# NOVEL CHEMICAL ELECTRON TRANSFER MEDIATED CARBON-HETEROATOM BOND FORMING REACTIONS AND RELATED CHEMISTRY

THESIS SUBMITTED TO THE
UNIVERSITY OF KERALA FOR THE DEGREE OF
**DOCTOR OF PHILOSOPHY**
IN CHEMISTRY UNDER THE FACULTY OF SCIENCE

BY

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UNDER THE SUPERVISION OF

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APRIL 2002

## DECLARATION

I hereby declare that the matter embodied in the thesis entitled "**NOVEL CHEMICAL ELECTRON TRANSFER MEDIATED CARBON-HETEROATOM BOND FORMING REACTIONS AND RELATED CHEMISTRY**" is the result of the investigations carried out by me in the Organic Chemistry Division of Regional Research Laboratory [CSIR], Thiruvananthapuram, under the supervision of Dr. Vijay Nair and the same has not been submitted elsewhere for a degree.

Anu

Thiruvananthapuram
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# CERTIFICATE

Certified that the work described in this thesis entitled **"NOVEL CHEMICAL ELECTRON TRANSFER MEDIATED CARBON-HETEROATOM BOND FORMING REACTIONS AND RELATED CHEMISTRY"** has been carried out by **Ms. Anu Augustine** under my supervision in the Organic Chemistry Division of Regional Research Laboratory [CSIR], Thiruvananthapuram and the same has not been submitted elsewhere for a degree.

G. Vijay Nair
(Thesis Supervisor)

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*Thiruvananthapuram* **Anu Augustine**

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## CONTENTS

## PREFACE

Carbon-carbon and carbon-heteroatom bond forming reactions occupy a pivotal position in organic synthesis. Radical methodology deserves special attention among such bond forming reactions. The generation of radicals involving chemical, electrochemical and photochemical processes are known. Of the different methods developed for the generation of radicals, chemical electron transfer reactions mediated by one electron oxidants especially cerium(IV) ammonium nitrate(CAN) are of current interest to us. A survey of the literature reveals that although CAN has found much use in carbon-carbon bond forming reactions, its use in carbon-heteroatom bond formation has not received much attention. In view of the growing interest in such reactions, we have carried out some investigations to explore the synthetic utility of CAN in carbon-heteroatom bond forming reactions and the results are presented in the thesis entitled **"NOVEL CHEMICAL ELECTRON TRANSFER MEDIATED CARBON-HETEROATOM BOND FORMING REACTIONS AND RELATED CHEMISTRY"**. The thesis is divided into four chapters. Relevant references are given at the end of each chapter.

Some recent developments in the use of CAN in various synthetic transformations with special emphasis on carbon-heteroatom bond forming reactions are presented in chapter 1. A statement of the present research problem has also been incorporated in this chapter.

The second chapter of the thesis deals with novel CAN mediated carbon-sulfur bond forming reactions. This chapter is divided into three parts. Oxidative addition of sulfinate to styrenes is described in the first part. Part two deals with the one pot synthesis of vinyl sulfones *via* CAN mediated reaction of aryl sulfinates and alkenes, mainly styrenes. A one-pot synthesis of acetylenic

sulfones forms the subject matter of part three. General information on the experimental procedure is also given in this chapter.

The third chapter deals with carbon-selenium bond forming reactions mediated by CAN. This chapter is divided into two parts. The first part covers the oxidative addition of selenocyanate to styrenes whereas CAN mediated selenocyanation of electron rich aromatics is outlined in part two.

The fourth chapter deals with some preliminary experiments on diastereoselective azidation mediated by CAN.

It may be noted that each chapter of the thesis is presented as a separate unit, and therefore, figures, schemes and structures are numbered accordingly. A summary of the work is given towards the end of the thesis.

## ABBREVIATIONS

| | |
|---|---|
| AIBN | : azobisisobutyronitrile |
| brs | : broad singlet |
| CAN | : cerium(IV) ammonium nitrate |
| d | : doublet |
| DCM | : dichloromethane |
| DMF | : dimethyl formamide |
| dd | : double doublet |
| Et | : ethyl |
| IR | : infrared |
| *J* | : coupling constant |
| KHMDS | : potassium hexamethyl disilazide |
| LDA | : lithium diisopropylamide |
| *m*CPBA | : *meta*-chloroperbenzoic acid |
| m | : multiplet |
| Me | : methyl |
| mg | : milligram |
| mL | : milliliter |
| mp | : melting point |
| NBS | : *N*-bromosuccinimide |
| NMR | : nuclear magnetic resonance |
| *o* | : ortho |
| *p* | : para |
| PDC | : pyridinium dichromate |
| Ph | : phenyl |
| PPTS | : pyridinium *p*-toluene sulfonate |
| s | : singlet |
| TBACN | : tetrabutyl ammonium cerium(IV) nitrate |
| THF | : tetrahydrofuran |
| t | : triplet |
| tlc | : thin layer chromatography |
| US | : ultrasonication |

Chapter 1

# RECENT DEVELOPMENTS IN CERIUM(IV) AMMONIUM NITRATE MEDIATED CARBON-HETEROATOM BOND FORMING REACTIONS

## 1.1 GENERAL INTRODUCTION

The origin of radical chemistry can be traced to the epoch making discovery of triphenylmethyl radical by Gomberg in 1900.[1] Inspite of the seminal contributions of Hey and Waters[2] and Kharasch,[3] radical chemistry did not find much acceptance in organic synthesis, especially in carbon-carbon bond formation, because of the persistent but erroneous notion that radical reactions lack selectivity and are uncontrollable. A dramatic change in this situation consequent on a paradigm shift attributable in large measure to the conceptualization and demonstration by Stork that the controlled formation as well as the addition of vinyl radicals to alkenes constitutes a unique and powerful method for complex carbocyclic construction led to an explosive growth in the area of radical methodology during the last two decades .[4] Important contributions made by many research groups, most notably those of Julia,[5] Beckwith,[6] Giese,[7] Ingold,[8] Curran[9] and Pattenden[10] have also contributed to the general acceptance of radical methodology.

The advantages of radical reactions over polar or pericyclic reactions are the high chemoselectivity and regioselectivity. Also, most radical reactions are carried out under mild conditions. Procedures involving chemical,[11]

electrochemical[12] and photochemical[13] methods have been established for the generation of radicals. Of these, oxidative methods involving one electron-oxidants are of current interest. Oxidative methods mediated by transition metal salts like those of Mn(III), Co(III), Cu(II), Fe(III) and V(V) have been explored in varying detail.[14] Although $Mn(OAc)_3$ occupies a unique position among the various one electron oxidants,[15] procedural problems associated with the use of this reagent often limit its application. Hence there has been growing interest in developing other reagents and methods for generating radicals.

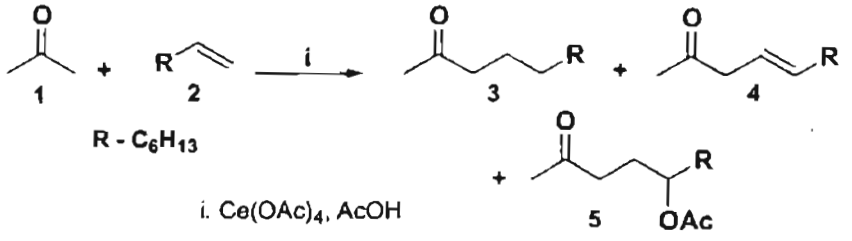
Recently, cerium(IV) compounds, especially cerium(IV) ammonium nitrate (CAN) has emerged as an effective reagent in this area.[16] The advantages associated with the use of CAN in chemical electron transfer reactions are mild and non-anhydrous reaction conditions, good to excellent yields of products and short reaction time. Being a non-hygroscopic solid, this reagent is readily available in pure form and can be handled easily. Also it is highly soluble in common organic solvents like methanol and acetonitrile.

The versatility of CAN in various chemical transformations with special emphasis on carbon-heteroatom bond formation is delineated in the following section.

## 1. 2 CAN MEDIATED CARBON-CARBON BOND FORMING REACTIONS

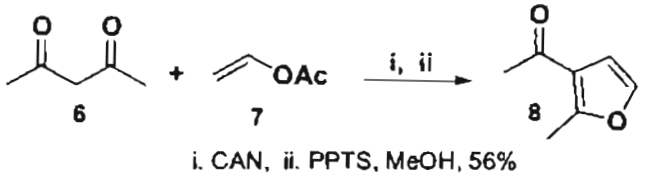
In 1971, Heiba and Dessau[17] generated carbon centered radicals using Ce(IV) reagents and they have shown that the radicals thus generated can react with alkenes producing a number of interesting products.

Cerium(IV) acetate mediated addition of acetone to 1-octene resulted in the formation of ketone **3**, unsaturated ketone **4** and keto acetate **5** (Scheme 1).



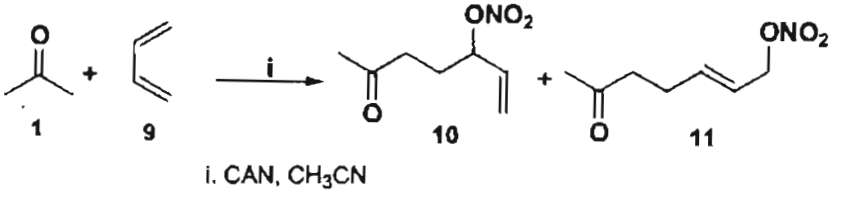

**Scheme 1**

Baciocchi *et al.* have carried out the CAN mediated addition of 1,3-dicarbonyl compounds to activated alkenes. An illustrative example is the addition of acetylacetone and ethyl acetoacetate to activated alkenes such as vinyl acetate to produce furan derivatives (Scheme 2).[18]



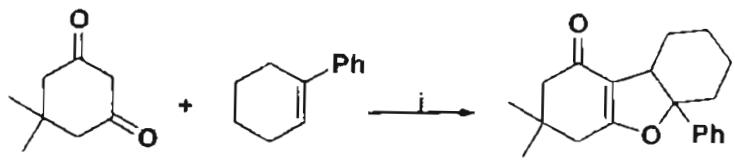

**Scheme 2**

They have also studied the 1,4-addition of carbonyl compounds such as acetone and ethyl acetoacetate to 1,3-butadiene (Scheme 3).[19]



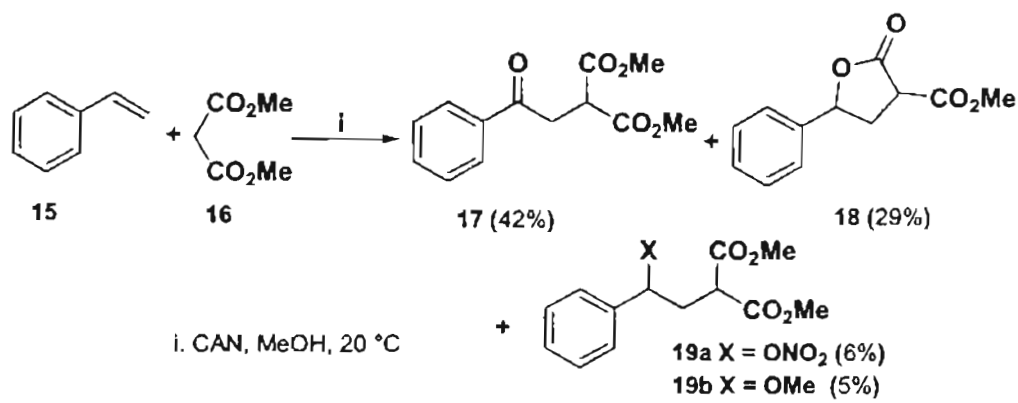

**Scheme 3**

Extensive studies in this area carried out in our laboratory have shown that the oxidative addition of dicarbonyl compounds such as dimedone, acetylacetone and ethyl acetoacetate to alkenes afforded dihydrofurans in excellent yields. The reaction of dimedone **12** with phenylcyclohexene **13** is illustrated in Scheme 4.[20]



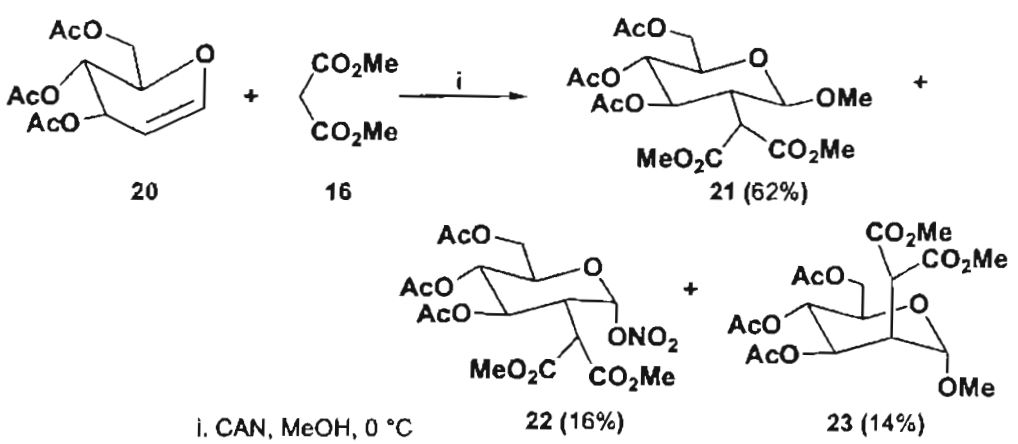

**Scheme 4**

CAN mediated oxidative addition of dimethyl malonate to styrenes resulted in a mechanistically interesting reaction (Scheme 5).[21]




**Scheme 5**

Linker has reported the addition of dimethyl malonate to triacetyl-D-glucal in the presence of CAN (Scheme 6).[22]



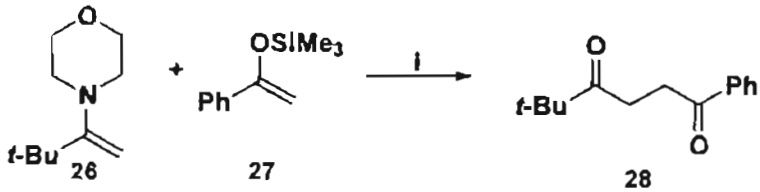

**Scheme 6**

Free radical nitromethylation, acetonylation and malonylation of arenes using CAN are reported in the literature.[23] Kurz *et al.* have reported the CAN mediated nitromethylation of arenes (Scheme 7).[23a]


24 i. CAN, AcOH, reflux, 24 h, 100% 25

**Scheme 7**

Narasaka *et al.* have reported the oxidative addition of enamines to electron-rich olefins such as silyl enol ethers leading to the formation of diketones (Scheme 8).[24]

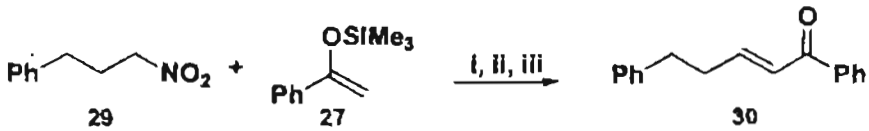



26 27 28

i. CAN, MeCN, 0.5 h, rt, 63%

**Scheme 8**

Nitroalkyl radicals generated by the oxidation of potassium salts of nitroalkanes by CAN add to silyl enol ethers to afford $\beta$-nitroketones which are further transformed to $\alpha,\beta$-unsaturated ketones (Scheme 9).[25]



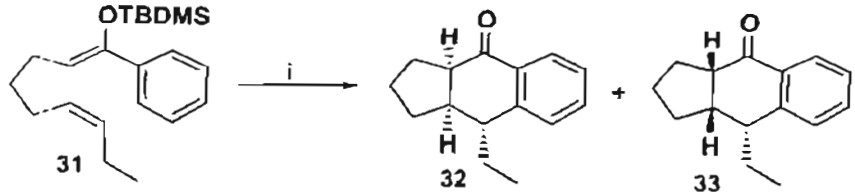

29 27 30

i. KOH, MeOH, rt ii. CAN, MeOH, -78 °C
iii. $Et_3N$, MeOH, rt

**Scheme 9**

Unlike the intermolecular carbon-carbon bond forming reactions mediated by CAN, only very few reports are available on the intramolecular reactions. Snider *et al.* have reported the intramolecular oxidative cyclization

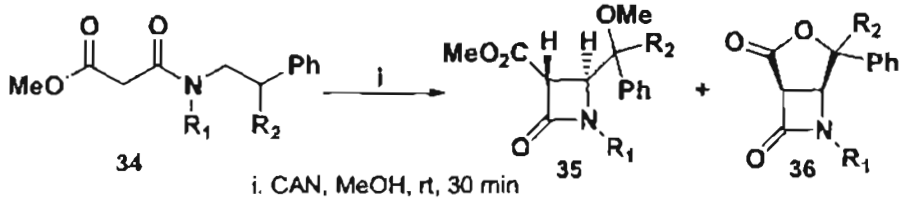
of $\delta,\varepsilon$ and $\varepsilon,\xi$-unsaturated silyl enol ether resulting in a tricyclic ketone. The reaction proceeds with excellent stereocontrol and in good yields (Scheme 10).[26]




i. CAN, $NaHCO_3$, MeCN, 25 °C, 73%, (1:20)

**Scheme 10**

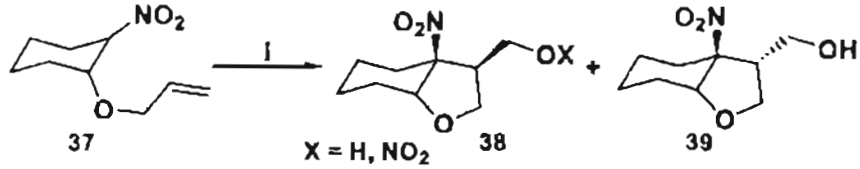
CAN mediated Pictet-Spengler cyclization, and cyclization of enamides leading to various functionalized $\beta$-lactams have been reported by Annibale *et al.* (Scheme 11).[27]




i. CAN, MeOH, rt, 30 min

**Scheme 11**

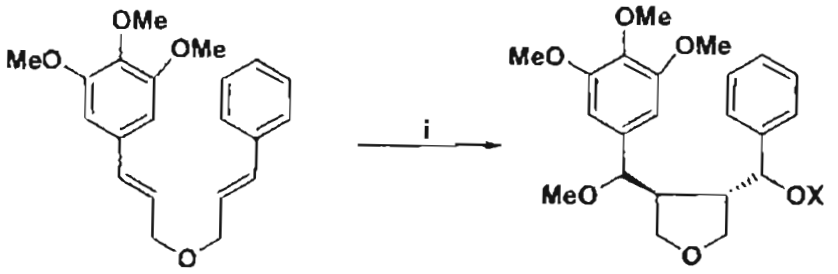
Intramolecular cyclization using nitroalkenyl radicals generated from nitro acyl anions forming tetrahydrofurans has been reported by Durand *et al.* (Scheme 12).[28]




i. CAN, THF, -78 °C, 0.1 N $Na_2S_2O_3$

**Scheme 12**

Recently, our group has reported the oxidative cyclization of cinnamyl ethers mediated by CAN leading to the stereoselective formation of 3,4-*trans* substituted tetrahydrofuran derivatives in good yields (Scheme 13).[29]



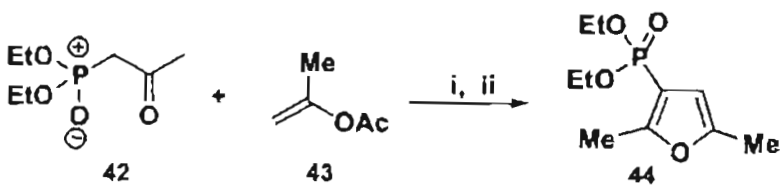

40 41

X = Me, $NO_2$

i. CAN, dry MeOH, rt, argon, 90 min, 56%, (2:1)

**Scheme 13**

Oxidative addition of β-ketophosphonates to vinylic acetates and subsequent acid catalyzed Pall-Knorr cyclization constitutes a convenient route to substituted diethyl-3-furyl phosphonates (Scheme 14).[30]

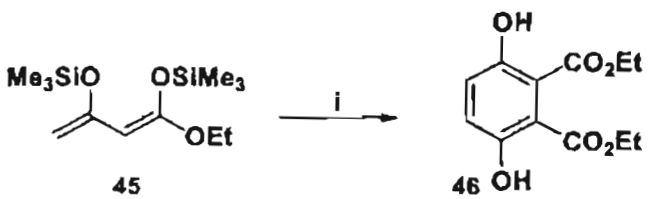



42 43 44

i. CAN, MeOH, rt ii. Amberlyst-15, toluene, reflux, 70%

**Scheme 14**

A very recent report illustrates the oxidative cyclization of 1,3-bis(trimethylsilyloxy)-buta-1,3-dienes mediated by CAN (Scheme 15).[31]

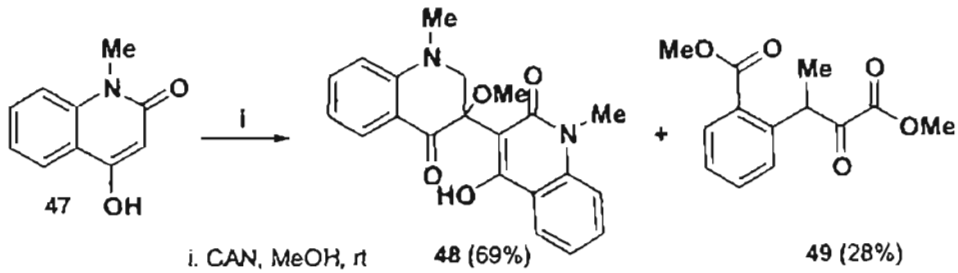



45 46

i. CAN, $NaHCO_3$, MeCN, 56%

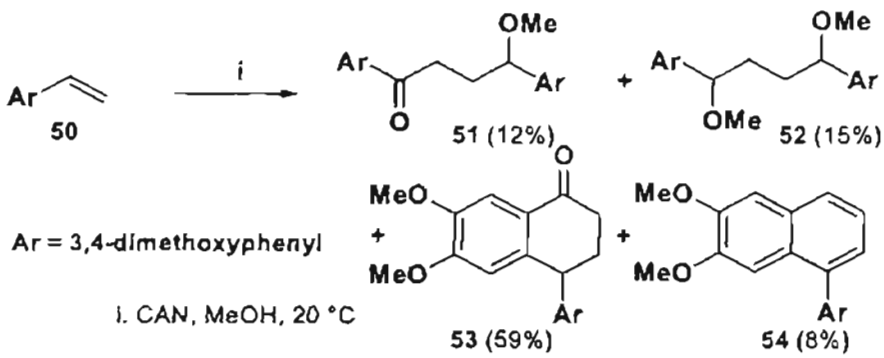
**Scheme 15**

There are several reports on the CAN mediated dimerization reactions. Dimerization of 4-hydroxyquinoline-2-(*1H*)-ones in presence of CAN in methanol has been reported recently (Scheme 16).[32]




**Scheme 16**

In the presence of CAN, methoxystyrenes are found to undergo a facile dimerization reaction and this has been studied in detail as shown in Scheme 17.[33]



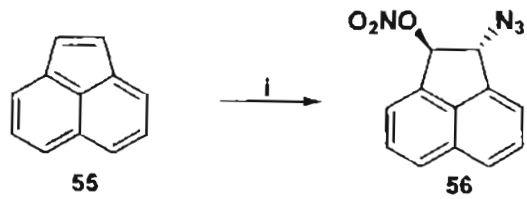

**Scheme 17**

## 1.3 CAN MEDIATED CARBON-HETEROATOM BOND FORMING REACTIONS

Though CAN has found much use in carbon-carbon bond forming reactions, the use of this reagent in carbon-heteroatom bond formation has not been much explored. An overview of various carbon-heteroatom bond forming reactions mediated by CAN is presented here.

### 1.3.1 Carbon-Nitrogen Bond Forming Reactions

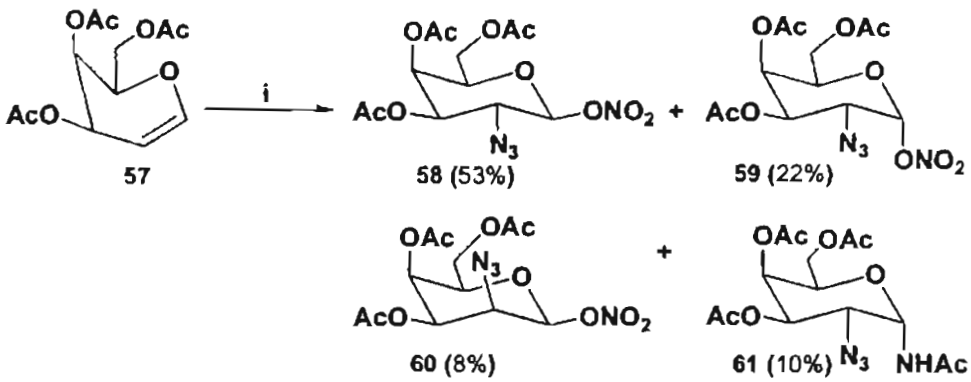
The first report on CAN mediated carbon-heteroatom bond forming reaction may be attributed to Trahanovsky, who in 1971 observed the addition of azide to alkenes resulting in azidonitrates (Scheme 18).[34]




i. $NaN_3$, CAN, MeCN, rt, 90%

**Scheme 18**

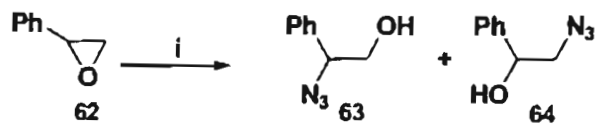
Subsequently, Lemieux has applied this reaction to glycals in the synthesis of azidosugars which are important intermediates in the synthesis of aminosugars (Scheme 19).[35]




i. CAN, $NaN_3$, MeCN, 0 °C-rt, argon

**Scheme 19**

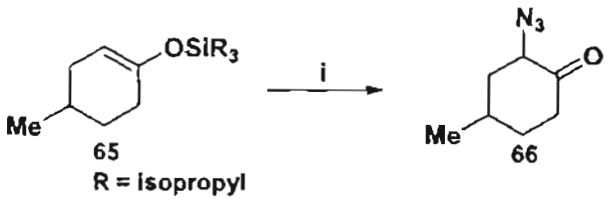
Regioselective conversion of epoxides to 1,2-azidoalcohols using catalytic amount of CAN has also been reported (Scheme 20).[36]




i. CAN (0.2 M), $NaN_3$, *t*-BuOH, rt, 96% (95:5)

**Scheme 20**

Oxidative addition of azide to triisopropylsilyl enol ethers resulted in the formation of $\alpha$-azidoketones in moderate to good yields (Scheme 21).[37]



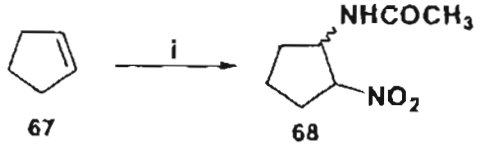

65 66

R = isopropyl

i. CAN, $NaN_3$, MeCN, -20 °C, argon, 81%

**Scheme 21**

CAN mediated nitroacetamidation *via* the Ritter reaction has also been reported (Scheme 22).[38]

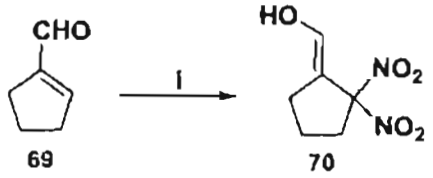



67 68

i. $NaNO_2$, CAN, MeCN, 64%

**Scheme 22**

The conversion of cyclopentene carboxaldehyde to dinitrooxime using the same combination of reagents has been reported (Scheme 23).[39]

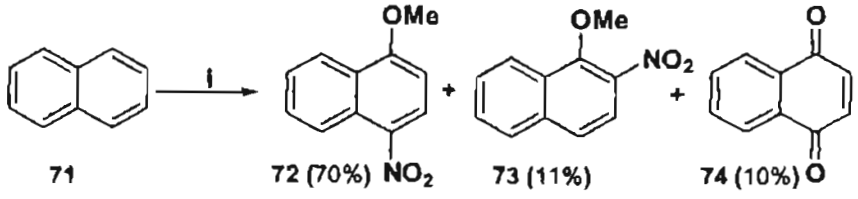



69 70

i. $NaNO_2$, CAN, MeCN, 21%

**Scheme 23**

Nitration of naphthalenes using CAN, tetrabutylammonium nitrite and acid afforded alkoxynitronaphthalenes (Scheme 24).[40]

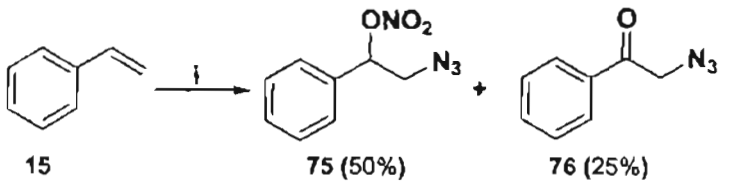



71 72 (70%) 73 (11%) 74 (10%)

i. $Bu_4NNO_2$, CAN, $H_2SO_4$, MeOH

**Scheme 24**

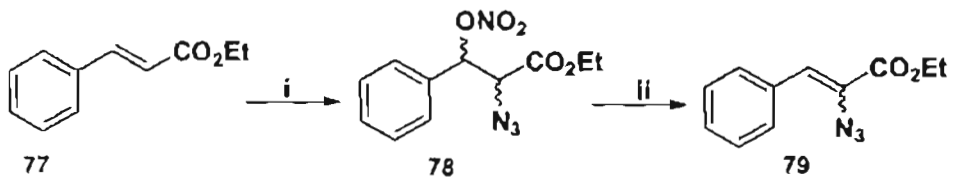
Recent work in our laboratory has demonstrated an expeditious route to the synthesis of phenacylazides and nitratoazides from styrene using sodium azide and CAN in acetonitrile (Scheme 25).[41]




i. $NaN_3$, CAN, MeCN, 0 °C, 15 min

**Scheme 25**

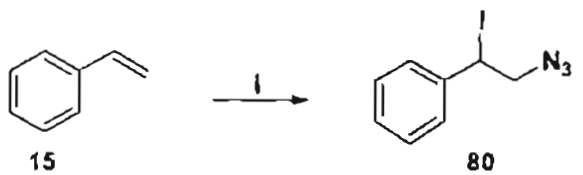
CAN mediated addition of azide to cinnamic acids, esters and $\alpha,\beta$–unsaturated ketones followed by reaction with sodium acetate afforded $\alpha$-azidocinnamates, $\alpha$-azidostyrenes and $\alpha$-azido-$\alpha,\beta$-unsaturated ketones in good yields (Scheme 26).[42]




i. $NaN_3$, CAN, dry MeCN, 0 °C, argon, 70%
ii.$CH_3COONa$, dry acetone, reflux, overnight, 66%

**Scheme 26**

A facile synthesis of azidoiodides from alkenes was achieved in good yields using a reagent combination of $NaN_3$, NaI and CAN (Scheme 27).[43]

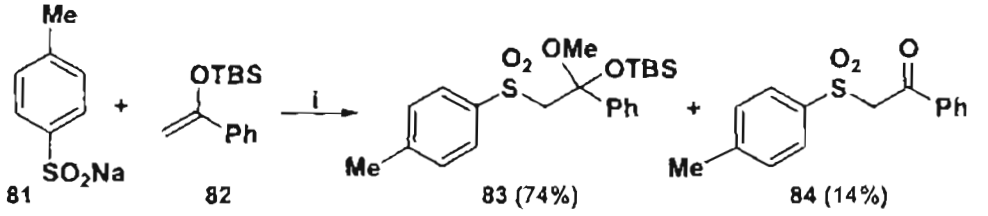



i. $NaN_3$, NaI, CAN, MeOH, 0 °C, 30 min, 71%

**Scheme 27**

### 1.3.2 Carbon-Sulfur Bond Forming Reactions

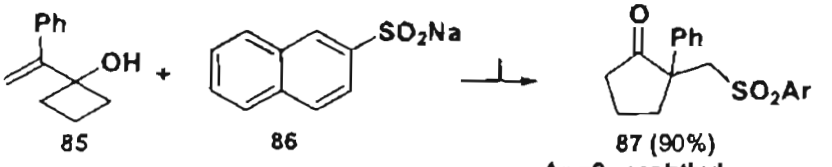
There are only a few reports available on carbon-sulfur bond forming reactions mediated by cerium(IV). Sulfonylation of electron rich olefins with tetrabutyl ammonium cerium(IV) nitrate(TBACN) in presence of potassium carbonate was reported by Narasaka *et al.* (Scheme 28).[44]




i. TBACN, $K_2CO_3$, MeOH, 0 °C, overnight

**Scheme 28**

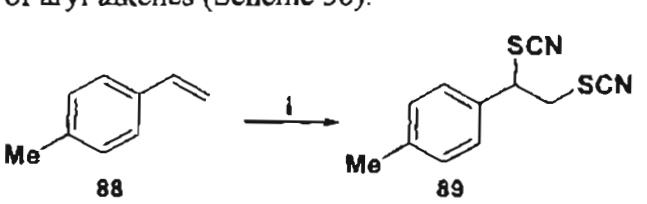
They have also reported the sulfonylation of 1-vinyl cyclic alcohols using CAN, which proceeded with ring enlargement (Scheme 29).[45]




i. CAN, $CH_3CN$, 0 °C, 2 h

**Scheme 29**

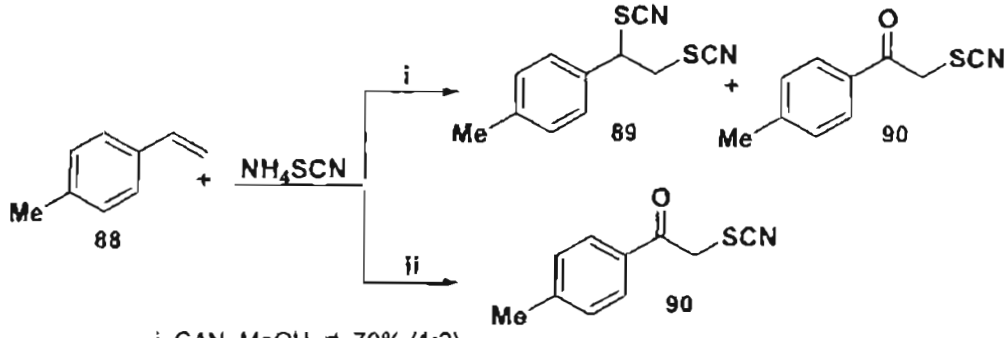
Work carried out in our laboratory has shown that CAN mediates a facile dithiocyanation of aryl alkenes (Scheme 30).[46]




i. $NH_4SCN$, CAN, MeCN, rt, 15 min, 95%

**Scheme 30**

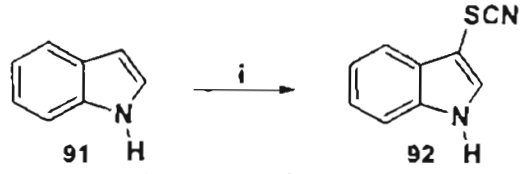
CAN also mediates an efficient synthesis of phenacylthiocyanates from aryl alkenes as well as other alkenes (Scheme 31).[41]




i. CAN, MeOH, rt, 70% (1:2)
ii. CAN, MeOH, oxygen, 0 °C, 70%

**Scheme 31**

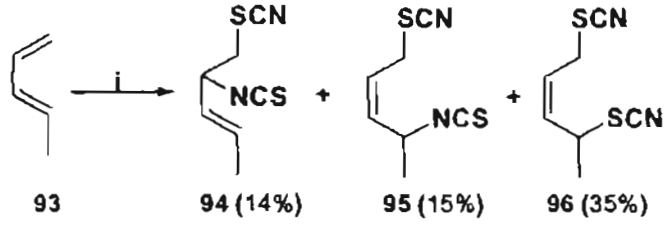
Thiocyanation of indole to afford 3-thiocyanatoindole has been achieved in quantitative yield by the reaction with thiocyanate and CAN (Scheme 32).[47]




i. $NH_4SCN$, CAN, MeOH, rt, 100%

**Scheme 32**

CAN mediated thiocyanation of dienes leading to isothiocyanato thiocyanates *via* a [3,3] sigmatropic rearrangement has been reported (Scheme 33).[48]

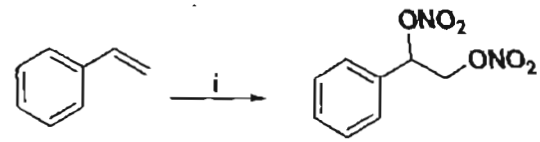



i. $NH_4SCN$, CAN, MeCN, 0 °C, 30 min

**Scheme 33**

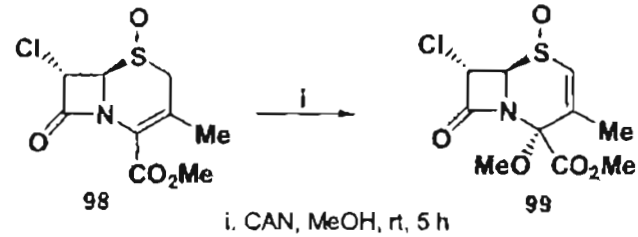
### 1.3.3 Carbon-Oxygen Bond Forming Reactions

Baciocchi *et al.* have reported the formation of dinitrates from styrenes using CAN in acetonitrile (Scheme 34).[49]



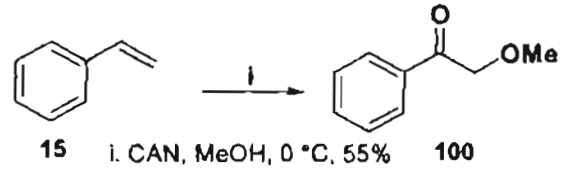

**Scheme 34**

Alpegiani *et al.* have reported the CAN mediated methoxylation of cephem sulfoxides (Scheme 35).[50]



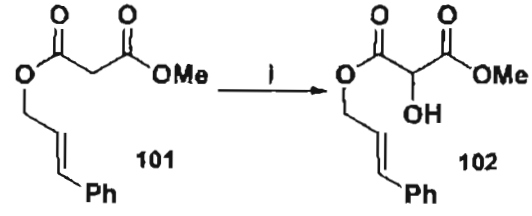

**Scheme 35**

α-Methoxyacetophenones have been synthesized by the reaction of styrenes with CAN in methanol (Scheme 36).[51]



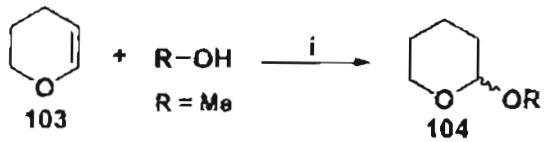

**Scheme 36**

CAN mediated oxygenation of alkyl malonates leading to tartronic acid derivatives has been reported (Scheme 37).[52]




**Scheme 37**

Very recently, Vankar *et al.* have reported the CAN catalyzed tetrahydropyranylation of alcohols (scheme 38).[53]

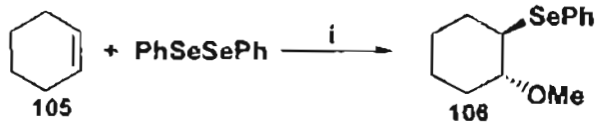



i. CAN (2 mol%), MeCN, rt, 5-15 min, 78%

**Scheme 38**

### 1.3.4 Carbon-Selenium Bond Forming Reactions

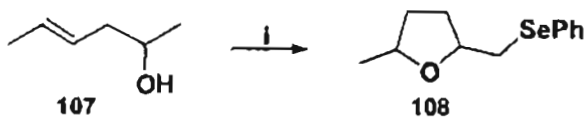
The only report on carbon-selenium bond formation using CAN involves the selenomethoxylation of alkenes reported by Bosman *et al.* (Scheme 39).[54]




i. CAN, MeOH, rt, argon, 30 min, 93%

**Scheme 39**

They have also shown that with 4-hexene-2-ol, the intramolecular reaction afforded the selenide substituted tetrahydrofuran (Scheme 40).[54]

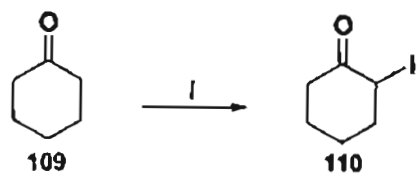



i. PhSeSePh, CAN, MeOH, 86%

**Scheme 40**

### 1.3.5 Carbon-Halogen Bond Forming Reactions

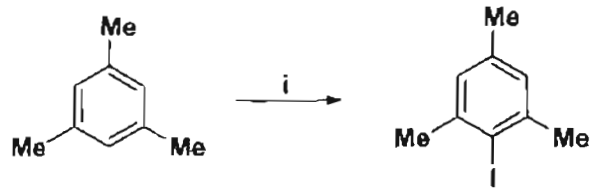
Horiuchi *et al.* have reported a facile $\alpha$-iodination of ketones using iodine and CAN in acetic acid (Scheme 41).[55]




i. $I_2$, CAN, AcOH, MeOH, 84%

**Scheme 41**

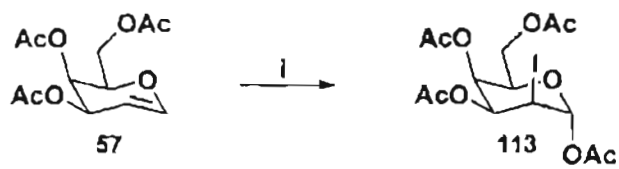
Iodination of polymethylbenzene, polymethoxybenzene and naphthalene using alkali metal iodides or elemental iodine and CAN in acetonitrile has been reported (Scheme 42).[56]




111 i. $Bu_4NI$, CAN, MeCN, 83% 112

**Scheme 42**

Roush *et al.* have reported the stereoselective iodo-acetoxylation of glycals with CAN and sodium iodide in the presence of acid (Scheme 43).[57]

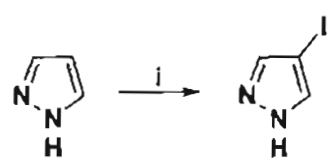



57 113

i. NaI, CAN, AcOH, MeCN, 75%

**Scheme 43**

Very recently, the regioselective iodination of pyrazoles using iodine and CAN has been reported (Scheme 44).[58]

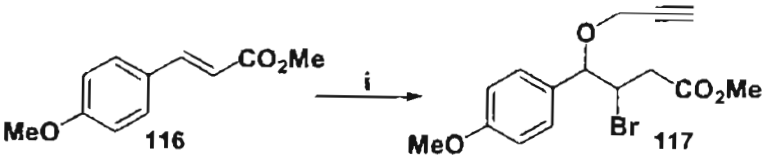



114 115

i. $I_2$, CAN, MeCN, 98%

**Scheme 44**

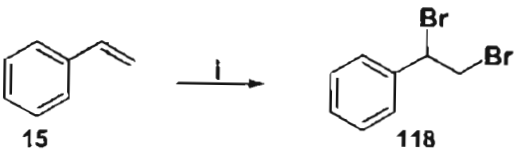
It has been reported recently that activated cinnamyl esters or ketones on reaction with CAN and lithium bromide with an excess of propargyl alcohol at room temperature afforded the bromoethers (Scheme 45).[59]




i. LiBr, CAN, propargyl alcohol, MeCN, 87%

**Scheme 45**

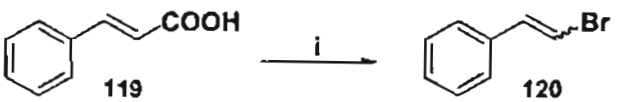
A novel method for the dibromination of alkenes developed in our laboratory involves the use of potassium bromide and CAN in a biphasic system of water and dichloromethane (Scheme 46).[60]




i. KBr, CAN, $CH_2Cl_2$, $H_2O$, rt, 91%

**Scheme 46**

Recently, we have observed a facile CAN mediated synthesis of $\beta$-vinyl bromides from $\alpha,\beta$-unsaturated aromatic acids (Scheme 47).[61a] Very recently, a similar process has been reported by another group.[61b]

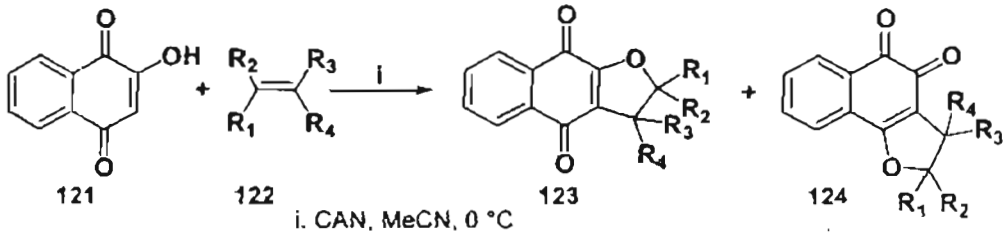



i. KBr, CAN, DCM-$H_2O$, rt, 45 min
ii. $Et_3N$, DMF, rt, 55%

**Scheme 47**

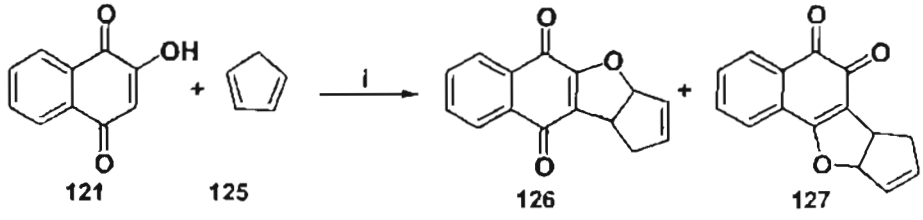
### 1.3.6 Miscellaneous CAN Mediated Reactions

Other than carbon-heteroatom bond forming reactions, there are reports of other oxidative transformations including cycloaddition reactions mediated by CAN. [3+2] cycloaddition of 2-hydroxy-1,4-naphthoquinones and 2-hydroxy-1,4-benzoquinones with alkenes resulted in the formation of furo-*p*-quinones as well as *o*-quinone derivatives (Scheme 48).[62]



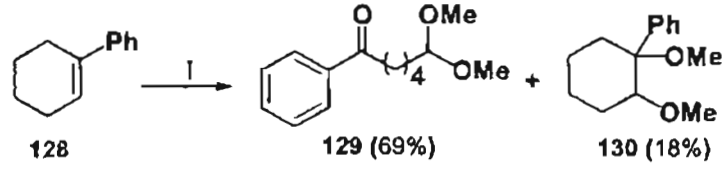

**Scheme 48**

Studies in our own laboratory have also shown that CAN induced oxidative addition of 2-hydroxy-1,4-naphthoquinone to dienes offers a simple and rapid one-step procedure for the synthesis of naphthofuran diones. An illustrative example is depicted in Scheme 49.[63]



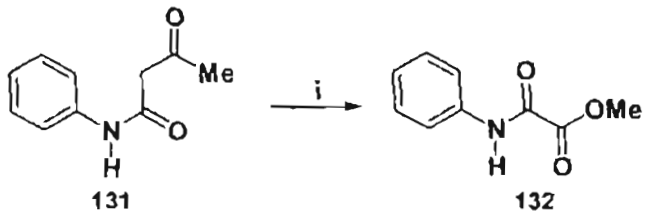

**Scheme 49**

An interesting CAN mediated fragmentation of phenylcycloalkenes leading to the synthesis of 1,n-dicarbonyl compounds along with the dimethoxy compound was observed in our laboratory (Scheme 50).[64]




**Scheme 50**

Work in our laboratory has also unraveled a facile CAN mediated transformation of acetoacetamides to oxamates (Scheme 51).[65]

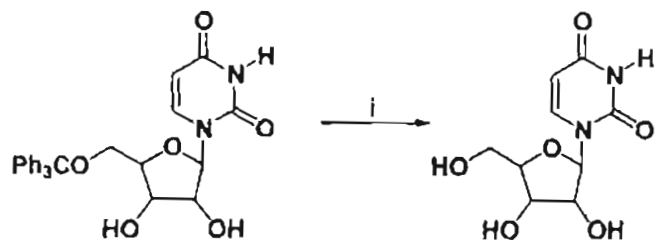



i. CAN, MeOH, oxygen, rt, 15 min, 70%

**Scheme 51**

CAN has also been used in a number of other oxidative transformations. CAN mediated deprotection of TBDMS ethers,[66] THP ethers,[66] *t*-butoxycarbonyl group[67] and acetals[68] have been reported.

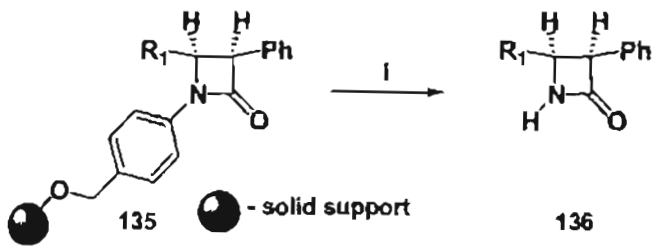
Rapid and selective removal of trityl group from protected nucleosides and nucleotides under mild conditions using catalytic amount of CAN has been reported (Scheme 52).[69]




i. CAN-silica, DCM, 25 °C, 80%

**Scheme 52**

A novel solid phase synthesis of N-sustituted β-lactams and secondary amines which utilizes the oxidative cleavage of benzyloxy aniline linker using CAN has been reported (Scheme 53).[70]




i. CAN, MeCN-$H_2O$ (2:1), rt, 30 min, 88%

**Scheme 53**

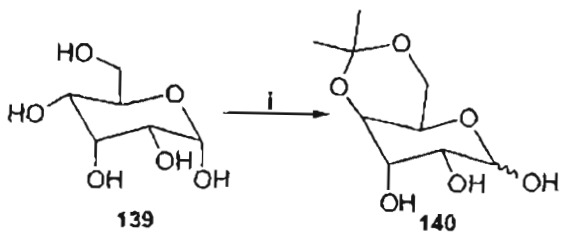
Debenzylation of tertiary amines using CAN has been reported by Bull and co-workers.(Scheme 54).[71]


137 138

i. CAN, MeCN-$H_2O$, 90%

**Scheme 54**

A novel CAN mediated acetonation of carbohydrates using 2,2-dimethoxy propane in anhydrous DMF has been reported recently (Scheme 55).[72]




139 140

i. CAN, DMP, dry DMF, 1 h, rt, 89%

**Scheme 55**

## 1.4 DEFINITION OF THE PROBLEM

The various synthetic transformations brought about by CAN clearly indicate that it is an excellent one-electron oxidant. A survey of the literature revealed that carbon-heteroatom bond forming reactions mediated by CAN have not been much explored, *vis a vis* carbon-carbon bond forming reactions. Though carbon-sulfur bond formation (thiocyanation) has been studied in some detail there are only isolated reports on the introduction of sulfonyl group mediated by CAN. In this context, it was of interest to study the CAN mediated addition of sulfinate to styrenes, alkenes and alkynes with the assumption that this would lead to sulfones which are versatile intermediates in organic synthesis.

Since it was also evident from the literature survey that CAN mediated carbon-selenium bond fomation has received only scant attention, it was of interest to explore the selenocyanation of styrenes. This constitutes the second phase of our work.

In the final phase of the work, we carried out some preliminary investigations on the stereoselectivity in CAN mediated azidation reactions, using the chiral auxiliary approach.

The results of our studies constitute the subject matter of the following chapters of the thesis.

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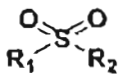
# CERIUM(IV) AMMONIUM NITRATE MEDIATED ADDITION OF SULFINATE TO STYRENES AND ACETYLENES

## 2.1 INTRODUCTION

The ability of sulfur to exist in variable oxidation states makes the organosulfur chemistry interesting. Furthermore, sulfur functionalities are amenable to a variety of synthetically useful transformations, most of which occur under mild conditions and are highly selective. Among the various organosulfur compounds, sulfones are of interest as intermediates in organic synthesis,[1] and as pharmaceutical agents.[2] The sulfone group is defined as **1**; the adjacent carbon substituents can be any combination of alkyl, vinyl, alkynyl or aryl groups (Figure 1).



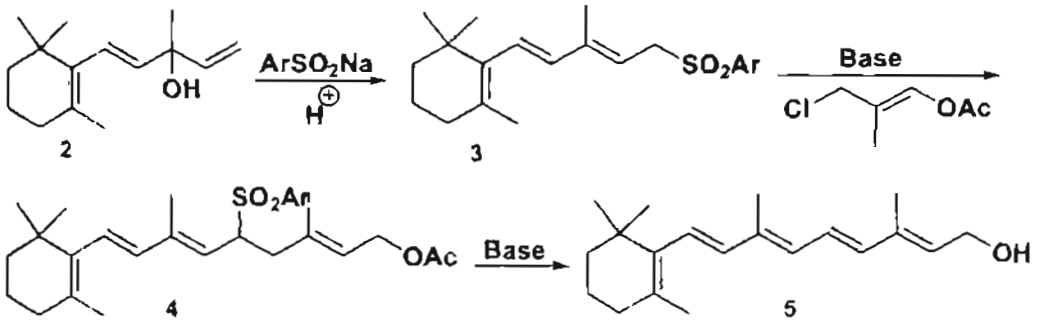
**1**

**$R_1$ and/or $R_2$ = alkyl, aryl, vinyl or alkynyl**

**Figure 1**

Perhaps the most well known and extensively studied reaction involving the sulfone functional group is the Ramberg-Bäcklund reaction,[3] which was discovered in 1940. The sulfone group is strongly electron withdrawing and has the ability to stabilize an $\alpha$-carbanion and hence the formation and reactions of $\alpha$-sulfonyl carbanions have been much studied.[4] Most uses of sulfone group in the synthesis ultimately involve its reductive removal.[5] There are several

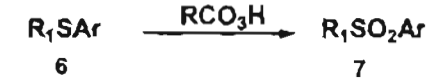
examples of the utility of sulfone group in the synthesis of natural products. The synthesis of Vitamin A alcohol is illustrative. Vitamin A alcohol 5 has been synthesized *via* the route outlined in Scheme 1. The facile elimination of aryl sulfinic acid to create the completely conjugated system is of particular interest. This type of chemistry, first described by Julia has been the corner stone of a number of polyene synthesis (Scheme 1).[6]




Scheme 1

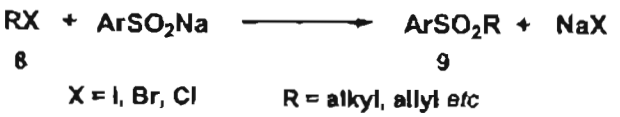
## 2.2 GENERAL METHODS FOR THE PREPARATION OF SULFONES

The most common method for the preparation of sulfones consists of the oxidation of sulfides and sulfoxides by peracids (Scheme 2).[7,8]



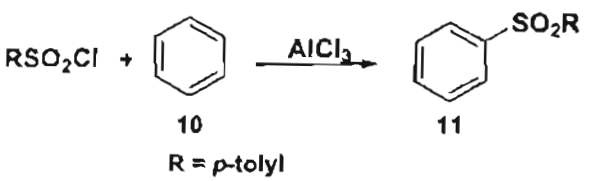

Scheme 2

Another procedure for the preparation of sulfones involves the alkylation of sulfinates with reactive halides (Scheme 3).[8]



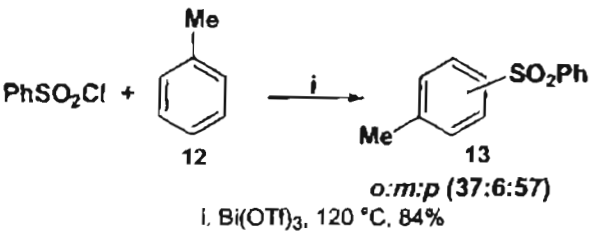

Scheme 3

The sulfonylation of aromatics has been well studied. The reaction of sulfonyl chlorides with aromatics under Friedel-Crafts condition constitutes an excellent route to diaryl or alkyl aryl sulfones (Scheme 4).[7,8]



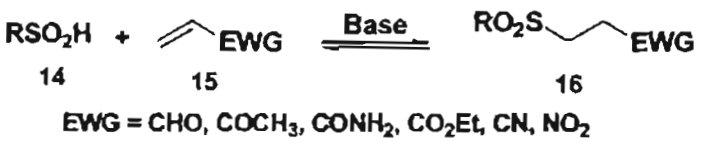

**Scheme 4**

Recently, Friedel-Crafts sulfonylation of aromatics employing the solid acid catalyst, $Fe^{3+}$-montmorillonite has been reported.[9] Also, Dubac *et al.* have reported that bismuth(III) trifluoromethane sulfonate serves as an excellent catalyst for the sulfonylation of aromatics (Scheme 5).[10]



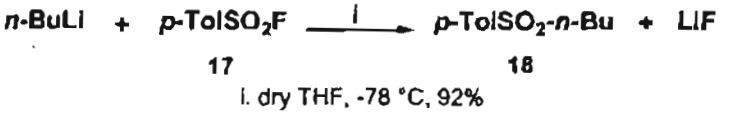

**Scheme 5**

Another convenient method involves the addition of sulfinic acids to polarized double bonds to form compounds of the type **16** as shown in Scheme 6.[11] This reaction is reversible.




**Scheme 6**

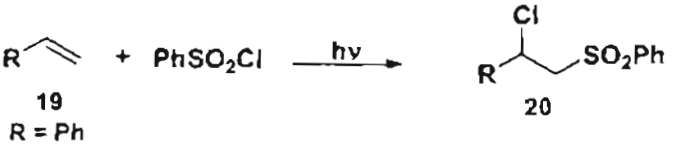
A wide variety of alkylaryl and diaryl sulfones can be synthesized by sulfonylation of organometallic reagents (Scheme 7).[12]




**Scheme 7**

In addition to ionic reactions there are several reports of sulfonylation reactions mediated by radicals including those generated by one electron oxidants.

Free radical addition of sulfonyl chlorides to alkenes and acetylenes catalyzed by light or typical chemical radical initiators was first investigated by Kharasch[13] and Skell[14] in the 1950s (Scheme 8).

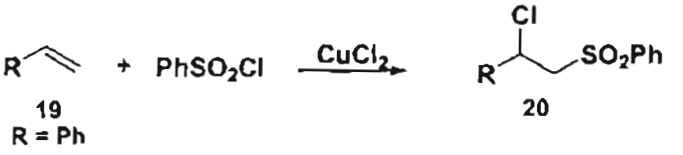



19
R = Ph

20

**Scheme 8**

Asscher *et al.* have reported the $CuCl_2$-catalyzed addition of sulfonyl chlorides to activated alkenes such as styrene affording compounds like **20** (Scheme 9).[15]

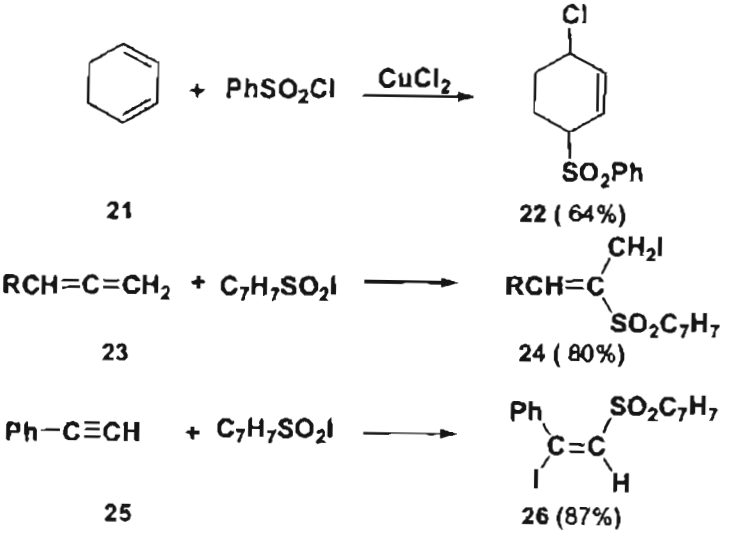



19
R = Ph

20

**Scheme 9**

Truce and co-workers have studied the addition of sulfonyl chlorides and iodides to 1,3-dienes,[16a] allenes[16b] and acetylenes[16c] under both sets of conditions and obtained products of the type **22**, **24** and **26** (Scheme 10).




21

22 ( 64%)

23

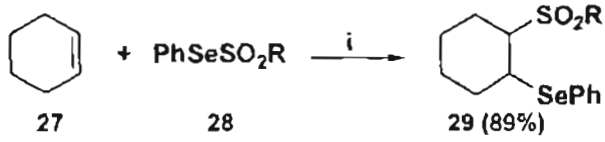
24 ( 80%)

25

26 (87%)

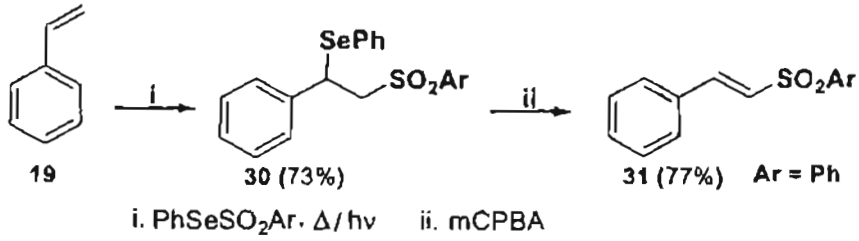
**Scheme 10**

Back and Collins have reported that phenylarene selenosulfonates add to olefins to give β-phenylseleno sulfones (Scheme 11).[17]




**Scheme 11**

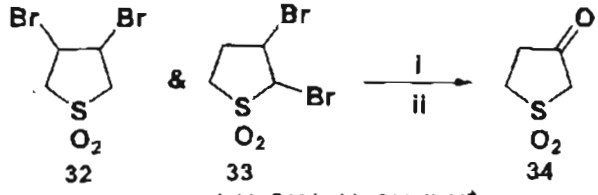
Photodecomposition of arene selenosulfonates and their facile photoaddition to alkenes have been reported by Kice and co-workers (Scheme 12).[18]




**Scheme 12**

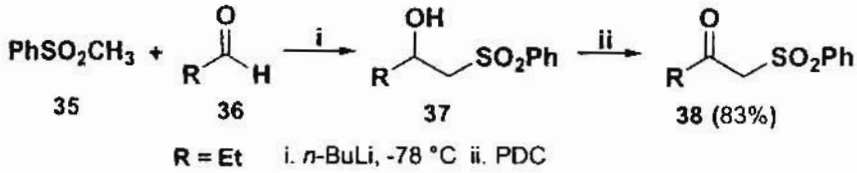
### 2.2.1 Synthesis of β-Ketosulfones and β-Hydroxysulfones

β-Ketosulfones are an important class of sulfone derivatives. These can be prepared by oxidation of the corresponding β-ketosulfides and β-ketosulfoxides.[18] The dibromides from 2,3-sulfolene on treatment with sodium hydroxide in MeOH followed by acid treatment yielded β-ketosulfone (Scheme 13).[19]



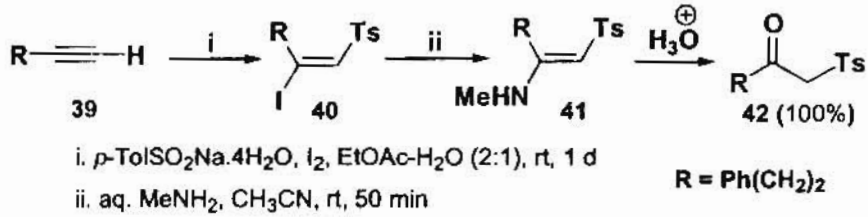

**Scheme 13**

The addition of lithio-(phenylsulfonylmethane) to aldehydes followed by oxidation of the crude β-hydroxysulfone using PDC gives β-ketosulfone (Scheme 14).[20]



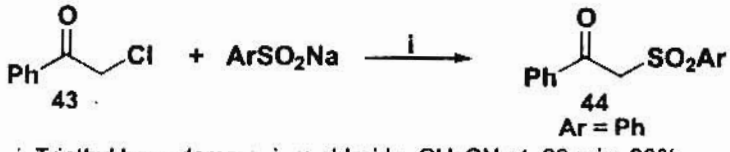

**Scheme 14**

Iwata *et al.* have reported that *(E)*-2-iodo-1-tosyl-1-alkenes can be readily synthesized by iodosulfonylation of 1-alkynes and these were found to be synthons for the preparation of α-tosyl ketones (Scheme 15).[21]



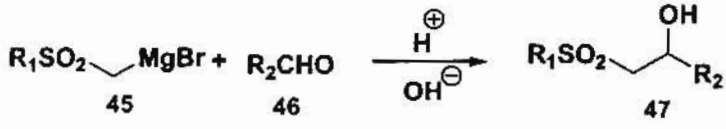

**Scheme 15**

Recently, a facile phase-transfer catalyzed synthesis of β-ketosulfones has been reported by Dubey *et al.* (Scheme 16).[22]



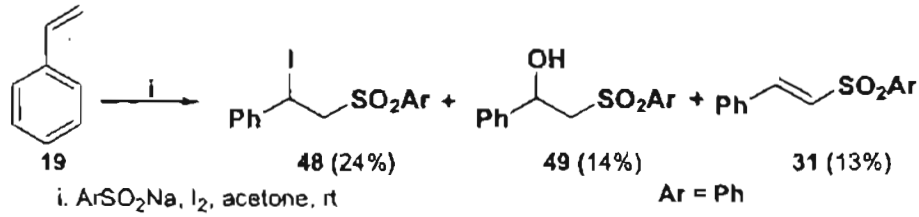

**Scheme 16**

The reaction between an α–sulfonyl carbanion and aldehydes or ketones represents the most general approach to β-hydroxysulfones (Scheme 17).[23]




**Scheme 17**

Reaction of olefins with sodium benzenesulfinate and iodine in acetone led to the formation of β-iodosulfone. When styrene was subjected to the same reaction β-hydroxysulfone was obtained along with the vinyl sulfone and β-iodo sulfone (Scheme 18).[24]

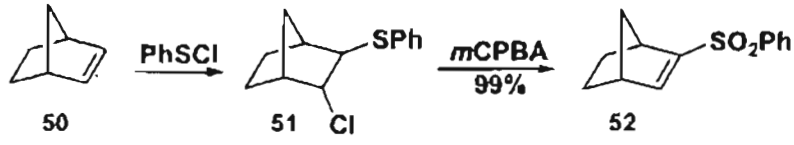



**Scheme 18**

## 2.2.2 Synthesis of Vinyl Sulfones

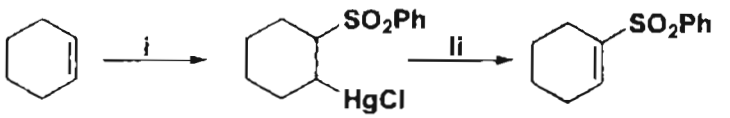
Vinyl sulfones (α, β –unsaturated sulfones) have been generally accepted as useful intermediates in organic synthesis[25] as amply demonstrated by the synthetic efforts of Fuchs.[25a] Vinyl sulfones serve as efficient Michael acceptors and as excellent 2π partners in cycloaddition reactions. In cycloaddition reactions, vinyl sulfones can serve useful function as convenient equivalents for ethylene, acetylene, ketene *etc.*

A versatile approach involving chlorosulfenylation dehydrochlorination has been used by Fuchs to prepare a variety of cyclic vinyl sulfones (Scheme 19).[26]




**Scheme 19**

The reaction of $HgCl_2$ with sodium benzenesulfinate results in the formation of arenesulfonyl mercury salts, which can then be eliminated under basic conditions (Scheme 20).[27]

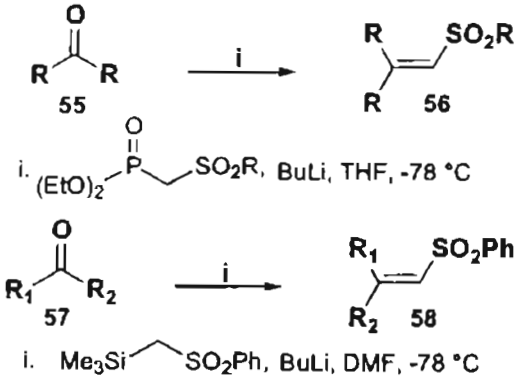



27 53 54

i. $HgCl_2$, $PhSO_2Na$, $H_2O$ ii. 50% NaOH, aq. dioxane, 79%

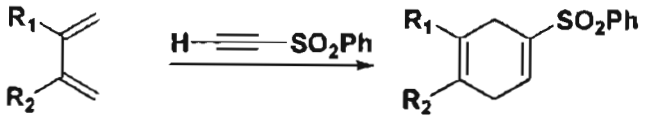
**Scheme 20**

The sulfonylphosphonates[28] and the silyl sulfones[29] take part in Horner-Emmons and Peterson reactions respectively, each process giving substituted vinyl sulfones (Scheme 21).



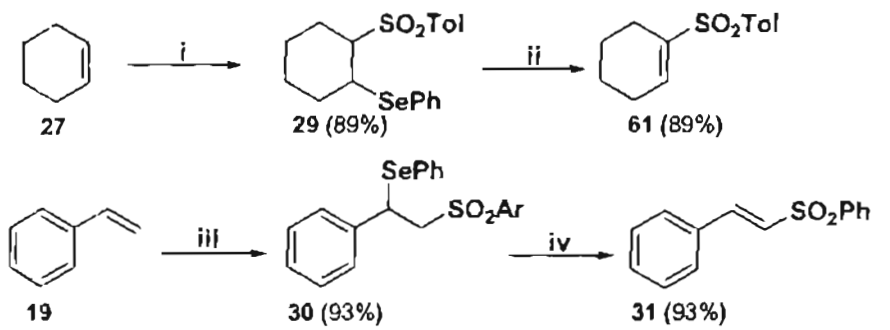

**Scheme 21**

A useful strategy for the synthesis of cyclohexenyl sulfones employs the Diels-Alder reaction. For example acetylenic sulfones react with 1, 3-dienes to afford the sulfone substituted 1, 4-diene (Scheme 22).[30]




**Scheme 22**

Back and Collins have reported the regio- and stereocontrolled synthesis of vinyl sulfones *via* either borontrifluoride catalyzed or thermal addition of selenosulfonates to olefins (Scheme 23).[17]

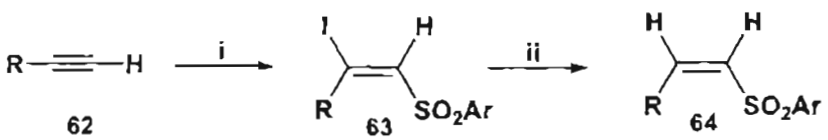



i. $PhSeSO_2Tol$ , $BF_3.OEt_2$ ii. *m*CPBA

iii. $PhSeSO_2Ph$, $\Delta$ / hv iv. *m*CPBA

**Scheme 23**

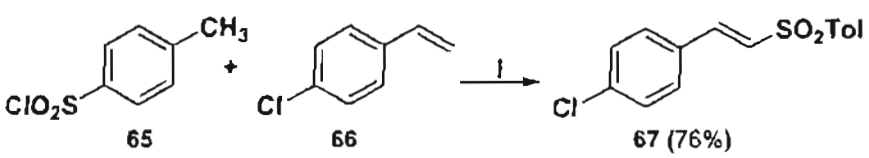
Truce *et al.* have reported that vinyl sulfones can be prepared from acetylenes through the reduction of the intermediate $\beta$-iodovinyl sulfone[16c] (Scheme 24).




i. $ArSO_2I$, hv ii. $H_2$, Pd-C, AcONa

**Scheme 24**

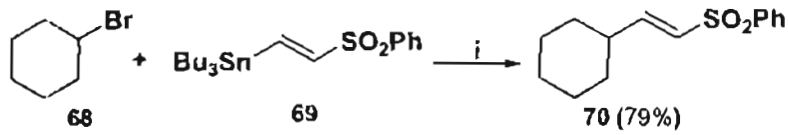
Kamigata *et al.* have reported that arenesulfonyl chlorides react with vinylarenes in the presence of Ruthenium(II) complex to form *(E)*-$\alpha$, $\beta$–unsaturated sulfones (Scheme 25).[31]




i. $RuCl_2(PPh_3)_2$, $Et_3N$, 60 °C, 72 h

**Scheme 25**

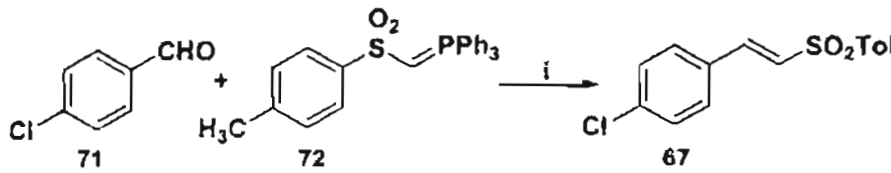
A free radical addition-fragmentation reaction for the preparation of vinyl sulfones has been reported by Feringa *et al.* (Scheme 26).[32]




i. AIBN, benzene

**Scheme 26**

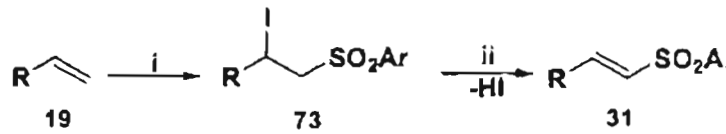
*Trans* disubstituted vinyl sulfones have been prepared *via* the Wittig reaction of aromatic aldehydes with (*p*-tolylsulfonylmethylene)triphenyl phosphorane under microwave irradiation (Scheme 27).[33]




i. microwave, silica gel, 15 min

**Scheme 27**

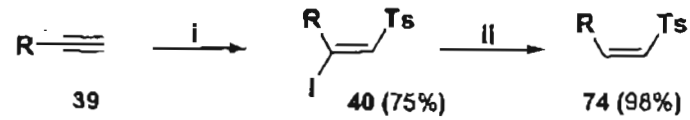
Julia *et al.* have reported the synthesis of vinyl sulfones from $\beta$-iodosulfones (Scheme 28).[24]




R = Ar = Ph i. $ArSO_2Na$, $I_2$, acetone, r.t
ii. $Et_3N$, DCM, rt, 24 h, 75%

**Scheme 28**

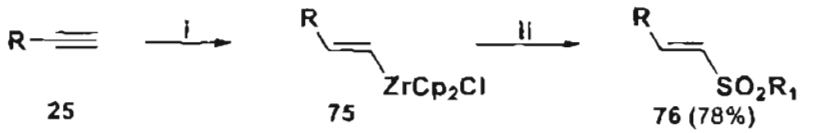
Iwata *et al.* have reported the synthesis of *(Z)*-vinyl sulfones through the iodosulfonylation of 1-alkynes (Scheme 29).[21]




$R = Ph(CH_2)_2$ i. $p\text{-}TolSO_2Na.4H_2O$, $I_2$, $EtOAc\text{-}H_2O$ (2:1), rt, 1 d
ii. $H_2$, 5% Pd-C, AcONa, rt, 5 h

**Scheme 29**

Recently, Huang *et al.* have reported a facile regio- and stereocontrolled synthesis of *E*-disubstituted vinyl sulfones *via* the reaction of alkenyl zirconocenes with sulfonyl chlorides (Scheme 30).[34]

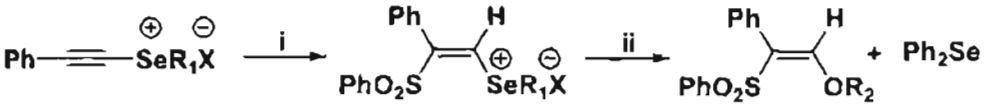



25 75 76 (78%)

R = Ph i. $Cp_2Zr(H)Cl$, THF, rt, 0.5-1 h ii. $R_1SO_2Cl$, 40 °C, 1.5-3 h

**Scheme 30**

Kataoka *et al.* have reported a simple stereoselective synthesis of *(Z)*-vinyl sulfones using a novel approach (Scheme 31).[35] The treatment of alkynylselenonium salt with benzenesulfinic acid in isopropanol gives *(Z)*-*β*-sulfonylvinylselenonium salt in good yield. The alkenylselenonium salts thus prepared react with nucleophiles such as alkoxides, halides and acetylides to yield *β*-functionalized *(Z)*-vinyl sulfones in high yields.

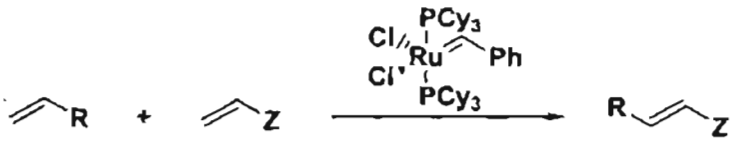



77 78 79 (76%)

i. $PhSO_2Na$, $^iPrOH$, rt, 2 h ii. $R_2ONa$, $R_2OH$, rt, 3 h

**Scheme 31**

Grela *et al.* have reported the cross metathesis reaction between functionalized olefins and phenyl vinyl sulfone by using the Grubbs' catalyst (Scheme 32).[36]

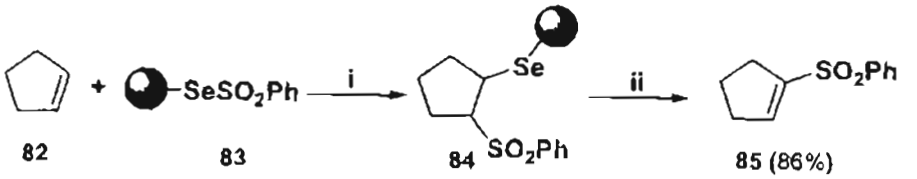



19 80 81

R = Ph Z = $CO_2R$, CHO, COR, CN, $SO_2Ph$

**Scheme 32**

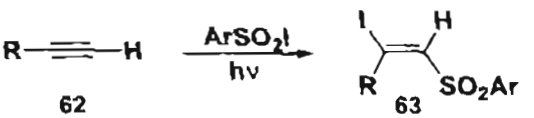
Very recently, it has been reported that polystyrene-supported selenosulfonates serve as efficient reagents for regio-and stereocontrolled synthesis of vinyl sulfones (Scheme 33).[37]




**Scheme 33**

### 2.2.3 Synthesis of β-Iodovinyl sulfones

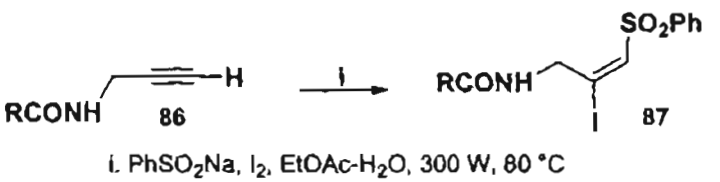
Truce *et al.* have reported that sulfonyl iodides add readily and stereoselectively to acetylenes to form 1:1 adducts in good to excellent yields, the addition occurs in a *trans* manner (Scheme 34).[16c]




**Scheme 34**

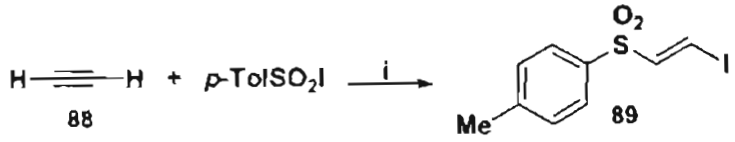
Julia *et al.* have reported the formation of β-iodosulfones from olefins (Scheme 28).[24] Also, Iwata *et al.* have reported the iodosulfonylation of 1-alkynes (Scheme 29).[21]

Short and Ziegler have reported that *N*-propargylamides when reacted with sodium sulfinate and iodine under photolytic conditions afforded iodovinyl sulfone (Scheme 35).[38]




**Scheme 35**

Very recently, Zoller and Uguen have reported an efficient preparartion of *E*-$\beta$-iodovinyl phenyl sulfone from alkynes (Scheme 36).[39]




i. EtOAc, -78 °C-rt, 5 d, 45%

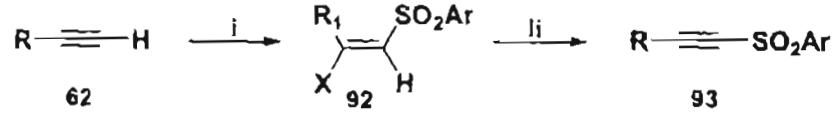
**Scheme 36**

## 2.2.4 Synthesis of Acetylenic Sulfones

Acetylenic sulfones are well recognized as useful reagents in organic synthesis.[40]The earliest procedure for preparing acetylenic sulfones involved oxidation of the corresponding sulphide wth *m*CPBA (Scheme 37).[41]


**Scheme 37**

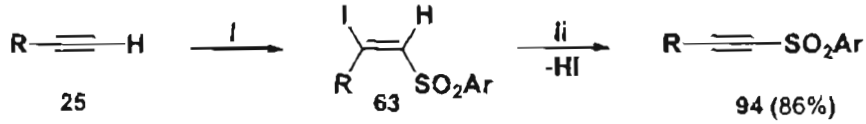
The free radical addition of sulfonyl chlorides,[16a,42] bromides[43] and iodides[16c,44] to terminal acetylenes was exploited to produce $\beta$-halovinyl sulfones, which underwent dehydrohalogenation with a base such as triethylamine to afford acetylenic sulfones (Scheme 38).




i. $RSO_2X$, $CuX_2$ ii. Triethylamine

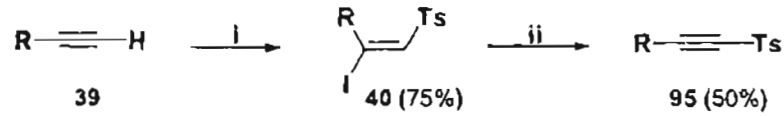
**Scheme 38**

Truce *et al.* have reported the synthesis of acetylenic sulfones from 1-alkynes (Scheme 39).[16c]



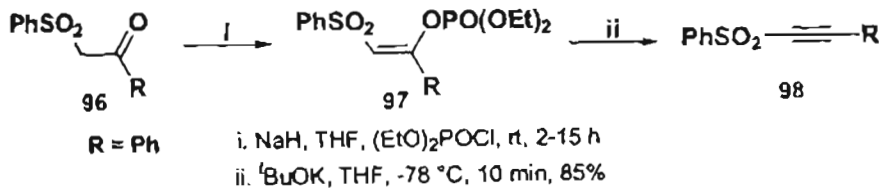

**Scheme 39**

Iwata *et al.* have used a related strategy for the synthesis of acetylenic sulfones and it is shown in Scheme 40.[21]



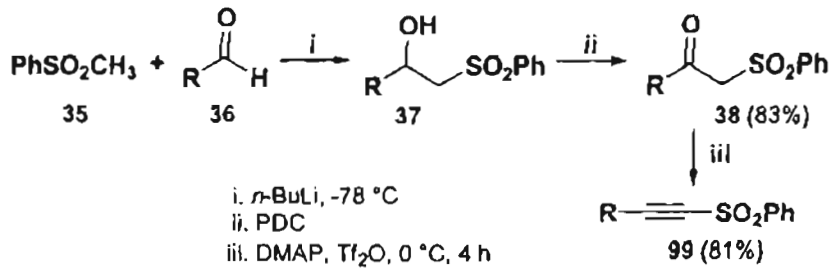

**Scheme 40**

The conversion of *β*-ketosulfones to acetylenic sulfones as shown in Scheme 41 was reported by Oh.[45]



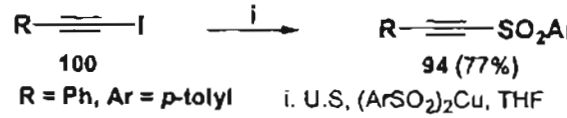

**Scheme 41**

Craig and Clasby have reported a convenient method for the preparation of acetylenic sulfones from *β*-ketosulfones which is illustrated in Scheme 42.[20]



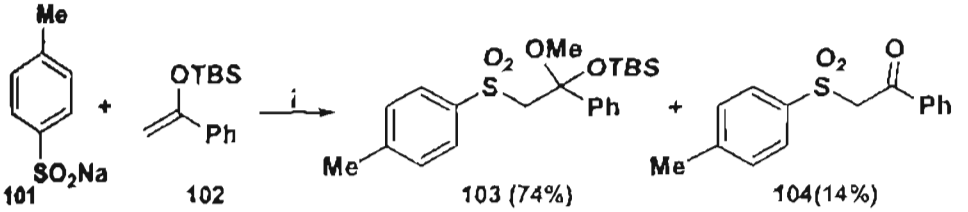

**Scheme 42**

Very recently, Suzuki and Abe have reported a new synthesis of alkynyl sulfones *via* the sonochemical coupling between alkynyl halides and copper sulfinates (Scheme 43).[46]




**Scheme 43**

Alhough a sulfonyl radical can be generated from the corresponding sulfinic acid by one-electron oxidation,[47] the synthetic utility of such an oxidative method has not been demonstrated. Recently, Narasaka *et al.* have reported briefly that sulfonyl radicals can be generated from sodium sulfinates under mild reaction conditions by the use of metallic oxidants like Manganese(III)-2-pyridine carboxylate($Mn(pic)_3$) and Tetrabutyl ammonium cerium(IV) nitrate(TBACN) which are found to react with olefinic compounds (Scheme 44).[48]

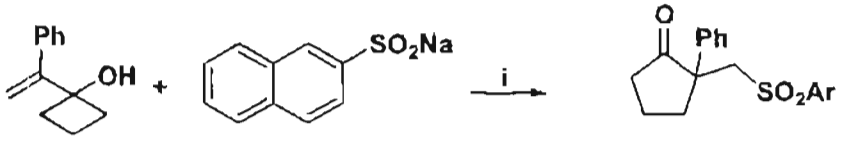



101 102 103 (74%) 104(14%)

*i.* TBACN, $K_2CO_3$, MeOH, 0 °C, overnight

**Scheme 44**

They have also reported the sulfonylation of 1-vinyl cyclic alcohols by utilizing CAN mediated oxidation of naphthalenesulfinate (Scheme 45).[49]




105 106 107 (90%)

i. CAN, $CH_3CN$, 0 °C, 2 h Ar = 2-Naphthyl

**Scheme 45**

## 2.3 STATEMENT OF THE PROBLEM

A complete survey of the literature revealed that despite the known methods of generation of sulfonyl radical from sulfinate, its synthetic utility has not been explored in detail. With the premise that the reaction can give rise to $\alpha$-sulfonyl-$\beta$-nitrato compounds that can serve as precursors of vinyl sulfones, it

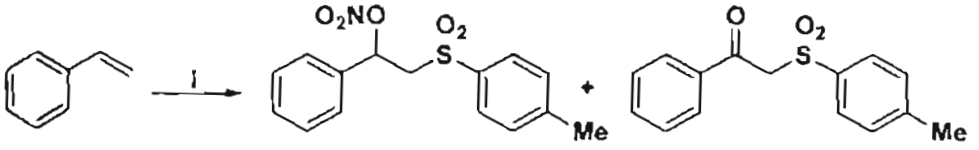
was considered worthwhile to undertake a detailed investigation in this area. The results of our investigations are presented in the following section.

## 2.4 RESULTS AND DISCUSSION

Against the literature background presented above, we have undertaken a systematic investigation of the Cerium(IV) ammonium nitrate (CAN) mediated addition of sulfinate to styrenes and acetylenes and the results are presented here. This section is divided mainly into three parts. First part deals with the sulfonylation of styrenes and the second part describes the one-pot synthesis of vinyl sulfones. The third part focusses on the synthesis of acetylenic sulfones.

### 2.4.1 Sulfonylation of Styrenes

Our studies were initiated with the reaction of styrene and sodium *p*-toluenesulfinate. A suspension of sodium *p*-toluenesulfinate and styrene **19** in acetonitrile on treatment with a solution of CAN in the same solvent, afforded the products **108** and **104** in 61% and 22% yields respectively (Scheme 46).




**19** **108 (61%)** **104 (22%)**

i. *p*-TolSO$_2$Na, CAN, CH$_3$CN, rt, 40 min

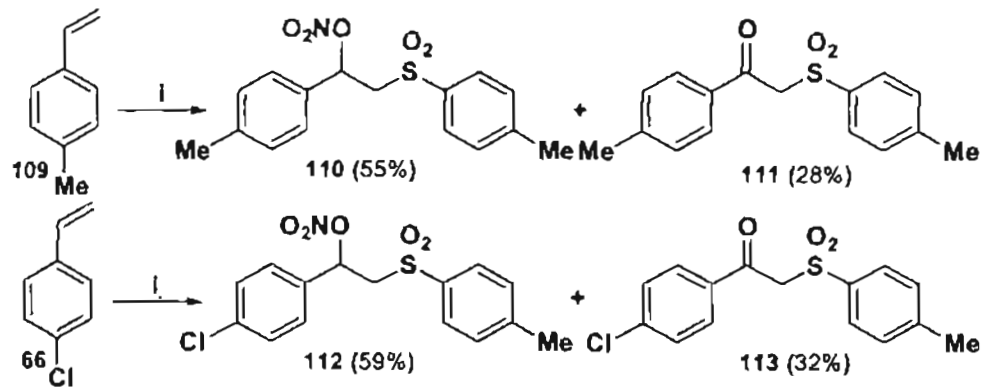
**Scheme 46**

The products were purified by silica gel column chromatography and characterized by the usual spectroscopic methods. The IR spectrum of **108** showed the characteristic absorption of $ONO_2$ group at 1645 cm$^{-1}$. The absorptions due to $SO_2$ group were visible at 1314 and 1145 cm$^{-1}$. In the $^1$H NMR spectrum, the benzylic proton resonated at δ 6.34 as doublet of a doublet ($J$ = 3.4 Hz, $J$ = 9.3 Hz). The two protons on the terminal carbon gave two

double doublets at δ 3.80 ($J$ = 9.3 Hz, $J$ = 15.0 Hz) and at δ 3.47 ($J$ = 3.4 Hz, $J$ = 15.0 Hz). A singlet observed at δ 2.40 was attributed to the $CH_3$ protons. In the $^{13}C$ NMR spectrum, the signal due to the benzylic carbon was visible at δ 78.82 and the methylene carbon resonated at δ 59.32. All other signals were in agreement with the assigned structure. The structure was further supported by analytical data.

The IR spectrum of **104** showed the characteristic absorption of benzoyl group at 1682 $cm^{-1}$. The absorptions visible at 1320 and 1148 $cm^{-1}$ were attributed to the $SO_2$ group. In the $^1H$ NMR spectrum, the $CH_2$ protons appeared as a singlet at δ 4.68. The $CH_3$ protons appeared as a singlet at δ 2.45. In the $^{13}C$ NMR spectrum, the carbonyl carbon was discernible at δ 187.86 and the $CH_2$ carbon appeared at δ 63.56. Analytical data further supported the integrity of the compound.

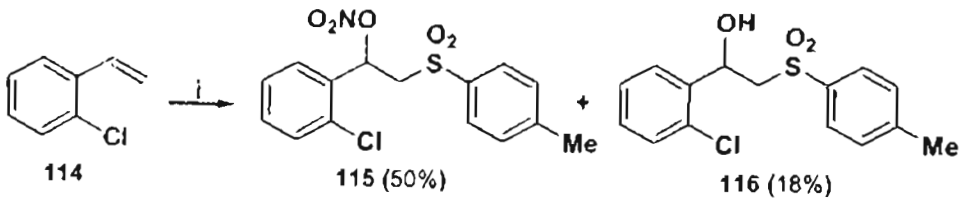
4-methylstyrene **109**, and 4-chlorostyrene **66** afforded the corresponding nitratosulfones **110**, **112** and ketosulfones **111**, **113** under similar reaction conditions (Scheme 47). The products were characterized on the basis of spectroscopic data.




i. *p*-TolSO$_2$Na, CAN, $CH_3CN$, rt, 40 min

**Scheme 47**

However, the reaction of 2-chlorostyrene **114** proceeded somewhat differently, affording the 2-hydroxy compound **116** in addition to the 2-nitrato compound **115** as shown in Scheme 48. No ketosulfone was obtained in this reaction.




**114** **115** (50%) **116** (18%)

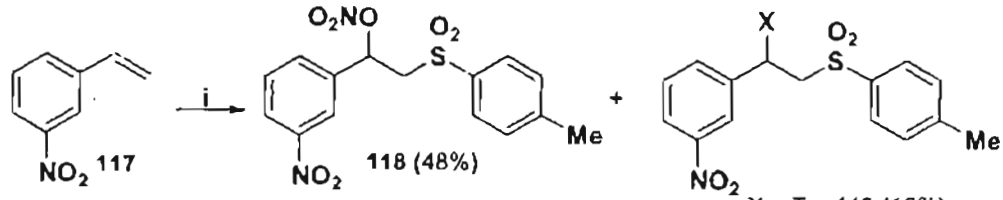
i. *p*-TolSO$_2$Na, CAN, CH$_3$CN, rt, 40 min

**Scheme 48**

In the IR spectrum of **115**, the absorption due to $ONO_2$ group was visible at 1645 cm$^{-1}$. In the $^1$H NMR spectrum, the benzylic proton resonated at δ 6.71 as doublet of a doublet ($J$ = 2.3 Hz, $J$ = 9.8 Hz). The two double doublets at δ 3.68 ($J$ = 9.8 Hz, $J$ = 15.2 Hz) and at δ 3.49 ($J$ = 2.3 Hz, $J$ = 15.2 Hz) were attributed to the methylene protons ($CH_2SO_2$). The $CH_3$ protons were visible as a singlet at δ 2.43. In the $^{13}$C NMR spectrum, the signal at δ 75.17 was attributed to the benzylic carbon and the methylene carbon resonated at δ 57.86. The methyl carbon signal appeared at δ 21.38. All other signals were in agreement with the assigned structure.

The IR spectrum of **116** showed strong absorption due to OH at 3505 cm$^{-1}$. In the $^1$H NMR spectrum, the benzylic proton appeared as a doublet at δ 5.41 ($J$ = 9.8 Hz) and one of the $CH_2$ protons appeared as a doublet at δ 3.48 ($J$ =14.6 Hz) and the other as doublet of a doublet at δ 3.24 ($J$ = 9.8 Hz, $J$ = 14.6 Hz) respectively. The OH proton appeared as a broad singlet at δ 4.52 (exchangeable with $D_2O$). In the $^{13}$C NMR spectrum, the benzylic carbon appeared at δ 65.42 and the methylene carbon at δ 61.85.

The reaction of 3-nitrostyrene **117** with *p*-toluenesulfinate in the presence of CAN in acetonitrile afforded the *β*-nitratosulfone **118** along with the disulfinate **119** and *β*-hydroxysulfone **120** as presented in Scheme 49.



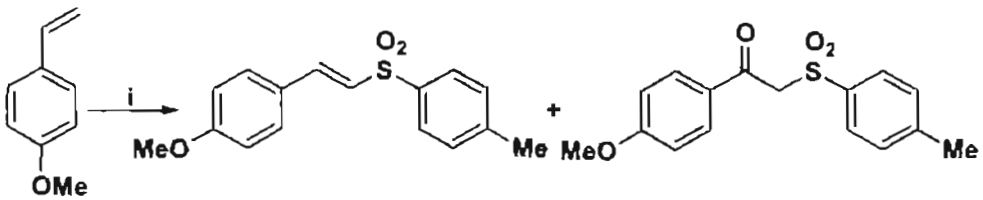

**Scheme 49**

The IR spectrum of **118** showed the characteristic absorption of $ONO_2$ group at 1645 $cm^{-1}$. The absorptions due to $SO_2$ group were visible at 1351 and 1145 $cm^{-1}$. In the $^1H$ NMR spectrum, the benzylic proton resonated at δ 6.41 as doublet of a doublet ($J$ = 4.5 Hz, $J$ = 8.2 Hz). The methylene protons appeared as two double doublets at δ 3.79 ($J$ = 8.4 Hz, $J$ = 14.9 Hz) and at δ 3.52 ($J$ = 4.5 Hz, $J$ = 14.9 Hz). A singlet observed at δ 2.46 was attributed to the $CH_3$ protons. In the $^{13}C$ NMR spectrum, the benzylic carbon was visible at δ 77.26 and the methylene carbon resonated at δ 58.99. All other signals were in agreement with the assigned structure.

In the IR spectrum of **119** the absorptions due to $SO_2$ group were visible at 1351 and 1145 $cm^{-1}$. In the $^1H$ NMR spectrum, the benzylic proton resonated at δ 4.64 as doublet of a doublet ($J$ = 2.0 Hz, $J$ = 11.7 Hz). The methylene protons gave two double doublets; one at δ 4.06 ($J$ = 2.1 Hz, $J$ = 14.3 Hz) and the other at δ 3.92 ($J$ = 11.7 Hz, $J$ = 14.3 Hz). The singlets observed at δ 2.42 and δ 2.35 were attributed to the $CH_3$ protons. In the $^{13}C$ NMR spectrum, the benzylic carbon appeared at δ 63.47 and the methylene carbon resonated at δ 51.84. All other signals were in agreement with the assigned structure.

In the IR spectrum of **120** the absorptions due to $SO_2$ group were visible at 1309 and 1151 $cm^{-1}$ and the absorption due to OH group appeared at 3440 $cm^{-1}$. In the $^1H$ NMR spectrum, the benzylic proton resonated at δ 5.37 as a doublet ($J$ = 9.8 Hz). The broad singlet at δ 4.10 was attributed to the OH proton (exchangeable with $D_2O$). The methylene protons appeared as a multiplet centered at δ 3.40. The singlet observed at δ 2.47 was attributed to the $CH_3$ protons. In the $^{13}C$ NMR spectrum, the benzylic carbon appeared at δ 66.65 and the methylene carbon resonated at δ 63.04. The $CH_3$ carbon appeared at δ 20.80. All other signals were in agreement with the assigned structure

The reaction of 4-methoxystyrene **121** with *p*-toluenesulfinate in the presence of CAN in acetonitrile afforded the vinyl sulfone **122** along with the β-ketosulfone **123** as presented in Scheme 50.




**121** **122** (40%) **123** (20%)

i. *p*-TolSO$_2$Na, CAN, CH$_3$CN, rt, 40 min

**Scheme 50**

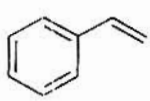
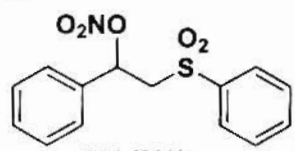
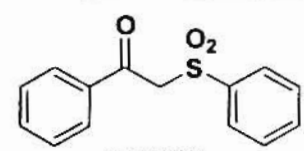
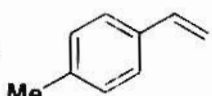
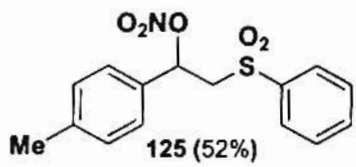
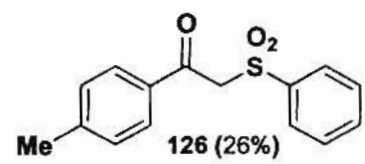
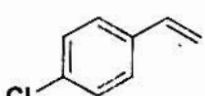
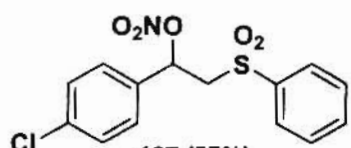
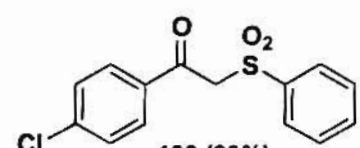
The IR spectrum of **122** showed the characteristic absorptions of $SO_2$ group at 1308 and 1142 $cm^{-1}$. In the $^1H$ NMR spectrum, the olefinic protons resonated as doublets at δ 7.57 ($J$ = 15.3 Hz) and at δ 6.68 ($J$ = 15.3 Hz) respectively. The peaks at δ 3.80 and δ 2.44 were attributed to the OMe and Me protons respectively. In the $^{13}C$ NMR spectrum, the signals at δ 55.06 and 21.32 were attributed to the $OCH_3$ and $CH_3$ carbons and all other signals were in agreement with the assigned structure.

In the IR spectrum of **123**, the carbonyl absorption was visible at 1672 $cm^{-1}$. In the $^1H$ NMR spectrum, the $CH_2$ protons appeared as a singlet at δ 4.63.

Also, the signals at δ 3.86 and δ 2.43 were attributed to the $OCH_3$ and $CH_3$ protons respectively. In the $^{13}C$ NMR spectrum, the carbonyl carbon resonated at δ 186.15 and the signals corresponding to the $OCH_3$ and $CH_3$ carbons were visible at δ 55.44 and δ 21.65 respectively.

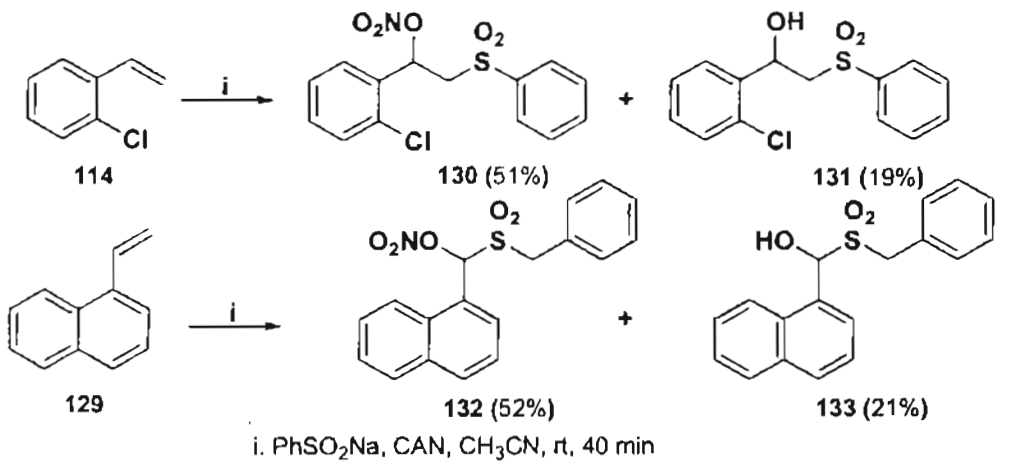
In order to examine the genarality of the reaction, we carried out some experiments with benzenesulfinate and the results are summarized in Table 1. The products were characterized by the usual spectroscopic methods.

**Table 1**: Sulfonylation of Styrenes

| Entry | Substrate | Products/Yield (%)[a] | |
|---|---|---|---|
| 1 |  19 |  124 (56%) |  44 (20%) |
| 2 |  109 |  125 (52%) |  126 (26%) |
| 3 |  66 |  127 (57%) |  128 (28%) |

[a] Reaction Conditions: $PhSO_2Na$, CAN, $CH_3CN$, rt, 40 min

The reaction of 2-chlorostyrene **114** with benzenesulfinate in the presence of CAN in acetonitrile afforded the nitratosulfinate **130** along with the β-hydroxysulfone **131**. Similar results were obtained with 1-vinylnaphthalene also as shown in Scheme 51.




i. $PhSO_2Na$, CAN, $CH_3CN$, rt, 40 min

**Scheme 51**

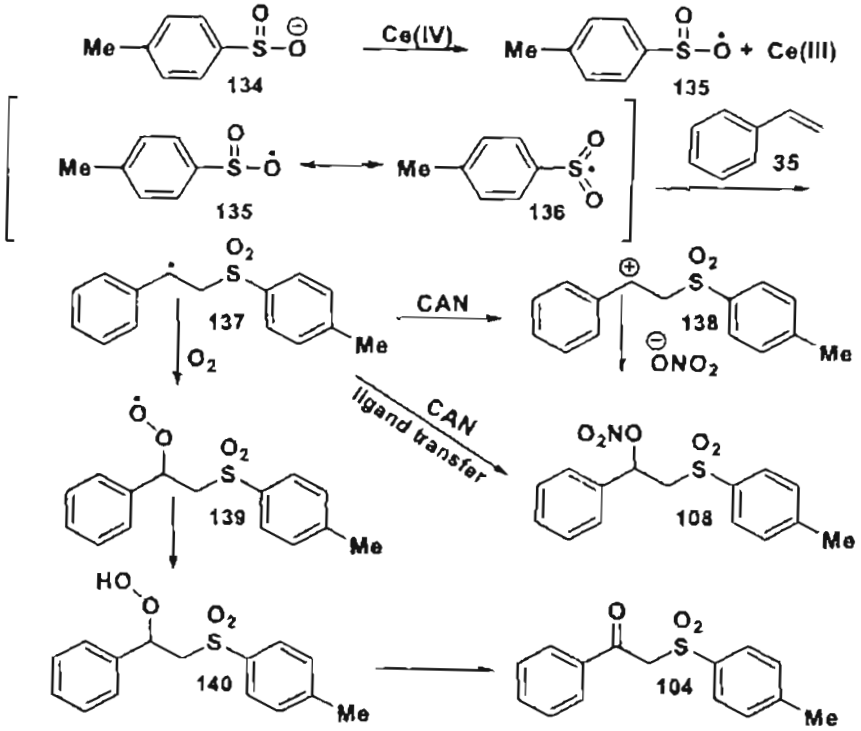
The IR spectra of both **130** and **132** showed strong absorption due to $ONO_2$ at 1651 and 1643 $cm^{-1}$ respectively. In the $^1H$ NMR spectrum of **130**, the benzylic proton appeared as doublet of a doublet at δ 6.71 ($J$ = 2.5 Hz, $J$ = 9.8 Hz). In the $^{13}C$ NMR spectrum, the benzylic carbon appeared at δ 75.19 and the $CH_2$ carbon at δ 58.01. In the $^{13}C$ NMR spectrum of **132**, the benzylic carbon appeared at δ 75.80 and the $CH_2$ carbon at δ 59.21.

The IR spectra of both the β-hydroxysulfones **131** and **133** showed strong absorption due to OH at 3501 $cm^{-1}$. In the $^1H$ NMR spectrum of **131**, the benzylic proton appeared as a doublet at δ 5.43 ($J$ = 9.8 Hz) and one of the $CH_2$ protons resonated as a doublet at δ 3.44 ($J$ = 14.4 Hz) and the other as doublet of a doublet at δ 3.28 ($J$ = 9.9 Hz, $J$ = 14.4 Hz). The OH proton resonated as a broad singlet at δ 4.55 (exchangeable with $D_2O$). In the $^{13}C$ NMR spectrum, the benzylic carbon appeared at δ 65.29 and the $CH_2$ carbon at δ 61.76.

In the $^1H$ NMR spectrum of **133**, the OH proton was visible as a broad singlet at δ 3.95 (exchangeable with $D_2O$). In the $^{13}C$ NMR spectrum, the benzylic carbon was discernible at δ 65.05.

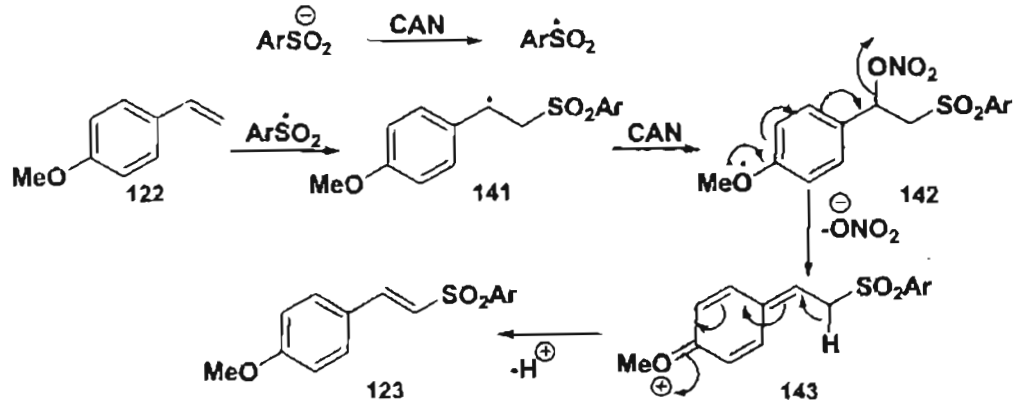
## 2.4.2 Mechanistic Considerations

The reaction can be rationalized along the lines depicted in Scheme 52. An oxygen centered radical generated by the oxidation of sulfinate with CAN resonates with a sulfonyl radical. This radical adds to styrene to give a benzylic radical **137** which is quenched by molecular oxygen to form the peroxy intermediate and which undergoes further transformations to give the keto product **104**. The product **108** can arise by ligand transfer of nitrate from CAN. Alternatively, CAN can oxidize the benzylic radical to the cation which combines with nitrate anion to form **108**.




**Scheme 52**

A mechanistic rationalization for the formation of the vinyl sulfone **123** can be given as shown in Scheme 53. The sulfonyl radical adds to 4-methoxystyrene **122** to form the benzylic radical which is then converted to the $\alpha$-sulfonyl-$\beta$-nitrato compound **142**. This can undergo spontaneous elimination of nitric acid to form the vinyl sulfone.

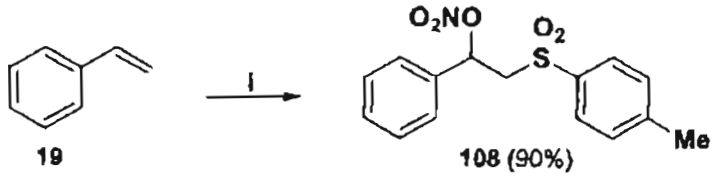



Scheme 53

### 2.4.3 Sulfonylation of Styrenes Under Argon Atmosphere: Synthesis of α-Sulfonyl-β-Nitrato Compounds

Since the ketoproduct is formed by the trapping of oxygen by the benzylic radical (*vide infra*), we expected that the nitrato product would be formed predominantly, if the reactions were carried out in a deoxygenated atmosphere. Accordingly, we performed the reaction in an atmosphere of argon and the results are described in the following paragraphs.

When a mixture of sodium *p*-toluenesulfinate and styrene **19** in anhydrous acetonitrile was treated with a solution of CAN in the same solvent in a deoxygenated atmosphere, a reaction leading to the exclusive formation of the β-nitrato product **108** in 90% yield occurred (Scheme 54).

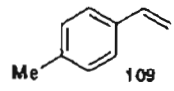
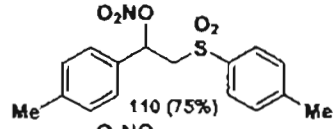
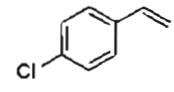
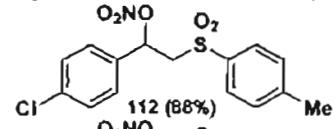
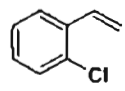
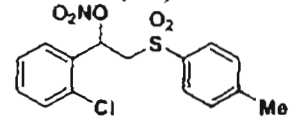
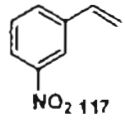
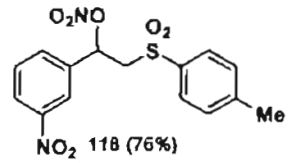
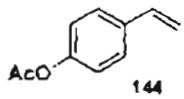
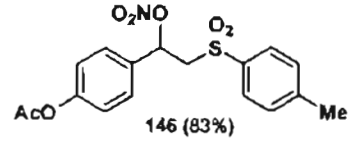
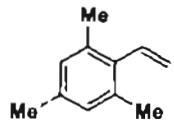
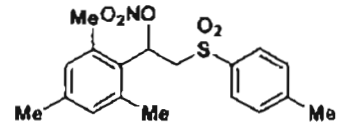



I. *p*-TolSO$_2$Na, CAN, dry CH$_3$CN, argon, rt, 40 min

Scheme 54

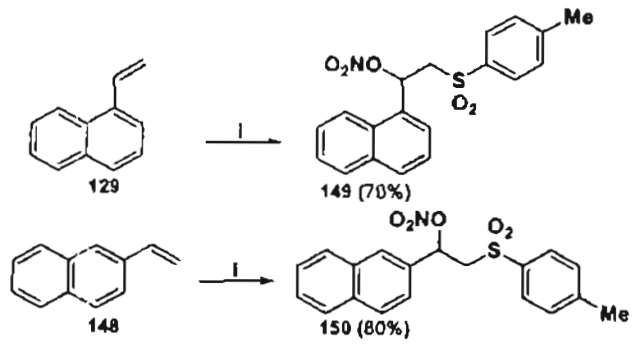
Similar reactions were observed with 4-methylstyrene **109**, 4-chlorostyrene **66**, 2-chlorostyrene **114**, 3-nitrostyrene **117**, 4-acetoxystyrene **144** and mesitylstyrene **145** and the results are summarized in Table 2.

**Table 2:** Sulfonylation of Styrenes Under Argon Atmosphere

| Entry | Substrate | Products/Yield (%)[a] |
|---|---|---|
| 1 |  109 |  110 (75%) |
| 2 |  66 |  112 (88%) |
| 3 |  114 |  115 (72%) |
| 4 |  117 |  118 (76%) |
| 5 |  144 |  146 (83%) |
| 6 |  145 |  147 (65%) |

[a] Reaction Conditions: *p*-TolSO$_2$Na, CAN, dry CH$_3$CN, argon, rt, 40 min

Analogous reactivity was observed with vinylnaphthalenes and the results are presented in Scheme 55.

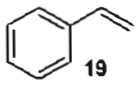
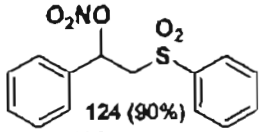
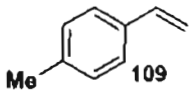
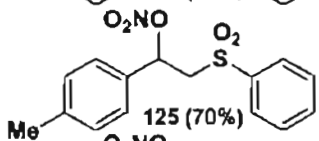
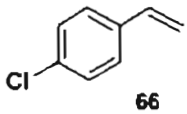
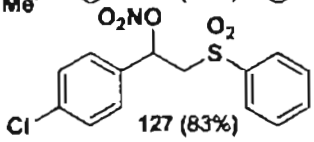
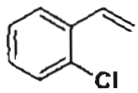
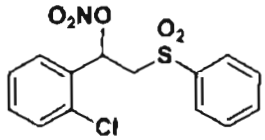
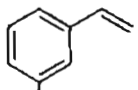
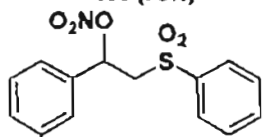
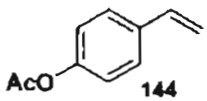
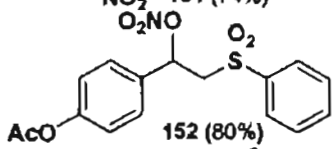
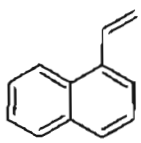
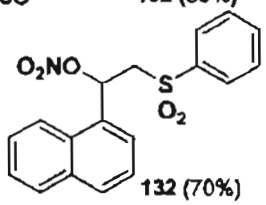
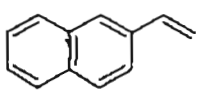
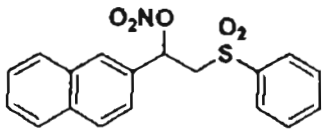



i. *p*-TolSO$_2$Na, CAN, dry CH$_3$CN, argon, rt, 40 min

Scheme 55

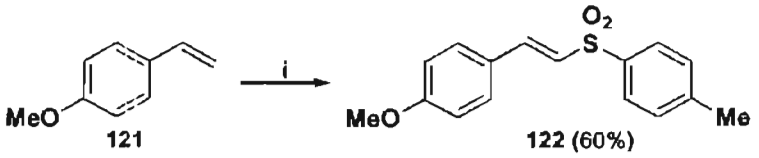
Similar results were obtained when the reaction was carried out with sodium benzenesulfinate and these are summarized in Table 3.

**Table 3:** Synthesis of $\alpha$-Sulfonyl-$\beta$-Nitrato Compounds

| Entry | Substrate | Products/Yield (%)[a] |
|---|---|---|
| 1 |  19 |  124 (90%) |
| 2 |  109 |  125 (70%) |
| 3 |  66 |  127 (83%) |
| 4 |  114 |  130 (76%) |
| 5 |  117 |  151 (74%) |
| 6 |  144 |  152 (80%) |
| 7 |  129 |  132 (70%) |
| 8 |  148 |  153 (76%) |

[a] Reaction Conditions: $PhSO_2Na$, CAN, dry $CH_3CN$, argon, rt, 40 min

The reaction of 4-methoxystyrene with *p*-toluenesulfinate in the presence of CAN in acetonitrile under these conditions afforded the vinyl sulfone **122** (Scheme 56).




i. *p*-TolSO$_2$Na, CAN, dry CH$_3$CN, argon, rt, 40 min

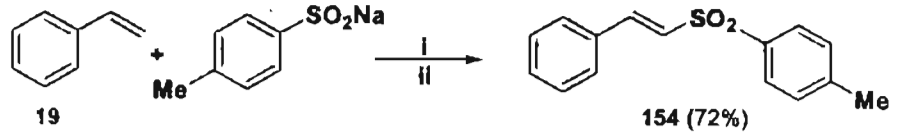
**Scheme 56**

Intrigued by the possibility of transforming the *β*-nitratosulfone to vinyl sulfone, we exposed **108** to potassium carbonate in refluxing anhydrous acetone. In the event, the nitrato compound was smoothly converted to the vinyl sulfone **154** (Scheme 57).


i. K$_2$CO$_3$, dry acetone, reflux, 2h, 85%

**Scheme 57**

Prompted by the success of the above reaction we attempted a one-pot conversion in which the crude product derived from the CAN induced addition of sulfinate to styrene (Scheme 54) was refluxed with potassium carbonate in anhydrous acetone at 65 °C for 3 h, when it was converted to the corresponding vinyl sulfone **154** (Scheme 58).



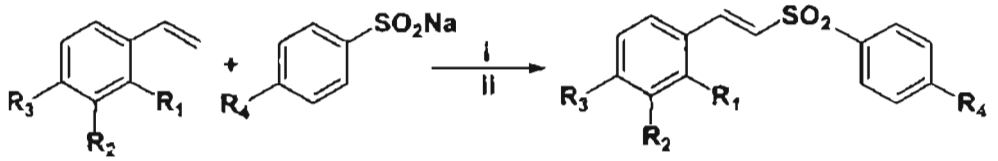

i. CAN, dry CH$_3$CN, argon, rt, 45 min
ii. K$_2$CO$_3$, acetone, 65 °C, 3h

**Scheme 58**

The IR spectrum of the product **154** showed the characteristic absorptions due to $SO_2$ group at 1301 and 1143 $cm^{-1}$. In the $^1H$ NMR spectrum, the olefinic protons appeared as doublets at δ 7.64 (J = 15.4 Hz) and δ 6.82 (J = 15.4 Hz). The signal at δ 2.44 was attributed to the $CH_3$ protons. All other signals were in agreement with the assigned structure. The $^{13}C$ NMR spectrum was also in complete agreement with the assigned structure. Elemental analysis also lent support for the integrity of the compound.

The reaction was found to be general with various substituted styrenes and the results are summarized in Table 4.

**Table 4** Synthesis of Vinyl Sulfones

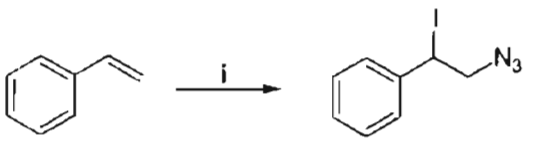



i. CAN, dry $CH_3CN$, argon, rt, 45 min
ii. $K_2CO_3$, acetone, 65 °C, 3h

| Entry | Substrate | $R_1$ | $R_2$ | $R_3$ | $R_4$ | Products/Yield (%) | |
|---|---|---|---|---|---|---|---|
| 1 | **19** | H | H | H | H | **31** | 66 |
| 2 | **109** | H | H | Me | Me | **155** | 75 |
| 3 | **109** | H | H | Me | H | **156** | 58 |
| 4 | **66** | H | H | Cl | Me | **157** | 51 |
| 5 | **66** | H | H | Cl | H | **158** | 46 |
| 6 | **114** | Cl | H | H | Me | **159** | 41 |
| 7 | **114** | Cl | H | H | H | **160** | 40 |
| 8 | **117** | H | $NO_2$ | H | Me | **161** | 38 |
| 9 | **117** | H | $NO_2$ | H | H | **162** | 36 |
| 10 | **129** | 1-naphthyl | | | Me | **163** | 38 |
| 11 | **148** | 2-naphthyl | | | H | **164** | 50 |

### 2.4.4 One-Pot Synthesis of Vinyl Sulfones Mediated by Cerium(IV) Ammonium Nitrate(CAN)

Oxidative addition of soft anions to alkenes mediated by Cerium(IV) ammonium nitrate has recently been shown to offer a practical method for carbon-heteroatom (C-N, C-S, C-Br *etc*) bond formation (see **Chapter 1**). In view of the success of these reactions and in the context of our recent observation of a very efficient azidoiodination[50] (Scheme 59), we surmised that CAN mediated addition of sulfinate and iodine to alkenes would lead to iodo sulfones, which are versatile intermediates in organic synthesis.

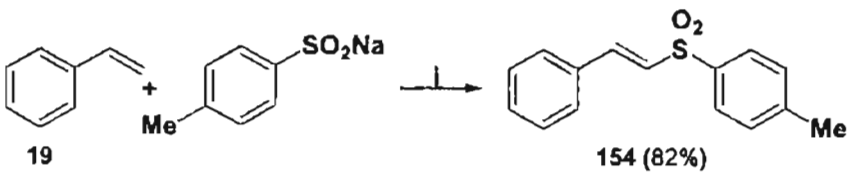



**19** **165**

i. CAN, NaI, $NaN_3$, MeOH, 0 °C, 30 min, 71%

**Scheme 59**

With the expectation as stated above, a mixture of styrene, *p*-toluenesulfinate and sodium iodide in anhydrous acetonitrile was treated with a solution of CAN in the same solvent under deoxygenated atmosphere. A facile reaction occurred, but instead of the expected $\beta$-iodosulfone, the vinyl sulfone **154** was formed in 82% yield (Scheme 60).



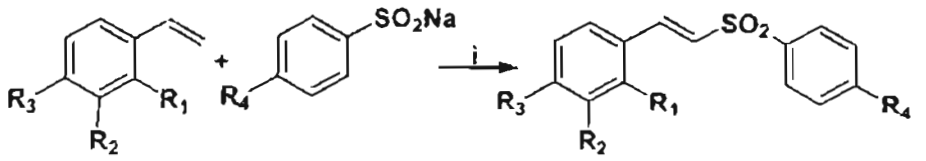

**19** **154 (82%)**

i. NaI, CAN, dry $CH_3CN$, argon, rt, 45 min

**Scheme 60**

Impressed by the efficiency of the reaction we extended it to a number of styrenes. The reaction was found to be general and the results are summarized in Table 5.

**Table 5:** One-pot Synthesis of Vinyl Sulfones



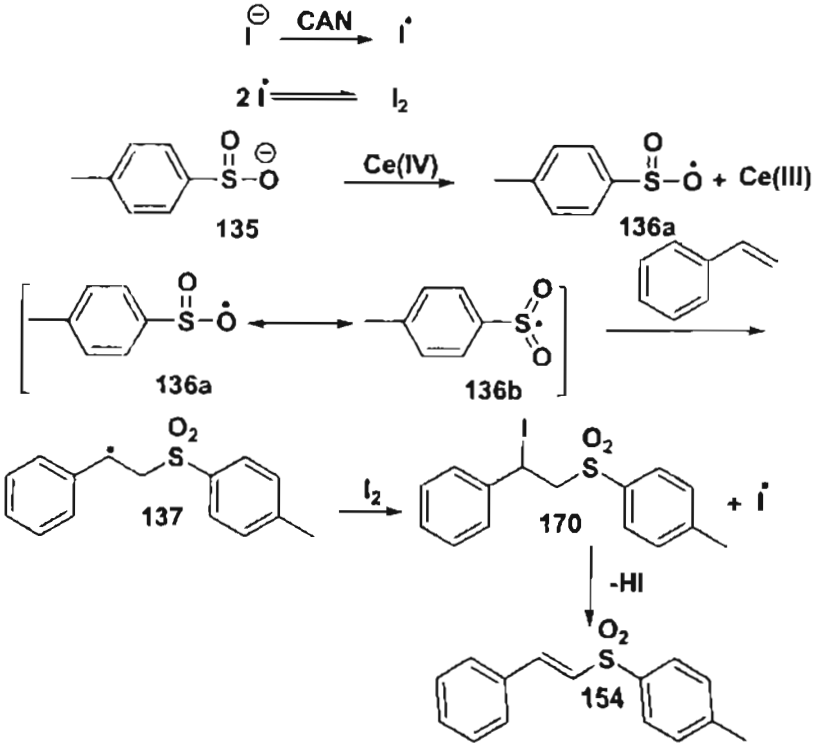

i. NaI, CAN, dry $CH_3CN$, argon, rt, 45 min

| Entry | Substrate | $R_1$ | $R_2$ | $R_3$ | $R_4$ | Products/yield(%) | |
|---|---|---|---|---|---|---|---|
| 1 | **19** | H | H | H | H | **31** | 76 |
| 2 | **109** | H | H | Me | Me | **155** | 83 |
| 3 | **109** | H | H | Me | H | **156** | 80 |
| 4 | **66** | H | H | Cl | Me | **157** | 88 |
| 5 | **66** | H | H | Cl | H | **158** | 85 |
| 6 | **114** | Cl | H | H | Me | **159** | 87 |
| 7 | **114** | Cl | H | H | H | **160** | 86 |
| 8 | **117** | H | $NO_2$ | H | Me | **161** | 80 |
| 9 | **117** | H | $NO_2$ | H | H | **162** | 81 |
| 10 | **144** | H | H | AcO | Me | **166** | 72 |
| 11 | **144** | H | H | AcO | H | **167** | 70 |
| 12 | **129** | 1-naphthyl | | | Me | **163** | 77 |
| 13 | **129** | 1-naphthyl | | | H | **168** | 76 |
| 14 | **148** | 2-naphthyl | | | Me | **169** | 70 |
| 15 | **148** | 2-naphthyl | | | H | **164** | 83 |

### 2.4.5 Mechanistic Considerations

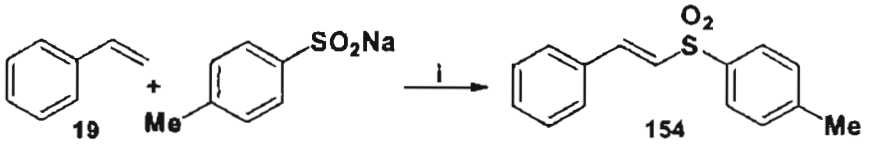
Mechanistically, the formation of the vinyl sulfone can be rationalized as shown in Scheme 61. An oxygen centered radical generated by the oxidation of sulfinate with CAN resonates with a sulfonyl radical. This radical adds to styrene to give a benzylic radical which is trapped by molecular iodine produced by the fast combination of two iodine radicals to give $\beta$-iodo sulfone.

Spontaneous elimination of a molecule of hydrogen iodide from this iodo sulfone would then afford the corresponding vinyl sulfone.




**Scheme 61**

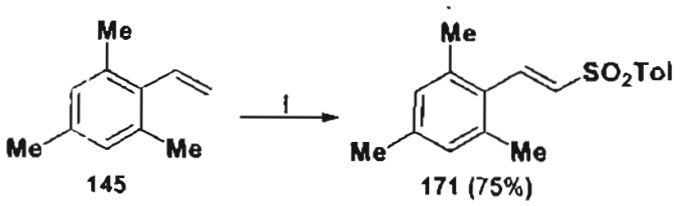
In order to obtain support for the suggested mechanism, we carried out the reaction of styrene with *p*-toluenesulfinate and iodine, which resulted in the formation of the vinyl sulfone in low yield (Scheme 62).




i. $I_2$, CAN, dry $CH_3CN$, rt, 45 min, 54%

**Scheme 62**

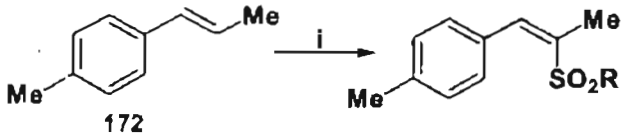
With mesitylstyrene also the reaction led to the formation of the corresponding vinyl sulfone (Scheme 63).




i. $p$-TolSO$_2$Na, NaI, CAN, dry CH$_3$CN, argon, rt, 45 min

**Scheme 63**

$\beta$-methylstyrene also showed similar reactivity as shown in Scheme 64.



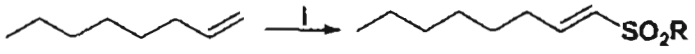

R = $p$-tolyl 173 (65%)
R = phenyl 174 (55%)

i. RSO$_2$Na, NaI, CAN, dry CH$_3$CN, argon, rt, 45 min

**Scheme 64**

With a view to examine the generality of the reaction, we have done some preliminary investigations on the sulfonylation of $n$-alkenes as well as cyclic alkenes.

The reaction of 1-octene with sodium $p$-toluenesulfinate in acetonitrile afforded the vinyl sulfone in 65% yield. Similar result was obtained with benzenesulfinate also (Scheme 65).




175

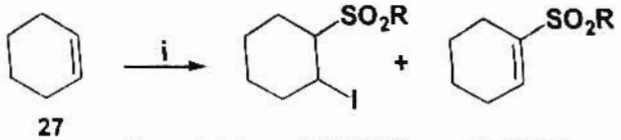
R = $p$-tolyl 176 (65%)
R = phenyl 177 (63%)

i. RSO$_2$Na, NaI, CAN, dry CH$_3$CN, argon, rt, 45 min

**Scheme 65**

The structures of the products were assigned on the basis of IR, $^1$H NMR and $^{13}$C NMR spectroscopic data.

Cyclohexene under similar reaction conditions afforded the cyclohexenyl sulfone along with the iodosulfone (Scheme 66).



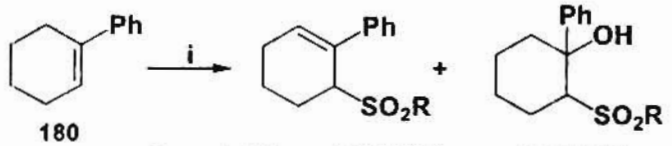

27

R = *p*-tolyl **178** (30%) **61** (25%)
R = phenyl **179** (28%) **54** (23%)

i. $RSO_2Na$, NaI, CAN, dry $CH_3CN$, argon, rt, 45 min

**Scheme 66**

However, phenylcyclohexene exhibited a different type of reactivity under similar reaction conditions affording the products shown in Scheme 67.



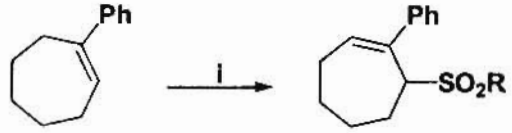

**180**

R = *p*-tolyl **181** (20%) **182** (55%)
R = phenyl **183** (10%) **184** (50%)

i. $RSO_2Na$, NaI, CAN, dry $CH_3CN$, argon, rt, 45 min

**Scheme 67**

The reaction of phenylcycloheptene resulted in the formation of the allylic sulfone as shown in Scheme 68.



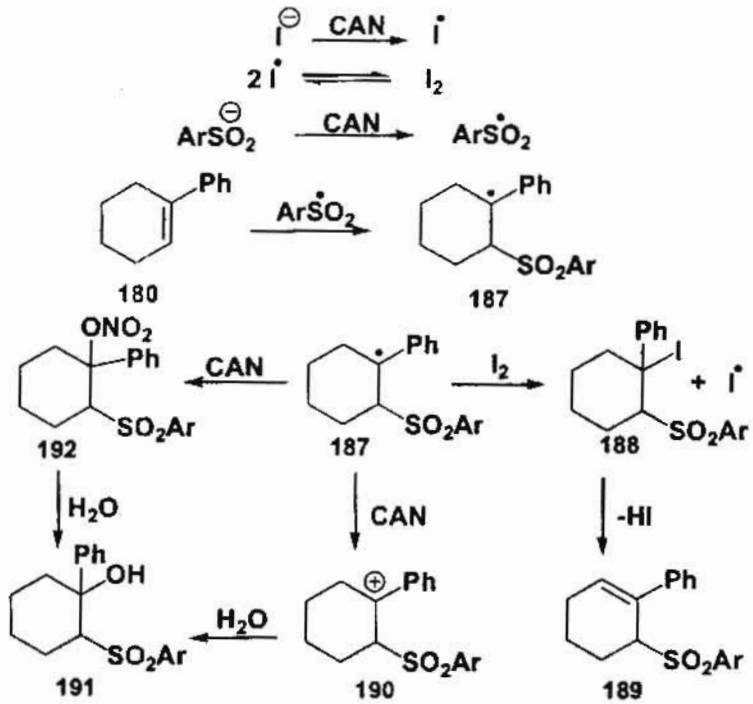

**185** R = *p*-tolyl **186** (52%)

i. $RSO_2Na$, NaI, CAN, dry $CH_3CN$, argon, rt, 45 min

**Scheme 68**

Invoking the mechanistic rationale presented earlier (*vide supra*), the initial event may be considered to be the formation of the benzylic radical from the arylcycloalkene and the sulfinate radical generated by the oxidation of sulfinate anion by CAN. This radical undergoes oxidation by CAN, followed by quenching of the resulting cation to afford **191**. Alternatively, the benzylic radical can be trapped by iodine, formed by the fast combination of iodine radicals, to form the $\beta$-iodo sulfone, which suffers the loss of a molecule of HI

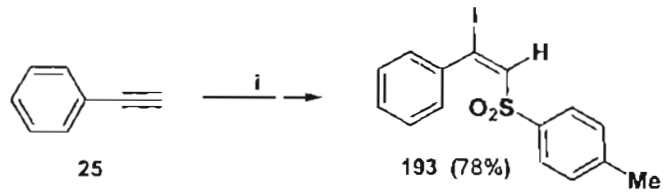
to form the allyl sulfone **189** (Scheme 69). The hydroxysulfone **191** can also be formed by the solvolysis of the nitrato compound **192**. It is also likely that some of the iodo compound **188** is undergoing solvolysis during work-up to give the carbinol **191** whereas part of it is undergoing elimination to give the allylic sulfone **189**.




**Scheme 69**

## 2.4.6 Synthesis of β–Iodovinyl Sulfones

As a logical extension of the work presented above, it was of interest to study the oxidative addition of sulfinate and iodine to alkynes. Our efforts were initiated by the reaction of phenyl acetylene with sodium *p*-toluenesulfinate and sodium iodide in the presence of CAN in acetonitrile to afford the β-iodovinyl sulfone in 78% yield (Scheme 70).



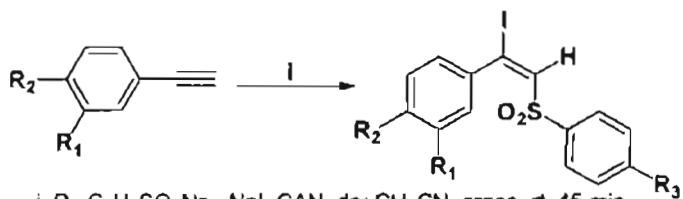

i. *p*-TolSO$_2$Na, NaI, CAN, dry CH$_3$CN, argon, rt, 45 min

**Scheme 70**

The product was purified by column chromatography on neutral alumina and was characterized by spectroscopic methods. The IR spectrum of the product **193** showed the characteristic absorptions due to $SO_2$ group at 1337 and 1155 cm$^{-1}$. In the $^1$H NMR spectrum, the peak corresponding to the olefinic proton was enveloped by the signals due to aromatic protons. The signal at δ 2.37 was attributed to the $CH_3$ protons. All other signals were in agreement with the assigned structure. In the $^{13}$C NMR spectrum the iodine bearing carbon resonated at δ 114.09 and the signal at δ 21.59 was attributed to the $CH_3$ carbon.

This reaction was found to be general as attested by the results presented in Table 6

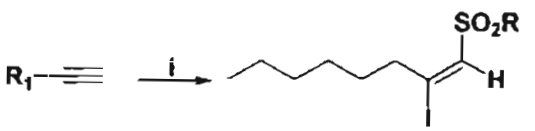
**Table 6:** Synthesis of *β*-Iodovinyl Sulfones




i. $R_3$-$C_6H_4SO_2Na$, NaI, CAN, dry $CH_3CN$, argon, rt, 45 min

| Entry | Substrate | $R_1$ | $R_2$ | $R_3$ | Products/Yield(%) | |
|---|---|---|---|---|---|---|
| 1 | **25** | H | H | H | **198** | 82 |
| 2 | **194** | H | Me | Me | **199** | 80 |
| 3 | **194** | H | Me | H | **200** | 79 |
| 4 | **195** | H | MeO | Me | **201** | 75 |
| 5 | **195** | H | MeO | H | **202** | 70 |
| 6 | **196** | MeO | H | Me | **203** | 68 |
| 7 | **197** | $NO_2$ | H | Me | **204** | 65 |
| 8 | **197** | $NO_2$ | H | H | **205** | 62 |

Similarly a normal alkyne such as 1-octyne when subjected to the same reaction afforded the iodovinyl sulfone as shown in Scheme 71. The product was characterized on the basis of spectroscopic data.



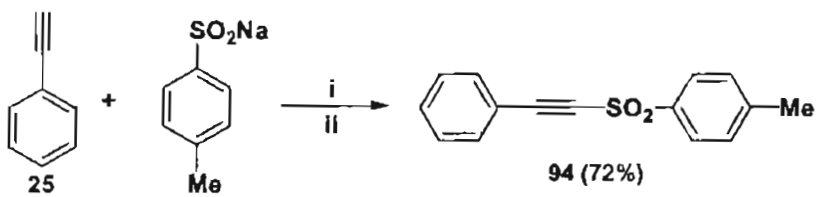

$R_1 = C_6H_{13}$ R = *p*-tolyl 207(65%)
206 R = phenyl 208 (60%)

i. $RSO_2Na$. NaI, CAN, dry $CH_3CN$, argon, rt, 45 min

**Scheme 71**

## 2.4.7 One-pot Synthesis of Acetylenic Sulfones

Following the synthesis of vinyl sulfones, we attempted the one-pot synthesis of acetylenic sulfones. In a prototype experiment the crude product derived from the reaction between phenyl acetylene and *p*-toluenesulfinate was refluxed with potassium carbonate in anhydrous acetone for 5 h; this resulted in the formation of acetylenic sulfone in 72% yield (Scheme 72).




i. NaI, CAN, dry $CH_3CN$, argon, rt, 45 min
ii. $K_2CO_3$, acetone, reflux, 5h

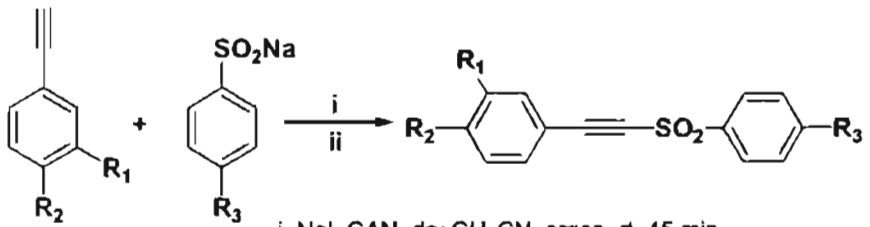
**Scheme 72**

The product **94** was purified by column chromatography on neutral alumina and was characterized by spectroscopic methods. Its IR spectrum showed the characteristic absorptions due to carbon-carbon triple bond at 2180 $cm^{-1}$ and the absorptions due to $SO_2$ group were visible at 1337 and 1162 $cm^{-1}$. In the $^1H$ NMR spectrum, the signal at $\delta$ 2.46 was attributed to the $CH_3$ protons. All other signals were in agreement with the assigned structure. In the $^{13}C$ NMR spectrum, the acetylenic carbon adjacent to the sulfone moiety resonated at

δ 92.76 while the other sp carbon resonated at δ 85.85. The signal at δ 21.77 was attributed to the $CH_3$ carbon. Elemental analysis provided support for the integrity of the compound.

Similar reactivity was observed with other substituted phenyl acetylenes and the results are summarized in Table 7.

**Table 7:** One-pot synthesis of Acetylenic Sulfones




i. NaI, CAN, dry $CH_3CN$, argon, rt, 45 min
ii. $K_2CO_3$, acetone, reflux, 5h

| Entry | Substrate | $R_1$ | $R_2$ | $R_3$ | Products/Yield(%) | |
|---|---|---|---|---|---|---|
| 1 | **25** | H | H | H | **98** | 68 |
| 2 | **194** | H | Me | Me | **209** | 75 |
| 3 | **194** | H | Me | H | **210** | 74 |
| 4 | **195** | H | MeO | Me | **211** | 75 |
| 5 | **195** | H | MeO | H | **212** | 70 |
| 6 | **196** | MeO | H | Me | **213** | 65 |

Interestingly, 1-octyne also underwent similar type of reaction as shown in Scheme 73.


$R_1 = C_6H_{13}$ **206** | **R = *p*-tolyl** **214 (60%)**

i. *p*-Tol$SO_2$Na, NaI, CAN, dry $CH_3CN$, argon, rt, 45 min
ii. $K_2CO_3$, acetone, reflux, 5h

**Scheme 73**

## 2.5 CONCLUSION

In conclusion, we have found that CAN serves as an excellent reagent for the oxidative addition of sulfinates to styrenes, other alkenes and acetylenes. This methodology offers a facile route to the synthesis of vinyl sulfones, $\beta$-iodovinyl sulfones and acetylenic sulfones which are useful intermediates in organic synthesis. The experimental simplicity and mild reaction conditions make these reactions particularly attractive.

## 2.6 EXPERIMENTAL DETAILS

### 2.6.1 General Experimental Procedure

All reactions were carried out in oven dried glassware. Melting points were recorded on MEL TEMP II melting point apparatus and were uncorrected. The IR spectra were recorded on Nicolet Impact 400D FT-IR and Bomem MB series FT-IR spectrophotometers. The NMR spectra were recorded at 300 MHz ($^1$H) and 75 MHz ($^{13}$C) on a Bruker 300 MHz FT- NMR spectrometer using $CDCl_3$-$CCl_4$ mixture as the solvent. Chemical shifts are reported on $\delta$ scale with TMS ($^1$H NMR) and $CDCl_3$ ($^{13}$C NMR) as the internal standards. Elemental analyses were carried out using Perkin-Elmer 2400 CHNS analyzer. GC/MS were recorded on a Hewlett Packard Model 5791 Mass Spectrometer. Analytical thin layer chromatography was performed on glass plate coated with silica containing 13% calcium sulfate as the binder. Products were purified by gravity column chromatography either on silica gel (100-200 mesh) or alumina (neutral) in hexane-ethyl acetate mixture as eluent.

Solvents used for the experiments were distilled and dried according to the standard procedures in laboratory manuels. CAN used for the reaction was purchased from Aldrich Co. and was used without purification. Styrene, 4-methylstyrene and 4-acetoxystyrene were purchased from Aldrich Co. All the other styrenes were prepared from the corresponding aldehydes by Wittig

reaction. 1-octene and 1-octyne were purchased from E. Merck and cyclohexene was available from local source. The phenylcycloalkenes were prepared from the corresponding cycloalkanones and phenylmagnesium bromide prepared from bromobenzene by Grignard protocol, followed by acid catalyzed dehydration.

### 2.6.2 CAN Mediated Addition of Sulfinate to Styrenes: General Procedure

To a suspension of sodium *p*-toluenesulfinate (2 mmol) and styrene (1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (2.3 mmol) in acetonitrile (10 mL) at room temperature for 40 minutes. On completion of the reaction as shown by tlc, acetonitrile was evaporated off, the reaction mixture was diluted with water (75 mL) and extracted with dichloromethane (3 x 25 mL). The combined organic extracts were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator *in vacuo* and the residue was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane-ethyl acetate afforded the pure products.

### 2.6.3 CAN Mediated Addition of Sulfinate to Styrenes Under Deoxygenated Conditions: General Procedure

A mixture of styrene (1 mmol) and sodium *p*-toluenesulfinate (1.2 mmol) was taken in anhydrous acetonitrile (5 mL) in a two necked round-bottomed flask fitted with a pressure equalizing funnel containing CAN (2.3 mmol) dissolved in anhydrous acetonitrile (10 mL). Both the solutions were simultaneously bubbled with argon, which was deoxygenated by passing through Fieser's[51] solution for 15 minutes. Then the solution of CAN was added dropwise at room temperature and the reaction mixture was stirred vigorously under argon atmosphere for 40 minutes. When the starting material was fully

consumed as shown by tlc, acetonitrile was evaporated off, the reaction mixture was diluted with water (75 mL) and extracted using dichloromethane (3 x 25 mL). The combined organic extracts were washed with water, then with saturated brine and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to obtain the crude residue, which was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane-ethyl acetate afforded the pure products.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-phenylethane (108) and 1-(4'-Methylphenylsulfonyl)acetophenone (104)***

To a suspension of sodium *p*-toluenesulfinate (356 mg, 2 mmol) and styrene **19** (104 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 196 mg of **108** (61%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 60 mg of **104** (22%).

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-phenylethane (108)***

colourless solid: recrystallized from hexane-dichloromethane

mp 76-78 °C

IR (KBr) $\nu_{max}$ : 3074, 2937, 1645, 1595, 1495, 1457, 1395, 1314, 1270, 1145, 1083, 977, 852, 752, 696 $cm^{-1}$.

$^1H$ NMR : δ 7.74 (d, 2H, ArH, $J$ = 8.2 Hz), 7.29 (m, 7H, ArH), 6.34 (dd, 1H, $CHONO_2$, $J$ = 3.4 Hz, $J$ = 9.3 Hz), 3.80 (dd, 1H, $CH_2SO_2$, $J$ = 9.3 Hz, $J$ = 15.0 Hz), 3.47 (dd, 1H, $CH_2SO_2$, $J$ = 3.4 Hz, $J$ = 15.0 Hz), 2.40 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 145.16, 136.33, 135.20, 129.95, 129.68, 129.07, 127.96, 126.57, 78.82, 59.32, 21.51.

Anal. Calcd. for $C_{15}H_{15}NO_5S$: C, 56.06; H, 4.70; N, 4.36; S, 9.98. Found: C, 56.42; H, 5.10; N, 4.46; S, 10.06.

***1-(4'-Methylphenylsulfonyl)acetophenone (104)***[48,49]

colourless solid: recrystallized from hexane-dichloromethane

mp 105-108 °C

IR (KBr) $\nu_{max}$ : 2986, 1682, 1601, 1495, 1445, 1407, 1320, 1264, 1208, 1148, 1083, 821, 683 $cm^{-1}$.

$^1H$ NMR : δ 7.95 (d, 2H, ArH, $J$ = 7.6 Hz), 7.74 (d, 2H, ArH, $J$ = 8.1 Hz), 7.61 (t, 1H, ArH, $J$ = 7.4 Hz), 7.47 (t, 2H, ArH, $J$ = 7.5 Hz), 7.32 (d, 2H, ArH, $J$ = 8.0 Hz), 4.68 (s, 2H, $CH_2SO_2$), 2.45 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 187.86, 145.07, 135.80, 135.75, 134.13, 129.68, 129. 31, 128.71, 128.61, 63.56, 21.64.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(4'-methylphenyl)ethane (110) and 1-(4'-Methylphenylsulfonyl)-(4'-methyl)acetophenone (111)***

To a suspension of sodium *p*-toluenesulfinate (356 mg, 2 mmol) and 4-methylstyrene **109** (118 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 184 mg of **110** (55%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 81 mg of **111** (28%).

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(4'-methylphenyl)ethane (110)***

colourless solid: recrystallized from hexane-dichloromethane

mp 87-89 °C

IR (KBr) $\nu_{max}$ : 3037, 2937, 1638, 1595, 1513, 1445, 1314, 1270, 1145, 1083, 833, 777, 714, $cm^{-1}$.

$^1$H NMR : δ 7.74 (d, 2H, ArH, $J$ = 8.2 Hz), 7.32 (d, 2H, ArH, $J$ = 7.9 Hz), 7.17 (d, 2H, ArH, $J$ = 8.2 Hz), 7.12 (d, 2H, ArH, $J$ = 8.0 Hz), 6.29 (dd, 1H, $CHONO_2$, $J$ = 3.5 Hz, $J$ = 9.3 Hz), 3.77 (dd, 1H, $CH_2SO_2$, $J$ = 9.3 Hz, $J$ = 15.1 Hz), 3.44 (dd, 1H, $CH_2SO_2$, $J$ = 3.5 Hz, $J$ = 15.1 Hz), 2.44 (s, 3H, $CH_3$), 2.31 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 145.09, 139.79, 136.36, 132.21, 129.92, 129.71, 127.99, 126.57, 78.76, 59.45, 21.58, 21.14.

Anal. Calcd. for $C_{16}H_{17}NO_5S$: C, 57.30; H, 5.11; N, 4.18; S, 9.56. Found: C, 57.58; H, 5.22; N, 4.35; S, 9.34.

***1-(4'-Methylphenylsulfonyl)-(4'-methyl)acetophenone (111)***

colourless solid: recrystallized from hexane-dichloromethane

mp 100-102 °C

IR (KBr) $\nu_{max}$ : 2956, 1676, 1607, 1407, 1314, 1276, 1183, 1145, 1083, 995, 808, 771, 733 $cm^{-1}$.

$^1$H NMR : δ 7.85 (d, 2H, ArH, $J$ = 8.1 Hz), 7.74 (d, 2H, ArH, $J$ = 8.1 Hz), 7.33 (d, 2H, ArH, $J$ = 8.1 Hz), 7.28 (d, 2H, ArH, $J$ = 8.1 Hz), 4.66 (s, 2H, $CH_2SO_2$), 2.45 (s, 3H, $CH_3$), 2.44 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 187.36, 145.25, 144.98, 135.83, 133.36, 129.65, 129.50, 129.42, 128.60, 63.55, 21.71, 21.64.

Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.68; H, 5.65; S, 11.16.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(4'-chlorophenyl)ethane (112) and 1-(4'-Methylphenylsulfonyl)-(4'-chloro)acetophenone (113)***

To a suspension of sodium *p*-toluenesulfinate (356 mg, 2 mmol) and 4-chlorostyrene **66** (138.5 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room

temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 210 mg of **112** (59%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 99 mg of **113** (32%).

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(4'-chlorophenyl)ethane (112)***

colourless solid: recrystallized from hexane-dichloromethane

mp 94-96 °C

IR (KBr) $\nu_{max}$ : 2960, 1635, 1601, 1495, 1301, 1276, 1233, 1133, 1083, 970, 870, 764 $cm^{-1}$.

$^1H$ NMR : δ 7.72 (d, 2H, ArH, $J$ = 8.1 Hz), 7.35-7.30 (m, 4H, ArH), 7.24 (d, 2H, ArH, $J$ = 8.2 Hz), 6.29 (dd, 1H, $CHONO_2$, $J$ = 3.8 Hz, $J$ = 8.6 Hz), 3.74 (dd, 1H, $CH_2SO_2$, $J$ = 8.7 Hz, $J$ = 14.9 Hz), 3.44 (dd, 1H, $CH_2SO_2$, $J$ = 3.8 Hz, $J$ = 14.9 Hz), 2.46 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 145.29, 136.23, 135.93, 133.68, 129.98, 129.37, 128.02, 127.98, 77.98, 59.31, 21.61.

Anal. Calcd. for $C_{15}H_{14}ClNO_5S$: C, 50.64; H, 3.97; N, 3.94; S, 9.01. Found: C, 50.87; H, 4.17; N, 4.43; S, 8.83.

***1-(4'-Methylphenylsulfonyl)-(4'-chloro)acetophenone (113)***

colourless solid: recrystallized from hexane-dichloromethane

mp 138-139 °C

IR (KBr) $\nu_{max}$ : 2098, 1682, 1595, 1482, 1320, 1283, 1145, 1076, 1002, 846, 777, 714 $cm^{-1}$.

$^1H$ NMR : δ 7.91 (d, 2H, ArH, $J$ = 8.2 Hz), 7.72 (d, 2H, ArH, $J$ = 7.9 Hz), 7.45 (d, 2H, ArH, $J$ = 8.2 Hz), 7.33 (d, 2H, ArH, $J$ = 7.9 Hz), 4.65 (s, 2H, $CH_2SO_2$), 2.45 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 186.76, 145.25, 140.99, 135.61, 134.04, 130.76, 129.76,

129.09, 128.54, 63.69, 21.65.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(2'-chlorophenyl)ethane (115) and 1-(4'-Methylphenylsulfonyl)-2-hydroxy-2-(2'-chlorophenyl)ethane (116)***

To a suspension of sodium *p*-toluenesulfinate (356 mg, 2 mmol) and 2-chlorostyrene **114** (138.5 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 178 mg of **115** (50%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 56 mg of **116** (18%).

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(2'-chlorophenyl)ethane (115)***

colourless solid: recrystallized from hexane-dichloromethane

mp 66-68 °C

IR (KBr) $\nu_{max}$ : 3074, 2930, 1645, 1588, 1476, 1439, 1313, 1283, 1145, 989, 827, 752 $cm^{-1}$.

$^1H$ NMR : δ 7.79 (d, 2H, ArH, $J$ = 8.1 Hz), 7.35 (d, 2H, ArH, $J$ = 8.2 Hz), 7.32-7.24 (m, 4H, ArH), 6.71 (dd, 1H, $CHONO_2$, $J$ = 2.3 Hz, $J$ = 9.8 Hz), 3.68 (dd, 1H, $CH_2SO_2$, $J$ = 9.8 Hz, $J$ = 15.2 Hz), 3.49 (dd, 1H, $CH_2SO_2$, $J$ = 2.3 Hz, $J$ = 15.2 Hz), 2.43 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 145.14, 135.93, 132.98, 131.62, 130.48, 129.92, 129.85, 127.88, 127.57, 126.65, 75.17, 57.86, 21.38.

Anal. Calcd. for $C_{15}H_{14}ClNO_5S$: C, 50.64; H, 3.97; N, 3.94; S, 9.01. Found: C, 51.05; H, 3.96; N, 3.65; S, 9.13.

***1-(4'-Methylphenylsulfonyl)-2-hydroxy-2-(2'-chlorophenyl)ethane (116)***

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3505, 3086, 2924, 1651, 1588, 1439, 1299, 1139, 1076,

819, 746, 664, 637cm$^{-1}$.

$^1$H NMR : δ 7.86 (d, 2H, ArH, $J$ = 8.3 Hz), 7.66 (d, 1H, ArH, $J$ = 7.3 Hz), 7.38 (d, 2H, ArH, $J$ = 8.3 Hz), 7.29-7.18 (m, 3H, ArH), 5.41 (d, 1H, CHOH, $J$ = 9.8 Hz), 4.52 (brs, 1H, OH, exchangeable with $D_2O$), 3.48 (d, 1H, $CH_2SO_2$, $J$ = 14.6 Hz), 3.24 (dd, 1H, $CH_2SO_2$, $J$ = 9.8 Hz, $J$ = 14.6 Hz), 2.47 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 145.17, 137.98, 133.24, 131.40, 130.03, 129.35, 129.16, 128.25, 127.38, 127.27, 65.42, 61.85, 21.73.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(3'-nitrophenyl)ethane (118), 1-2-Di-(4'-methylphenylsulfonyl)-2-(3'-nitrophenyl)ethane (119) and 1-(4'-Methylphenylsulfonyl)-2-hydroxy-2-(3'-nitrophenyl)ethane (120)***

To a suspension of sodium *p*-toluenesulfinate (356 mg, 2 mmol) and 3-nitrostyrene **117** (149 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 177 mg of **118** (48%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 22 mg (10%) of **119** and 58 mg (18%) of **120**.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(3'-nitrophenyl)ethane (118)***

colourless solid: recrystallized from hexane-dichloromethane

mp 163-165 °C

IR (neat) $\nu_{max}$ : 3087, 2980, 1645, 1526, 1351, 1270, 1145, 1083, 983, 864, 808, 696 cm$^{-1}$.

$^1$H NMR : δ 8.22 (d, 2H, ArH, $J$ = 8.0 Hz), 8.13 (s, 1H, ArH), 7.73 (d, 2H, ArH, $J$ = 8.0 Hz), 7.59 (t, 1H, ArH, $J$ = 7.9 Hz), 7.35 (d, 2H, ArH, $J$ = 7.8 Hz), 6.41 (dd, 1H, $CHONO_2$, $J$ =

4.5 Hz, $J$ = 8.2 Hz), 3.79 (dd, 1H, $CH_2SO_2$, $J$ = 8.4 Hz, $J$ = 14.9 Hz), 3.52 (dd, 1H, $CH_2SO_2$, $J$ = 4.5 Hz, $J$ = 14.9 Hz), 2.46 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 148.54, 145.44, 137.35, 136.06, 132.70, 130.19, 130.04, 127.92, 124.52, 121.58, 77.26, 58.99, 21.57.

***1-2-Di-(4'-methylphenylsulfonyl)-2-(3'-nitrophenyl)ethane (119)***

colourless solid: recrystallized from hexane-dichloromethane

mp 228-230 °C

IR (KBr) $\nu_{max}$ : 2948, 1613, 1536, 1351, 1310, 1148, 888, 811, 548 cm$^{-1}$.

$^1$H NMR : δ 8.07 (d, 1H, ArH, $J$ = 7.8 Hz), 7.63 (s, 1H, ArH), 7.45-7.33 (m, 5H, ArH), 7.25-7.22 (m, 3H, ArH), 7.14-7.11 (m, 2H, ArH), 4.64 (d, 1H, $CHSO_2$, $J$ = 2.0 Hz, $J$ = 11.7 Hz), 4.06 (dd, 1H, $CH_2SO_2$, $J$ = 2.1 Hz, $J$ = 14.3 Hz), 3.92 (dd, 1H, $CH_2SO_2$, $J$ = 11.7 Hz, $J$ = 14.3 Hz), 2.42 (s, 3H, $CH_3$), 2.35 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 146.19, 144.17, 135.16, 128.35, 128.13, 127.79, 127.69, 126.48, 123.30, 121.98, 63.47, 51.84, 20.05, 19.79.

***1-(4'-Methylphenylsulfonyl)-2-hydroxy-2-(3'-nitrophenyl)ethane (120)***

colourless solid: recrystallized from hexane-dichloromethane

mp 116-119 °C

IR (KBr) $\nu_{max}$ : 3440, 3058, 2921, 1532, 1407, 1351, 1309, 1151, 1087, 1023, 948, 812 cm$^{-1}$.

$^1$H NMR : δ 8.15-8.10 (m, 2H, ArH), 7.82 (d, 2H, ArH, $J$ = 7.9 Hz), 7.70-7.64 (m, 1H, ArH), 7.53-7.48 (m, 1H, ArH), 7.38 (d, 2H, ArH, $J$ = 7.8 Hz), 5.37 (d, 1H, CHOH, $J$ = 9.8 Hz), 4.10, (brs, 1H, OH, exchangeable with $D_2O$), 3.40 (m, 2H, $CH_2SO_2$), 2.47 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 144.23, 143.75, 136.42, 131.53, 128.95, 128.69, 128.54,

127.27, 121.74, 120.24, 66.65, 63.04, 20.80.

***1-(4'-Methylphenylsulfonyl)-2-(4'-methoxyphenyl)ethene (122) and 1-(4'-Methylphenylsulfonyl)-(4'-methoxy)acetophenone (123)***

To a suspension of sodium *p*-toluenesulfinate (356 mg, 2 mmol) and 4-methoxystyrene **121** (134 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 115 mg of **122** (40%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 61 mg of **123** (20%).

***1-(4'-Methylphenylsulfonyl)-2-(4'-methoxyphenyl)ethene (122)***

colourless solid: recrystallized from hexane-dichloromethane

mp 178-180 °C

IR (KBr) $\nu_{max}$ : 3058, 2946, 2927, 1601, 1574, 1512, 1308, 1258, 1174, 1142, 1085, 1026, 810, 758, 656 $cm^{-1}$.

$^1H$ NMR : δ 7.79 (d, 2H, ArH, *J* = 7.9 Hz), 7.57 (d, 1H, olefinic, *J* = 15.3 Hz), 7.40 (d, 2H, ArH, *J* = 8.5 Hz), 7.30 (d, 2H, ArH, *J* = 7.9 Hz), 6.86 (d, 2H, ArH, *J* = 8.4 Hz), 6.68 (d, 1H, olefinic, *J* = 15.3 Hz), 3.80 (s, 3H, $OCH_3$), 2.44 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 161.69, 143.67, 141.37, 138.11, 130.02, 129.51, 129.32, 127.32, 124.80, 114.20, 55.06, 21.32.

***1-(4'-Methylphenylsulfonyl)-(4'-methoxy)acetophenone (123)***

colourless liquid

IR (neat) $\nu_{max}$ : 3062, 2949, 2843, 1672, 1599, 1570, 1511, 1466, 1293, 1149, 1088, 814, 737$cm^{-1}$.

$^1H$ NMR : δ 7.91 (d, 2H, ArH, *J* = 8.7 Hz), 7.72 (d, 2H, ArH, *J* = 8.2

Hz), 7.30 (d, 2H, ArH, $J$ = 8.1 Hz), 6.91 (d, 2H, ArH, $J$ = 8.7 Hz), 4.63 (s, 2H, $CH_2SO_2$), 3.86 (s, 3H, $OCH_3$), 2.43 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 186.15, 144.96, 135.90, 131.88, 129.94, 129.67, 128.56, 128.01, 126.90, 113.95, 63.46, 55.44, 21.65.

***1-Phenylsulfonyl-2-nitrato-2-phenylethane (124)***
***and 1-Phenylsulfonylacetophenone (44)***

To a suspension of sodium benzenesulfinate (328 mg, 2 mmol) and styrene **19** (104 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 172 mg of **124** (56%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 52 mg of **44** (20%).

***1-Phenylsulfonyl-2-nitrato-2-phenylethane (124)***

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3065, 2986, 2932, 1639, 1585, 1541, 1496, 1448, 1308, 1274, 1144, 1084, 979, 835, 746 cm$^{-1}$.

$^1$H NMR : δ 7.86 (d, 2H, ArH, $J$ = 7.3 Hz), 7.61-7.46 (m, 3H, ArH), 7.33-7.27 (m, 5H, ArH), 6.37 (dd, 1H, $CHONO_2$, $J$ = 3.5 Hz, $J$ = 9.2 Hz), 3.85 (dd, 1H, $CH_2SO_2$, $J$ = 9.3 Hz, $J$ = 15.1 Hz), 3.51 (dd, 1H, $CH_2SO_2$, $J$ = 3.5 Hz, $J$ = 15.1 Hz).

$^{13}$C NMR : δ 139.00, 134.77, 133.84, 129.53, 129.13, 128.85, 127.64, 126.41, 78.58, 58.86.

***1-Phenylsulfonylacetophenone (44)***[20]

colourless solid: recrystallized from hexane-dichloromethane

mp 86-88 °C

IR (KBr) $\nu_{max}$ : 3006, 2952, 1684, 1603, 1448, 1414, 1327, 1279, 1165, 1084, 1003, 760 $cm^{-1}$.

$^1H$ NMR : δ 7.95-786 (m, 4H, ArH ), 7.68-7.45 (m, 6H, ArH), 4.71 (s, 2H, $CH_2SO_2$).

$^{13}C$ NMR : δ 187.82, 138.92, 135.86, 134.31, 134.16, 129.40, 129.19, 128.87, 128.72, 63.56.

***1-Phenylsulfonyl-2-nitrato-2-(4'-methylphenyl)ethane (125)***

***and 1-Phenylsulfonyl-(4'-methyl)acetophenone (126)***

To a suspension of sodium benzenesulfinate (328 mg, 2 mmol) and 4-methylstyrene **109** (118 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 167 mg of **125** (52%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 71 mg of **126** (26%).

***1-Phenylsulfonyl-2-nitrato-2-(4'-methylphenyl)ethane (125)***

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3065, 2927, 1640, 1514, 1446, 1315, 1278, 1147, 1058, 855, 793, 743 $cm^{-1}$.

$^1H$ NMR : δ 7.85 (d, 2H, ArH, $J$ = 7.3 Hz), 7.60 (t, 1H, ArH, $J$ = 7.3 Hz), 7.49 (t, 2H, ArH, $J$ = 7.5 Hz), 7.16 (d, 2H, ArH, $J$ = 7.9 Hz), 7.09 (d, 2H, ArH, $J$ = 7.9 Hz), 6.32 (dd, 1H, $CHONO_2$, $J$ = 3.5 Hz, $J$ = 9.2 Hz), 3.83 (dd, 1H, $CH_2SO_2$, $J$ = 9.2 Hz, $J$ = 15.0 Hz), 3.49 (dd, 1H, $CH_2SO_2$, $J$ = 3.5 Hz, $J$ = 15.0 Hz), 2.27 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 139.66, 139.14, 133.82, 131.85, 129.54, 129.16, 127.73, 126.52, 78.64, 59.00, 20.93.

***1-Phenylsulfonyl-(4'-methyl)acetophenone (126)***

colourless solid: recrystallized from hexane-dichloromethane

mp 123-125 °C

IR (KBr) $\nu_{max}$ : 3070, 3002, 2942, 1681, 1613, 1452, 1314, 1175, 1094, 1013, 798, 697 $cm^{-1}$.

$^1H$ NMR : δ 7.88-7.82 (m, 4H, ArH), 7.67-7.51 (m, 3H, ArH), 7.27-7.25 (m, 2H, ArH), 4.68 (s, 2H, $CH_2SO_2$), 2.42 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 187.26, 145.35, 138.88, 134.02, 133.39, 129.51, 129.08, 128.63, 125.57, 63.44, 21.77.

***1-Phenylsulfonyl-2-nitrato-2-(4'-chlorophenyl)ethane (127)***
***and 1-Phenylsulfonyl-(4'-chloro)acetophenone (128)***

To a suspension of sodium benzenesulfinate (328 mg, 2 mmol) and 4-chlorostyrene **66** (138.5 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 195 mg of **127** (57%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 82 mg of **128** (28%).

***1-Phenylsulfonyl-2-nitrato-2-(4'-chlorophenyl)ethane (127)***

colourless solid: recrystallized from hexane-dichloromethane

mp 67-69 °C

IR (KBr) $\nu_{max}$ : 3071, 2934, 1645, 1599, 1495, 1415, 1319, 1280, 1090, 984, 852, 756, 691 $cm^{-1}$.

$^1H$ NMR : δ 7.85 (d, 2H, ArH, $J$ = 7.3 Hz), 7.60-7.50 (m, 3H, ArH), 7.30 (d, 2H, ArH, $J$ = 7.4 Hz), 7.29-7.23 (m, 2H, ArH), 6.33 (dd, 1H, $CHONO_2$, $J$ = 3.9 Hz, $J$ = 8.9 Hz), 3.83 (dd, 1H, $CH_2SO_2$, $J$ = 8.9 Hz, $J$ = 15.0 Hz), 3.52 (dd, 1H,

$CH_2SO_2$, $J$ = 3.7 Hz, $J$ = 15.0 Hz),

$^{13}$C NMR : δ 139.12, 135.75, 134.08, 133.47, 129.36, 129.27, 128.17, 127.84, 78.00, 58.90.

***1-Phenylsulfonyl-(4'-chloro)acetophenone (128)***

colourless solid: recrystallized from hexane-dichloromethane

mp 125-127 °C

IR (KBr) $\nu_{max}$ : 2948, 2901, 1690, 1587, 1337, 1303, 1148, 1094, 993, 831, 697 $cm^{-1}$.

$^1$H NMR : δ 7.90 (d, 2H, ArH, $J$ = 8.6 Hz), 7.86 (d, 2H, ArH, $J$ = 8.0 Hz), 7.67 (t, 1H, ArH, $J$ = 7.4 Hz), 7.55 (t, 3H, ArH, $J$ = 7.6 Hz), 7.45 (d, 2H, ArH, $J$ = 8.6 Hz), 4.69 (s, 2H, $CH_2SO_2$).

$^{13}$C NMR : δ 186.57, 141.07, 138.56, 134.16, 133.99, 130.72, 129.13, 128.76, 128.53, 63.56.

***1-Phenylsulfonyl-2-nitrato-2-(2'-chlorophenyl)ethane (130) and 1-Phenylsulfonyl-2-hydroxy-2-(2'-chlorophenyl)ethane(131)***

To a suspension of sodium benzenesulfinate (328 mg, 2 mmol) and 2-chlorostyrene **114** (138.5 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the mixture was stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 174 mg of **130** (51%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 56 mg of **131** (19%).

***1-Phenylsulfonyl-2-nitrato-2-(2'-chlorophenyl)ethane (130)***

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3064, 2934, 1651, 1583, 1476, 1446, 1309, 1276, 1146, 1085, 866, 752 $cm^{-1}$.

$^1$H NMR : δ 7.94-7.88 (m, 2H, ArH), 7.71-7.52 (m, 3H, ArH), 7.35-7.25 (m, 4H, ArH), 6.71 (dd, 1H, $CHONO_2$, $J$ = 2.5 Hz, $J$ = 9.8 Hz), 3.68 (dd, 1H, $CH_2SO_2$, $J$ = 9.8 Hz, $J$ = 15.2 Hz), 3.52 (dd, 1H, $CH_2SO_2$, $J$ = 2.5 Hz, $J$ = 15.0 Hz).

$^{13}$C NMR : δ 139.04, 136.23, 134.15, 133.14, 130.63, 130.14, 129.41, 128.02, 127.69, 126.71, 75.19, 58.01.

***1-Phenylsulfonyl-2-hydroxy-2-(2'-chlorophenyl)ethane(131)***

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3501, 3083, 1600, 1465, 1310, 1155, 1101, 1054, 771, 697 cm$^{-1}$.

$^1$H NMR : δ 7.99 (d, 2H, ArH, $J$ = 7.5 Hz), 7.68-7.57 (m, 4H, ArH), 7.27-7.18 (m, 3H, ArH), 5.43 (d, 1H, CHOH, $J$ = 9.8 Hz), 4.55 (brs, 1H, OH, exchangeable with $D_2O$), 3.44 (d, 1H, $CH_2SO_2$, $J$ = 14.4 Hz), 3.28 (dd, 1H, $CH_2SO_2$, $J$ = 9.9 Hz, $J$ = 14.4 Hz).

$^{13}$C NMR : δ 138.71, 137.96, 133.99, 131.31, 129.32, 129.24, 129.09, 128.19, 127.28, 127.21, 65.29, 61.76.

***1-Phenylsulfonyl-2-nitrato-2-(1-naphthyl)ethane (132) and***

***1-Phenylsulfonyl-2-hydroxy-2-(1-naphthyl)ethane (133)***

To a suspension of sodium benzenesulfinate (328 mg, 2 mmol) and 1-vinylnaphthalene **129** (154 mg, 1 mmol) in acetonitrile (5 mL) was added dropwise a solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature and the was mixture stirred for about 40 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (95:5) afforded 186 mg of **132** (52%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 66 mg of **133** (21%).

***1-Phenylsulfonyl-2-nitrato-2-(1-naphthyl)ethane (132)***

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3064, 2933, 1643, 1512, 1448, 1308, 1286, 1144, 1084, 980, 867, 836, 776, 741 $cm^{-1}$.

$^1H$ NMR : δ 7.97-7.89 (m, 3H, ArH), 7.86-7.79 (m, 2H, ArH), 7.68-7.49 (m, 5H, ArH), 7.46-7.38 (m, 2H, ArH), 7.13 (dd, 1H, $CHONO_2$, $J$ = 2.2 Hz, $J$ = 9.5 Hz), 3.83 (dd, 1H, $CH_2SO_2$, $J$ = 9.5 Hz, $J$ = 15.4 Hz), 3.57 (dd, 1H, $CH_2SO_2$, $J$ = 2.3 Hz, $J$ = 15.4 Hz).

$^{13}C$ NMR : δ 139.04, 136.22, 134.18, 131.18, 130.16, 129.45, 129.26, 128.03, 127.54, 126.43, 125.19, 123.53, 121.79, 75.80, 59.21.

***1-Phenylsulfonyl-2-hydroxy-2-(1-naphthyl)ethane (133)***

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3501, 3063, 2935, 1526, 1458, 1310, 1142, 1088, 980, 737, 690 $cm^{-1}$.

$^1H$ NMR : δ 7.91-7.88 (m, 2H, ArH), 7.74-7.71 (m, 1H, ArH), 7.66-7.57 (m, 3H, ArH), 7.51-7.46 (m, 3H, ArH), 7.43-7.31 (m, 3H, ArH), 5.96 (dd, 1H, CHOH, $J$ = 2.7 Hz, $J$ = 8.0 Hz), 3.95 (brs, 1H, OH, exchangeable with $D_2O$), 3.87-3.83 (m, 1H, $CH_2SO_2$).

$^{13}C$ NMR : δ 139.20, 136.26, 133.90, 133.56, 129.32, 129.13, 129.04, 128.51, 128.06, 126.53, 125.60, 125.42, 123.20, 121.77, 65.05, 63.34.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(4'-acetoxyphenyl)ethane (146)***

To a deoxygenated suspension of sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and 4-acetoxystyrene **144** (162 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in

acetonitrile (10 mL) at room temperature for 40 minutes. On completion of the reaction it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (80:20) afforded 315 mg (83%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 3049, 1769, 1642, 1610, 1506, 1317, 1209, 1142, 1088, 987, 804 $cm^{-1}$.

$^1H$ NMR : δ 7.70 (d, 2H, ArH, *J* = 8.2 Hz), 7.31-7.27 (m, 4H, ArH), 7.04 (d, 2H, ArH, *J* = 8.4 Hz), 6.32 (dd, 1H, $CHONO_2$, *J* = 3.6 Hz, *J* = 9.1 Hz), 3.77 (dd, 1H, $CH_2SO_2$, *J* = 9.2 Hz, *J* = 15.0 Hz), 3.46 (dd, 1H, $CH_2SO_2$, *J* = 3.6 Hz, *J* = 15.0 Hz), 2.41 (s, 3H, $OCOCH_3$), 2.25 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 168.55, 151.46, 145.09, 136.13, 132.40, 129.86, 127.81, 127.64, 122.21, 78.08, 59.04, 21.40, 20.78.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(2',4',6'-trimethylphenyl)ethane (147)***

To a deoxygenated suspension of sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and mesitylstyrene **145** (146 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature for 40 minutes. On completion of the reaction it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (90:10) afforded 236 mg (65%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 2930, 1632, 1451, 1314, 1276, 1139, 1083, 1026, 927, 864, 802, 689 $cm^{-1}$.

$^1H$ NMR : δ 7.78 (d, 2H, ArH, *J* = 8.1 Hz), 7.36 (d, 2H, ArH, *J* = 7.9 Hz), 6.77-6.75 (m, 2H, ArH merged with 1H, $CHONO_2$), 3.95 (dd, 1H, $CH_2SO_2$, *J* = 9.1 Hz, *J* = 15.3 Hz), 3.37 (dd, 1H, $CH_2SO_2$, *J* = 2.5 Hz, *J* = 15.3 Hz), 2.47 (s, 3H, $CH_3$), 2.33 (s, 6H, $CH_3$), 2.22 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 145.21, 139.17, 136.56, 136.16, 130.10, 130.01, 128.89, 128.18, 75.67, 58.28, 21.75, 20.90, 20.20.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(1-naphthyl)ethane (149)***

To a deoxygenated suspension of sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and 1-vinylnaphthalene **129** (154 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature for 40 minutes. On completion of the reaction it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (90:10) afforded 260 mg (70%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 3058, 2927, 1639, 1595, 1508, 1303, 1284, 1141, 1091, 979, 867, 836, 774 cm$^{-1}$.

$^{1}$H NMR : δ 7.92 (d, 2H, ArH, *J* = 8.0 Hz), 7.81-7.73 (m, 3H, ArH), 7.54-7.42 (m, 3H, ArH), 7.36-7.31 (m, 1H, ArH), 7.27 (d, 2H, ArH, *J* = 8.0 Hz), 7.11 (dd, 1H, $CHONO_2$, *J* = 2.1 Hz, *J* = 9.2 Hz), 3.79 (dd, 1H, $CH_2SO_2$, *J* = 9.4 Hz, *J* = 15.3 Hz), 3.51 (dd, 1H, $CH_2SO_2$, *J* = 2.1 Hz, *J* = 15.3 Hz), 2.38 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 145.15, 135.87, 133.67, 131.07, 129.95, 129.87, 129.08, 129.03, 127.88, 127.30, 126.24, 125.06, 123.51, 121.68, 75.81, 59.03, 21.42.

***1-(4'-Methylphenylsulfonyl)-2-nitrato-2-(2-naphthyl)ethane (150)***

To a deoxygenated suspension of sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and 2-vinylnaphthalene **148** (154 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature for 40 minutes. On completion of the reaction it was processed as described in the general procedure. The residue

on column chromatography on silica gel using hexane-ethyl acetate (90:10) afforded 297 mg (80%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 3052, 2934, 1639, 1595, 1315, 1297, 1278, 1141, 1085, 967, 861, 811, 749 $cm^{-1}$.

$^1H$ NMR : δ 7.70-7.67 (m, 4H, ArH), 7.68 (d, 2H, ArH, $J$ = 7.9 Hz), 7.43-7.40 (m, 2H, ArH), 7.28-7.25 (m, 2H, ArH), 7.13 (d, 2H, ArH, $J$ = 7.9 Hz), 6.50 (dd, 1H, $CHONO_2$, $J$ = 4.0 Hz, $J$ = 8.7 Hz), 3.88 (dd, 1H, $CH_2SO_2$, $J$ = 8.8 Hz, $J$ = 15.0 Hz), 3.58 (dd, 1H, $CH_2SO_2$, $J$ = 4.0 Hz, $J$ = 15.0 Hz), 2.24 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 144.88, 136.01, 133.36, 132.58, 131.90, 129.63, 129.01, 127.93, 127.70, 127.47, 126.89, 126.60, 123.06, 78.95, 58.90, 21.20.

***1-Phenylsulfonyl-2-nitrato-2-(3'-nitrophenyl)ethane (151)***

To a deoxygenated suspension of sodium benzenesulfinate (197 mg, 1.2 mmol) and 3-nitrostyrene **117** (149 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature for 40 minutes. On completion of the reaction it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (90:10) afforded 260 mg (74%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 3070, 2933, 1649, 1533, 1325, 1307, 1277, 1148, 1085, 836, 753, 685 $cm^{-1}$.

$^1H$ NMR : δ 8.22 -8.15(m, 2H, ArH), 7.88-7.81 (m, 2H, ArH), 7.75-7.51 (m, 5H, ArH), 6.48 (dd, 1H, $CHONO_2$, $J$ = 4.3 Hz, $J$ = 8.7 Hz), 3.93 (dd, 1H, $CH_2SO_2$, $J$ = 8.7 Hz, $J$ = 14.9 Hz), 3.66 (dd, 1H, $CH_2SO_2$, $J$ = 4.3 Hz, $J$ = 14.9 Hz).

$^{13}C$ NMR : δ 148.29, 138.92, 137.01, 134.15, 132.87, 130.24, 129.36,

127.74, 124.44, 121.70, 77.38, 58.47.

***1-Phenylsulfonyl-2-nitrato-2-(4'-acetoxyphenyl)ethane (152)***

To a deoxygenated suspension of sodium benzenesulfinate (197 mg, 1.2 mmol) and 4-acetoxystyrene **144** (162 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature for 40 minutes. On completion of the reaction it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (80:20) afforded 292 mg (80%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 3045, 1764, 1640, 1608, 1513, 1308, 1214, 1130, 1094, 980, 801 $cm^{-1}$.

$^1H$ NMR : δ 7.82 (d, 2H, ArH, $J$ = 8.3 Hz), 7.63-7.57 (m, 1H, ArH), 7.51-7.46 (m, 2H, ArH), 7.29-7.27 (m, 2H, ArH), 7.02 (d, 2H, ArH, $J$ = 8.4 Hz), 6.34 (dd, 1H, $CHONO_2$, $J$ = 2.4 Hz, $J$ = 9.0 Hz), 3.81 (dd, 1H, $CH_2SO_2$, $J$ = 9.2 Hz, $J$ = 15.0 Hz) 3.48 (dd, 1H, $CH_2SO_2$, $J$ = 2.5 Hz, $J$ = 15.0 Hz), 2.23 (s, 3H, $OCOCH_3$).

$^{13}C$ NMR : δ 168.56, 151.42, 139.00, 133.92, 132.19, 129.56, 129.21, 127.83, 127.66, 122.18, 78.00, 58.77, 20.71.

***1-Phenylsulfonyl-2-nitrato-2-(2-naphthyl)ethane (153)***

To a deoxygenated suspension of sodium benzenesulfinate (197 mg, 1.2 mmol) and 2-vinylnaphthalene **148** (154 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature for 40 minutes. On completion of the reaction it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (90:10) afforded 271 mg (76%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 3064, 2983, 2927, 1641, 1586, 1510, 1309, 1278, 1142,

1085, 863, 750 $cm^{-1}$.

$^1H$ NMR : δ 7.86-7.73 (m, 6H, ArH), 7.57-7.41 (m, 5H, ArH), 7.31-7.28 (m, 1H, ArH), 6.51 (dd, 1H, $CHONO_2$, $J$ = 3.6 Hz, $J$ = 9.1 Hz), 3.89 (dd, 1H, $CH_2SO_2$, $J$ = 9.1 Hz, $J$ = 15.1 Hz), 3.56 (dd, 1H, $CH_2SO_2$, $J$ = 3.6 Hz, $J$ = 15.1 Hz).

$^{13}C$ NMR : δ 139.16, 133.92, 133.54, 132.76, 132.10, 129.23, 128.07, 127.85, 127.64, 127.09, 126.81, 126.65, 123.00, 78.88, 59.19.

### 2.6.4 General Procedure for the Synthesis of Vinyl Sulfones and β-Iodovinyl Sulfones from Styrenes

A mixture of of styrene (1 mmol), sodium *p*-toluenesulfinate (1.2 mmol) and sodium iodide (1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. After the completion of the reaction, the reaction mixture was washed with water and extracted with dichloromethane (3 x 20 mL). The combined organic extracts were washed with saturated sodium thiosulfate solution followed by brine and dried over anhydrous sodium sulfate. The solvent was evaporated off and the residue on column chromatography on neutral alumina using hexane-ethyl acetate mixture as the eluent afforded the product.

***1-(4'-Methylphenylsulfonyl)-2-(phenyl)ethene (154)***[17c,18b,31,34,37]

A mixture of styrene **19** (104 mg, 1 mmol), *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 212

mg (82%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 119-121 °C

IR (KBr) $\nu_{max}$ : 3046, 2915, 1613, 1594, 1447, 1301, 1143, 1085, 974, 858, 742, 692 $cm^{-1}$.

$^1H$ NMR : δ 7.82 (d, 2H, ArH, $J$ = 8.1 Hz), 7.64 (d, 1H, olefinic, $J$ = 15.4 Hz), 7.48-7.45 (m, 2H, ArH), 7.39-7.37 (m, 3H, ArH), 7.33 (d, 2H, ArH, $J$ = 8.1 Hz), 6.82 (d, 1H, olefinic, $J$ = 15.4 Hz), 2.44 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 144.12, 141.72, 137.89, 132.43, 130.95, 129.85, 128.95, 128.44, 127.78, 127.67, 21.53.

GC-MS *(m/z)* : 258[$M^+$] (26),194 (13), 193 (26), 178 (19), 139 (73), 119 (21), 103 (47), 91 (100), 77 (61), 65 (36), 51 (26).

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 70.00; H, 5.60; S, 12.63.

***1-(4'-Methylphenylsulfonyl)-2-(4'-methylphenyl)ethene (155)***[31]

A mixture of 4-methylstyrene **109** (118 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 226 mg (83%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 154-156 °C

IR (KBr) $\nu_{max}$ : 3045, 2952, 1605, 1594, 1514, 1492, 1447, 1303, 1183, 1140, 1084, 974, 864, 795 $cm^{-1}$.

$^1H$ NMR : δ 7.81 (d, 2H, ArH, $J$ = 8.1 Hz), 7.82-7.79 (m, 2H, ArH), 7.60 (d, 1H, olefinic, $J$ = 15.4 Hz), 7.37-7.31 (m, 4H,

ArH), 7.17 (d, 2H, ArH, $J$ = 7.9 Hz), 6.77 (d, 1H, olefinic, $J$ = 15.4 Hz), 2.43 (s, 3H, $CH_3$), 2.36 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 144.00, 141.82, 141.48, 138.16, 129.84, 129.76, 129.71, 128.51, 127.67, 126.60, 21.57, 21.48.

Anal. Calcd. for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; S, 11.77. Found: C, 70.83; H, 5.91; S, 11.73.

***1-(4'-Methylphenylsulfonyl)-2-(4'-chlorophenyl)ethene (157)***[31]

A mixture of 4-chlorostyrene **66** (138.5 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 257 mg (88%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 138-140 °C

IR (KBr) $\nu_{max}$ : 3058, 1616, 1594, 1488, 1404, 1305, 1288, 1143, 1085, 1015, 971, 862, 790 cm$^{-1}$.

$^1$H NMR : δ 7.81 (d, 2H, ArH, $J$ = 8.2 Hz), 7.58 (d, 1H, olefinic, $J$ = 15.4 Hz), 7.40 (d, 2H, ArH, $J$ = 8.5 Hz), 7.35 (d, 2H, ArH, $J$ = 8.6 Hz), 7.34 (d, 2H, ArH, $J$ = 8.3 Hz), 6.81 (d, 1H, olefinic, $J$ = 15.4 Hz), 2.45 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 144.37, 140.29, 137.73, 137.15, 131.02, 129.99, 129.67, 129.37, 128.46, 127.83, 21.65.

***1-(4'-Methylphenylsulfonyl)-2-(2'-chlorophenyl)ethene(159)***

A mixture of 2-chlorostyrene **114** (138.5 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for

nutes. The reaction mixture after work up and purification on neutral na column afforded 254 mg (87%) of the product; colourless crystalline recrystallized from hexane-dichloromethane.

105-107 °C

KBr) $\nu_{max}$ : 3058, 3027, 1647, 1611, 1592, 1491, 1465, 1323, 1299, 1145, 1089, 1029, 810, 748 $cm^{-1}$.

NMR : δ 8.03 (d, 1H, olefinic, $J$ = 15.4 Hz), 7.83 (d, 2H, ArH, $J$ = 8.1 Hz), 7.50 (d, 1H, ArH, $J$ = 7.6 Hz), 7.42 (d, 1H, ArH, $J$ = 7.7 Hz), 7.34 (d, 1H, ArH, $J$ = 8.0 Hz), 7.32-7.22 (m, 3H, ArH), 6.86 (d, 1H, olefinic, $J$ = 15.4 Hz), 2.45 (s, 3H, $CH_3$).

NMR : δ 144.40, 137.80, 137.59, 135.37, 131.72, 130.96, 130.63, 130.41, 130.01, 128.25, 127.99, 127.14, 21.68.

l. Calcd. for $C_{15}H_{13}ClO_2S$: C, 61.53; H, 4.48; S, 10.95. Found: C, 62.05; H, ; S, 11.13

***'-Methylphenylsulfonyl)-2-(3'-nitrophenyl)ethene (161)***[31]

A mixture of 3-nitrostyrene **117** (149 mg, 1 mmol), sodium luenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in ydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in ydrous acetonitrile (15 mL) at room temperature under argon atmosphere for minutes. The reaction mixture after work up and purification on neutral mina column afforded 242 mg (80%) of the product; colourless crystalline id: recrystallized from hexane-dichloromethane.

ip 142-145 °C

ν (KBr) $\nu_{max}$ : 3070, 3058, 1624, 1594, 1531, 1351, 1317, 1297, 1199, 1142, 1083, 981, 844, 729 $cm^{-1}$.

H NMR : δ 8.33 (s, 1H, ArH), 8.25 (d, 1H, ArH, $J$ = 8.2 Hz), 7.83 (d, 2H, ArH, $J$ = 8.2 Hz), 7.78 (d, 1H, ArH, $J$ = 7.8 Hz),

7.68 (d, 1H, olefinic, $J$ = 15.4 Hz), 7.59 (t, 1H, ArH, $J$ = 8.0 Hz), 7.36 (d, 2H, ArH, $J$ = 8.0 Hz), 6.99 (d, 1H, olefinic, $J$ = 15.4 Hz), 2.46 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 148.80, 144.83, 138.69, 137.17, 134.39, 134.09, 131.37, 130.15, 128.04, 125.21, 122.75, 21.70.

Anal. Calcd. for $C_{15}H_{13}NO_4S$: C, 59.39; H, 4.32; N: 4.62; S, 10.57. Found: C, 59.20; H, 4.54; N: 4.83; S, 10.74

***1-(4'-Methylphenylsulfonyl)-2-(1-naphthyl)ethene(163)***

A mixture of 1-vinylnaphthalene **129** (154 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 237 mg (77%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 132-134 °C

IR (KBr) $\nu_{max}$ : 3063, 1613, 1310, 1155, 1088, 973, 852, 804, 744, 676, 555 cm$^{-1}$.

$^1$H NMR : δ 8.47 (d, 1H, olefinic, $J$ = 15.1 Hz), 8.16 (d, 1H, ArH, $J$ = 8.1 Hz), 7.90-7.85 (m, 4H, ArH), 7.65-7.41 (m, 5H, ArH), 7.35 (d, 1H, ArH, $J$ = 8.0 Hz), 6.92 (d, 1H, olefinic, $J$ = 15.1 Hz), 2.44 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 144.26, 138.92, 137.92, 133.72, 131.34, 130.18, 130.01, 129.73, 128.85, 127.89, 127.31, 126.50, 125.63, 125.28, 123.16, 21.68 .

Anal. Calcd. for $C_{19}H_{16}O_2S$: C, 74.00; H, 5.23; S, 10.40. Found: C, 74.36; H, 5.88; S, 10.54

***1-(4'-Methylphenylsulfonyl)-2-(2-naphthyl)ethene (169)***

A mixture of 2-vinylnaphthalene **148** (154 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 216 mg (70%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 156-158 °C

IR (KBr) $\nu_{max}$ : 3045, 3021, 1613, 1591, 1302, 1146, 1082, 980, 849, 830, 745 $cm^{-1}$.

$^1H$ NMR : δ 7.89-7.62 (m, 6H, ArH), 7.83 (d, 1H, olefinic, $J$ = 15.4 Hz), 7.53-7.48 (m, 3H, ArH), 7.32 (d, 2H, ArH, $J$ = 8.0 Hz), 6.93 (d, 1H, olefinic, $J$ = 15.4 Hz), 2.42 (*s*, 3H, $CH_3$).

$^{13}C$ NMR : δ 144.21, 141.92, 138.10, 134.51, 133.20, 130.82, 129.98, 128.94, 128.69, 127.89, 127.84, 127.73, 126.98, 21.59.

***1-(4'-Methylphenylsulfonyl)-2-(4'-acetoxyphenyl)ethene (166)***

A mixture of 4-acetoxystyrene **144** (162 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 228 mg (72%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 127-129 °C

IR (KBr) $\nu_{max}$ : 3049, 1769, 1613, 1506, 1371, 1317, 1209, 1142, 1088, 987, 919, 804, 589 $cm^{-1}$.

$^1H$ NMR : δ 7.80 (d, 2H, ArH, $J$ = 8.1 Hz), 7.61 (d, 1H, olefinic, $J$ =

15.4 Hz), 7.48 (d, 2H, ArH, $J$ = 8.5 Hz), 7.33 (d, 2H, ArH, $J$ = 8.0 Hz), 7.11 (d, 2H, ArH, $J$ = 8.5 Hz), 6.78 (d, 1H, olefinic, $J$ = 15.4 Hz), 2.44 (s, 3H, $OCOCH_3$), 2.29 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 168.50, 152.61, 144.14, 140.60, 137.83, 130.07, 129.86, 129.60, 127.88, 127.70, 122.26, 21.57, 21.00.

Anal. Calcd. for $C_{17}H_{16}O_4S$: C, 64.54; H, 5.10; S, 10.14. Found: C, 64.43; H, 5.53; S, 10.22

***1-Phenylsulfonyl-2-phenylethene (31)***[24,31,32,34,37,54]

A mixture of styrene **19** (104 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 185 mg (76%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 70-71 °C

IR (KBr) $\nu_{max}$ : 3058, 1714, 1608, 1570, 1446, 1303, 1191, 1141, 1085, 1023, 973, 855, 811, 742 $cm^{-1}$.

$^1$H NMR : δ 7.94-7.91 (m, 2H, ArH), 7.65 (d, 1H, olefinic, $J$ = 15.4 Hz), 7.59-7.49 (m, 3H, ArH), 7.46-7.43 (m, 2H, ArH), 7.39-7.36 (m, 3H, ArH), 6.85 (d, 1H, olefinic, $J$ = 15.4 Hz).

$^{13}$C NMR : δ 142.25, 140.79, 133.18, 132.28, 131.05, 129.20, 128.95, 128.49, 127.57, 127.37.

***1-Phenylsulfonyl-2-(4'-methylphenyl)ethene (156)***[31]

A mixture of 4-methylstyrene **109** (118 mg, 1 mmol) sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in

anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 206 mg (80%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 132-135 °C

IR (KBr) $\nu_{max}$ : 3064, 1607, 1507, 1445, 1308, 1140, 1084, 974, 869, 829, 785, 754 $cm^{-1}$.

$^1H$ NMR : δ 7.93 (m, 2H, ArH), 7.63 (d, 1H, olefinic, $J$ = 15.4 Hz), 7.62-7.51 (m, 3H, ArH), 7.37 (d, 2H, ArH, $J$ = 8.0 Hz), 7.17 (d, 2H, ArH, $J$ = 7.9 Hz), 6.78 (d, 1H, olefinic, $J$ = 15.4 Hz), 2.37 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 142.38, 141.64, 141.10, 133.11, 129.74, 129.66, 129.21, 128.57, 127.59, 126.25, 21.49.

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.93; H, 5.54; S, 12.52.

***1-Phenylsulfonyl-2-(4'-chlorophenyl)ethene (158)***[31,53]

A mixture of 4-chlorostyrene **66** (138.5 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 237 mg (85%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 129-130 °C

IR (KBr) $\nu_{max}$ : 2921, 2846, 1614, 1483, 1446, 1346, 1303, 1147, 1116, 1079, 786, 749, 687 $cm^{-1}$.

$^1H$ NMR : δ 7.93 (d, 2H, ArH, $J$ = 7.0 Hz), 7.62 (d, 1H, olefinic, $J$ =

15.2 Hz), 7.62-7.57 (m, 1H, ArH), 7.53 (d, 2H, ArH, $J$ = 7.0 Hz), 7.42 (d, 2H, ArH, $J$ = 8.5 Hz), 7.35 (d, 2H, ArH, $J$ = 8.5 Hz), 6.83 (d, 1H, olefinic, $J$ = 15.4 Hz).

$^{13}$C NMR : δ 140.85, 140.70, 137.29, 133.41, 130.92, 129.74, 129.40, 129.36, 128.13, 127.77.

***1-Phenylsulfonyl-2-(2'-chlorophenyl)ethene (160)***

A mixture of 2-chlorostyrene **114** (138.5 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 240 mg (86%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 102-104 °C

IR (KBr) $\nu_{max}$ : 3056, 1607, 1479, 1445, 1303, 1155, 1081, 980, 831, 757, 683 cm$^{-1}$.

$^{1}$H NMR : δ 8.06 (d, 1H, olefinic, $J$ = 15.4 Hz), 7.96-7.93 (m, 2H, ArH), 7.65-7.49 (m, 4H, ArH), 7.42-7.22 (m, 3H, ArH), 6.89 (d, 1H, olefinic, $J$ = 15.4 Hz).

$^{13}$C NMR : δ 140.45, 138.17, 135.25, 133.39, 131.80, 130.69, 130.30, 130.21, 129.30, 128.22, 127.78, 127.13.

***1-Phenylsulfonyl-2-(3'-nitrophenyl)ethene (162)***[54]

A mixture of 3-nitrostyrene **117** (149 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral

alumina column afforded 234 mg (81%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 126-128 °C

IR (KBr) $\nu_{max}$ : 3058, 1622, 1585, 1530, 1478, 1446, 1352, 1300, 1145, 1083, 976, 846, 811, 752 $cm^{-1}$.

$^1H$ NMR : δ 8.34 (s, 1H, ArH), 8.24 (d, 1H, ArH, *J* = 8.0 Hz), 7.96 (d, 2H, ArH, *J* = 7.3 Hz), 7.81 (d, 1H, ArH, *J* = 7.6 Hz), 7.72 (d, 1H, olefinic, *J* = 15.4 Hz), 7.65-7.55 (m, 4H, ArH), 7.04 (d, 1H, olefinic, *J* = 15.4 Hz).

$^{13}C$ NMR : δ 148.59, 139.98, 139.20, 134.14, 133.65, 130.81, 130.12, 129.40, 129.14, 127.81, 125.20, 122.72.

Anal. Calcd. for $C_{14}H_{11}NO_4S$: C, 58.12; H, 3.83; N,4.84 S, 11.08. Found: C, 58.30; H, 4.06; N, 4.89; S, 11.43.

***1-Phenylsulfonyl-2-(1-naphthyl)ethene (168)***

A mixture of 1-vinylnaphthalene **129** (154 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 223 mg (76%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 93-94 °C

IR (KBr) $\nu_{max}$ : 3056, 1607, 1580, 1512, 1458, 1310, 1148, 1094, 980, 852, 798, 751 $cm^{-1}$.

$^1H$ NMR : δ 8.51 (d, 1H, olefinic, *J* = 15.1 Hz), 8.18-7.85 (m, 5H, ArH), 7.67-7.51 (m, 6H, ArH), 7.46-7.41 (m, 1H, ArH), 6.94 (d, 1H, olefinic, *J* = 15.1 Hz).

$^{13}C$ NMR : δ 142.76, 140.87, 139.45, 133.72, 133.32, 131.45, 131.39,

129.82, 129.61, 129.35, 128.85, 127.81, 127.36, 126.52, 125.69, 125.26, 123.10.

Anal. Calcd. for $C_{18}H_{14}O_2S$: C, 73.44; H, 4.79; S, 10.89. Found: C, 73.71; H, 4.88; S, 10.83.

***1-Phenylsulfonyl-2-(2-naphthyl)ethene (164)***

A mixture of 2-vinylnaphthalene **148** (154 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 244 mg (83%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 99-101 °C

IR (KBr) $\nu_{max}$ : 3052, 1611, 1595, 1479, 1448, 1306, 1289, 1142, 1067, 964, 846 $cm^{-1}$.

$^1H$ NMR : δ 7.87-7.84 (m, 2H, ArH), 7.73-7.64 (m, 3H, ArH), 7.63 (d, 1H, olefinic, $J$ = 15.2 Hz), 7.45-7.34 (m, 6H, ArH), 6.84 (d, 1H, olefinic, $J$ = 15.3 Hz).

$^{13}C$ NMR : δ 142.29, 140.86, 134.32, 133.14, 132.93, 130.74, 129.65, 129.18, 128.75, 128.53, 127.66, 127.60, 127.54, 127.35, 126.80, 123.33.

***1-Phenylsulfonyl-2-(4'-acetoxyphenyl)ethene (167)***

A mixture of 4-acetoxystyrene **144** (162 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) in anhydrous acetonitrile (10 mL) was treated with CAN (1.37 g, 2.5 mmol) in anhydrous acetonitrile (15 mL) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral

alumina column afforded 211 mg (70%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 126-127 °C

IR (KBr) $\nu_{max}$ : 3049, 1755, 1613, 1506, 1445, 1378, 1317, 1135, 1088, 1013, 973, 818, 690 $cm^{-1}$.

$^1H$ NMR : δ 7.94-7.92 (m, 2H, ArH), 7.68-7.56 (m, 3H, ArH), 7.57 (d, 1H, olefinic, $J$ = 15.1 Hz), 7.50 (d, 2H, ArH, $J$ = 8.5 Hz), 7.12 (d, 2H, ArH, $J$ = 8.5 Hz), 6.79 (d, 1H, olefinic, $J$ = 15.3 Hz), 2.30 (s, 3H, $OCOCH_3$).

$^{13}C$ NMR : δ 168.53, 152.71, 141.19, 133.24, 129.66, 129.23, 127.62, 127.52, 122.29, 20.99.

***1-(4'-Methylphenylsulfonyl)-2-(2',4',6'-trimethylphenyl)ethene (171)***

A mixture of mesitylstyrene **145** (145 mg, 1 mmol), sodium sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 225 mg (75%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 94-95 °C

IR (KBr) $\nu_{max}$ : 3056, 2975, 1600, 1452, 1303, 1290, 1148, 1081, 987, 858, 663 $cm^{-1}$.

$^1H$ NMR : δ 7.81 (d, 2H, ArH, $J$ = 8.3 Hz), 7.80 (d, 1H, olefinic, $J$ = 14.9 Hz), 7.33 (d, 2H, ArH, $J$ = 8.0 Hz), 6.84 (s, 2H, ArH), 6.49 (d, 1H, olefinic, $J$ = 15.1 Hz), 2.44 (s, 3H, $CH_3$), 2.27 (s, 6H, $CH_3$), 2.25 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 144.02, 140.15, 139.12, 138.16, 136.94, 132.14, 129.89, 129.37, 128.58, 127.64, 21.61, 21.08, 21.01.

Anal. Calcd. for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.76; S, 10.67. Found: C, 72.16; H, 6.83; S, 10.90.

***1-(4'-Methylphenylsulfonyl)-1-methyl-2-(4'-methylphenyl)ethene(173)***

A mixture of β-methyl-4-methylstyrene **172** (132 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol, 224 mg) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 186 mg (65%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 113-115 °C

IR (KBr) $\nu_{max}$ : 3036, 2982, 2928, 1600, 1445, 1303, 1155, 1108, 1081, 966, 818, 744, 663, $cm^{-1}$.

$^1H$ NMR : δ 7.80-7.74 (m, 3H, ArH), 7.33-7.27 (m, 3H, ArH + 1H olefinic), 7.20-7.15 (m, 2H, ArH), 2.44 (s, 3H, $CH_3$), 2.37 (s, 3H, $CH_3$), 2.09 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 143.92, 139.42, 137.01, 136.51, 131.11, 129.76, 129.71, 129.38, 128.28, 127.95, 21.64, 21.42, 13.26.

***1-Phenylsulfonyl)-1-methyl-2-(4'-methylphenyl)ethene(174)***[52,53,54]

A mixture of β-methyl-4-methylstyrene **172** (132 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 150 mg (55%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 89-90 °C

IR (KBr) $\nu_{max}$ : 3056, 1634, 1506, 1303, 1155, 1115, 1088, 973, 818, 764,

697 $cm^{-1}$.

$^1H$ NMR : δ 7.92-7.89 (m, 2H, ArH), 7.77 (s, 1H, ArH), 7.62-7.49 (m, 2H, ArH + 1H olefinic), 7.29 (d, 2H, ArH, $J$ = 8.0 Hz), 7.19 (d, 2H, ArH, $J$ = 8.0 Hz), 2.36 (s, 3H, $CH_3$), 2.10 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 139.49, 139.33, 137.35, 136.09, 133.04, 130.85, 129.62, 129.31, 129.04, 128.03, 21.30, 13.18.

***1-(4'-Methylphenylsulfonyl)-1-octene (176)***[34]

A mixture of 1-octene **175** (112 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 173 mg (65%) of the product; colourless viscous liquid

IR (neat) $\nu_{max}$ : 2962, 2942, 2854, 1607, 1499, 1330, 1297, 1155, 1094, 980, 818, 670 $cm^{-1}$.

$^1H$ NMR : δ 7.73 (d, 2H, ArH, $J$ = 8.1 Hz), 7.31 (d, 2H, ArH, $J$ = 8.1 Hz), 6.98-6.88 (m, 1H, olefinic), 6.30-6.24 (m, 1H, olefinic), 2.42 (s, 3H, $CH_3$), 2.24-2.18 (m, 2H, $CH_2$), 1.44-1.42 (m, 2H, $CH_2$), 1.25 (brs, 6H, $CH_2$), 0.86 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 146.32, 143.87, 130.76, 129.73, 128.64, 127.56, 31.38, 28.64, 27.53, 22.40, 21.51, 13.95.

GC-MS *(m/z)* : 265[$M^+$-1] (10), 196 (15), 179 (16), 157 (45), 155 (36), 139 (100), 119 (65), 109 (55).

***1-(Phenylsulfonyl)-1-octene (177)***[31]

A mixture of 1-octene **175** (112 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under

argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 159 mg (63%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 2962, 2942, 2861, 1640, 1458, 1330, 1310, 1162, 1094, 973, 831, 764 $cm^{-1}$.

$^1H$ NMR : δ 7.87-7.85 (m, 2H, ArH), 7.62-7.45 (m, 3H, ArH), 7.02-6.93 (m, 1H, olefinic), 6.32-6.27 (m, 1H, olefinic), 2.26-2.19 (m, 2H, $CH_2$), 1.45-1.43 (m, 2H, $CH_2$), 1.25 (brs, 6H, $CH_2$), 0.86 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 146.98, 140.84, 133.01, 130.41, 129.08, 127.46, 31.36, 28.60, 27.47, 22.37, 13.92.

***1-(4'-Methylphenylsulfonyl)-2-iodocyclohexane (178)***
***and 1-(4'-Methylphenylsulfonyl)-cyclohexene (61)***

A mixture of cyclohexene **27** (82 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 109 mg (30%) of **178** and 59 mg (25%) of **61.**

***1-(4'-Methylphenylsulfonyl)-2-iodocyclohexane (178)***[24]

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3062, 2943, 2862, 1634, 1595, 1446, 1313, 1272, 1145, 1084, 1000, 865, 813, 714, 677 $cm^{-1}$.

$^1H$ NMR : δ 7.74 (d, 2H, ArH, $J$ = 7.9 Hz), 7.35 (d, 2H, ArH, $J$ = 7.8 Hz), 5.09 (s, 1H, $CHSO_2$), 3.29 (s, 1H, CHI), 2.45 (s, 3H, $CH_3$), 2.20-2.16 (m, 2H, $CH_2$), 1.96-1.91 (m, 2H, $CH_2$), 1.66-1.51 (m, 4H, $CH_2$).

$^{13}C$ NMR : δ 144.77, 135.28, 129.93, 128.51, 67.40, 33.26, 25.39,

22.34, 21.66, 21.52, 20.89.

***1-(4'-Methylphenylsulfonyl)-cyclohexene (61)***[17c,18a,37,55]

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 79-80 °C

IR (KBr) $\nu_{max}$ : 2962, 2867, 1600, 1447, 1317, 1290, 1155, 1094, 818, 744, 676, 602 $cm^{-1}$.

$^1H$ NMR : δ 7.72 (d, 2H, ArH, $J$ = 8.1 Hz), 7.30 (d, 2H, ArH, $J$ = 8.0 Hz), 7.02-7.01 (m, 1H, olefinic) 2.44 (s, 3H, $CH_3$), 2.27-2.25 (m, 2H, $CH_2$), 2.15 (m, 2H, $CH_2$), 1.64-1.56 (m, 4H, $CH_2$).

$^{13}C$ NMR : δ 143.79, 140.25, 137.64, 129.67, 128.61, 128.18, 25.48, 22.85, 21.90, 21.64, 20.92.

Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 66.09; H, 6.76; S, 14.00.

***1-(Phenylsulfonyl)-2-iodocyclohexane (179)***
***and 1-(Phenylsulfonyl)-cyclohexene (54)***

A mixture of 1-octene **27** (82 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 98 mg (28%) of **179** and 52 mg (23%) **54**.

***1-(Phenylsulfonyl)-2-iodocyclohexane (179)***[24]

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3062, 2943, 2856, 1447, 1305, 1147, 1083, 861, 722, 688, 655 $cm^{-1}$.

$^1H$ NMR : δ 7.90-7.84 (m, 2H, ArH), 7.71-7.52 (m, 3H, ArH), 5.11 (s, 1H, $CHSO_2$), 3.34 (s, 1H, CHI), 2.26-2.17 (m, 2H, $CH_2$), 1.97 (m, 2H, $CH_2$), 1.80-1.53 (m, 4H, $CH_2$).

$^{13}$C NMR : δ 138.15, 133.86, 129.32, 128.47, 67.38, 33.40, 25.00, 22.38, 21.60, 20.91.

***1-(Phenylsulfonyl)-cyclohexene (54)***[37]

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3070, 2942, 2867, 1701, 1647, 1452, 1303, 1290, 1162, 1094, 1027, 757 cm$^{-1}$.

$^{1}$H NMR : δ 7.86-7.83 (m, 2H, ArH), 7.63-7.50 (m, 3H, ArH), 7.07-7.04 (m, 1H, olefinic), 2.28-2.26 (m, 2H, $CH_2$), 2.16-2.15 (m, 2H, $CH_2$), 1.68-1.55 (m, 4H, $CH_2$).

$^{13}$C NMR : δ 139.84, 139.48, 138.23, 132.99, 128.97, 127.96, 25.42, 22.77, 21.76, 20.76.

GC-MS *(m/z)* : 222[M$^{+}$] (71), 125 (26), 97 (29), 77 (100), 55 (19), 51 (76).

***2-(4'-Methylphenylsulfonyl)-1-phenyl-1-cyclohexene (181) and***

***2-(4'-Methylphenylsulfonyl)-1-hydroxy-1-phenylcyclohexane (182)***

A mixture of 1-phenyl-1-cyclohexene **180** (158 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 62 mg (20%) of **181** and 182 mg (55%) **182**.

***2-(4'-Methylphenylsulfonyl)-1-phenyl-1-cyclohexene (181)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 127-130 °C

IR (KBr) $\nu_{max}$ : 3029, 2948, 2908, 1607, 1452, 1297, 1142, 1088, 912, 771, 730 cm$^{-1}$.

$^{1}$H NMR : δ 7.50-7.48 (m, 2H, ArH), 7.38-7.16 (m, 2H, ArH), 7.04-6.95 (m, 5H, ArH), 6.21-6.20 (m, 1H, olefinic), 4.32 (m, 1H, $CHSO_2$), 2.82-2.77 (m, 1H, $CH_2$), 2.35-2.14 (m, 3H,

$CH_2$), 2.30 (s, 3H, $CH_3$), 1.92-1.89 (m, 1H, $CH_2$), 1.87-1.76 (m, 1H, $CH_2$).

$^{13}$C NMR : δ 143.48, 137.17, 135.07, 131.24, 129.05, 128.70, 128.04, 127.19, 126.55, 126.39, 62.78, 25.57, 23.49, 21.50, 17.45.

***2-(4'-Methylphenylsulfonyl)-1-hydroxy-1-phenylcyclohexane (182)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 157-159 °C

IR (KBr) $\nu_{max}$ : 3494, 2942, 2867, 1607, 1449, 1310, 1290, 1135, 1081, 973, 746 $cm^{-1}$.

$^1$H NMR : δ 7.63-7.61 (m, 2H, ArH), 7.48 (d, 2H, ArH, *J* = 8.1 Hz), 7.25-7.23 (m, 3H, ArH), 7.19 (d, 2H, ArH, *J* = 8.1 Hz), 4.33 (brs, 1H, OH, exchangeable with $D_2O$), 3.60-3.55 (m, 1H, $CHSO_2$), 2.41 (s, 3H, $CH_3$), 2.33-1.35 (m, 8H, $CH_2$).

$^{13}$C NMR : δ 144.03, 143.76, 137.10, 129.51, 128.30, 127.84, 127.49, 127.12, 74.98, 73.49, 25.30, 24.38, 21.58, 21.33.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71; S, 9.70. Found: C, 69.03; H, 7.06; S, 9.65

***2-(Phenylsulfonyl)-1-phenyl-1-cyclohexene (183) and***

***2-(Phenylsulfonyl)-1-hydroxy-1-phenylcyclohexane (184)***

A mixture of 1-phenyl-1-cyclohexene **181** (158 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 30 mg (10%) of **183** and 149 mg (50%) **184**.

***2-(Phenylsulfonyl)-1-phenyl-1-cyclohexene (183)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 86-89 °C

IR (KBr) $\nu_{max}$ : 3063, 2948, 1445, 1297, 1135, 1081, 724, 697, 622 $cm^{-1}$.

$^1H$ NMR : δ 7.50-7.47 (m, 2H, ArH), 7.38-7.33 (m, 1H, ArH), 7.21-7.16 (m, 2H, ArH), 7.02-7.00 (m, 5H, ArH), 6.22-6.21 (m, 1H, olefinic), 4.36 (m, 1H, $CHSO_2$), 2.85-2.80 (m, 1H, $CH_2$), 2.42-2.10 (m, 3H, $CH_2$), 1.95-1.89 (m, 1H, $CH_2$), 1.83-1.73 (m, 1H, $CH_2$).

$^{13}C$ NMR : δ 140.84, 140.21, 134.98, 132.67, 131.11, 128.50, 128.34, 128.02, 126.80, 126.30, 62.72, 25.47, 23.36, 17.43.

***2-(Phenylsulfonyl)-1-hydroxy-1-phenylcyclohexane (184)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 131-133 °C

IR (KBr) $\nu_{max}$ : 3505, 3062, 2943, 2862, 1495, 1447, 1301, 1139, 1082, 1035, 971, 763, 688 $cm^{-1}$.

$^1H$ NMR : δ 7.59-7.51 (m, 5H, ArH), 7.42-7.37 (m, 2H, ArH), 7.25-7.21 (m, 3H, ArH), 4.18 (brs, 1H, OH, exchangeable with $D_2O$), 3.64-3.59 (m, 1H, $CHSO_2$), 2.34-1.45 (m, 8H, $CH_2$).

$^{13}C$ NMR : δ 143.69, 139.99, 132.94, 128.77, 128.03, 127.78, 127.50, 126.97, 74.65, 73.09, 25.01, 24.02, 21.21.

***1-(4'-Methylphenylsulfonyl)-2-phenyl-1-cycloheptene (186)***

A mixture of 1-phenyl-1-cycloheptene **185** (172 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 170 mg (52%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 122-124 °C

IR (KBr) $\nu_{max}$ : 3029, 2921, 2861, 1600, 1452, 1317, 1290, 1142, 1088,

852, 771, 676 $cm^{-1}$.

$^1H$ NMR : δ 7.55 (d, 2H, ArH, $J$ = 8.2 Hz), 7.06-7.03 (m, 5H, ArH), 6.93-6.90 (m, 2H, ArH), 6.30-6.25 (m, 1H, olefinic), 4.39-4.36 (m, 1H, $CHSO_2$), 2.91-2.82 (m, 1H, $CH_2$), 2.63-2.57 (m, 1H, $CH_2$), 2.46-2.36 (m, 1H, $CH_2$), 2.30 (s, 3H, $CH_3$), 1.99-1.85 (m, 3H, $CH_2$), 1.54-1.35 (m, 2H, $CH_2$).

$^{13}C$ NMR : δ 144.30, 143.79, 139.05, 136.67, 135.53, 129.20, 128.69, 127.83, 126.35, 126.28, 69.65, 27.42, 26.79, 26.13, 25.55, 21.50.

Anal. Calcd. for $C_{20}H_{22}O_2S$: C, 73.58; H, 6.79; S, 9.82. Found: C, 73.70; H, 6.82; S, 9.84.

***1-(4'-Methylphenylsulfonyl)-2-iodo-2-phenylethene (193)***[16b]

A mixture of phenylacetylene **25** (102 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (197 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 300 mg (78%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 77-79 °C

IR (KBr) $\nu_{max}$ : 3070, 1600, 1445, 1337, 1276, 1155, 1094, 865, 778, 710, 555 $cm^{-1}$.

$^1H$ NMR : δ 7.43 (d, 2H, ArH, $J$ = 7.0 Hz), 7.34 (s, 1H, olefinic), 7.27-7.22 (m, 3H, ArH,),7.26 (d, 2H, ArH, $J$ = 7.8 Hz), 7.16 (d, 2H, ArH, $J$ = 7.8 Hz), 2.37 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 144.41, 141.30, 139.61, 137.39, 137.36, 129.71, 129.60, 127.84, 127.68, 114.09, 21.59.

***1-Phenylsulfonyl-2-iodo-2-phenylethene (198)***[24]

A mixture of phenylacetylene **25** (102 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 303 mg (82%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 3043, 1604, 1584, 1485, 1444, 1324, 1147, 1080, 863, 772, 744, 686 $cm^{-1}$.

$^1H$ NMR : δ 7.54-7.46 (m, 3H, ArH), 7.36 (s, 1H, olefinic), 7.35-7.30 (m, 2H, ArH), 7.25-7.19 (m, 5H, ArH).

$^{13}C$ NMR : δ 140.89, 139.97, 139.27, 133.22, 129.53, 128.75, 127.67, 127.47, 127.40, 114.49.

***1-(4'-Methylphenylsulfonyl)-2-iodo-2-(4'-methylphenyl)ethene (199)***

A mixture of 4-methylphenylacetylene **194** (116 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (197 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 318 mg (80%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 114-116 °C

*IR (KBr) $\nu_{max}$ : 3043, 1607, 1499, 1337, 1155, 1088, 825, 791, 744, 676 $cm^{-1}$.*

$^1H$ NMR : δ 7.49 (d, 2H, ArH, $J$ = 8.2 Hz), 7.28 (s, 1H, olefinic), 7.21-7.15 (m, 4H, ArH), 7.09 (d, 2H, ArH, $J$ = 8.1 Hz), 2.40 (s, 3H, $CH_3$), 2.36 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 144.35, 140.72, 140.09, 136.89, 129.61, 128.54, 127.92,

127.90, 114.65, 21.66, 21.50.

GC-MS *(m/z)* : 398[$M^+$] (2), 271 (9), 207 (16), 155 (10), 115 (96), 91 (100), 65 (38).

Anal. Calcd. for $C_{20}H_{22}O_2S$: C, 48.25; H, 3.80; S, 8.05. Found: C, 48.21; H, 3.58; S, 7.58.

***1-Phenylsulfonyl-2-iodo-2-(4'-methylphenyl)ethene (200)***

A mixture of 4-methylphenylacetylene **194** (116 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 303 mg (79%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 3043, 1613, 1512, 1452, 1330, 1162, 1088, 872, 831, 703 $cm^{-1}$.

$^1$H NMR : δ 8.07-8.04 (m, 2H, ArH), 7.59 (d, 2H, ArH, $J$ = 7.5 Hz), 7.39 (d, 2H, ArH, $J$ = 7.6 Hz), 7.31 (s, 1H, olefinic), 7.16-7.05 (m, 3H, ArH), 2.36 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 142.26, 140.60, 133.94, 132.71, 129.42, 129.28, 128.91, 127.85, 127.37, 114.83, 21.78.

***1-(4'-Methylphenylsulfonyl)-2-iodo-2-(4'-methoxyphenyl)ethene (201)***

A mixture of 4-methoxylphenylacetylene **195** (132 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 311 mg (75%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 134-136 °C

IR (KBr) $\nu_{max}$ : 2962, 2908, 1681, 1600, 1573, 1317, 1263, 1182, 1142, 1034, 993, 818, 764.

$^1$H NMR : δ 7.49 (d, 2H, ArH, *J* = 8.3 Hz), 7.25 (s, 1H, olefinic), 7.23-7.18 (m, 4H, ArH), 6.78 (d, 2H, ArH, *J* = 8.4 Hz), 3.83 (s, 3H, $OCH_3$), 2.40 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 160.84, 144.30, 142.38, 140.40, 137.75, 131.88, 130.05, 129.62, 127.90, 113.23, 55.31, 21.66.

***1-Phenylsulfonyl-2-iodo-2-(4'-methoxyphenyl)ethene (202)***

A mixture of 4-methoxylphenylacetylene **195** (132 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 280 mg (70%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 3047, 2959, 2845, 1610, 1499, 1322, 1253, 1152, 1078, 842, 821, 705 $cm^{-1}$.

$^1$H NMR : δ 7.59-7.49 (m, 3H, ArH), 7.39-7.34 (m, 2H, ArH), 7.29 (s, 1H, olefinic), 7.20 (d, 2H, ArH, *J* = 8.7 Hz), 6.75 (d, 2H, ArH, *J* = 8.7 Hz), 3.78 (s, 3H, $OCH_3$).

$^{13}$C NMR : δ 160.63, 140.32, 140.01, 134.49, 133.21, 131.54, 129.79, 129.14, 128.79, 127.54, 113.09, 55.15.

GC-MS *(m/z)* : 385[$M^+$] (5), 257 (64), 251 (36), 227 (10), 190 (25), 163 (55), 143 (61), 141 (100), 109 (74).

***1-(4'-Methylphenylsulfonyl)-2-iodo-2-(3'-methoxyphenyl)ethene (203)***

A mixture of 3-methoxyphenylacetylene **196** (132 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room

temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 252 mg (68%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 104-106 °C

IR (KBr) $\nu_{max}$ : 3043, 2996, 1593, 1479, 1324, 1236, 1155, 1081, 818, 737, 649 $cm^{-1}$.

$^1H$ NMR : δ 7.52 (d, 2H, ArH, $J$ = 8.1 Hz), 7.33-7.32 (m, 2H, ArH), 7.29 (s, 1H, olefinic), 7.21 (d, 2H, ArH, $J$ = 8.0 Hz), 6.74-6.71 (m, 2H, ArH), 3.75 (s, 3H, $OCH_3$), 2.40 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 158.30, 144.73, 142.02, 140.11, 136.66, 133.55, 130.20, 129.71, 128.40, 128.19, 117.23, 113.80, 55.51, 21.65.

***1-(4'-Methylphenylsulfonyl)-2-iodo-2-(3'-nitrophenyl)ethene (204)***

A mixture of 3-nitrophenylacetylene **197** (147 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (197 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 279 mg (65%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 156-157°C

IR (KBr) $\nu_{max}$ : 3090, 3049, 1610, 1533, 1351, 1297, 1155, 1088, 912, 858, 751, 649 $cm^{-1}$.

$^1H$ NMR : δ 8.20-8.17 (m, 1H, ArH), 7.89 (s, 1H, ArH), 7.67-7.65 (m, 1H, ArH), 7.58-7.49 (m, 3H, ArH), 7.41 (s, 1H, olefinic), 7.27-7.24 (m, 2H, ArH), 2.41 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 147.57, 145.26, 143.21, 141.27, 137.07, 133.55, 131.40, 130.06, 129.19, 127.89, 124.24, 122.31, 108.84, 21.63.

***1-Phenylsulfonyl-2-iodo-2-(3'-nitrophenyl)ethene (205)***

A mixture of 3-nitrophenylacetylene **197** (147 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 257 mg (62%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 117-119 °C

IR (KBr) $\nu_{max}$ : 3083, 3043, 1526, 1351, 1297, 1155, 1094, 912, 831, 757, 690 $cm^{-1}$.

$^1H$ NMR : δ 8.20-8.18 (m, 2H, ArH), 7.94 (s, 1H, ArH), 7.65-7.46 (m, 6H, ArH), 7.42 (s, 1H, olefinic).

$^{13}C$ NMR : δ 147.62, 142.78, 141.22, 140.02, 134.02, 133.52, 129.45, 129.23, 127.84, 124.36, 122.37, 109.50.

***1-(4'-Methylphenylsulfonyl)-2-iodo-1-octene (207)***[16b,24]

A mixture of 1-octyne **206** (110 mg, 1 mmol), sodium *p*-toluenesulfinate (214 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 255 mg (65%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 2956, 2930, 2856, 1595, 1451, 1320, 1145, 1076, 808, 764, 677 $cm^{-1}$.

$^1H$ NMR : δ 7.77 (d, 2H, ArH, $J$ = 8.1 Hz), 7.35 (d, 2H, ArH, $J$ = 8.1 Hz), 6.98 (s, 1H, olefinic), 3.04-2.99 (m, 2H, $CH_2$), 2.45 (s, 3H, $CH_3$), 1.56-1.52 (m, 2H, $CH_2$), 1.29-1.25 (m, 6H, $CH_2$), 0.90-0.87.86 (m, 3H, $CH_3$).

$^{13}$C NMR : δ 144.67, 139.03, 138.27, 130.07, 127.56, 125.52, 40.01, 31.55, 29.87, 28.18, 22.52, 21.68, 14.08.

***1-Phenylsulfonyl-2-iodo-1-octene(208)***

A mixture of 1-octyne **206** (110 mg, 1 mmol), sodium benzenesulfinate (197 mg, 1.2 mmol) and sodium iodide (179 mg, 1.2 mmol) was treated with CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes. The reaction mixture after work up and purification on neutral alumina column afforded 227 mg (60%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 2935, 2854, 1593, 1438, 1324, 1155, 1088, 798, 744, 683, 548 cm$^{-1}$.

$^{1}$H NMR : δ 7.91-7.88 (m, 2H, ArH), 7.68-7.63 (m, 1H, ArH), 7.58-7.53 (m, 2H, ArH), 6.99 (s, 1H, olefinic), 3.05-3.00 (m, 2H, $CH_2$), 1.53-1.50 (m, 2H, $CH_2$), 1.29-1.25 (m, 6H, $CH_2$), 0.89-0.87 (m, 3H, $CH_3$).

$^{13}$C NMR : δ 141.15, 138.69, 133.60, 129.40, 127.45, 126.02, 40.04, 31.49, 29.85, 28.13, 22.46, 14.05.

GC-MS *(m/z)* : 379[$M^+$+1] (25), 309 (11), 252 (30), 237 (100), 209 (11), 181 (52), 141 (22), 128 (42), 109 (50).

***1-(4'-Methylphenylsulfonyl)-2-phenylethyne (94)***[16b,46,56]

Phenylacetylene **25** (102 mg, 1 mmol) on treatment with sodium *p*-toluenesulfinate (214 mg, 1.2 mmol), sodium iodide (179 mg, 1.2 mmol)and CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes afforded the β-iodo vinyl sulfone which was refluxed with potassium carbonate in anhydrous acetone (5 mL) for 5 hours. The reaction mixture after work up and purification afforded 184 mg (72%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 78-79 °C

IR (KBr) $\nu_{max}$ : 3036, 2180, 1593, 1492, 1337, 1162, 1094, 852, 771, 697, 548 $cm^{-1}$.

$^1H$ NMR : δ 7.94 (d, 2H, ArH, $J$ = 8.1 Hz), 7.50-7.42 (m, 3H, ArH), 7.39-7.32 (m, 4H, ArH), 2.46 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 145.27, 139.15, 132.72, 131.44, 130.01, 128.68, 127.56, 118.10, 92.76, 85.85, 21.77.

Anal. Calcd. for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72; S, 12.51. Found: C, 70.43; H, 4.93; S, 12.60

***1-Phenylsulfonyl-2-phenylethyne (98)***[45,46]

Phenylacetylene **25** (102 mg, 1 mmol) on treatment with sodium benzenesulfinate (197 mg, 1.2 mmol), sodium iodide (179 mg, 1.2 mmol) and CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes afforded the β-iodovinyl sulfone which was refluxed with potassium carbonate in anhydrous acetone (5 mL) for 5 hours. The reaction mixture after work up and purification afforded 165 mg (68%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane.

mp 68-69 °C

IR (KBr) $\nu_{max}$ : 3063, 2187, 2079, 1580, 1492, 1317, 1162, 1081, 845, 764, 730 $cm^{-1}$.

$^1H$ NMR : δ 8.07-8.04 (m, 2H, ArH), 7.70-7.65 (m, 1H, ArH), 7.61-7.55 (m, 2H, ArH) 7.51-7.42 (m, 3H, ArH), 7.37-7.32 (m, 2H, ArH).

$^{13}C$ NMR : δ 141.95, 134.06, 132.73, 131.50, 129.33, 128.65, 127.42, 117.93, 93.23, 85.51.

Anal. Calcd. for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16; S, 13.23. Found: C, 69.54; H, 4.40; S, 13.37

***1-(4'-Methylphenylsulfonyl)-2-(4'-methylphenyl)ethyne (209)***[46]

4-methylphenylacetylene **194** (116 mg, 1 mmol) on treatment with sodium *p*-toluenesulfinate (214 mg, 1.2 mmol), sodium iodide (179 mg, 1.2 mmol) and CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes afforded the β-iodovinyl sulfone which was refluxed with potassium carbonate in anhydrous acetone (5 mL) for 5 hours. The reaction mixture after work up and purification afforded 203 mg (75%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane

| | | |
|---|---|---|
| mp | | 103-105 °C |
| IR (KBr) $\nu_{max}$ | : | 3043, 2989, 2173, 1600, 1499, 1330, 1155, 1081, 858, 825, 778, 670 $cm^{-1}$. |
| $^1$H NMR | : | δ 7.92 (d, 2H, ArH, $J$ = 8.1 Hz), 7.37-7.34 (m, 4H, ArH), 7.13 (d, 2H, ArH, $J$ = 7.9 Hz), 2.44 (s, 3H, $CH_3$), 2.34 (s, 3H, $CH_3$). |
| $^{13}$C NMR | : | δ 145.01, 142.08, 139.09, 132.47, 129.81, 129.29, 127.26, 114.71, 93.28, 85.26, 21.60, 21.55. |

Anal. Calcd. for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22; S, 11.86. Found: C, 71.47; H, 5.31; S, 11.60

***1-Phenylsulfonyl-2-(4'-methylphenyl)ethyne (210)***

4-methylphenylacetylene **194** (116 mg, 1 mmol) on treatment with sodium benzenesulfinate (197 mg, 1.2 mmol), sodium iodide (179 mg, 1.2 mmol) and CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes afforded the β-iodovinyl sulfone which was refluxed with potassium carbonate in anhydrous acetone (5 mL) for 5 hours. The reaction mixture after work up and purification afforded 189 mg (74%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 87-88 °C

IR (KBr) $\nu_{max}$ : 3056, 2180, 1613, 1580, 1452, 1344, 1169, 1088, 865, 811, 724 $cm^{-1}$.

$^1H$ NMR : δ 8.08-8.05 (m, 2H, ArH), 7.67-7.56 (m, 3H, ArH), 7.40 (d, 2H, ArH, $J$ = 8.0 Hz), 7.16 (d, 2H, ArH, $J$ = 7.9 Hz), 2.37 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 142.26, 142.10, 133.94, 132.69, 129.42, 129.27, 127.35, 114.80, 93.90, 85.10, 21.77.

Anal. Calcd. for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72; S, 12.51. Found: C, 70.33; H, 4.76; S, 12.70.

***1-(4'-Methylphenylsulfonyl)-2-(4'-methoxyphenyl)ethyne (211)***

4-Methoxyphenylacetylene **195** (132 mg, 1 mmol) on treatment with sodium *p*-toluenesulfinate (214 mg, 1.2 mmol), sodium iodide (179 mg, 1.2 mmol) and CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes afforded the β-iodovinyl sulfone which was refluxed with potassium carbonate in anhydrous acetone (5 mL) for 5 hours. The reaction mixture after work up and purification afforded 215 mg (75%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 123-124 °C

IR (KBr) $\nu_{max}$ : 2955, 2894, 2362, 1674, 1607, 1317, 1270, 1182, 1142, 1000, 845, 771, 683 $cm^{-1}$.

$^1H$ NMR : δ 7.91 (d, 2H, ArH, $J$ = 8.2 Hz), 7.41 (d, 2H, ArH, $J$ = 8.9 Hz), 7.35 (d, 2H, ArH, $J$ = 8.0 Hz), 6.83 (d, 2H, ArH, $J$ = 8.9 Hz), 3.79 (s, 3H, $OCH_3$), 2.43 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 161.94, 144.87, 139.23, 134.40, 129.76, 127.16, 114.26, 109.36, 93.78, 84.88, 55.22, 21.52.

***1-Phenylsulfonyl-2-(4'-methoxyphenyl)ethyne (212)***[45]

4-Methoxyphenylacetylene **195** (132 mg, 1 mmol) on treatment with sodium benzenesulfinate (197 mg, 1.2 mmol), sodium iodide (179 mg, 1.2 mmol) and CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes afforded the $\beta$-iodovinyl sulfone which was refluxed with potassium carbonate in anhydrous acetone (5 mL) for 5 hours. The reaction mixture after work up and purification afforded 190 mg (70%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 103-105 °C

IR (KBr) $\nu_{max}$ : 2996, 2935, 1667, 1607, 1512, 1317, 1263, 1162, 1088, 804, 737 $cm^{-1}$.

$^1H$ NMR : $\delta$ 8.06-8.03 (m, 2H, ArH), 7.67-7.54 (m, 3H, ArH), 7.40 (d, 2H, ArH, $J$ = 8.7 Hz), 6.84 (d, 2H, ArH, $J$ = 8.8 Hz), 3.78 (s, 3H, $OCH_3$).

$^{13}C$ NMR : $\delta$ 161.98, 141.92, 134.41, 133.78, 129.13, 126.98, 114.25, 109.07, 94.34, 84.53, 55.18.

***1-(4'-Methylphenylsulfonyl)-2-(3'-methoxyphenyl)ethyne (213)***

3-Methoxyphenylacetylene **196** (132 mg, 1 mmol) on treatment with sodium *p*-toluenesulfinate (214 mg, 1.2 mmol), sodium iodide (179 mg, 1.2 mmol) and CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes afforded the $\beta$-iodovinyl sulfone which was refluxed with potassium carbonate in anhydrous acetone (5 mL) for 5 hours. The reaction mixture after work up and purification afforded 186 mg (65%) of the product; colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 129-130 °C

IR (KBr) $\nu_{max}$ : 2962, 2908, 1688, 1607, 1330, 1263, 1155, 1182, 1034,

993, 764 $cm^{-1}$.

$^1H$ NMR : δ 7.93 (d, 2H, ArH, *J* = 8.0 Hz), 7.37 (d, 2H, ArH, *J* = 8.0 Hz), 7.24 (t, 1H, ArH, *J* = 7.8 Hz), 7.08 (d, 2H, ArH, *J* = 7.4 Hz), 6.99 (m, 2H, ArH), 3.77 (s, 3H, $OCH_3$), 2.46 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 159.26, 145.17, 138.95, 129.89, 129.70, 127.43, 125.07, 118.78, 118.19, 116.95, 92.57, 85.34, 55.22, 21.65.

***1-(4'-Methylphenylsulfonyl)-1-octyne (214)***

A mixture of 1-octyne **206** (110 mg, 1 mmol), on treatment with sodium *p*-toluenesulfinate (214 mg, 1.2 mmol), sodium iodide (179 mg, 1.2 mmol) and CAN in anhydrous acetonitrile (1.37 g, 2.5 mmol) at room temperature under argon atmosphere for 45 minutes afforded the β-iodo vinyl sulfone which was refluxed with potassium carbonate in anhydrous acetone (5 mL) for 5 hours. The reaction mixture after work up and purification afforded 158 mg (60%) of the product; colourless viscous liquid.

IR (neat) $\nu_{max}$ : 2955, 2935, 2867, 1600, 1472, 1344, 1169, 1094, 818, 690, 629, 562 $cm^{-1}$.

$^1H$ NMR : δ 7.86 (d, 2H, ArH, *J* = 8.2 Hz), 7.34 (d, 2H, ArH, *J* = 8.1 Hz), 2.46 (s, 3H, $CH_3$), 2.34 (t, 2H, $CH_2$, *J* = 7.1 Hz), 1.59-1.49 (m, 2H, $CH_2$), 1.37-1.17 (m, 6H, $CH_2$), 0.88-0.83 (m, 3H, $CH_3$).

$^{13}C$ NMR : δ 144.73, 139.38, 129.71, 127.22, 96.86, 78.56, 30.96, 28.32, 26.89, 22.27, 21.60, 18.33, 13.85.

## 2.7 REFERENCES

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Chapter 3

# CERIUM(IV) AMMONIUM NITRATE MEDIATED SELENOCYANATION OF STYRENES AND ELECTRON RICH AROMATICS

## 3.1 INTRODUCTION

Although the first synthetic organoselenium compound, diethyl selenide, was prepared by Löwing as early as 1836,[1] the highly malodorous nature of selenium compounds coupled with the instability of many of the derivatives hampered the development of organoselenium chemistry for a very long time. Thus, major developments in organoselenium chemistry intensified only in the 1970s, well over a century after the discovery of the first organoselenium compound. Interest in the use of organoselenium compounds in biochemistry started with the findings that organoselenium compounds are much less toxic compared with the inorganic selenium species.[2] Since then there has been growing interest in the synthesis of organoselenium compounds with respect to their use in enzymology and bioorganic chemistry.[3]

It has been reported that a number of organoselenium compounds exhibit considerable anticancer properties.[4] For example, benzyl selenocyanate has been shown to be a potent inhibitor of tumour cells.[5] Therefore, the design and synthesis of organoselenium compounds have received much attention in synthetic organic chemistry.[2, 6]

The structures of organoselenium compounds are closely related to those of analogous sulfur compounds. However, there are remarkable differences in

their properties. Also the use of selenium intermediates is facilitated by simpler and milder conditions.

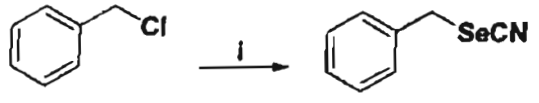
## 3.2 GENERAL METHODS FOR THE SYNTHESIS OF SELENOCYANATES

Selenium is most commonly introduced into organic structures through alkyl and aryl selenocyanate synthesis. Because of the similarity in the chemical behaviour of selenocyanate to that of halide ions, it is considered as a "pseudohalide". It is ten times more nucleophilic than the thiocyanate ion.

Aliphatic selenocyanates[7] are usually prepared by the nucleophilic displacement of a halide or any other good leaving group, by selenocyanate anion (Scheme 1).


**Scheme 1**

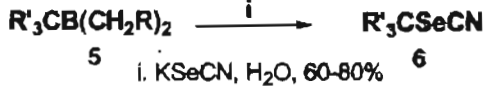
Benzyl selenocyanate is easily prepared from benzyl chloride[8] by the reaction with potassium selenocyanate (Scheme 2).




i. KSeCN, EtOH, 20 °C, 83%

**Scheme 2**

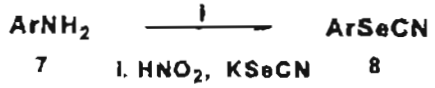
Selenocyanate anion also substitutes a dialkylboron moiety linked to a secondary or tertiary carbon (Scheme 3).[9]




i. KSeCN, $H_2O$, 60-80%

**Scheme 3**

A more satisfactory procedure for the preparation of arylselenocyanates utilizes the reaction of a diazonium salt, obtained from an aniline precursor, with potassium selenocyanate (Scheme 4).[10]

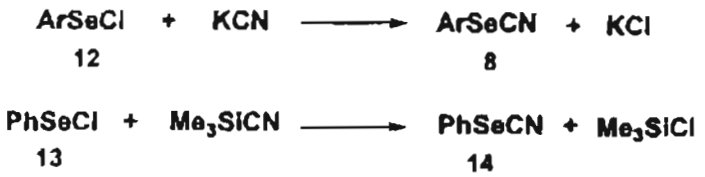



**Scheme 4**

The compound **10**, obtained from the reaction between triphenyl phosphine and selenocyanogen, has been used to prepare primary alkyl and benzylic selenocyanates from the corresponding alcohols (Scheme 5).[11]

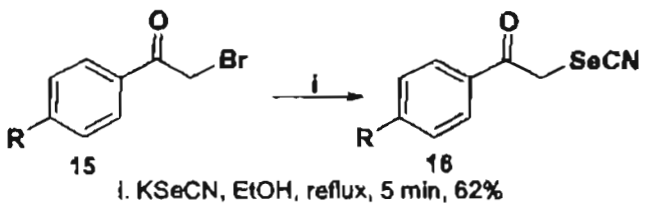

**Scheme 5**

The nucleophilic substitution on areneselenenyl chlorides can be accomplished by the cyanide ion using either potassium cyanide[12] or trimethylsilyl cyanide[13]as reagents (Scheme 6).



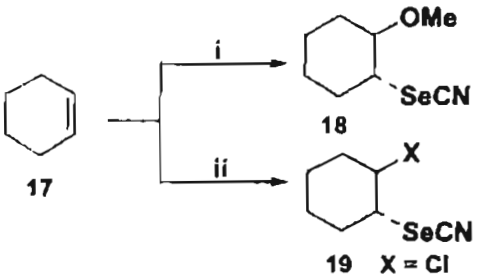

**Scheme 6**

Hassaneen *et al.* have reported the synthesis of phenacylselenocyanates from the corresponding phenacylbromides (Scheme 7).[14]




**Scheme 7**

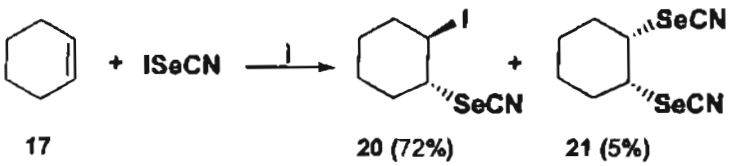
Uemura *et al.* have reported a novel oxidative method for the alkoxyselenocyanation[15] and halogenoselenocyanation[16] of olefins (Scheme 8).




i. KSeCN, $CuBr_2$, MeOH, 65 °C, 0.5 h, 60%
ii. KSeCN, $CuCl_2$, MeCN, 82 °C, 0.5 h, 69%

**Scheme 8**

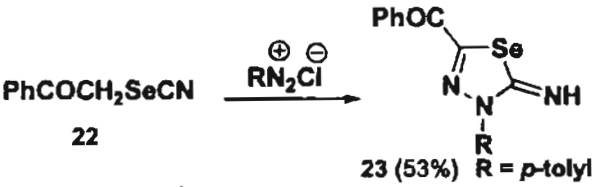
Woodgate *et al.* have reported the formation of iodoselenocyanates[17] by the reaction of iodine selenocyanide and alkene; diselenocyanates[2] are obtained as minor products (Scheme 9).




i. $CHCl_3$, 0-3 °C, 48 h

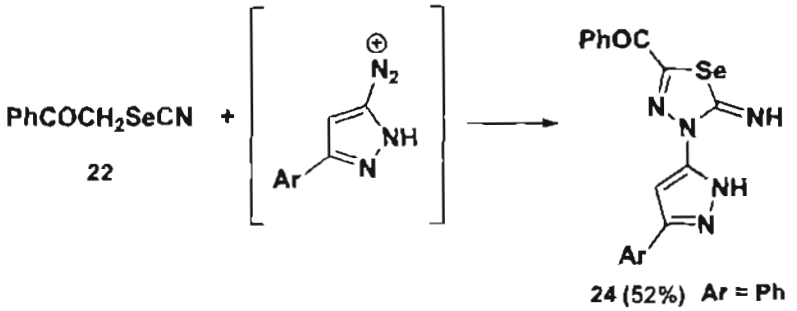
**Scheme 9**

Takahashi *et al.*[18] have reported that phenacylselenocyanates undergo coupling with aromatic diazonium salts to yield the corresponding 2-imino-2,3-dihydro-1,3,4-selenadiazoles **23** which have been shown to possess significant antibacterial activity (Scheme 10).[19]



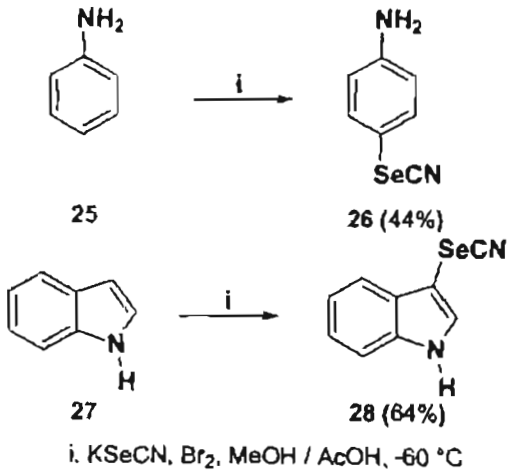

**Scheme 10**

In 1987 Shawali *et al.*[20] have reported that the reaction of phenacyl selenocyanate with diazotized arylamines led to one step synthesis of 2-imino-3-(3-phenyl-5-pyrazolyl)-5-benzoyl-2,3-dihydro-1,3,4-selenadiazole **24** (Scheme 11).



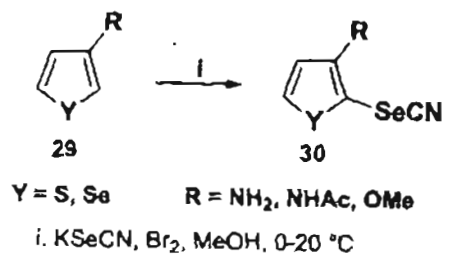

**Scheme 11**

It may be noted that, with aromatic and heteroaromatic nuclei bearing electron donating groups, the electrophilic substitution reaction using selenocyanogen formed *in situ* at low temperature, leads to aryl[21] and hetero aryl[22] selenocyanates in moderate yields (Scheme 12).



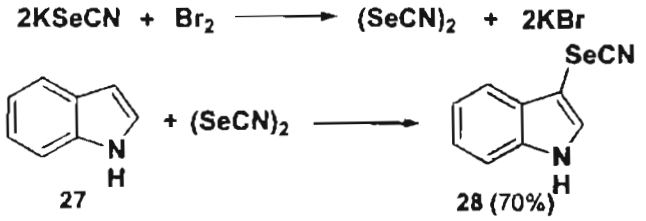

**Scheme 12**

Subsequently, Paulmier has reported the selenocyanation of thiophenes[23] and selenophenes [24](Scheme 13).




**Scheme 13**

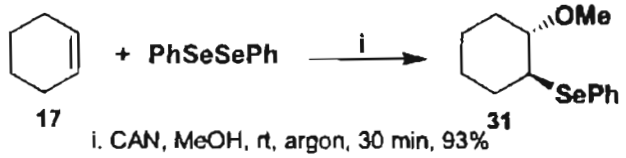
Agenas has reported that indole reacts with selenocyanogen at -60 °C to give 3-selenocyanatoindole (Scheme 14).[22c]




**Scheme 14**

## 3.3 THE PRESENT WORK

In comparison to the carbon-nitrogen, carbon-sulfur and carbon-halogen bond forming reactions mediated by CAN (for details see **Chapter 1**) there is only one report on carbon-selenium bond forming reaction mediated by CAN. Bosman and co-workers have reported the methoxyphenylselenation of alkenes using CAN in methanol (Scheme 15).[25]




**Scheme 15**

A complete survey of the literature (*vide supra*) revealed that, other than ionic reactions, selenocyanation reactions mediated by one-electron oxidants are hitherto unknown. It is noteworthy that although the alkoxyselenocyanation[15, 16] and halogenoselenocyanation[16,17] of alkenes have been reported, the synthesis of diselenocyanates[2 (p. 109)] and phenacylselenocyanates[14, 26] has received only very little attention. In view of the versatility of selenocyanato group in heterocyclic construction, it was considered worthwhile to undertake an investigation in this area. In particular, it was also evident from the literature survey that there has been no investigation on the selenocyanation of styrenes using one-electron oxidants. Therefore, it was of interest to explore the CAN mediated addition of

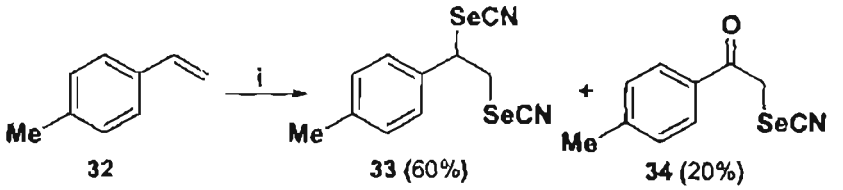
selenocyanate to styrenes and electron rich-arenes and the results are described in the following section.

## 3.4 RESULTS AND DISCUSSION

This section is divided mainly into two parts. The first part deals with the selenocyanation of styrenes and the second part describes the selenocyanation of electron rich aromatic compounds such as indole, pyrrole and *N,N*-dimethylaniline.

### 3.4.1 CAN Mediated Selenocyanation of Styrenes

The present investigations were initiated with the reaction of potassium selenocyanate and 4-methylstyrene. A methanolic solution of 4-methylstyrene **32** and potassium selenocyanate on treatment with CAN in methanol afforded the diselenocyanate **33** and phenacylselenocyanate **34** in 60% and 20% yields respectively (Scheme 16).




i. KSeCN, CAN, MeOH, 0 °C, 30 min

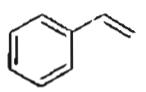
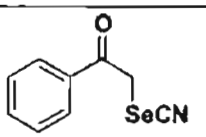
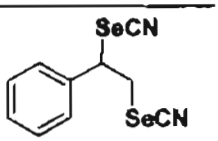
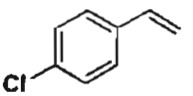
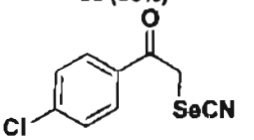
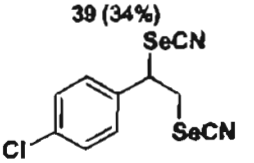
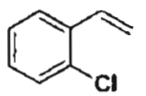
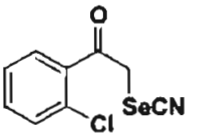
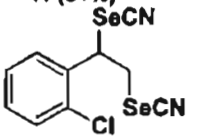
**Scheme 16**

The structures of the products **33** and **34** were assigned on the basis of spectroscopic data. The IR spectrum of **33** showed a strong absorption at 2152 $cm^{-1}$ characteristic of the SeCN group. In the $^1H$ NMR spectrum, the aromatic protons resonated as a multiplet centered at δ 7.26. The benzylic proton resonated at δ 4.97 as a double doublet ($J$ = 4.9 Hz, $J$ = 11.7 Hz). The methylene protons resonated as a multiplet centered at δ 3.93. The $CH_3$ protons appeared as a singlet at δ 2.38. In the $^{13}C$ NMR spectrum, the characteristic signals due to the selenocyanate carbons appeared at δ 100.86 and 99.53. Analytical data were also in good agreement with the assigned structure.

The IR spectrum of **34** showed characteristic absorption of benzoyl group at 1657 $cm^{-1}$ and that of SeCN group at 2150 $cm^{-1}$. In the $^1H$ NMR spectrum, the aromatic protons were visible as doublets at δ 7.84 ($J$ = 8.1 Hz) and at δ 7.31 ($J$ = 8.0 Hz). The resonance signal due to the $CH_2$ protons of **34** was visible as a sharp singlet at δ 4.92. A singlet observed at δ 2.45 was attributed to $CH_3$ protons. In the $^{13}C$ NMR spectrum, the carbonyl carbon was discernible at δ 192.61, and signal due to the selenocyanate carbon appeared at δ 101.82. The carbon attached to SeCN appeared at δ 38.73 and the signal at δ 22.03 was attributed to the methyl carbon. The assigned structure was further supported by analytical data.

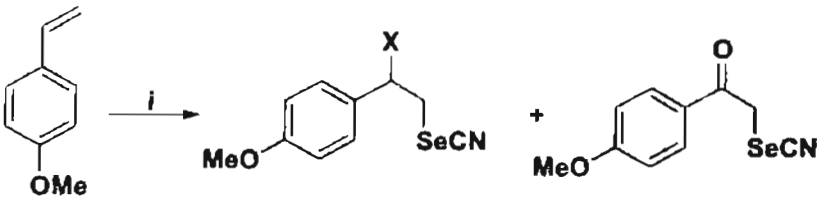
Similar reactivity was observed with styrene **35**, 4-chlorostyrene **36** and 2-chlorostyrene **37**; the corresponding ketoselenocyanates **38, 40** and **42** and diselenocyanates **39, 41** and **43** were obtained under similar reaction conditions and the results are summarized in Table 1. All the products were characterized on the basis of spectroscopic data.

**Table 1:** Selenocyanation of Styrenes

| Entry | Substrate | Products/Yield (%)[a] | |
|---|---|---|---|
| 1 |  35 |  38 (36%) |  39 (34%) |
| 2 |  36 |  40 (35%) |  41 (31%) |
| 3 |  37 |  42 (33%) |  43 (28%) |

[a] Reaction Conditions: KSeCN, CAN, MeOH, 0 °C, 30 min

The reaction of 4-methoxystyrene **44** with potassium selenocyanate in presence of CAN in methanol afforded *β*-methoxyselenocyanate **45** along with the diselenocyanate **46** and ketoselenocyanate **47** (Scheme 17).




i. KSeCN, CAN, MeOH, 0 °C, 30 min

**Scheme 17**

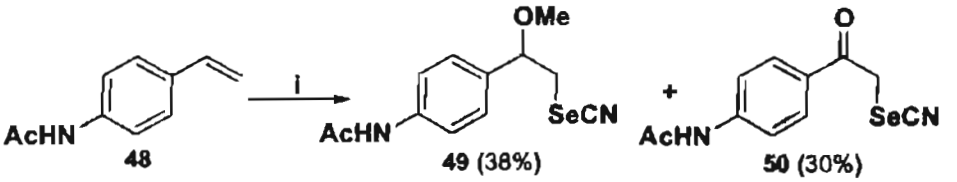
The IR spectrum of **45** showed the characteristic absorption of SeCN group at 2149 $cm^{-1}$. In the $^1H$ NMR spectrum of **45**, the benzylic proton appeared at δ 4.40 as a double doublet ($J$ = 4.0 Hz, $J$ = 9.6 Hz). The protons of the methylene group resonated as a multiplet centered at δ 3.34. The OMe protons resonated as singlets at δ 3.80 and at δ 3.22. In the $^{13}C$ NMR spectrum, the selenocyanato carbon was discernible at δ 102.03.

The IR spectrum of **46** showed a strong absorption at 2143 $cm^{-1}$ characteristic of the SeCN group. In the $^1H$ NMR spectrum, the aromatic protons were visible as doublets at δ 7.30 ($J$ = 8.5 Hz) and at δ 6.93 ($J$ = 8.5 Hz). The benzylic proton resonated at δ 5.00 as a double doublet ($J$ = 4.8 Hz, $J$ = 11.7 Hz). The two $CH_2$ protons resonated as a multiplet centered at δ 3.95. The OMe protons appeared as a singlet at δ 3.83. In the $^{13}C$ NMR spectrum, the characteristic signals due to the selenocyanato carbons appeared at δ 100.99 and 99.52. All other signals were in good agreement with the suggested structure.

The IR spectrum of **47** showed characteristic absorption of carbonyl group at 1645 $cm^{-1}$ and that of SeCN group at 2149 $cm^{-1}$. In the $^1H$ NMR spectrum, the aromatic protons were visible as doublets at δ 7.91 ($J$ = 8.8 Hz) and at δ 6.96 ($J$ = 8.8 Hz). The resonance due to the two protons attached to the

terminal carbon of **47** was visible as a sharp singlet at δ 4.90. A singlet observed at δ 3.90 was attributed to the OMe protons. In the $^{13}C$ NMR spectrum, the carbonyl carbon was discernible at δ 191.18, and the signal due to the selenocyanato carbon appeared at δ 101.77. The assigned structure was further supported by analytical data.

4-Acetamidostyrene **48** on treatment with potassium selenocyanate in the presence of CAN in methanol afforded the β-methoxyselenocyanate **49** along with the phenacylselenocyanate **50** (Scheme 18).




i. KSeCN, CAN, MeOH, 0° C, 30 min

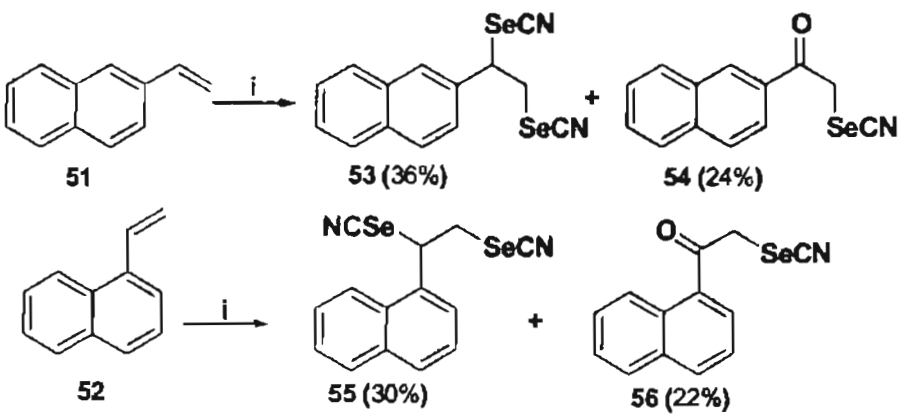
**Scheme 18**

The IR spectrum of **49** showed the characteristic absorption of SeCN group at 2149 $cm^{-1}$and the absorptions due to NH were visible at 3295 and 3257 $cm^{-1}$. The acetamido group showed the characteristic carbonyl absorption at 1664 $cm^{-1}$. In the $^1H$ NMR spectrum of **49** the NH proton appeared at δ 8.73 (exchangeable with $D_2O$) and the benzylic proton appeared at δ 4.42 as a double doublet ($J$ = 4.0 Hz, $J$ = 9.2 Hz). The protons on the terminal carbon resonated as a multiplet centered at δ 3.34. The OMe protons resonated as a singlet at δ 3.25 and the singlet at δ 2.27 was attributed to the acetamido methyl group. In the $^{13}C$ NMR spectrum, the carbonyl of acetamido group was visible at δ 168.29 and the selenocyanato carbon was discernible at δ 102.18.

The IR spectrum of **50** showed the characteristic absorptions of acetamido carbonyl group at 1689 $cm^{-1}$, and the benzoyl group at 1639 $cm^{-1}$ and the SeCN group at 2156 $cm^{-1}$. In the $^1H$ NMR spectrum, the NH proton appeared at δ 9.94 (exchangeable with $D_2O$) and the aromatic protons were visible as doublets at δ

7.90 ($J$ = 8.6 Hz) and at δ 7.76 ($J$ = 8.6 Hz). The resonance due to the $CH_2$ protons of **50** was visible as a sharp singlet at δ 4.93. A singlet observed at δ 2.16 was attributed to the acetamido methyl group. In the $^{13}C$ NMR spectrum, the carbonyl carbons were discernible at δ 191.66 and δ 169.29, and the signal due to the selenocyanate carbon appeared at δ 102.05. The assigned structure was further supported by analytical data.

Similar reactivity was observed with vinylnaphthalenes and the results are presented in Scheme 19.




i. KSeCN, CAN, MeOH, 0 °C, 30 min

**Scheme 19**

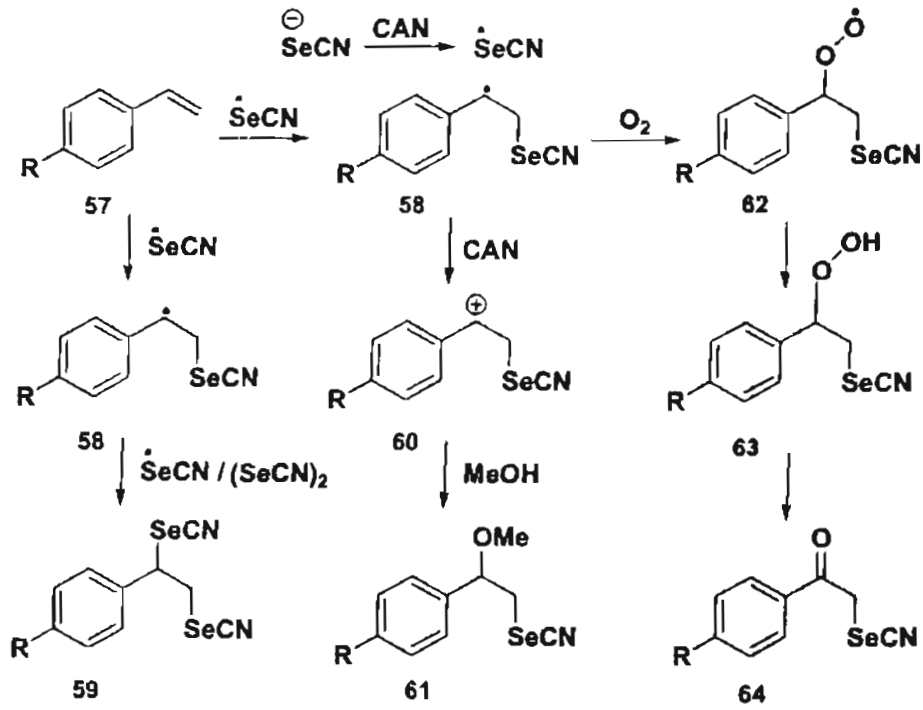
The IR spectrum of **53** showed a strong absorption at 2149 $cm^{-1}$ characteristic of the SeCN group. In the $^1H$ NMR spectrum, the benzylic proton resonated at δ 5.14 as a double doublet ($J$ =. 4.8 Hz, $J$ = 11.6 Hz). The two $CH_2$ protons resonated as a multiplet centered at δ 4.05. In the $^{13}C$ NMR spectrum, the characteristic signals due to the selenocyanate carbons appeared at δ 100.60 and 99.49. Analytical data was also in good agreement with the assigned structure. The IR spectrum of **55** showed a strong absorption at 2149 $cm^{-1}$ characteristic of the SeCN group. In the $^1H$ NMR spectrum, the benzylic proton resonated as a multiplet centered at δ 5.81. The two $CH_2$ protons resonated as a multiplet centered at δ 4.20. In the $^{13}C$ NMR spectrum, the characteristic signals

due to the selenocyanate carbons appeared at δ 100.94 and 99.98. Analytical data were also in good agreement with the assigned structure.

Similar diagnostic spectroscopic data (IR, $^{1}H$ NMR and $^{13}C$ NMR) were obtained for **54** and **56**. In the IR spectra, both the ketoselenocyanates **54** and **56** showed strong absorptions due to carbonyl groups at 1651 $cm^{-1}$ and 1640 $cm^{-1}$ respectively. In both compounds the absorption due to SeCN group was visible at 2149 $cm^{-1}$. In the $^{1}H$ NMR spectrum of **54**, the two methylene protons resonated as a sharp singlet at δ 5.07 and in the case of **56**, the corresponding signal appeared at δ 5.08. In the $^{13}C$ NMR spectrum of **54**, the characteristic signals due to the carbonyl carbon and selenocyanato carbon appeared at δ 192.77and 101.51 respectively. The $^{13}C$ NMR spectrum of **56** showed two signals at δ 195.25 and 101.57 corresponding to the carbonyl carbon and selenocyanato carbon respectively. Analytical data further supported the assigned structures.

### 3.4.2 Mechanistic Considerations

Mechanistically, this reaction can be rationalized as illustrated in Scheme 20. Oxidation of the selenocyanate anion by CAN would give rise to the selenocyanato radical which on addition to the styrene **57** would give rise to the benzylic radical. The addition of a second selenocyanato radical or selenocyanogen to the initially formed benzylic radical may result in the formation of the diselenocyanate **59**. The β-methoxy product **61** can result from the quenching of the benzylic cation **60** by methanol, the cation being formed by oxidation of the benzylic radical by CAN. The β-keto product **64** may be derived from the fragmentation / oxidation of the hydroperoxide **63**, which is formed by the quenching of benzylic radical **58** by molecular oxygen.



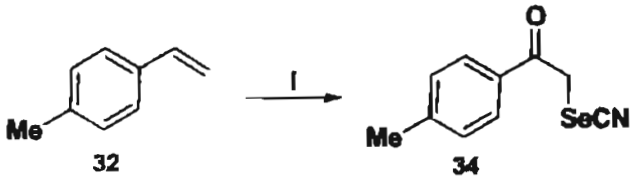

Scheme 20

### 3.4.3 CAN Mediated Synthesis of Phenacylselenocyanates

From the mechanistic point of view, it is assumed that the phenacylselenocyanate is formed by the trapping of oxygen by the initially formed benzylic radical followed by further transformations of the peroxy intermediate. Therefore we anticipated that if the reaction is carried out in an atmosphere of oxygen, it will result in the predominant formation of the keto product as a result of the quenching of the benzylic radical by oxygen. Accordingly, reactions of various substituted styrenes with potassium selenocyanate in methanol were repeated in an atmosphere of oxygen with the expectation that the phenacyl selenocyanate would be formed predominantly or exclusively.

In a typical experiment, an anhydrous methanolic solution of 4-methylstyrene **32** and potassium selenocyanate saturated with oxygen was

treated with a solution of CAN in methanol in an atmosphere of oxygen, at 0 °C for 45 minutes; the phenacylselenocyanate **33** was obtained exclusively as a colourless crystalline solid in 70 % yield (Scheme 21).




**32** **34**

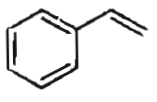
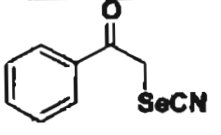
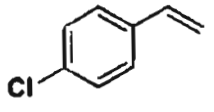
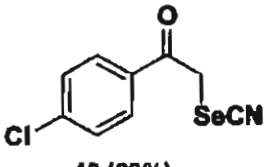
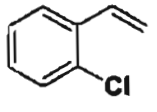
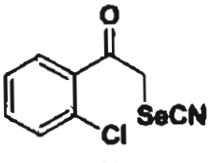
i. KSeCN, CAN, MeOH. oxygen, 0 °C, 45 min, 70%

**Scheme 21**

The product was characterized by IR, $^{1}H$ NMR, $^{13}C$ NMR and elemental analysis.

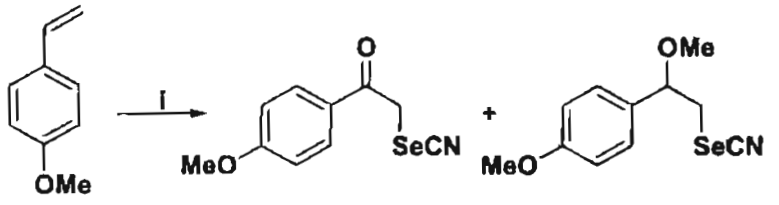
The reaction was found to be general with various substituted styrenes. Styrene **35**, 4-chlorostyrene **36** and 2-chlorostyrene **37** afforded the corresponding ketoselenocyanates **38, 40** and **42** under similar reaction conditions. The results are summarized in Table 2.

**Table 2:** Synthesis of Phenacylselenocyanates

| Entry | Substrate | Products/Yield (%)[a] |
|---|---|---|
| 1 |  **35** |  **38 (71%)** |
| 2 |  **36** |  **40 (68%)** |
| 3 |  **37** |  **42 (54%)** |

[a] Reaction Conditions: KSeCN, CAN, MeOH, oxygen, 0 °C, 45 min

The reaction of 4-methoxystyrene **44** with potassium selenocyanate in presence of CAN in methanol under an atmosphere of oxygen afforded ketoselenocyanate **47** along with the $\beta$-methoxyselenocyanate **45** (Scheme 22).

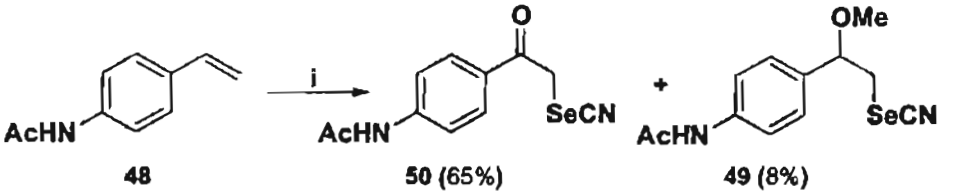



**44** **47 (45%)** **45 (31%)**

i. KSeCN, CAN, MeOH, oxygen, 0 °C, 45 min

**Scheme 22**

Similar reaction occurred with 4-acetamidostyrene **48** as shown in Scheme 23.

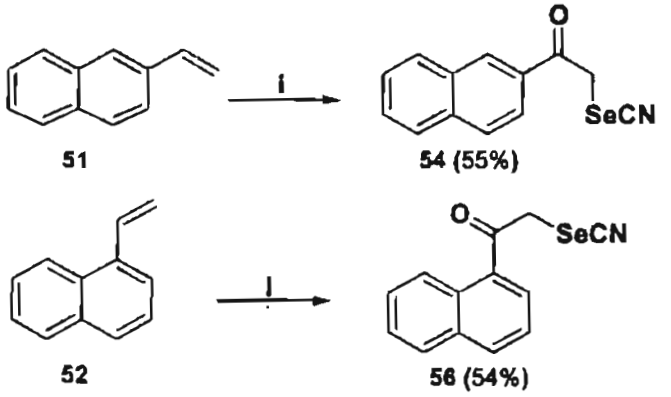



**48** **50 (65%)** **49 (8%)**

i . KSeCN, CAN, MeOH, oxygen, 0° C, 45 min

**Scheme 23**

Vinylnaphthalenes **51** and **52** also afforded the ketoselenocyanates as shown in Scheme 24.




**51** **54 (55%)**

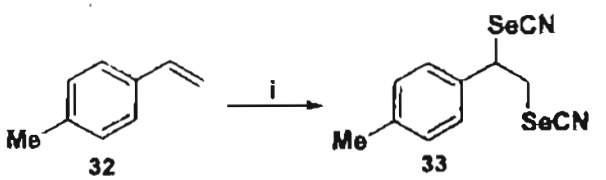
**52** **56 (54%)**

i. KSeCN, CAN, MeOH, oxygen, 0 °C, 45 min

**Scheme 24**

### 3.4.4 CAN Mediated Synthesis of Diselenocyanates

Since phenacylselenocyanate was formed as the major or exclusive product in an atmosphere of oxygen, it was reasonable to assume that the diselenocyanate would be formed predominantly in an oxygen free atmosphere. When a methanolic solution of 4-methylstyrene **32** and potassium selenocyanate saturated with argon was treated with CAN in methanol in an atmosphere of argon, the diselenocyanate **34** was obtained as a colourless solid in 66% yield (Scheme 25).



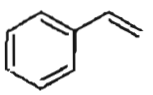
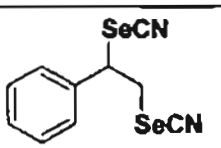
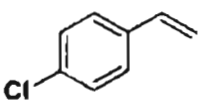
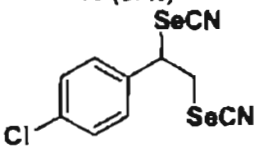
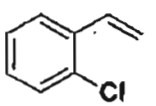
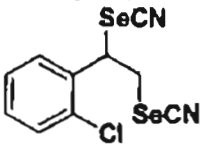

**32** **33**

i. KSeCN, CAN, MeOH, argon, 0 °C, 45 min, 66%

**Scheme 25**

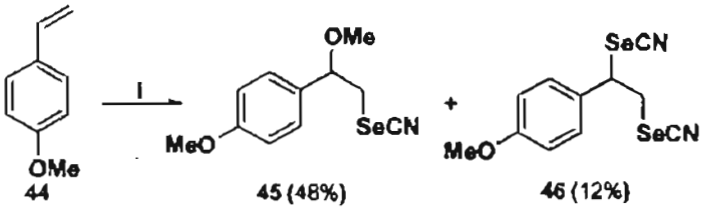
Other styrenes **35, 36** and **37** also underwent similar reaction and the results are summarized in Table.3.

Table 3: Synthesis of Diselenocyanates

| Entry | Substrate | Products/Yield (%)[a] |
|---|---|---|
| 1 |  **35** |  **39 (67%)** |
| 2 |  **36** |  **41 (52%)** |
| 3 |  **37** |  **43 (46%)** |

[a] Reaction Conditions: KSeCN, CAN, MeOH, argon, 0 °C, 45 min

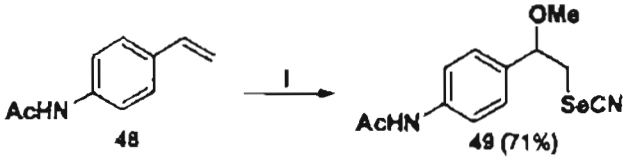
The reaction of 4-methoxystyrene **44** with potassium selenocyanate in presence of CAN in methanol under an atmosphere of argon afforded $\beta$-methoxyselenocyanate **45** along with a small amount of the diselenocyanate **46** as presented in Scheme 26.




i. KSeCN, CAN., MeOH, argon, 0 °C, 45 min

**Scheme 26**

With 4-acetamidostyrene **48**, the methoxyselenocyanate **49** was the only isolated product as shown in Scheme 27.

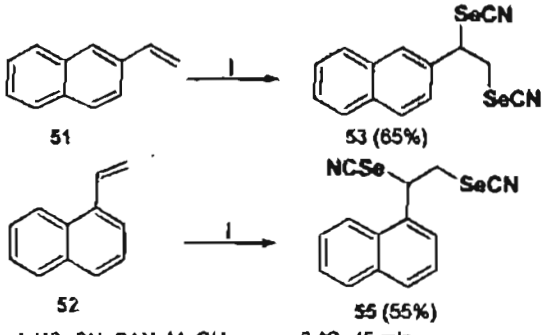



i. KSeCN, CAN, MeOH, argon, 0° C, 45 min

**Scheme 27**

Formation of the methoxy selenocyanate as the major or predominant product in these two cases may be attributed to the rapid oxidation of the benzylic radical intermediate to the cation and its facile quenching by methanol.

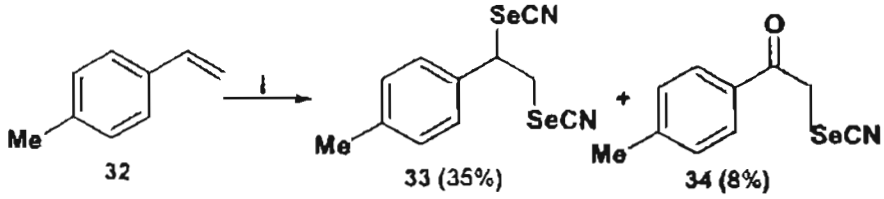
With vinylnaphthalenes, the reaction proceeded as expected to afford the diselenocyanates (Scheme 28).




i. KSeCN, CAN, MeOH, argon, 0 °C, 45 min

**Scheme 28**

In order to assess the effect of solvent on the selenocyanation reaction we studied the reaction of a number of styrenes in acetonitrile. Interestingly, the reactions proceeded to afford analogous products as in methanol *albeit* in lower yields. An illustrative example is shown in Scheme 29.




**Scheme 29**

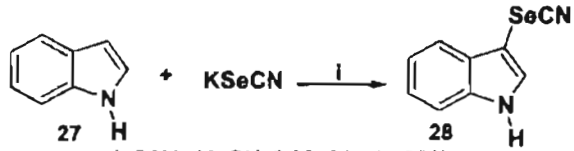
In order to probe the generality of the reaction we have done some preliminary investigations on the selenocyanation of normal alkenes such as 1-octene as well as cyclic alkenes such as 1-phenylcyclohexene. Although there was evidence of selenocyanation, the products decomposed on attempted purification by chromatography on silica gel column.

## 3.5 CAN MEDIATED SELENOCYANATION OF ELECTRON-RICH AROMATICS

From the literature survey it was evident that no work on selenocyanation of arenes using CAN has been reported. In view of this and as a logical extension of the selenocyanation of styrenes, it was of interest to examine the selenocyanation of electron-rich arenes. The aromatic compounds selected for our study are indoles, *N*-*N*-dimethylaniline, *N*-methylpyrrole and veratrole (1,2-dimethoxybenzene).

### 3.5.1 Selenocyanation of Indoles Mediated by CAN

Our work was initiated with the reaction of indole **27** with potassium selenocyanate and CAN in methanol, which led to the formation of 3-selenocyanatoindole **28** as the only isolable product as a colourless crystalline solid in 72% yield (Scheme 30).

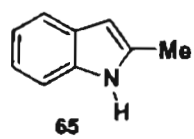
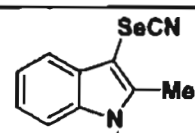
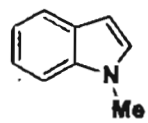
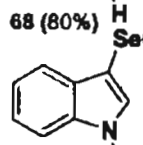
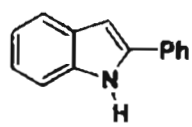
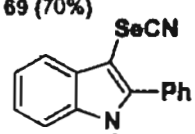



**Scheme 30**

The structure of the product was assigned on the basis of spectroscopic data. The IR spectrum of **28** showed strong absorptions at 2160 $cm^{-1}$ and 3339 $cm^{-1}$ indicating the presence of SeCN and NH moieties respectively. In the $^1H$ NMR spectrum, a broad singlet observed at δ 8.80 was attributed to NH proton (exchangeable with $D_2O$). The aromatic protons resonated as two separate multiplets centered at δ 7.68 and δ 7.27. In the $^{13}C$ NMR spectrum, the SeCN carbon was visible at δ 111.89 and the carbon bearing the selenocyanato group at δ 88.97. All other signals were in agreement with the assigned structure which was further supported by elemental analysis.

The reaction of 2-methylindole **65**, 1-methylindole **66** and 2-phenylindole **67** proceeded in a similar fashion affording 3-selenocyanated products **68**, **69** and **70** in good yields (Table 4).

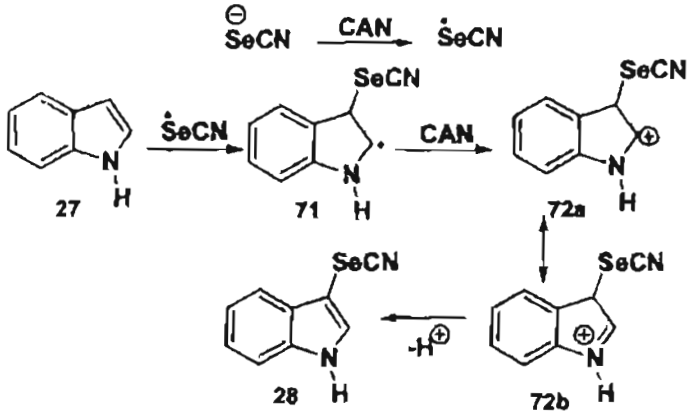
**Table 4:** Selenocyanation of Indoles

| Entry | Substrate | Products/Yield (%)[a] |
|---|---|---|
| 1 |  **65** |  **68** (80%) |
| 2 |  **66** |  **69** (70%) |
| 3 |  **67** |  **70** (73%) |

[a] Reaction Conditions: KSeCN, CAN, MeOH, 0 °C, 30 min

The products were characterized on the basis of spectroscopic data, which confirmed the assigned stuctures.

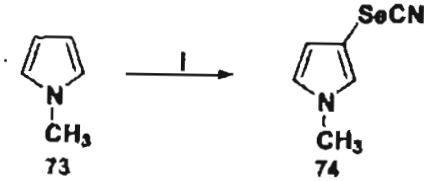
A mechanistic rationalization for the reaction can be given as follows (Scheme 31). Oxidation of selenocyanate anion by CAN would lead to the selenocyanate radical. This can conceivably add to indole **27** forming the radical **71**, which then undergoes further oxidation to form the resonance stabilized cation **72a**. The latter can easily lose a proton to form the 3-selenocyanatoindole **28**.




**Scheme 31**

### 3.5.2 Selenocyanation of Pyrrole and Aniline Mediated by CAN

Prompted by the facility with which indoles underwent the selenocyanation reaction, it was of interest to probe the selenocyanation of pyrrole and *N, N*-dimethylaniline under similar reaction conditions. The reaction of 1-methylpyrrole **73** with potassium selenocyanate and CAN in methanol afforded the selenocyanated product **74** in very low yield (Scheme 32).

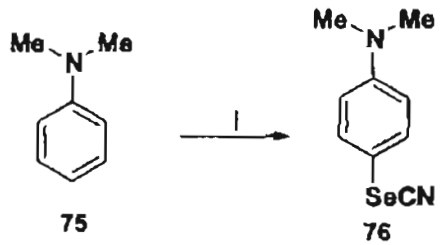



I. KSeCN, CAN, MeOH ,0 °C, 30 min, 25%

**Scheme 32**

The structure of the product **74** was assigned on the basis of spectroscopic data. The IR spectrum of **74** showed the SeCN absorption at 2150 $cm^{-1}$. In the $^1H$ NMR spectrum, the aromatic protons resonated as separate singlets at δ 6.89, 6.61 and 6.34. In the $^{13}C$ NMR spectrum, the signal corresponding to the methyl carbon appeared at δ 33.24. The attempted selenocyanation of pyrrole, furan and thiophene was not promising.

*N,N*-dimethylaniline **75** on treatment with potassium selenocyanate and CAN in methanol afforded the *p*-selenocyanated product **76** in 50% yield (Scheme 33).

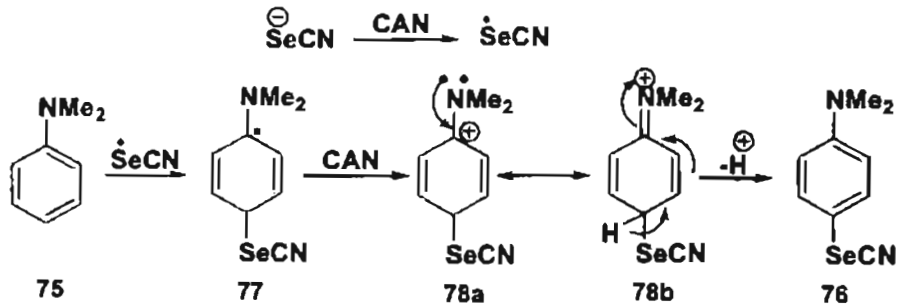



**75** **76**

i. KSeCN, CAN, MeOH, 0 °C, 30 min, 50%

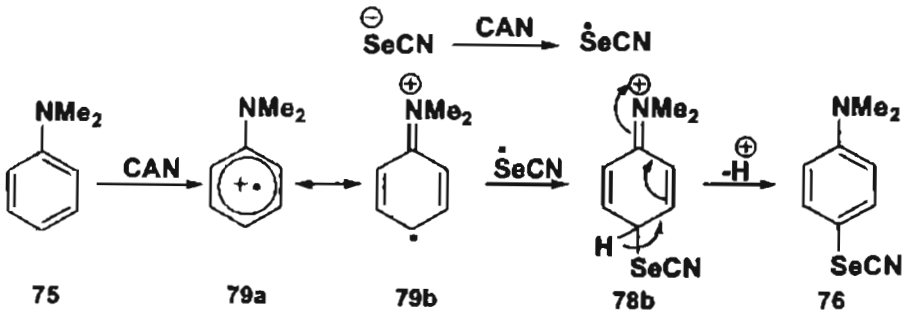
**Scheme 33**

The structure of the product **76** was established by the spectroscopic data. In the IR spectrum, the SeCN absorption was observed at 2144 $cm^{-1}$. In the $^1H$ NMR spectrum, the two doublets at δ 7.48 ($J$ = 9 Hz) and 6.62 ($J$ = 9 Hz) were attributed to the aromatic protons. The protons of the two methyl groups were visible as singlets at δ 2.98. In the $^{13}C$ NMR spectrum, the SeCN carbon resonated at 102.16. All other signals were in agreement with the assigned structure. Mechanistically, this reaction can be rationalized as shown in Scheme 34.




**Scheme 34**

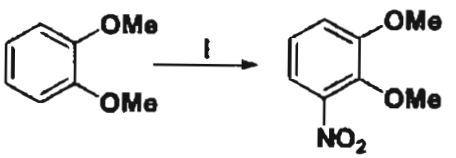
An alternative mechanism can be proposed which involves the formation of radical cation as shown in Scheme 35.




**Scheme 35**

With aniline and *N*-methylaniline, although the products were formed, they could not be isolated due to decomposition during attempted purification by column chromatography.

Subsequently, the selenocyanation of veratrole was attempted. However, in this case we were not able to isolate any selenocyanated product; instead the 4-nitrocompound was obtained as the only isolable product (Scheme 36).




I. KSeCN, MeOH, 0 °C, 30 min, 60%

**Scheme 36**

The structure of **81** was assigned on the basis of spectroscopic data. The two strong bands at 1532 $cm^{-1}$ and 1354 $cm^{-1}$ in the IR spectrum were attributed to the $NO_2$ absorption. In the $^{13}C$ NMR spectrum, the OMe signals appeared at δ 56.46 and δ 56.34.

## 3.6 CONCLUSION

In conclusion, we have devised an efficient procedure for the selenocyanation of styrenes, indoles and certain electron-rich aromatic systems such as pyrrole and *N,N*-dimethylaniline. The reaction appears to be interesting both from synthetic and mechanistic standpoints. In view of the experimental simplicity and good yields of the products, the present procedure appears to be attractive.

## 3.7 EXPERIMENTAL DETAILS

For general information , see section **2.6.** of **Chapter 2**, page 64.

### 3.7.1 Synthesis of selenocyanates from styrenes: General procedure

To a solution of styrene (1 mmol) and potassium selenocyanate (2 mmol) in methanol (10 mL) was added dropwise with stirring a solution of CAN (2.3 mmol) in methanol (15 mL) at 0 °C for 30 minutes. On completion of the reaction as shown by tlc, the reaction mixture was diluted with water (100 mL) and extracted with dichloromethane (3 x 25 mL). The combined organic extract was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed and the residue was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane and ethyl acetate afforded the products.

### 3.7.2 Synthesis of ketoselenocyanates under oxygenated conditions: General procedure

A mixture of styrene (1 mmol) and potassium selenocyanate (1.2 mmol) was taken in anhydrous methanol (10 mL) in a two necked round-bottomed flask fitted with a pressure equalizing funnel containing CAN (2.3 mmol) dissolved in anhydrous methanol (15 mL). The contents of the flask were kept cooled in an ice-bath. Both the solutions were simultaneously bubbled with oxygen, for 15 minutes. Then CAN solution was added dropwise and the reaction mixture was stirred vigorously (ice-bath) under oxygen atmosphere for 45 minutes. When the starting material was fully consumed as indicated by tlc, the reaction mixture was diluted with water (100 mL) and extracted with dichloromethane (3 x 25 mL). The combined organic extract was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed and the residue was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane and ethyl acetate afforded the products.

### 3.7.3 Synthesis of diselenocyanates under deoxygenated conditions: General procedure

A mixture of styrene (1 mmol) and potassium selenocyanate (2 mmol) was taken in anhydrous methanol (5 mL) in a two necked round-bottomed flask fitted with a pressure equalizing funnel containing CAN (2.3 mmol) dissolved in anhydrous methanol (10 mL). Both the solutions were simultaneously bubbled with argon, which was deoxygenated by passing through Fieser's solution, for 15 minutes. Then CAN solution was added dropwise to the contents of the flask kept in an ice-bath and the reaction mixture was stirred vigorously under argon atmosphere for 45 minutes. When the starting material was fully consumed as shown by tlc, the reaction mixture was diluted with water (100 mL) and extracted with dichloromethane (3 x 25 mL). The combined organic extract was

washed with brine and dried over anhydrous sodium sulfate. The solvent was removed and the residue was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane and ethyl acetate afforded the products.

***1,2-Diselenocyanato-2-(4'-methylphenyl)ethane (33) and***

***1-Selenocyanato-(4'-methyl)acetophenone (34)***

To a solution of 4-methylstyrene **32** (118 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) afforded 48 mg of **34** (20%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 197 mg of **33** (60%).

***1,2-Diselenocyanato-2-(4'-methylphenyl)ethane (33)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

| | | |
|---|---|---|
| mp | | 138-140 °C |
| IR (KBr) $\nu_{max}$ | : | 3009, 2921, 2152, 1613, 1533, 1431, 1169, 1148, 899, 831, 724 $cm^{-1}$. |
| $^1H$ NMR | : | δ 7.28-7.24 (m, 4H, ArH), 4.97 (dd, 2H, CHSeCN, $J$ = 4.9 Hz, $J$ = 11.7 Hz), 4.05-3.81 (m, 2H, $CH_2SeCN$), 2.38 (s, 3H, $CH_3$). |
| $^{13}C$ NMR | : | δ 140.50, 131.57, 130.51, 127.46, 100.86, 99.53, 48.04, 33.89, 21.39. |

Anal. Calcd. for $C_{11}H_{10}N_2Se_2$: C, 40.26; H, 3.07; N, 8.54. Found: C, 40.77; H, 3.15; N, 8.05.

***1-Selenocyanato-(4'-methyl)acetophenone (34)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 131-133 °C

IR (KBr) $\nu_{max}$ : 2987, 2924, 2150, 1657, 1607, 1569, 1382, 1294, 1176, 1003, 801, 741 $cm^{-1}$.

$^1H$ NMR : δ 7.84 (d, 2H, ArH, $J$ = 8.1 Hz), 7.31 (d, 2H, ArH, $J$ = 8.0 Hz), 4.92 (s, 2H, $CH_2SeCN$), 2.45 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 192.61, 146.14, 131.53, 129.93, 128.98, 101.82, 38.73, 22.03.

Anal. Calcd. for $C_{10}H_9NOSe$: C, 50.43; H, 3.81; N, 5.88. Found: C, 50.92; H, 3.66; N, 5.86.

***1-Selenocyanatoacetophenone (38) and***

***1,2-Diselenocyanato-2-phenylethane (39)***

To a solution of styrene **35** (104 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) afforded 81 mg of **38** (36%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 107 mg of **39** (34%).

***1-Selenocyanatoacetophenone (38)***[14,27]

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 82-85 °C

IR (KBr) $\nu_{max}$ : 3064, 2921, 2154, 1670, 1589, 1446, 272, 1172, 991, 736, 687 $cm^{-1}$.

$^1H$ NMR : δ 7.97-7.94 (m, 2H, ArH), 7.69-7.65 (m, 1H, ArH), 7.55-7.50 (m, 2H, ArH), 4.94 (s, 2H, $CH_2SeCN$).

$^{13}C$ NMR : δ 192.69, 134.57, 133.63, 128.91, 128.50, 101.22, 38.20.

Anal. Calcd. for $C_9H_7NOSe$: C, 48.23; H, 3.15; N, 6.25. Found: C, 48.68; H, 3.41; N, 6.30.

***1,2-Diselenocyanato-2-phenylethane (39)***[16,17]

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 144-146 °C

IR (KBr) $\nu_{max}$ : 3008, 2149, 1496, 1452, 1427, 1222, 1135, 886, 761, 693 $cm^{-1}$.

$^1H$ NMR : δ 7.42-7.37 (m, 5H, ArH), 4.97 (dd, 2H, CHSeCN, $J$ = 4.8 Hz, $J$ = 11.6 Hz), 4.05-3.81 (m, 2H, $CH_2SeCN$).

$^{13}C$ NMR : δ 134.82, 130.30, 129.88, 127.57, 100.56, 99.30, 48.08, 33.82.

Anal. Calcd. for $C_{10}H_8N_2Se_2$: C, 38.24; H, 2.57; N, 8.92. Found: C, 38.72; H, 2.57; N, 8.35.

***1-Selenocyanato-(4'-chloro)acetophenone (40) and***

***1,2-Diselenocyanato-2-(4'-chlorophenyl)ethane (41)***

To a solution of 4-chlorostyrene **36** (138.5 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) afforded 90 mg of **40** (35%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 112 mg of **41** (31%).

***1-Selenocyanato-(4'-chloro)acetophenone (40)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 141-143 °C

IR (KBr) $\nu_{max}$ : 2921, 2155, 1657, 1595, 1483, 1297, 1185, 1091, 998, 817 $cm^{-1}$.

$^1$H NMR : δ 7.91 (d, 2H, ArH, $J$ = 8.4 Hz), 7.51 (d, 2H, ArH, $J$ = 8.4 Hz), 4.89 (s, 2H, $CH_2SeCN$).

$^{13}$C NMR : δ 192.00, 141.87, 132.37, 130.29, 129.77, 101.40, 38.11.

Anal. Calcd. for $C_9H_6ClNOSe$: C, 41.81; H, 2.34; N, 5.42. Found: C, 41.88; H, 2.61; N, 5.39.

***1,2-Diselenocyanato-2-(4'-chlorophenyl)ethane (41)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 136-138 °C

IR (KBr) $\nu_{max}$ : 2921, 2143, 1589, 1489, 1421, 1222, 1141, 1091, 1010, 886, 823, 774, 718, 662, 574 cm$^{-1}$.

$^1$H NMR : δ 7.43 (d, 2H, ArH, $J$ = 8.4 Hz), 7.33 (d, 2H, ArH, $J$ = 8.4 Hz), 4.92 (dd, 2H, CHSeCN, $J$ = 5.0 Hz, $J$ = 11.6 Hz), 4.06-3.74 (m, 2H, $CH_2SeCN$).

$^{13}$C NMR : δ 136.40, 133.62, 130.12, 128.85, 100.17, 99.18, 47.25, 33.41.

Anal. Calcd. for $C_{10}H_7ClN_2Se_2$: C, 34.46; H, 2.02; N, 8.04. Found: C, 34.80; H, 2.11; N, 7.83.

***1-Selenocyanato-(2'-chloro)acetophenone (42) and***

***1,2-Diselenocyanato-2-(2'-chlorophenyl)ethane (43)***

To a solution of 2-chlorostyrene **37** (138.5 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) afforded 85 mg of **42** (33%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 98 mg of **43** (28%).

***1-Selenocyanato-(2'-chloro)acetophenone (42)***

colourless viscous liquid

IR (neat) $\nu_{max}$ : 2996, 2934, 2155, 1670, 1589, 1564, 1477, 1427, 1384, 1290, 1178, 1060, 991, 755 $cm^{-1}$.

$^1H$ NMR : δ 7.78 (d, 2H, ArH, $J$ = 7.7 Hz), 7.56-7.51 (m, 2H, ArH), 7.44-7.40 (m, 1H, ArH), 4.91 (s, 2H, $CH_2SeCN$).

$^{13}C$ NMR : δ 194.10, 138.86, 133.99, 131.08, 130.88, 127.65, 127.34, 101.33, 40.22.

***1,2-Diselenocyanato-2-(2'-chlorophenyl)ethane (43)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 96-98 °C

IR (KBr) $\nu_{max}$ : 3071, 3021, 2143, 1589, 1570, 1471, 1440, 1340, 1278, 1228, 1191, 1147, 1122, 1029, 892, 755, 730 $cm^{-1}$.

$^1H$ NMR : δ 7.51-7.40 (m, 4H, ArH), 5.30 (dd, 2H, CHSeCN, $J$ = 6.5 Hz, $J$ = 10.3 Hz), 4.05-3.98 (m, 2H, $CH_2SeCN$).

$^{13}C$ NMR : δ 134.21, 133.24, 131.03, 130.90, 128.02, 127.62, 100.04, 99.34, 44.51, 32.73.

Anal. Calcd. for $C_{10}H_7ClN_2Se_2$: C, 34.46; H, 2.02; N, 8.04. Found: C, 34.64; H, 1.95; N, 7.77.

***1-Selenocyanato-2-methoxy-2-(4'-methoxyphenyl)ethane (45),***
***1,2-Diselenocyanato-2-(4'-methoxyphenyl)ethane (46) and***
***1-Selenocyanato-(4'-methoxy)acetophenone (47)***

To a solution of 4-methoxystyrene **44** (134 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate mixture (98:2) afforded 119 mg of **45** (44%)

and on further elution using hexane-ethyl acetate mixture (95:5) afforded 30 mg of **46** (12%). The product **47** (28 mg, 8%) was eluted in hexane-ethyl acetate mixture (90:10).

***1-Selenocyanato-2-methoxy-2-(4'-methoxyphenyl)ethane (45)***

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3002, 2934, 2834, 2149, 1608, 1508, 1458, 1247, 1172, 1097, 1023, 960, 823, 637, 562 $cm^{-1}$.

$^1H$ NMR : δ 7.22 (d, 2H, ArH, $J$ = 8.6 Hz), 6.89 (d, 2H, ArH, $J$ = 8.6 Hz), 4.40 (dd, 2H, $CHOCH_3$, $J$ = 4.0 Hz, $J$ = 9.6 Hz), 3.80 (s, 3H, $OCH_3$), 3.43-3.26 (m, 2H, $CH_2SeCN$), 3.22 (s, 3H, $OCH_3$).

$^{13}C$ NMR : δ 159.88, 130.52, 127.64, 114.18, 102.03, 81.43, 56.71, 55.07, 36.06.

***1,2-Diselenocyanato-2-(4'-methoxyphenyl)ethane (46)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 115-117 °C

IR (KBr) $\nu_{max}$ : 3008, 2959, 2840, 2143, 1614, 1514, 1465, 1253, 1178, 1135, 1023, 892, 830, 724, 705 $cm^{-1}$.

$^1H$ NMR : δ 7.30 (d, 2H, ArH, $J$ = 8.5 Hz), 6.93 (d, 2H, ArH, $J$ = 8.5 Hz), 5.00 (dd, 2H, CHSeCN, $J$ = 4.8 Hz, $J$ = 11.7 Hz), 4.05-3.85 (m, 2H, $CH_2SeCN$), 3.83 (s, 3H, $OCH_3$).

$^{13}C$ NMR : δ 160.98, 128.99, 126.17, 115.19, 100.99, 99.52, 55.37, 48.11, 34.08.

***1-Selenocyanato-(4'-methoxy)acetophenone (47)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 115-117 °C

IR (KBr) $\nu_{max}$ : 2966, 2940, 2846, 2149, 1645, 1595, 1570, 1421, 1297, 1259, 1172, 1023, 991, 817 $cm^{-1}$.

$^1$H NMR : δ 7.91 (d, 2H, ArH, $J$ = 8.8 Hz), 6.96 (d, 2H, ArH, $J$ = 8.8 Hz), 4.90 (s, 2H, $CH_2SeCN$), 3.90 (s, 3H, $OCH_3$).

$^{13}$C NMR : δ 191.18, 164.78, 131.09, 126.81, 114.25, 101.77, 55.50, 38.43.

Anal. Calcd. for $C_{10}H_9NO_2Se$: C, 47.26; H, 3.57; N, 5.51. Found: C, 47.28; H, 3.55; N, 5.34.

***1-Selenocyanato-2-methoxy-2-(4'-acetamidophenyl)ethane (49)***
***and 1-Selenocyanato-(4'-acetamido)acetophenone (50)***

To a solution of 4-acetamidostyrene **48** (161 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) afforded 112 mg of **49** (38%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 89 mg of **50** (30%).

***1-Selenocyanato-2-methoxy-2-(4'-acetamidophenyl)ethane (49)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 108-110 °C

IR (KBr) $\nu_{max}$ : 3295, 3257, 2940, 2834, 2149, 1664, 1602, 1558, 1408, 1321, 1265, 1085, 948, 830, 749, 730, 606 cm$^{-1}$.

$^1$H NMR : δ 8.73 (s, 1H, NH, exchangeable with $D_2O$), 7.54-7.23 (m, 4H, ArH), 4.42 (dd, 1H, $CHOCH_3$, $J$ = 4.0 Hz, $J$ = 9.2 Hz), 3.41-3.28 (m, 2H, $CH_2SeCN$), 3.25 (s, 3H, $OCH_3$), 2.17 (s, 3H, $NHCOCH_3$).

$^{13}$C NMR : δ 168.29, 138.56, 134.45, 127.24, 120.20, 102.18, 81.61, 57.14, 36.09, 24.53.

***1-Selenocyanato-(4'-acetamido)acetophenone (50)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 184-186 °C

*IR* (KBr) $\nu_{max}$ : 3326, 3289, 2940, 2156, 1689, 1639, 1595, 1521, 1440, 1378, 1322, 1291, 1160, 1004, 811 $cm^{-1}$.

$^1H$ NMR : δ 9.94 (s, 1H, NH, exchangeable with $D_2O$), 7.90 (d, 2H, ArH, *J* = 8.6 Hz), 7.76 (d, 2H, ArH, *J* = 8.6 Hz), 4.93 (s, 2H, $CH_2SeCN$), 2.16 (s, 3H, $NHCOCH_3$).

$^{13}C$ NMR : δ 191.66, 169.29, 145.10, 130.01, 128.36, 118.78, 102.05, 37.97, 24.34.

Anal. Calcd. for $C_{11}H_{10}N_2O_2Se$: C, 46.99; H, 3.58; N, 9.96. Found: C, 47.11; H, 3.59; N, 9.75.

***1,2-Diselenocyanato-2-(2-naphthyl)ethane (53) and***

***1-Selenocyanato-(2-naphthyl)ethanone (54)***

To a solution of 2-vinylnaphthalene **51** (154 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) afforded 66 mg of **53** (24%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 131 mg of **54** (36%).

***1,2-Diselenocyanato-2-(2-naphthyl)ethane (53)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 141-143 °C

IR (KBr) $\nu_{max}$ : 3064, 3008, 2149, 1620, 1595, 1502, 1427, 1365, 1265, 1147, 1128, 1054, 954, 892, 871, 742 $cm^{-1}$.

$^1H$ NMR : δ 7.93-7.85 (m, 4H, ArH), 7.57-7.42 (m, 3H, ArH), 5.14

(dd, 2H, CHSeCN, $J$ = 4.8 Hz, $J$ = 11.6 Hz), 4.16-3.93 (m, 2H, $CH_2SeCN$).

$^{13}C$ NMR : δ 133.85, 133.21, 132.00, 130.15, 128.30, 127.99, 127.62, 127.45, 127.38, 123.96, 100.60, 99.49, 48.44, 33.71.

Anal. Calcd. for $C_{14}H_{10}N_2Se_2$: C, 46.17; H, 2.77; N, 7.69. Found: C, 46.17; H, 2.67; N, 7.40.

***1-Selenocyanato-(2-naphthyl)ethanone (54)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 129-131 °C

IR (KBr) $\nu_{max}$ : 2996, 2946, 2149, 1651, 1626, 1465, 1371, 1297, 1163, 1122, 998, 848, 811, 736 $cm^{-1}$.

$^1H$ NMR : δ 8.47 (s, 1H, ArH), 7.99-7.88 (m, 4H, ArH), 7.69-7.58 (m, 2H, ArH), 5.07 (s, 2H, $CH_2SeCN$).

$^{13}C$ NMR : δ 192.77, 136.16, 132.27, 131.17, 129.69, 129.48, 129.10, 127.91, 127.38, 123.36, 101.51, 38.44.

Anal. Calcd. for $C_{13}H_9NOSe$: C, 56.95; H, 3.31; N, 5.11. Found: C, 57.17; H, 3.46; N, 5.09.

***1,2-Diselenocyanato-2-(1-naphthyl)ethane (55 )and***

***1-Selenocyanato-(1-naphthyl)ethanone (56)***

To a solution of 1-vinylnaphthalene **52** (154 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) afforded 60 mg of **55** (22%) and on further elution using hexane-ethyl acetate mixture (90:10) afforded 109 mg of **56** (30%).

***1,2-Diselenocyanato-2-(1-naphthyl)ethane (55)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

| | | |
|---|---|---|
| mp | | 108-110 °C |
| IR (KBr) $\nu_{max}$ | : | 3058, 3008, 2149, 1602, 1539, 1508, 1434, 1396, 1209, 1128, 886, 805, 774 $cm^{-1}$. |
| $^1H$ NMR | : | δ 8.08 (d, 1H, ArH, $J$ = 8.1 Hz), 7.93 (d, 2H, ArH, $J$ = 7.6 Hz), 7.70-7.65 (m, 1H, ArH), 7.60 (d, 1H, ArH, $J$ = 7.6 Hz), 7.56-7.49 (m, 2H, ArH), 5.84-5.79 (m, 1H, CHSeCN), 4.21-4.18 (m, 2H, $CH_2SeCN$). |
| $^{13}C$ NMR | : | δ 134.26, 131.06, 130.47, 130.17, 129.64, 127.78, 126.87, 125.31, 124.53, 121.86, 100.94, 99.98, 48.40, 33.67. |

Anal. Calcd. for $C_{14}H_{10}N_2Se_2$: C, 46.17; H, 2.77; N, 7.69. Found: C, 46.67; H, 2.46; N, 7.66.

***1-Selenocyanato-(1-naphthyl)ethanone (56)***

colourless crystalline solid: recrystallized from hexane-dichloromethane

| | | |
|---|---|---|
| mp | | 110-112 °C |
| IR (KBr) $\nu_{max}$ | : | 3046, 2921, 2149, 1640, 1564, 1508, 1377, 1290, 1253, 1209, 1166, 948, 799, 761 $cm^{-1}$. |
| $^1H$ NMR | : | δ 8.85 (d, 1H, ArH, $J$ = 8.5 Hz), 8.11 (d, 1H, ArH, $J$ = 8.2 Hz), 8.05 (d, 1H, ArH, $J$ = 7.2 Hz), 7.90 (d, 1H, ArH, $J$ = 8.0 Hz), 7.68-7.51 (m, 3H, ArH), 5.08 (s, 2H, $CH_2SeCN$). |
| $^{13}C$ NMR | : | δ 195.25, 135.49, 134.01, 130.76, 130.55, 130.33, 129.22, 128.67, 127.05, 125.70, 124.14, 101.57, 40.72. |

Anal. Calcd. for $C_{13}H_9NOSe$: C, 56.95; H, 3.31; N, 5.11. Found: C, 56.72; H, 3.19; N, 4.90.

### 3.7.4 Selenocyanation of Indoles: General Procedure

To a solution of indole (1 mmol) and potassium selenocyanate (2 mmol) in methanol (10 mL) was added dropwise a solution of CAN (2.3 mmol) in methanol (15 mL) at 0 °C during 30 minutes. On completion of the reaction as shown by tlc, the reaction mixture was diluted with water (100 mL) and extracted with dichloromethane (3 x 25 mL). The combined organic extract was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residue was subjected to column chromatography on basic alumina. Elution with an appropriate mixture of hexane and ethyl acetate afforded the products.

*3-Selenocyanatoindole (28)*[22]

To a solution of indole **27** (117 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on basic alumina using hexane-ethyl acetate mixture (90:10) afforded 159 mg of **28** (72%).

colourless crystalline solid: recrystallized from hexane-dichloromethane

| | | |
|---|---|---|
| mp | | 100-101 °C |
| IR (KBr) $\nu_{max}$ | : | 3339, 3050, 2160, 1574, 1505, 1451, 1411, 1324, 1229, 1094 $cm^{-1}$. |
| $^1H$ NMR | : | δ 8.80 (s, 1H, NH, exchangeable with $D_2O$), 7.69-7.67 (m, 1H, ArH), 7.32-7.22 (m, 4H, ArH). |
| $^{13}C$ NMR | : | δ 135.96, 131.74, 128.56, 123.56, 121.67, 119.31, 111.89, 101.96, 88.97. |

Anal. Calcd. for $C_9H_6N_2Se$: C, 48.89; H, 2.74; N, 12.67. Found: C, 48.56; H, 2.92; N, 12.34.

***2-Methyl-3-selenocyanatoindole (68)***[22b]

To a solution of 2-methylindole **65** (131 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on basic alumina using hexane-ethyl acetate mixture (90:10) afforded 188 mg of **68** (80%).

colourless crystalline solid: recrystallized from hexane-dichloromethane

| | | |
|---|---|---|
| mp | | 131-132 °C |
| IR (KBr) $\nu_{max}$ | : | 3386, 2144, 1620, 1576, 1539, 1451, 1389, 1283, 1220, 733, 633 $cm^{-1}$. |
| $^1H$ NMR | : | δ 8.61 (s, 1H, NH, exchangeable with $D_2O$), 7.63-7.61 (m, 1H, ArH), 7.31-7.19 (m, 3H, ArH), 2.51 (s, 3H, $CH_3$). |
| $^{13}C$ NMR | : | δ 141.73, 135.37, 129.72, 122.84, 121.45, 118.87, 110.92, 101.60, 87.84, 12.90 |

Anal. Calcd. for $C_{10}H_8N_2Se$: C, 51.08; H, 3.43; N, 11.91. Found: C, 51.48; H, 3.42; N, 11.74.

***1-Methyl-3-selenocyanatoindole (69)***[22b]

To a solution of 1-methylindole **66** (131 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on basic alumina using hexane-ethyl acetate mixture (90:10) afforded 165 mg of **69** (70%).

colourless crystalline solid: recrystallized from hexane-dichloromethane

| | |
|---|---|
| mp | 107-108 °C |

IR (KBr) $\nu_{max}$ : 3176, 3145, 3064, 2149, 1446, 1438, 1402, 1328, 1303, 1228, 1023, 742, 687 $cm^{-1}$.

$^1H$ NMR : δ 7.74-7.71 (m, 1H, ArH), 7.37-7.29(m, 4H, ArH), 3.81 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 137.11, 135.69, 129.45, 123.25, 121.47, 119.74, 109.86, 101.30, 87.25, 33.21

Anal. Calcd. for $C_{10}H_8N_2Se$: C, 51.08; H, 3.43; N, 11.91. Found: C, 51.18; H, 3.38; N, 11.49.

***2-Phenyl-3-selenocyanatoindole (70)***

To a solution of 2-phenylindole **67** (193 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on basic alumina using hexane-ethyl acetate mixture (90:10) afforded 217 mg of **70** (73%)

colourless crystalline solid: recrystallized from hexane-dichloromethane

mp 170-172 °C

IR (KBr) $\nu_{max}$ : 3176, 3145, 3064, 2149, 1483, 1446, 1402, 1328, 1303, 1228, 1023, 742, 687 $cm^{-1}$.

$^1H$ NMR : δ 11.11 (s, 1H, NH, exchangeable with $D_2O$), 7.73-7.71 (m, 3H, ArH), 7.50-7.42 (m, 4H, ArH), 7.30-7.23 (m, 2H, ArH).

$^{13}C$ NMR : δ 143.51, 136.30, 131.05, 130.69, 129.21, 128.93, 128.54, 123.27, 121.37, 119.49, 111.98, 101.97, 86.26

Anal. Calcd. for $C_{15}H_{10}N_2Se$: C, 60.62; H, 3.39; N, 9.43. Found: C, 61.19; H, 3.37; N, 9.40.

***N-Methyl-2-selenocyanatopyrrole (74)***

To a solution of N-methylpyrrole **73** (81 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on basic alumina using hexane-ethyl acetate mixture (90:10) afforded 46 mg of **74** (25%)

Light yellow viscous liquid

IR (neat) $\nu_{max}$ : 3150, 3042, 2930, 2150, 1424, 1507, 1312, 1108, 1020, 789, 652 $cm^{-1}$.

$^1H$ NMR : δ 6.89 (s, 1H, ArH), 6.61 (s, 1H, ArH), 6.34 (s, 1H, ArH), 3.69 (s, 3H, $CH_3$).

$^{13}C$ NMR : δ 127.24, 119.55, 108.55, 108.25, 101.10, 33.24.

***N, N-Dimethyl-4-selenocyanatoaniline (76)***[21]

To a solution of N,N-dimethylaniline **75** (121 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography on basic alumina using hexane-ethyl acetate mixture (90:10) afforded 113 mg of **76** (50%)

Light yellow viscous liquid

IR (neat) $\nu_{max}$ : 2906, 2812, 2144, 1582, 1507, 1432, 1370, 1226, 1195, 1064, 939, 802 $cm^{-1}$.

$^1H$ NMR : δ 7.48 (d, 2H, ArH, $J$ = 9.0 Hz), 6.62 (d, 2H, ArH, $J$ = 9.0 Hz), 2.98 (s, 6H, $NMe_2$).

$^{13}C$ NMR : δ 151.51, 136.16, 113.24, 112.60, 102.16, 40.00.

***1,2-Dimethoxy-4-nitrobenzene (81)***

To a solution of 1,2-dimethoxybenzene **80** (138 mg, 1 mmol) and potassium selenocyanate (288 mg, 2 mmol) in methanol (10 mL) kept in an ice-bath was added dropwise (30 min) a solution of CAN (1.26 gm, 2.3 mmol) in methanol (15 mL). On completion of the reaction, the reaction mixture was processed as described in the general procedure. The residue on column chromatography afforded 110 mg of **81** (60%)

yellow crystalline solid: recrystallized from hexane-dichloromethane

| | | |
|---|---|---|
| mp | | 94-95 °C |
| IR (KBr) $\nu_{max}$ | : | 2943, 2837, 1532, 1507, 1354, 1270, 1233, 1183, 1083, 846, 796 $cm^{-1}$. |
| $^1H$ NMR | : | δ 7.93 (dd, 1H, ArH, $J$ = 8.8 Hz, $J$ = 2.2 Hz), 7.75 (d, 2H, ArH, $J$ = 2.2 Hz), 6.92 (d, 1H, ArH, $J$ = 8.8 Hz), 3.98 (s, 3H, OMe), 3.97 (s, 3H, OMe). |
| $^{13}C$ NMR | : | δ 154.54, 148.92, 141.56, 117.82, 109.88, 106.52, 56.46, 56.34. |

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Chapter 4

# DIASTEREOSELECTIVE AZIDATION REACTIONS MEDIATED BY CERIUM(IV) AMMONIUM NITRATE

## 4.1 INTRODUCTION

Addition of free radicals to carbon-carbon double bonds has emerged as an important reaction in organic chemistry (see **Chapter 1**). Because of their high reactivity, organic free radicals have historically been regarded as intermediates poorly suited for selective reactions. Recently, however, remarkable progress has been made in stereochemical control in radical carbon-carbon bond formation.[1] Developments in diastereoselective radical reactions began in the 1980s and have culminated in guidelines for the use of auxiliaries and the understanding of substrate controlled processes.

Chiral auxiliary methodology continues to offer an effective approach in asymmetric synthesis.[2] An important condition for the success of the approach is that the chiral auxiliary must be efficiently introduced and it must be easily removed without disrupting the newly formed stereogenic centres. Currently, the most useful chiral auxiliaries are those which function by controlling the diastereoselectivity of attached acyl fragments. In this context, perhaps the most widely used auxiliaries are the versatile oxazolidin-2-ones **1** and **2** discovered by Evans[3] (Figure 1). The N-acyl derivatives of Evans' auxiliaries **1** and **2** have been utilized in numerous highly diastereoselective reactions including alkylation, amination, azidation, bromination, hydroxylation, aldol addition, Diels-Alder cycloadditions and conjugate additions.[4]

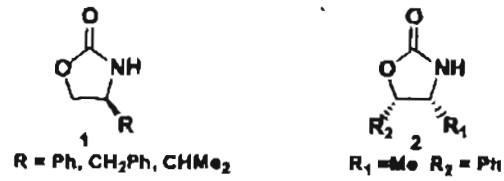
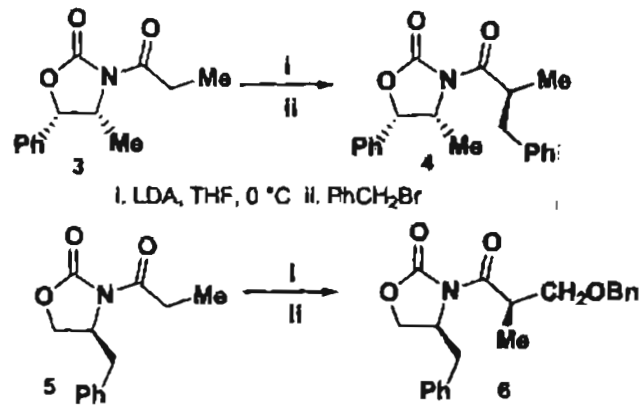


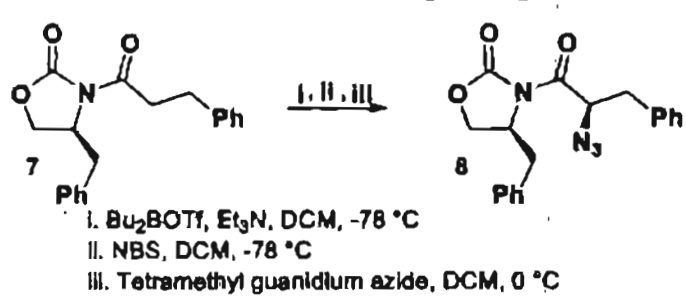

**Figure 1**

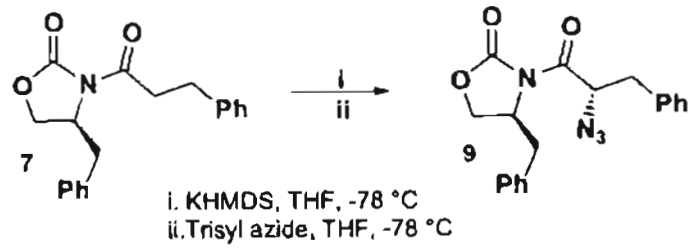
With the development of chiral enolate systems, it has been found that amide and imide enolates of 1 and 2 exhibit excellent levels of asymmetric induction for alkylation reactions (Scheme 1).[5]




**Scheme 1**

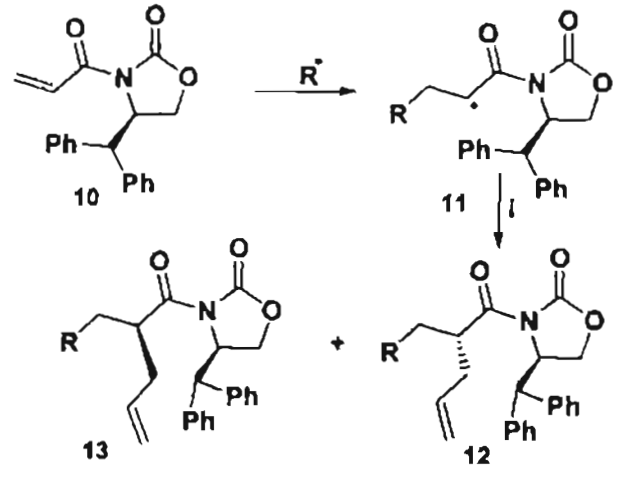
The electrophilic introduction of azide with chiral imide enolate has been used to synthesize $\alpha$-amino acids with high diastereoselection. The reaction can be performed with either the enolate directly[6] or through a halo intermediate,[7] the resultant azide can be reduced to the corresponding amine (Scheme 2).





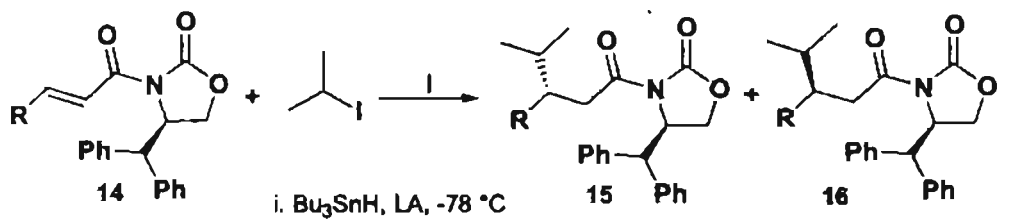

**Scheme 2**

Although there are numerous examples of diastereoselective Diels-Alder, Aldol and other reactions that are directed by chiral auxiliaries, there are only a few reports of diastereoselective radical reactions. The reaction of alkyl iodides, electron-deficient alkenes and allyl tributyl stannane has been used extensively to test the efficacy of auxiliary groups in free radical additions. The auxiliary can be used in a propagation sequence that involves radical addition to the acrylimide followed by trapping of the adduct radical with allyl stannane and this is exemplified in Scheme 3.[8]



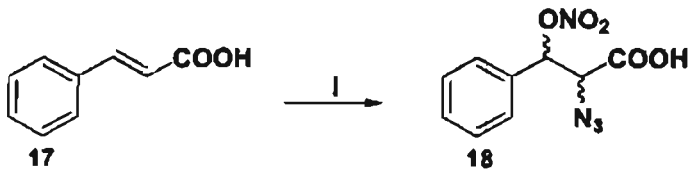

**Scheme 3**

The diphenyloxazolidinone in combination with Lewis acids provides a general solution for diastereoselective reactions (Scheme 4).[9]




**Scheme 4**

Recent work in our laboratory has shown that CAN mediated addition of azide to $\alpha$, $\beta$-unsaturated carboxylic acid under an atmosphere of argon leads to a facile synthesis of $\alpha$-azido-$\beta$-nitrato compounds that can serve as precursors to $\alpha$-amino-$\beta$-hydroxy acids (Scheme 5).[10] It is worthy of mention that the latter are of considerable biological importance.[11] Inter alia, they are components of various peptides possessing a wide range of biological activities such as antibiotic and immunosuppressive properties.



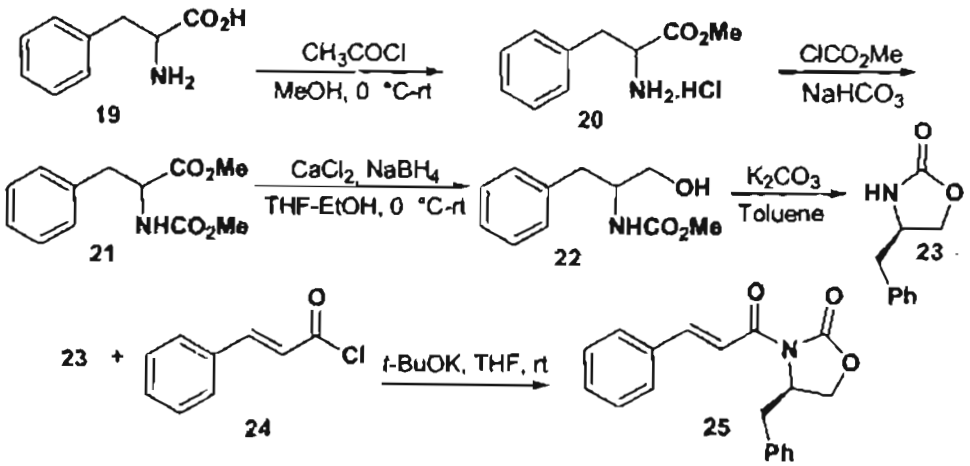

i. $NaN_3$, CAN, dry $CH_3CN$, argon, 0 °C-rt, overnight, 70%, *syn:anti* =1:1

**Scheme 5**

In this case, the reaction proceeded to afford the product as a 1:1 mixture of *syn* and *anti* isomers. Intrigued by the possibility of diastereoselective radical reactions, it was of interest to undertake the addition of azide radical to $\alpha$, $\beta$-unsaturated N-acyl oxazolidin-2-ones.

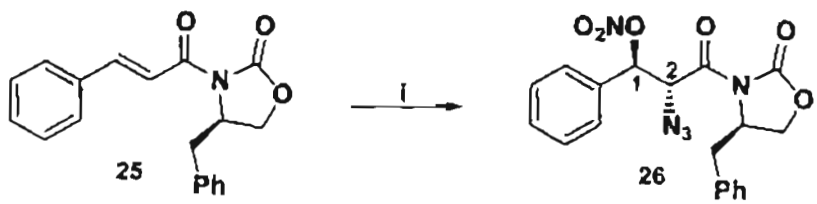
## 4.2 RESULTS AND DISCUSSION

The cinnamyloxazolidinone required for our study was synthesized according to the procedure as outlined in Scheme 6.[12]




**Scheme 6**

A deoxygenated solution of cinnamyloxazolidinone and sodium azide in anhydrous acetonitrile, on treatment with a deoxygenated solution of CAN in the same solvent afforded only the *anti* isomer **26** in 52% yield (Scheme 7).

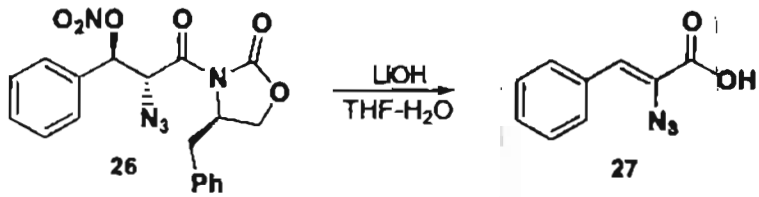



I. $NaN_3$, CAN, dry $CH_3CN$, argon, rt, 50 min, 52%

**Scheme 7**

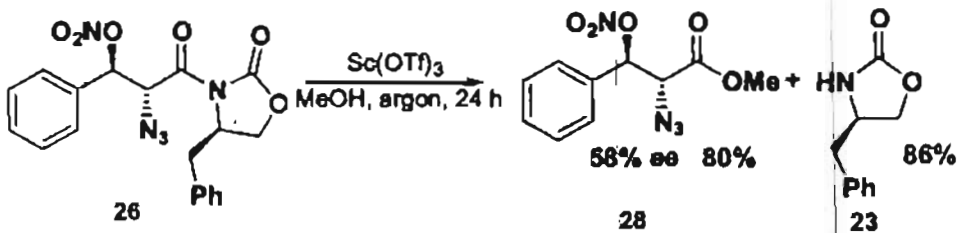
The product was purified by silica gel column chromatography and characterized by the usual spectroscopic methods. The IR spectrum of **26** showed the characteristic absorption of azide at 2115 $cm^{-1}$. The absorptions due to carbonyl groups were visible at 1781 and 1707 $cm^{-1}$ respectively. The absorption due to $ONO_2$ group was visible at 1645 $cm^{-1}$. In the $^1H$ NMR spectrum, the proton attached C-1 was visible as doublet at δ 6.22 (d, $J$ = 9.9 Hz). The proton on C-2 also appeared as doublet at δ 5.47 (d, $J$ = 7.2 Hz). In the $^{13}C$ NMR spectrum, the carbonyl carbons were discernible at δ 166.24 and 152.78. The C-1 carbon resonated at δ 81.55 and the C-2 carbon resonated at δ 66.60. All other signal were in good agreement with the assigned structure.

When we attempted the exocyclic cleavage of the chiral auxiliary using lithium hydroxide,[13] the product obtained was the 2-azidocinnamic acid (Scheme 8).



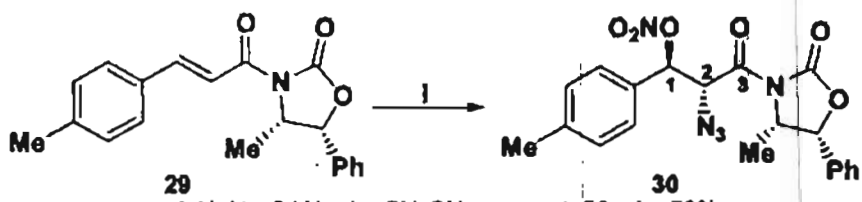

**Scheme 8**

Subsequently, we tried the Lewis acid mediated cleavage of the chiral auxiliary[14] for which a solution of the product in anhydrous methanol was treated with scandium triflate under an atmosphere of argon and was refluxed for 24 hours. The reaction proceeded to afford 80% of **28** with 58% of *ee* and 86% of **23** (Scheme 9). Enantiomeric excess of the product was determined by using chiral shift reagent, tris[3-heptafluoropropylhydroxymethylene(+)-camphorato]europium(III), $Eu(hfc)_3$.




**Scheme 9**

4-Methylcinnamyloxazolidinone also gave the *anti* isomer of the *α*-azido-*β*-nitrato product under similar reaction conditions (Scheme 10).

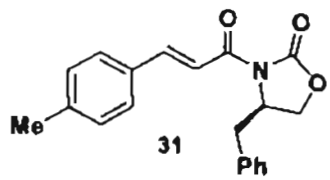
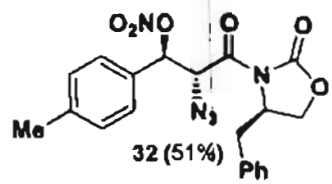
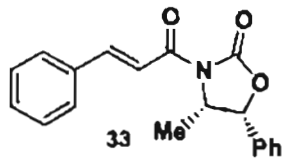
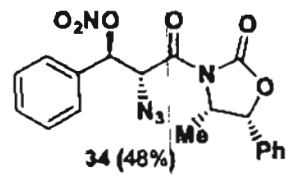
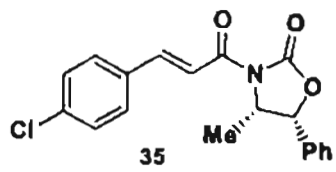
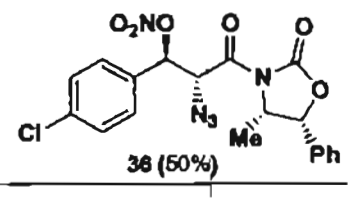



**Scheme 10**

The structure of the product **30** was established on the basis of spectroscopic data. The IR spectrum showed the absorption due to $N_3$ at 2118 $cm^{-1}$ and $ONO_2$ group at 1642 $cm^{-1}$. The absorptions due to the carbonyl groups were visible at 1787 and 1715 $cm^{-1}$. In the $^1H$ NMR spectrum, the proton attached to C-1 appeared as a doublet at δ 6.14 (d, $J$ = 9.9 Hz) and the proton on C-2 also appeared as doublet at δ 5.76 (d, $J$ = 7.2 Hz). In the $^{13}C$ NMR spectrum, the carbonyl peaks were discernible at δ 166.22 and 152.46. The C-1 carbon resonated at δ 81.76 and the C-2 carbon resonated at δ 79.62. All other signals were in good agreement with the assigned structure.

The reaction was found to proceed well with other substituted cinnamyloxazolidin-2-ones **31**, **33** and **35** and the results are presented in Table 1.The products were characterized on the basis of spectroscopic data.

**Table 1:** Azidation of cinnamyloxazolidin-2-ones

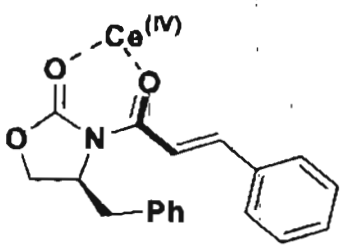
| Entry | Substrate | Product/Yield(%)[a] |
|---|---|---|
| 1 |  **31** |  **32** (51%) |
| 2 |  **33** |  **34** (48%) |
| 3 |  **35** |  **36** (50%) |

[a] Reaction Conditions: $NaN_3$, CAN, dry $CH_3CN$, argon, rt, 50 min

## 4.3 MECHANISTIC DETAILS

A working hypothesis for the stereoselectivity observed for the CAN mediated azidations with chiral auxiliary can be depicted as shown in Scheme

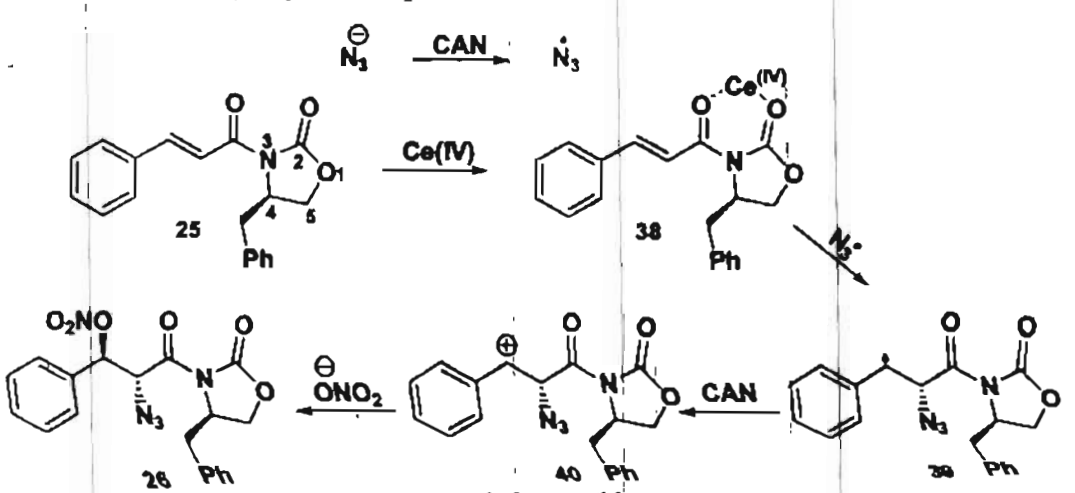
11. The success of the oxazolidinone template in providing high diastereoselectivity is attributed to the availability of two donor sites for chelation. In the first step Cerium(IV) co-ordinates with the oxygen atoms of the oxazolidinone to form the six membered chelated intermediate 37 (Figure 2).




37

**Figure 2**

A model 37 can account for the observed selectivity. The oxazolidinone 4-substituent provides shielding of the diastereotopic face and thus the azido radical formed by the oxidation of azide anion by CAN would add to this complex preferentially from only one face thus leading to the observed stereoselectivity. This radical can be oxidized to benzylic cation 40 by a second equivalent of CAN and the cation is then quenched by $ONO_2$ or by ligand transfer from CAN to yield the product.




**Scheme 11**

## 4.4 CONCLUSION

In conclusion, the preliminary results presented above suggest that the stereoselectivity achieved in the radical carbon-heteroatom bond forming reactions mediated by CAN makes further exploration obligatory. It is quite likely that such studies will result in much interesting results. Further work in this direction will be undertaken by other members of our research group.

## 4.5 EXPERIMENTAL DETAILS

For general information, see section **2.6** of **Chapter 2** page 64.

### 4.5.1 CAN mediated addition of azide to cinnamyloxazolidin-2-ones under deoxygenated conditions: General Procedure

A mixture of cinnamyloxazolidin-2-one (1 mmol) and sodium azide (1.2 mmol) was taken in anhydrous acetonitrile (5 mL) in a two necked round-bottomed flask fitted with a pressure equalizing funnel containing CAN (2.3 mmol) dissolved in anhydrous acetonitrile (10 mL). Both the solutions were simultaneously bubbled with argon, which was deoxygenated by passing through Fieser's[52] solution for 15 minutes. Then the solution of CAN in $CH_3CN$ was added dropwise at room temperature and the reaction mixture was stirred vigorously under argon atmosphere for 50 minutes. When the starting material was fully consumed as shown by tlc, acetonitrile was evaporated off, the reaction mixture was diluted with water (75 mL) and extracted using dichloromethane (3 x 25 mL). The combined organic extracts were washed with water, then with saturated brine and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to obtain the crude residue, which was subjected to column chromatography on silica gel. Elution with an appropriate mixture of hexane-ethyl acetate afforded the products.

***3-(2-Azido-3-nitrato-3-phenyl-1-oxopropyl)-4-(phenylmethyl)-2-oxazolidinone (26)***

To a deoxygenated solution of sodium azide (78 mg, 1.2 mmol) and cinnamyl oxazolidin-2-one **25** (307 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature over a period of 50 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (80:20) afforded 214 mg (52%) of the product.

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3024, 2918, 2115, 1781, 1707, 1645, 1458, 1390, 1273, 1211, 1111, 842, 700 $cm^{-1}$.

$^1H$ NMR : δ 7.51-7.44 (m, 5H, ArH), 7.33-7.25 (m, 3H, ArH), 7.21-7.18 (m, 2H, ArH), 6.22 (d, 1H, $CHONO_2$, $J$ = 9.9 Hz), 5.47 (d, 1H, $CHN_3$, $J$ = 7.2 Hz) 4.73-4.68 (m, 1H, CH), 4.28-4.20 (m, 1H, $CH_2$), 3.24 (dd, 1H, $CH_2$, $J$ = 2.9 Hz, $J$ = 13.3 Hz), 2.87 (dd, 1H, $CH_2$, $J$ = 9.1 Hz, $J$ = 13.5 Hz).

$^{13}C$ NMR : δ 166.24, 152.78, 134.35, 133.59, 130.12, 129.36, 129.13, 128.98, 127.78, 127.53, 81.55, 66.60, 60.82, 55.29, 37.45.

***3-(2-Azido-3-nitrato-3-(4'-methylphenyl)-1-oxopropyl)-4-(methyl)-2-(phenyl)-2-oxazolidinone (30)***

To a deoxygenated solution of sodium azide (78 mg, 1.2 mmol) and 4-methyl cinnamyl oxazolidin-2-one **29** (321 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature over a period of 50 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (80:20) afforded 213 mg (50%) of the product.

***3-(2-Azido-3-nitrato-3-phenyl-1-oxopropyl)-4-(phenylmethyl)-2-oxazolidinone (26)***

To a deoxygenated solution of sodium azide (78 mg, 1.2 mmol) and cinnamyl oxazolidin-2-one **25** (307 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature over a period of 50 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (80:20) afforded 214 mg (52%) of the product.

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3024, 2918, 2115, 1781, 1707, 1645, 1458, 1390, 1273, 1211, 1111, 842, 700 $cm^{-1}$.

$^1H$ NMR : δ 7.51-7.44 (m, 5H, ArH), 7.33-7.25 (m, 3H, ArH), 7.21-7.18 (m, 2H, ArH), 6.22 (d, 1H, $CHONO_2$, $J$ = 9.9 Hz), 5.47 (d, 1H, $CHN_3$, $J$ = 7.2 Hz) 4.73-4.68 (m, 1H, CH), 4.28-4.20 (m, 1H, $CH_2$), 3.24 (dd, 1H, $CH_2$, $J$ = 2.9 Hz, $J$ = 13.3 Hz), 2.87 (dd, 1H, $CH_2$, $J$ = 9.1 Hz, $J$ = 13.5 Hz).

$^{13}C$ NMR : δ 166.24, 152.78, 134.35, 133.59, 130.12, 129.36, 129.13, 128.98, 127.78, 127.53, 81.55, 66.60, 60.82, 55.29, 37.45.

***3-(2-Azido-3-nitrato-3-(4'-methylphenyl)-1-oxopropyl)-4-(methyl)-2-(phenyl)-2-oxazolidinone (30)***

To a deoxygenated solution of sodium azide (78 mg, 1.2 mmol) and 4-methyl cinnamyl oxazolidin-2-one **29** (321 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature over a period of 50 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (80:20) afforded 213 mg (50%) of the product.

colourless viscous liquid

IR (neat) $\nu_{max}$ : 2989, 2921, 2118, 1787, 1715, 1642, 1458, 1384, 1276, 1155, 1007, 852, 737 $cm^{-1}$.

$^1H$ NMR : δ 7.43-7.38 (m, 5H, ArH), 7.32-7.24 (m, 4H, ArH), 6.14 (d, 1H, $CHONO_2$, $J$ = 10.0 Hz), 5.76 (d, 1H, $CHN_3$, $J$ = 7.2 Hz), 5.49 (d, 1H, CH, $J$ = 10.0 Hz) 4.83-4.79 (m, 1H, CH), 2.39 (s, 3H, $CH_3$), 0.96 (d, 3H, $CH_3$).

$^{13}C$ NMR : δ 166.22, 152.46, 140.28, 132.66, 130.62, 129.90, 129.09, 128.87, 127.84, 125.65, 81.76, 79.62, 60.86, 55.27, 21.40, 14.33.

***3-(2-Azido-3-nitrato-3(4'-methylphenyl-1-oxopropyl)-4-(phenylmethyl)-2-oxazolidinone (32)***

To a deoxygenated solution of sodium azide (78mg, 1.2 mmol) and 4-methyl cinnamyl oxazolidin-2-one **31** (321 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature over a period of 50 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (80:20) afforded 217 mg (51%) of the product.

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3020, 2116, 1779, 1705, 1644, 1457, 1398, 1275, 1210, 1101, 850, 740 $cm^{-1}$.

$^1H$ NMR : δ 7.40-7.38 (m, 2H, ArH), 7.36-7.30 (m, 3H, ArH), 7.28-7.21 (m, 5H, ArH), 6.16 (d, 1H, $CHONO_2$, $J$ = 10.0 Hz), 5.49 (d, 1H, $CHN_3$, $J$ = 10.0 Hz) 4.76-4.71 (m, 1H, CH), 4.35-4.24 (m, 1H, $CH_2$), 3.29 (dd, 1H, $CH_2$, $J$ = 3.3 Hz, $J$ = 13.5 Hz), 2.88 (dd, 1H, $CH_2$, $J$ = 9.2 Hz, $J$ = 13.5 Hz), 2.40 (s, 3H, $CH_3$).

$^{13}$C NMR : δ 166.55, 152.65, 140.30, 134.47, 130.66, 129.93, 129.51, 129.14, 127.90, 127.69, 81.69, 66.69, 60.81, 55.38, 37.54, 21.42.

***3-(2-Azido-3-nitrato-3-(phenyl)-1-oxopropyl)-4-(methyl)-2-(phenyl)-2-oxazolidinone (34)***

To a deoxygenated solution of sodium azide (78 mg, 1.2 mmol) and methyl cinnamyl oxazolidin-2-one **33** (307 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature over a period of 50 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (80:20) afforded 197 mg (48%) of the product.

colourless viscous liquid

IR (neat) $\nu_{max}$ : 3012, 2104, 1783, 1702, 1645, 1450, 1390, 1256, 1230, 1103, 864, 710

$^{1}$H NMR : δ 7.50-7.32 (m, 10H, ArH), 6.18 (d, 1H, $CHONO_2$, $J$ = 10.0 Hz), 5.76 (d, 1H, $CHN_3$, $J$ = 7.2 Hz), 5.49 (d, 1H, CH, $J$ = 10.0 Hz) 4.84-4.79 (m, 1H, CH), 0.97 (d, 3H, $CH_3$).

$^{13}$C NMR : δ 165.97, 152.50, 136.44, 132.58, 132.34, 129.56, 129.21, 128.96, 125.69, 80.99, 79.78, 60.90, 55.28, 14.42.

***3-(2-Azido-3-nitrato-3-(4'-chlorophenyl)-1-oxopropyl)-4-(methyl)-2-(phenyl)-2-oxazolidinone (36)***

To a deoxygenated solution of sodium azide (78 mg, 1.2 mmol) and 4-chloro methyl cinnamyl oxazolidin-2-one **35** (341.5 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was added dropwise a deoxygenated solution of CAN (1.26 g, 2.3 mmol) in acetonitrile (10 mL) at room temperature over a period of 50 minutes. On completion of the reaction, it was processed as described in the general procedure. The residue on column chromatography on silica gel using hexane-ethyl acetate (80:20) afforded 223 mg (50%) of the product.

colourless viscous liquid

IR (neat) $\nu_{max}$ : 2989, 2124, 1790, 1708, 1650, 1506, 1391, 1283, 1202, 1155, 1094, 1000, 852, 771, $cm^{-1}$.

$^1H$ NMR : δ 7.45-7.39 (m, 9H, ArH), 6.14 (d, 1H, $CHONO_2$, $J$ = 10.0 Hz), 5.78 (d, 1H, $CHN_3$, $J$ = 7.2 Hz), 5.47 (d, 1H, CH, $J$ = 10.0 Hz) 4.86-4.77 (m, 1H, CH), 0.96 (d, 3H, $CH_3$).

$^{13}C$ NMR : δ 165.92, 152.48, 136.39, 132.57, 132.26, 129.53, 129.21, 129.14, 128.89, 125.64, 80.91, 79.69, 60.84, 55.27, 14.35 .

***2-Azido-3-nitrato-3-phenyl-methylpropanoate(27)***

A solution of azido oxazolidinone **26** (205 mg, 0.5 mmol) and scandium triflate (10 mol%) in methanol (2 mL) was heated under reflux under an atmosphere of argon for 24 hours. The reaction mixture was filtered through a silica gel pad to remove the catalyst. The filtrate was evaporated and the residue was subjected to column chromatography on silica gel to afford 213 mg (80%) of methyl cinnamate **28** and 152 mg (86%) of oxazolidinone **23**.

IR (neat) $\nu_{max}$ : 2990, 2119, 1735, 1647, 150, 1361, 1273, 1155, 1080, 1010, 842, 761, $cm^{-1}$.

$^1H$ NMR : δ 7.41 (s, 5H, ArH), 6.13 (d, 1H, $CHONO_2$, $J$ = 7.0 Hz), 4.34 (d, 1H, $CHN_3$, $J$ = 7.0 Hz), 3.84 (s, 3H, $OCH_3$).

$^{13}C$ NMR : δ 170.46, 132.81, 129.90, 128.99, 127.00, 82.02, 63.70.

Enantiomeric excess of the product was determined by chiral shift reagent, tris[3-heptafluoro propyl hydroxy methylene(+)-camphorato]europium(III), Eu(hfc)$_3$. For this racemic $\alpha$-azido-$\beta$-nitrato ester was prepared and 5 mg of the ester was dssolved in 0.5 ml of $CDCl_3$. To this shift reagent was added in 5 mg lots until a good seperation of the methoxy signals were obtained. The two $COOCH_3$ groups shifted on adding shift reagent and a good seperation of one of the methoxy groups were obtained with 40 mg

of the shift reagent. Similarly, in the case of **28** the *ee* was determined using 30 mg $Eu(hfc)_3$.

## 4.6 REFERENCES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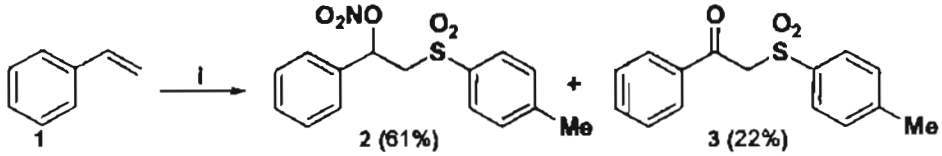
## SUMMARY

Carbon-carbon and carbon-heteroatom bond forming reactions are central to organic synthesis. Radical methodology occupies a unique position among such bond forming reactions. Of the different methods developed for the generation of radicals, chemical electron transfer reactions mediated by one electron oxidants are of current interest. Among the various one electron oxidants, cerium(IV) ammonium nitrate(CAN) has recently emerged as an effective reagent. A survey of the literature reveals that although CAN has been utilized widely in carbon-carbon bond forming reactions, the use of this reagent in carbon-heteroatom bond formation has not been studied extensively. In the context of our general interest in the synthetic utility of CAN, it was of interest to explore the potential of CAN in carbon-heteroatom bond forming reactions. As an introduction to this work, a brief description of various CAN mediated transformations with special emphasis on carbon-heteroatom bond forming reactions is presented in the first chapter of the thesis.

**1.1 Carbon-sulfur bond forming reactions mediated by CAN**

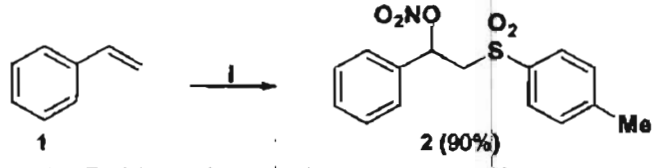
The second chapter of the thesis deals with carbon-sulfur bond forming reactions promoted by CAN. This chapter is divided into three parts. CAN mediated oxidative addition of sulfinate to styrenes is described in part one. The reaction of styrene and sodium *p*-toluenesulfinate with a solution of CAN in acetonitrile resulted in the formation of $\beta$-nitratosulfone **2** along with the $\beta$-ketosulfone **3** (Scheme 1).




i. $p$-TolSO$_2$Na, CAN, CH$_3$CN, rt, 40 min

**Scheme 1**

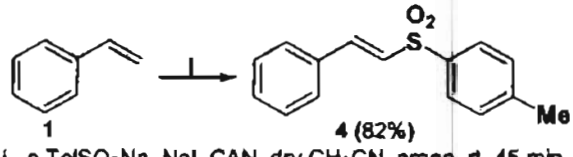
When the same reaction was done under argon atmosphere, the $\beta$-nitratosulfone **2** was formed exclusively (Scheme 2).




i. $p$-TolSO$_2$Na, CAN, dry CH$_3$CN, argon, rt, 40 min

**Scheme 2**

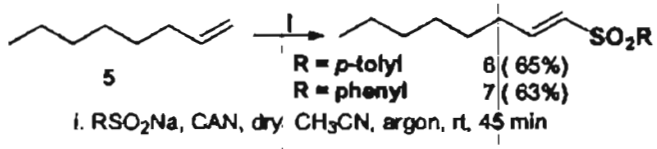
A one-pot synthesis of vinyl sulfones is described in the second part. A mixture of styrene, sodium $p$-toluenesulfinate and sodium iodide on treatment with a solution of CAN was found to yield the vinyl sulfone **4** instead of the expected $\beta$-iodovinyl sulfone (Scheme 3).




i. $p$-TolSO$_2$Na, NaI, CAN, dry CH$_3$CN, argon, rt, 45 min

**Scheme 3**

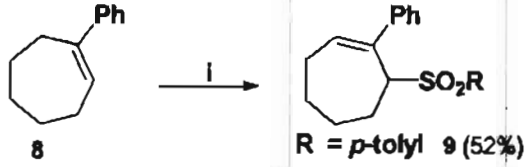
With a view to examine the generality of the reaction, we have done some preliminary investigations on the sulfonylation of $n$-alkenes as well as cyclic alkenes. The reaction of 1-octene with sodium $p$-toluenesulfinate in acetonitrile afforded the vinyl sulfone in 65% yield. Similar result was obtained with benzenesulfinate also (Scheme 4).




i. RSO$_2$Na, CAN, dry CH$_3$CN, argon, rt, 45 min

**Scheme 4**

The reaction of 1-phenylcycloheptene resulted in the formation of the allylic sulfone as shown in Scheme 5.

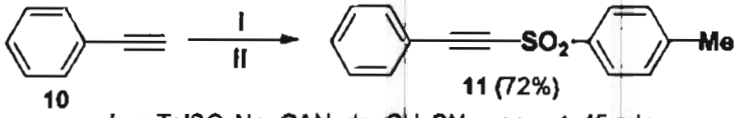



8 R = *p*-tolyl 9 (52%)

I. $RSO_2Na$, NaI, CAN, dry $CH_3CN$, argon, rt, 45 min

**Scheme 5**

Part three of chapter two describes the one pot synthesis of acetylenic sulfones. The crude $\beta$-iodovinyl sulfone derived from the reaction of phenylacetylene, sodium *p*-toluene sulfinate, sodium iodide and CAN on treatment with potassium carbonate under reflux afforded the acetylenic sulfone **11** (Scheme 6).



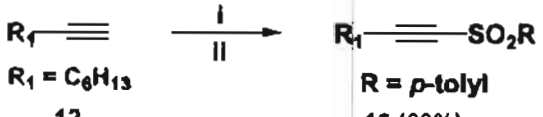

10 11 (72%)

I. *p*-$TolSO_2Na$, CAN, dry $CH_3CN$, argon, rt, 45 min

II. $K_2CO_3$, acetone, reflux, 5h

**Scheme 6**

Interestingly, 1-octyne also underwent similar type of reaction as shown in Scheme 7.




$R_1 = C_6H_{13}$ R = *p*-tolyl

12 13 (60%)

I. *p*-$TolSO_2Na$, NaI, CAN, dry $CH_3CN$, argon, rt, 45 min

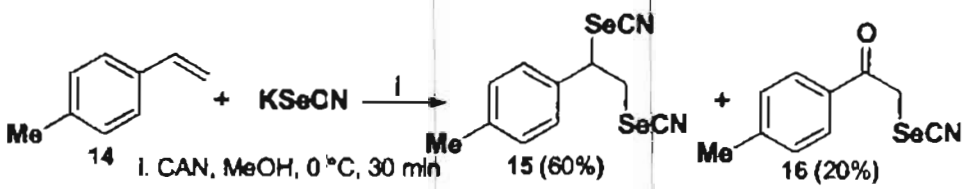
II. $K_2CO_3$, acetone, reflux, 5h

**Scheme 7**

## 1.2 Carbon-selenium bond forming reactions mediated by CAN

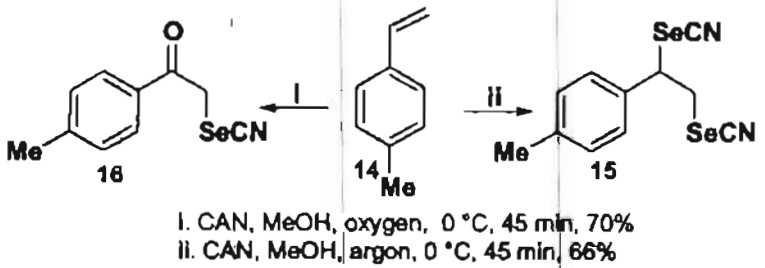
The third chapter of the thesis describes the CAN mediated carbon-selenium bond forming reactions. This is divided into two parts. The first part deals with the CAN mediated oxidative addition of selenocyanate to styrenes. A

methanolic solution of styrene and potassium selenocyanate on treatment with a methanolic solution of CAN afforded the diselenocyanate **15** along with the ketoselenocyanate **16** (Scheme 8).



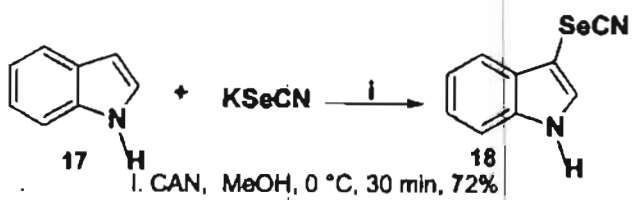

**Scheme 8**

When this reaction was done under oxygen atmosphere, ketoselenocyanate **16** was formed exclusively, whereas diselenocyanate **15** was the only product when the reaction was carried out under argon atmosphere (Scheme 9).




**Scheme 9**

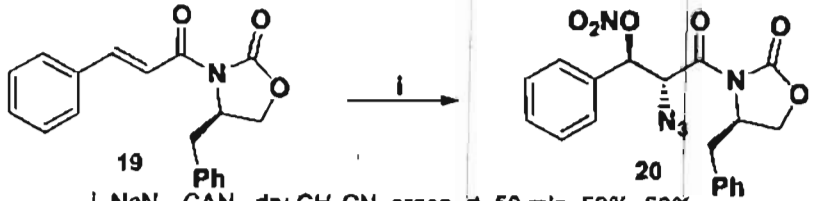
CAN mediated selenocyanation of electron rich aromatics is described in the second part. The reaction of indole and potassium selenocyanate with a methanolic solution of CAN resulted in the formation of 3-selenocyanatoindole **18** (Scheme 10).




**Scheme 10**

**1.3 Diastereoselective azidation reactions mediated by CAN**

One of the major objectives in organic synthesis has been the development of general strategies for stereoselective bond construction. Stereoselective radical reactions mediated by CAN are hitherto unknown. In view of the success of chiral auxiliary methodology in asymmetric synthesis, we undertook a preliminary study in this area and this forms the subject matter of the fourth chapter. A deoxygenated solution of cinnamyl oxazolidinone and sodium azide in anhydrous acetonitrile, on treatment with a solution of CAN in the same solvent afforded only the *anti* isomer **20** (Scheme 11).




i. $NaN_3$, CAN, dry $CH_3CN$, argon, rt, 50 min, 52%, 58% *ee*

**Scheme 11**

In conclusion, we have developed novel methods for the synthesis of sulfonyl compounds especially, vinyl sulfones, $\beta$-iodovinyl sulfones and acetylenic sulfones. We have also demonstrated that CAN is an efficient reagent for the selenocyanation of styrenes and electron-rich aromatics. Finally, our preliminary experiments have also shown the usefulness of CAN in diastereoselective azidation reactions.

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2. Cerium(IV) Ammonium Nitrate Mediated Addition of Thiocyanate and Azide to Styrenes: Expeditious Routes to Phenacyl Thiocyanates and Phenacyl Azides: Nair, V.; Nair, L. G.; George, T. G.; **Augustine, A.** *Tetrahedron* **2000**, *56*, 7607.
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6. An Efficient One-pot Synthesis of Vinyl Sulfones via CAN Mediated Reaction of Aryl Sulfinates and Alkenes: Nair, V.; **Augustine, A.**; George, T. G.; Nair, L. G. *Tetrahedron Lett.* **2001**, *42*, 6763.
7. Carbon-Heteroatom Bond Forming ReactionsMediated by Cerium(IV) Ammonium Nitrate:An Overview: Nair, V.; Panicker, S.B.; Nair, L. G.; George, T. G.; **Augustine, A**. *Synlett* (Account) **2002**, 0000.
8. A Facile CAN Mediated Synthesis of Selenocyanates from Aryl Alkenes and Heteroarenes: Nair, V.; **Augustine, A.**; George, T. G. *Eur. J. Org. Chem.* **2002**, 0000.

9. CAN Mediated Reaction of Aryl Sulfinates with Alkenes and Alkynes: Synthesis of Vinyl Sulfones, β-Iodovinyl Sulfones and Acetylenic Sulfones: Nair, V.; **Augustine, A.**; T. D. Suja. *Synthesis* **2002** (communicated).

## Posters presented at symposia

1. Cerium(IV) Ammonium Nitrate Mediated Fragmentation of Phenylcycloalkenes: Nair, V.; Panicker, S. B.; **Augustine, A.** National Symposium in Chemistry, Bangalore, January 1999, P-53.
2. Carbon-Heteroatom Bond Forming Reactions Mediated by Cerium(IV) Ammonium Nitrate: Nair, V.; Nair, L. G.; George, T. G.; **Augustine, A.** National Symposium in Chemistry, Hyderabad, January 2000, P-44.
3. An Efficient One-pot Synthesis of Vinyl Sulfones via CAN Mediated Reaction of Aryl Sulfinates and Alkenes: Nair, V.; **Augustine, A.** National Symposium in Chemistry, Pune, February 2002, P-15.