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# **LEVEL CYCLOADDITION REACTIONS OF [60] FULLERENE, 1, 2-DIONES AND RELATED CHEMISTRY**

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

BY

**D. SETHUMADHAVAN**

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ORGANIC CHEMISTRY DIVISION  
REGIONAL RESEARCH LABORATORY (CSIR)  
TRIVANDRUM-695 019, KERALA, INDIA

FEBRUARY, 2001

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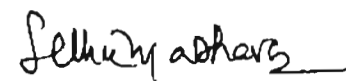
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**FEBRUARY, 2001**

## DECLARATION

I hereby declare that the thesis entitled “NOVEL CYCLOADDITION REACTIONS OF [60] FULLERENE, 1,2-DIONES AND RELATED CHEMISTRY” embodies the results of the investigations carried out by me at the Organic Chemistry Division of the Regional Research Laboratory (CSIR), Trivandrum, under the supervision of Dr. G. Vijay Nair and the same has not been submitted elsewhere for a degree.

  
D. Sethumadhavan

February, 2001.



COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH [CSIR]

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निदेशक

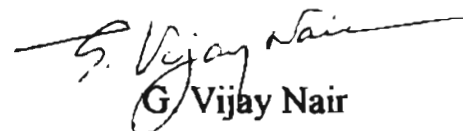
Dr. G. Vijay Nair, F.A.Sc.

Director

February 2001

## CERTIFICATE

This is to certify that the work contained in the thesis entitled "NOVEL CYCLOADDITION REACTIONS OF [60] FULLERENE, 1,2-DIONES AND RELATED CHEMISTRY" has been carried out by Mr. D. Sethumadhavan under my supervision at the Organic Chemistry Division of Regional Research Laboratory (CSIR), Trivandrum and the same has not been submitted elsewhere for any other degree.

  
G Vijay Nair

(Thesis Supervisor)

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*Thiruvananthapuram  
February 2001.*

*D. SETHUMADHAVAN*

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**Summary**

**List of Publications**

## PREFACE

Ever since fullerenes were discovered in 1985, the interest in their chemical modification has increased steadily. Functionalization of fullerenes continues to attract great attention and a major part of such effort is devoted to the synthesis of fullerene derivatives suitable for biological applications and in material science. The development of synthetic methods for the introduction of functional groups on a fullerene moiety is of much practical importance and it continues to be a challenge to synthetic chemist.

1,2 Diones like *o*-benzoquinones and isatins constitute an important class of organic compounds. Owing to the presence of two adjacent carbonyl groups, these compounds appeared interesting from the point of view of their transformations to a variety of structurally fascinating and potentially valuable compounds.

A systematic investigation of the dipolar cycloaddition reactions of [60] fullerene and isatins has been carried out. Cycloaddition reactions of *o*-benzoquinones with arylacetylenes has also been carried out and these results are presented in this thesis entitled "NOVEL CYCLOADDITION REACTIONS OF [60] FULLERENE, 1,2-DIONES AND RELATED CHEMISTRY".

The thesis is divided into four chapters. Relevant references are given at the end of each chapter. A general introduction to the cycloaddition reactions and nucleophilic addition reactions to [60] fullerene and cycloaddition reactions of 1,2-benzoquinones are presented in chapter 1. A definition of the present research problems is also incorporated.

The second chapter contains the results of our investigation of the dipolar cycloaddition of carbonyl ylides, and reaction of allenamides, with [60] fullerene. Results obtained from cyclic voltametry of the C<sub>60</sub> adducts are also incorporated. General information on the experimental procedures of the reactions of [60] fullerene is given in this chapter.

The third chapter deals with the dipolar cycloaddition reactions of nitrile ylides with isatins and 1,2-benzoquinones. Results of a limited study of the reaction of a five membered cyclic carbonyl ylide with isatins are also presented in this chapter.

The fourth chapter deals with a serendipitous synthesis of highly substituted tropolone derivatives from *o*-benzoquinones.

## ABBREVIATIONS

|                 |   |
|-----------------|---|
| br s            | : broad singlet                                       |
| C <sub>60</sub> | : [60] fullerene                                      |
| CV              | : cyclic voltametry                                   |
| d               | : doublet   |
| dd              | : double doublet                                      |
| DCB             | : dichlorobenzene                                     |
| DDQ             | : 2,3-dichloro-5,6-dicyano-1,4-benzoquinone           |
| DEPT            | : distortionless enhancement by polarization transfer |
| DMAD            | : dimethyl acetylenedicarboxylate                     |
| EI              | : electron impact                                     |
| Et              | : ethyl   |
| g               | : gram  |
| HETCORE         | : heterocosity  |
| HOMO            | : highest occupied molecular orbital                  |
| HRMS            | : high-resolution mass spectrum                       |
| IR              | : infrared  |
| <i>J</i>        | : coupling constant                                   |
| LDA             | : lithium diisopropylamide                            |
| LUMO            | : lowest unoccupied molecular orbital                 |
| m               | : multiplet   |
| Me              | : methyl  |
| mL              | : milliliter  |
| mp              | : melting point                                       |
| NMR             | : nuclear magnetic resonance                          |
| <i>o</i>        | : ortho   |
| <i>p</i>        | : para  |
| Ph              | : phenyl  |
| rt              | : room temperature                                    |
| s               | : singlet   |
| t               | : triplet   |
| TCNE            | : tetracyano ethylene                                 |
| <i>tert</i>     | : tertiary  |

# CHAPTER 1

## INTRODUCTION

The focal theme of the thesis is the functionalization reactions of [60] fullerene and cycloaddition reactions of 1,2-diones such as *o*-benzoquinones, isatins, acenaphthenequinone and phenanthrenequinone, along with some rearrangement reactions of the cycloadducts. To put things in perspective this chapter begins with a brief overview of the reactions of [60] fullerene and cycloaddition reactions of 1,2-diones.

For the sake of clarity, this chapter is divided into two parts. In the first part, a brief account of the cycloaddition and nucleophilic addition reactions of [60] fullerene is given. A very brief outline of the Diels-Alder and dipolar cycloadditions of *o*-benzoquinones is given in the second part. Since the information available on dipolar cycloadditions to isatins is very limited, it was considered more appropriate to include this in the introduction to the third chapter. Similarly the relevant background information to the work resulting in a synthesis of tropolone derivatives is presented in the fourth chapter.

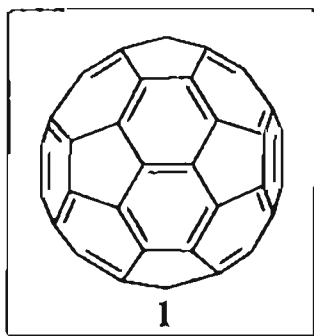
# PART 1

## CYCLOADDITION AND NUCLEOPHILIC ADDITION REACTIONS OF [60] FULLERENE

### 1.1 GENERAL

Fullerenes were discovered<sup>1</sup> by Kroto, Smalley and Curl in the year 1985 for which they were awarded the Nobel Prize for chemistry in 1996. Fullerenes are deemed to be the third allotrope of carbon after diamond and graphite. Synthetic chemists have been interested in the transformation of known matter and creating new materials. Elemental carbon played a minor role in the past. With the discovery of fullerenes this situation changed, because these molecules are soluble in a variety of organic solvents, an important requirement for chemical manipulations. The fullerenes are made up of fused pentagons and hexagons. Each fullerene  $C_n$  consists of 12 pentagonal rings and any number of hexagonal ones,  $m$ , such that  $m = (C_n - 20)/2$ .

The most important member of the fullerene family is the  $I_h$  symmetrical Buckminster fullerene,  $C_{60}$ , **1** (Figure 1).<sup>2</sup>



**Figure 1**

The smallest, stable and at the same time the most abundant, fullerene,  $C_{60}$  has the shape of a soccer ball. All the carbon atoms in the [60] fullerene are  $sp^2$  hybridized and is composed of 12 pentagons and 20 hexagons.

There is a tendency to avoid double bonds in the pentagonal ring and there is only one structure for  $C_{60}$  that avoids having any double bonds in the pentagonal rings. This has two important consequences. First, delocalization of electrons is poor, so  $C_{60}$  is much more reactive than originally expected. Second,  $C_{60}$  is not much of an aromatic molecule but a giant closed cage alkene. Unlike aromatics, fullerenes have no hydrogen atoms or other groups attached and so are unable to undergo substitution reactions. As the cage consists entirely of  $sp^2$  hybridized carbons, which have electron withdrawing  $-I$  inductive effects, the fullerenes are strongly electron attracting. They react readily with nucleophiles. The molecule appears to undergo all the reactions associated with poorly conjugated and electron deficient alkenes.

### 1.1.1 REACTIONS OF [60] FULLERENE

The two most important reactions of [60] fullerene explored<sup>3, 4</sup> so far are cycloadditions and nucleophilic additions. Reduction experiments performed chemically<sup>5,6</sup> and electrochemically<sup>7,8,9</sup> clearly show that  $C_{60}$  is a fairly electronegative system. Calculations as well as structure data demonstrate bond alternation with long bonds at the junction of five membered and six membered rings, called 5-6 bonds, and shorter bonds with double bond character at the junctions of two six membered rings, called 6-6 bonds (Figure 2).

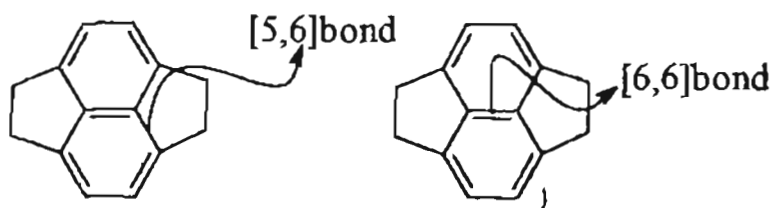


Figure 2

These geometric and electronic properties imply that  $C_{60}$  behaves like an electron poor conjugated polyolefin, consisting of fused [5] radialene and cyclohexatriene units, rather than a superaromatic molecule. Characteristic reactions of an electron poor olefin are nucleophilic addition and cycloaddition reactions.  $C_{60}$  undergoes both types of reactions. A brief account of these reactions is given below.

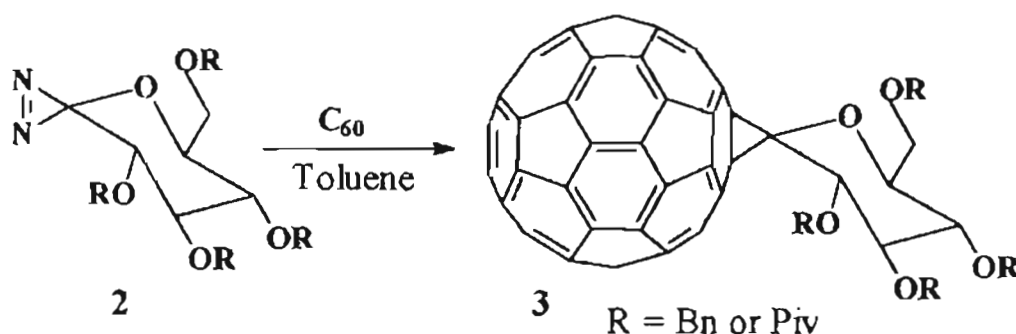
### 1.1.2 CYCLOADDITION REACTIONS OF [60] FULLERENE

Of all fullerene reactions, cycloadditions have received by far the most attention. This is mainly due to the ability to control the reaction so that only one addend becomes attached to the cage, making analysis of the products relatively easy. Six types of cycloadditions are known: [1+2], [2+2], [3+2], [4+2], [6+2] and [8+2] cycloaddition reactions.



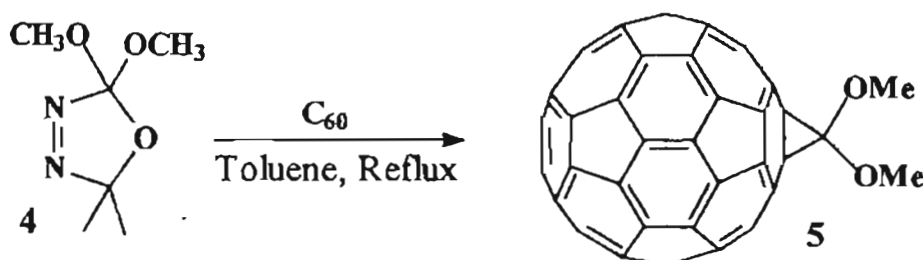
### [1+2] Cycloaddition reactions

Thermal extrusion of nitrogen from *o*-benzyl and *o*-pivaloyl protected diazirines **2** produces carbenes, which react with [60] fullerene in toluene. These [1+2] carbene additions cleanly lead to 1,2-methano bridged sugar monoadducts **3** (Scheme 1).<sup>10</sup>



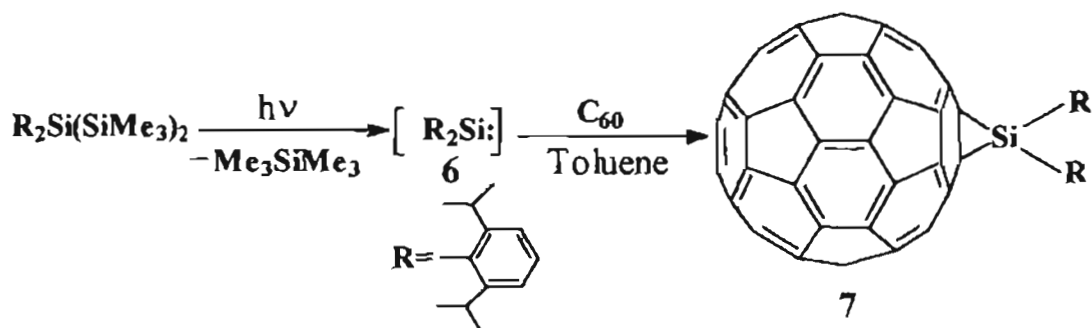
Scheme 1

The dimethoxy methano fullerene **5** has been synthesized *via* the corresponding carbene, which was prepared *in situ* by thermolysis of the oxadiazoline **4** (Scheme 2).<sup>11</sup>



Scheme 2

The addition of bis (2,6-diisopropylphenyl)silylene **6** as a reactive divalent species to C<sub>60</sub> yields the [2+1] cycloadduct as the ring closed 1,2 bridged adduct **7** (Scheme 3).<sup>12</sup>

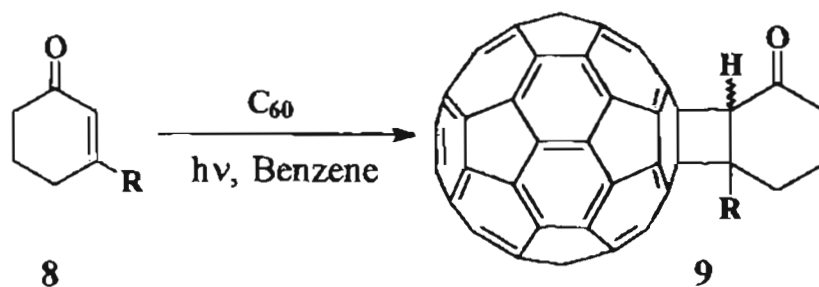


Scheme 3

### [2+2] Cycloaddition reactions

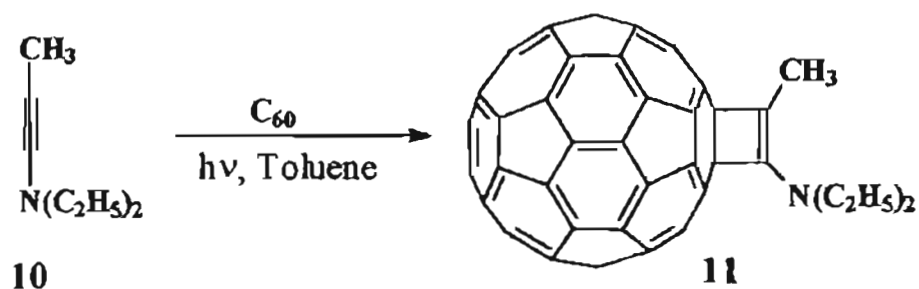
Photochemical [2+2] cycloaddition reactions take place with fullerene giving products with four membered rings fused to the fullerene cage. Further reactions may occur due to the strain in these rings. For orbital symmetry to be conserved, suprafacial addition should occur if the reactions are fully synchronous. When this is not the case biradical intermediates are implicated.

The photochemical [2+2] cycloaddition of enones **8** to  $\text{C}_{60}$  is possible by irradiation of benzene solution of the components with a high pressure mercury lamp. Analysis of the reaction products showed that the isolated monoadducts are a mixture of two isomers, which are *cis* and *trans* fused stereoisomers **9** arising from the [2+2] cycloaddition to a 6-6 bond of  $\text{C}_{60}$  (Scheme 4).<sup>13</sup>



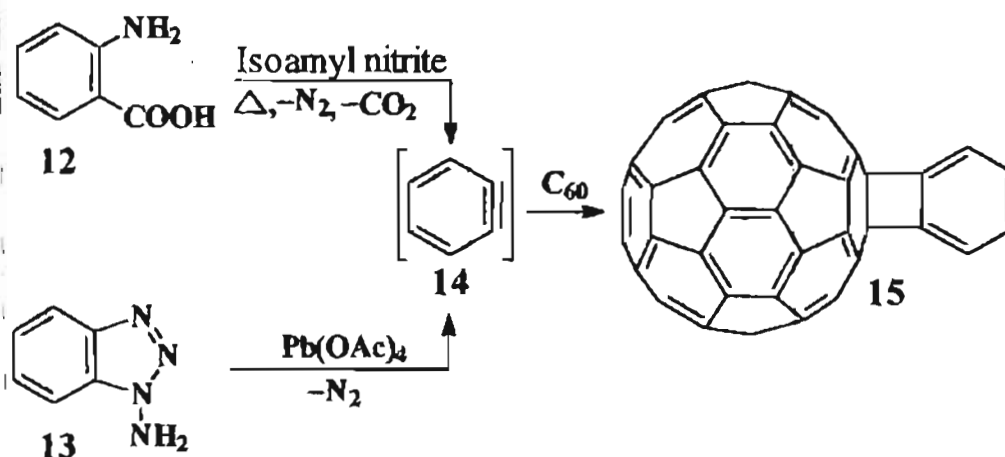
Scheme 4

The ease of photoreaction of [60] fullerene with electron rich organic molecules has been used to cycloadd N,N-diethyl propynyl amine 10 to C<sub>60</sub>. Upon irradiation of the components in oxygen free toluene solution for 20 minutes at room temperature, the [2+2] adduct 11 was obtained (Scheme 5).<sup>14</sup>



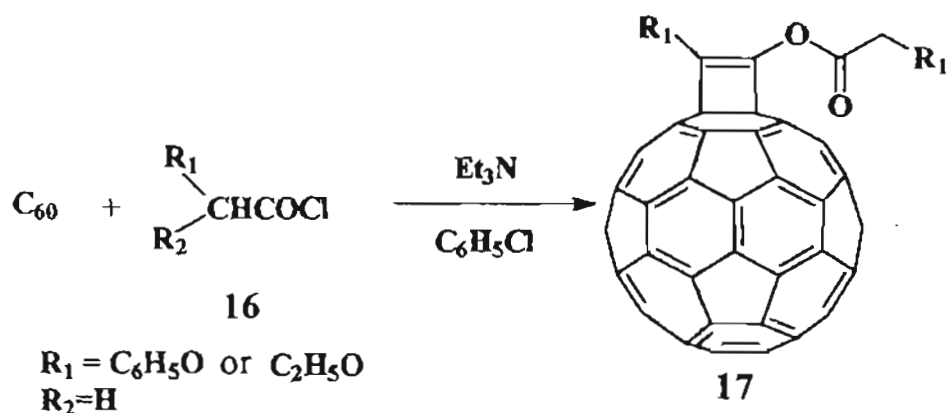
Scheme 5

Cycloaddition reaction of benzyne 14, generated by two routes, to C<sub>60</sub> leads to [2+2] cycloadduct 15 (Scheme 6).<sup>15,16</sup>



Scheme 6

Saigo *et al.* have reported that aryloxy and alkoxyketenes generated from acid chlorides 16 undergo facile [2+2] cycloaddition with C<sub>60</sub> (Scheme 7).<sup>17</sup>



Scheme 7

### [3+2] Cycloaddition reactions of [60] fullerene

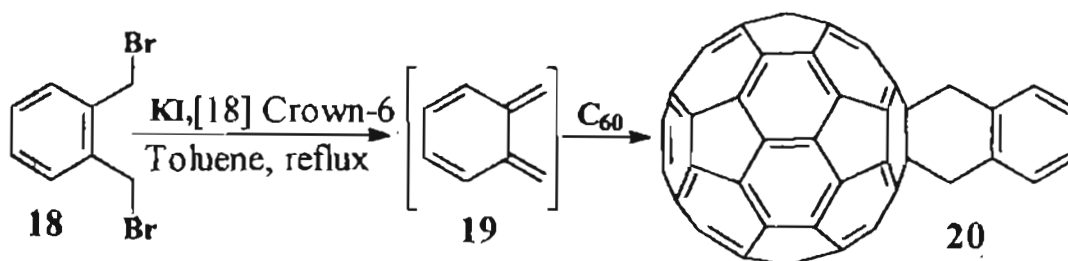
A large number of [3+2] cycloaddition reactions with C<sub>60</sub> have been reported. These are discussed in chapter 2.

### [4+2] Cycloaddition reactions of [60] fullerene

In [4+2] cycloaddition reactions, it is always the 6-6 double bonds of C<sub>60</sub> that act as dienophile. A large variety of cycloadditions have been carried out with C<sub>60</sub> and the complete characterization of the products, mainly monoadducts, has enhanced the knowledge of fullerene chemistry. The conditions for the cycloadduct formation strongly depend on the reactivity of the diene.

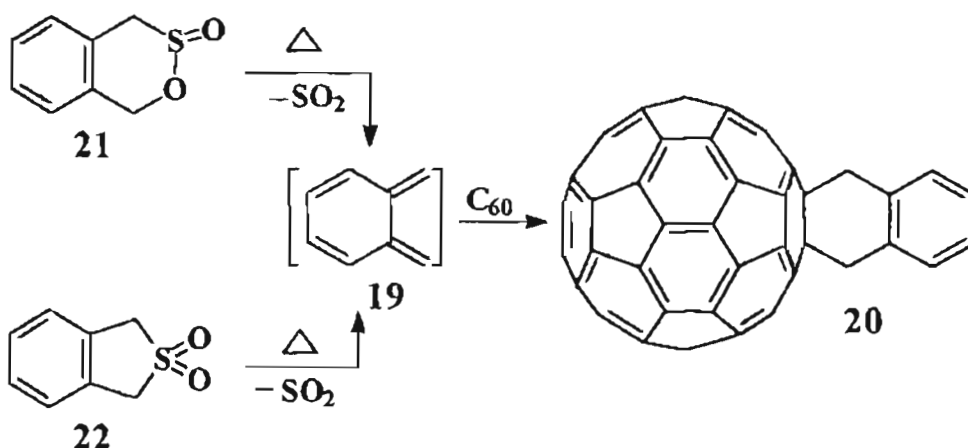
### Reactions of *o*-quinodimethanes with [60] fullerene

In an approach to synthesize stable Diels-Alder adducts of C<sub>60</sub>, Müllen *et al.* used 1,2-bis(bromomethyl)benzene 18 to generate *o*-quinodimethane 19 and added the latter to [60] fullerene (Scheme 8).<sup>18</sup>



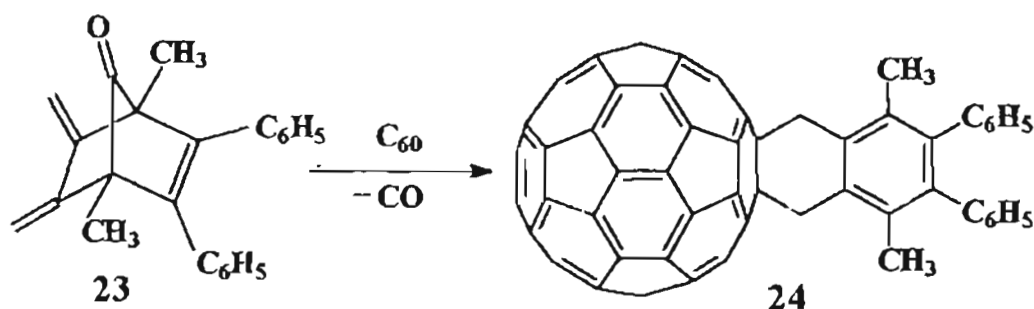
Scheme 8

Sultine 21 and sulphone 22 eliminate SO<sub>2</sub> on heating and the resulting *o*-quinodimethane has been trapped by C<sub>60</sub> (Scheme 9).<sup>19-21</sup>



Scheme 9

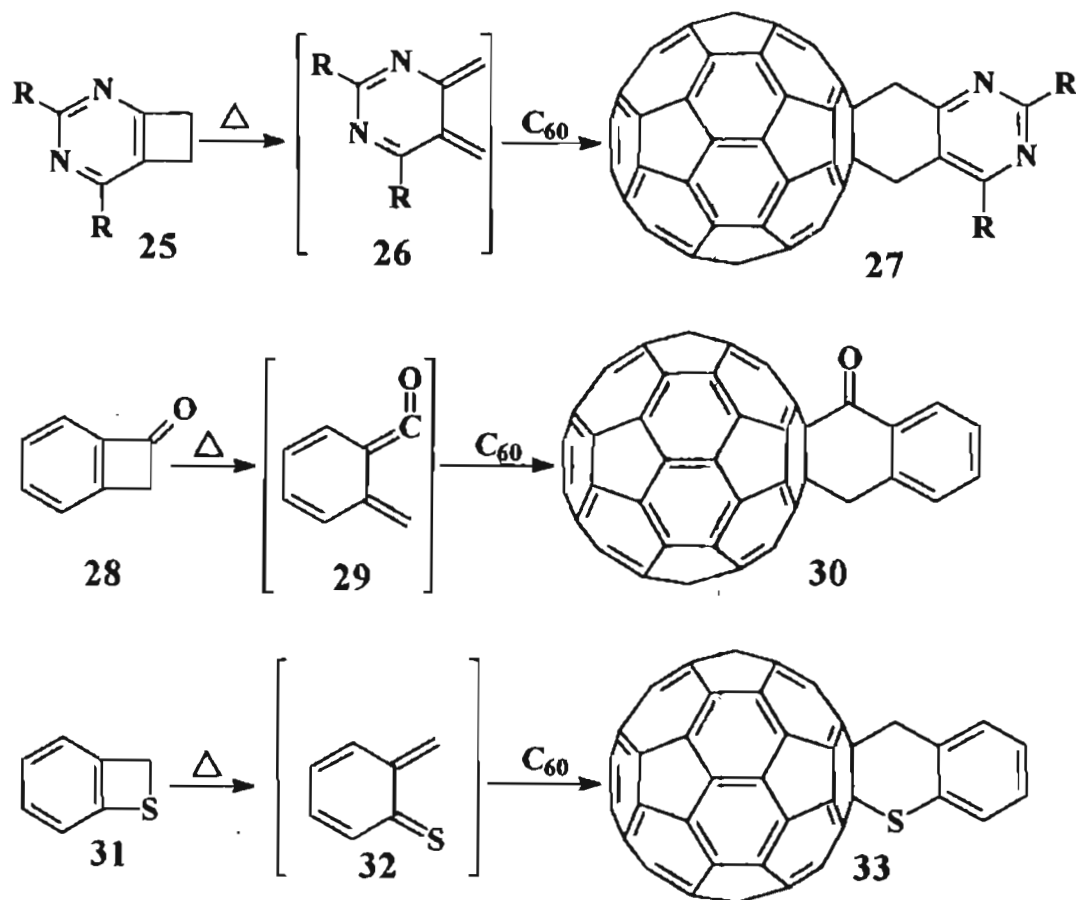
Another variation employed the ketone 23 which loses CO during the reaction to give the product 24 (Scheme 10).<sup>22</sup>



Scheme 10

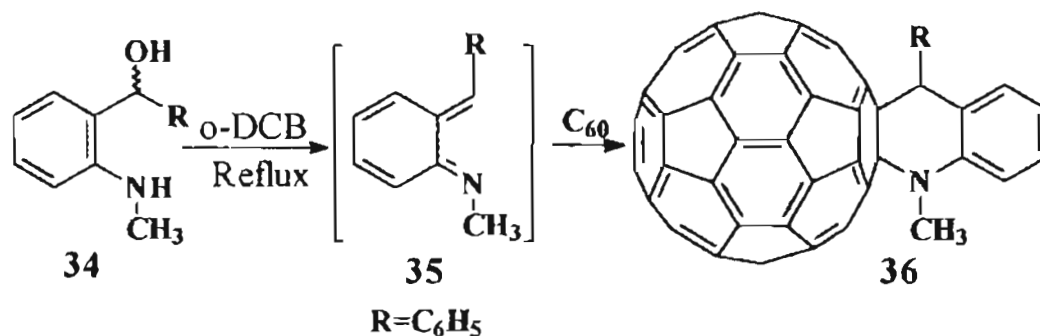
Thermal ring opening of arenocyclobutane produces *o*-quinodimethane and this method has also been applied to C<sub>60</sub>

functionalization<sup>23</sup>. Thus cyclobutane substituted pyrimidine **25**, benzocyclobutanone **28** and benzothiete **31** undergo ring opening at elevated temperatures and the resulting quinonemethides have been trapped by C<sub>60</sub> (Scheme 11).<sup>24-26</sup>



**Scheme 11**

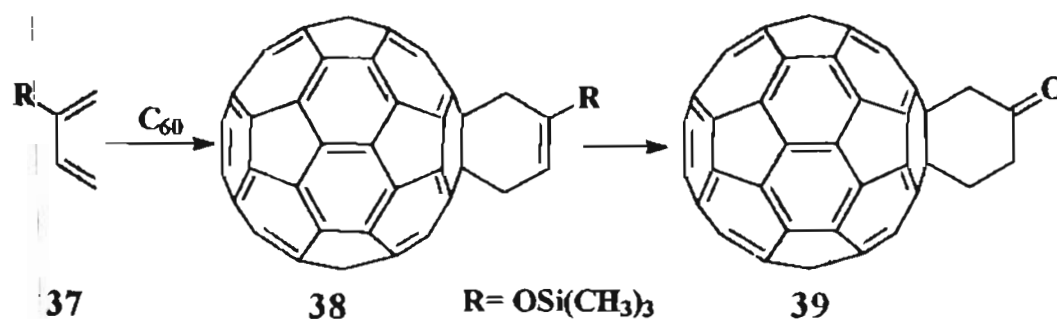
In analogous manner nitrogen bonded [60] fullerene derivatives have been prepared by a hetero Diels-Alder reaction. *o*-Quinonemethide imine **35** generated by thermolysis of *o*-amino benzyl alcohols **34** have been trapped efficiently by C<sub>60</sub>, leading to piperidine fused fullerene derivatives **36** (Scheme 12).<sup>27</sup>



Scheme 12

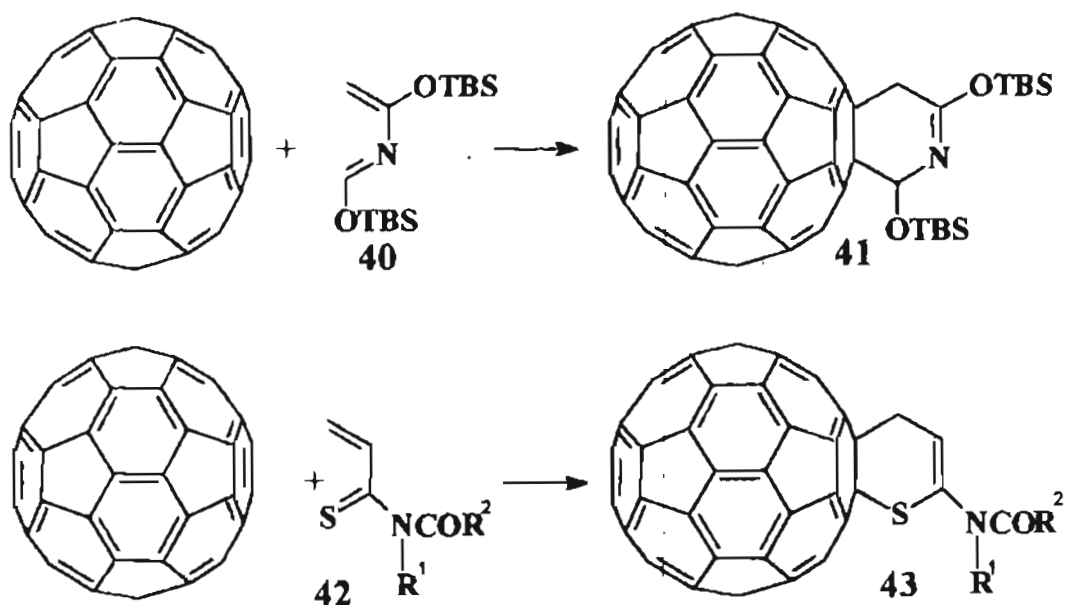
### Addition of buta-1, 3- diene derivatives

It has been reported that  $\text{C}_{60}$  reacts with 2-trimethyl silyloxy 1,3-butadiene **37** in toluene at reflux, leading to a stable Diels-Alder adduct **39**. The ketone is formed by hydrolysis of the intermediate silyl enolether **38** during flash chromatography (Scheme 13).<sup>28</sup>



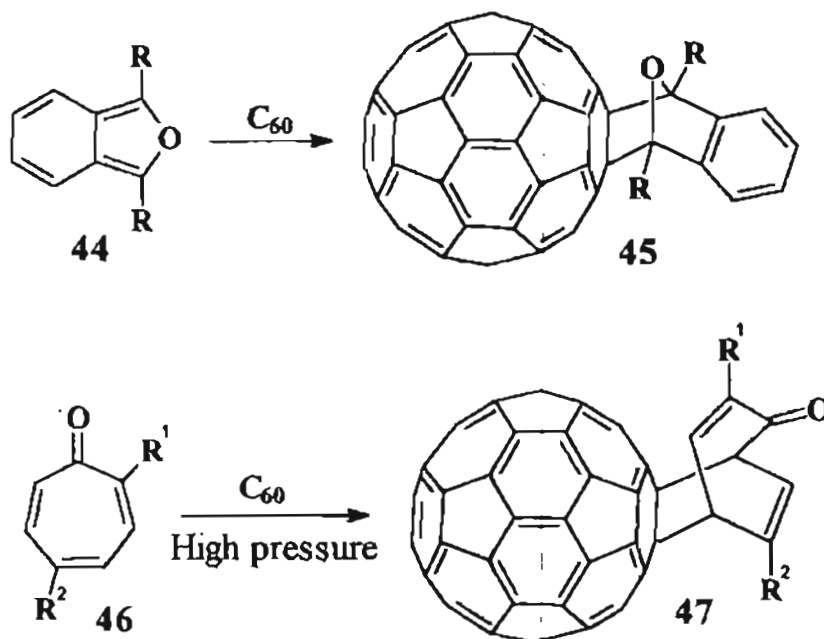
Scheme 13

Similar to the methodology involving quinonemethide imine<sup>27</sup> adopted for the synthesis of fulleroheterocycles, 1,3-butadiene derivatives can also be used. Thus 2-aza-1, 3-diene derivative **40** as well as *N*-acyl thioacrylamide **42** reacts smoothly with [60] fullerene leading to the respective cycloadducts (Scheme 14).<sup>29,30</sup>



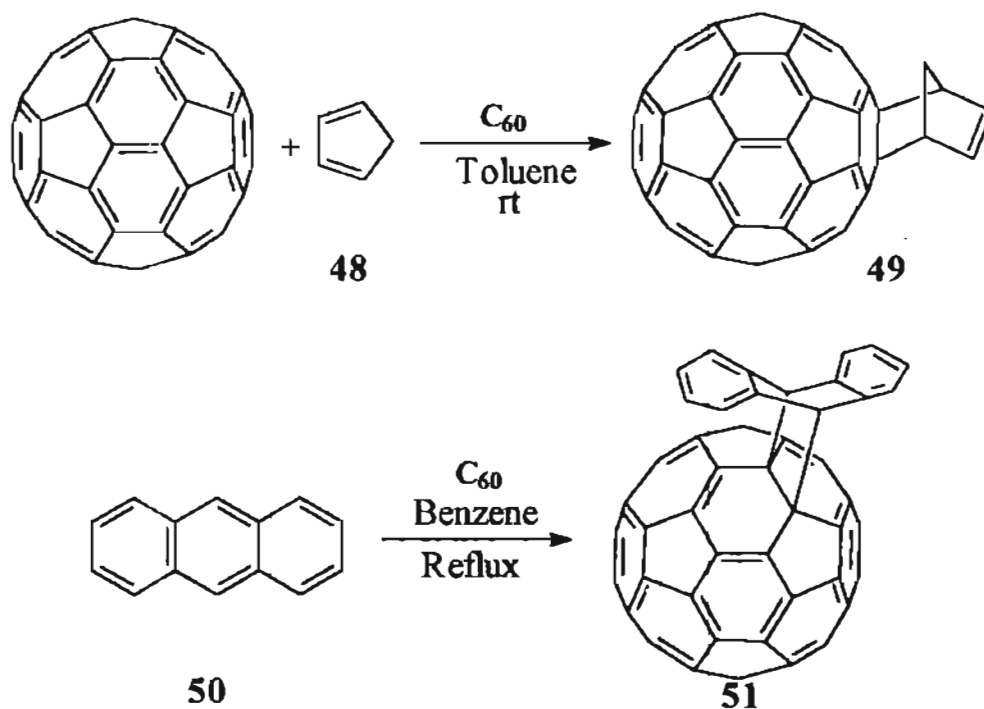
Scheme 14

In addition, a number of  $4\pi$  components like isobenzofuran 44, tropone 46, cyclopentadiene 48 and anthracene 50 have been added to [60] fullerene (Schemes 15a and 15b).<sup>31-34</sup>



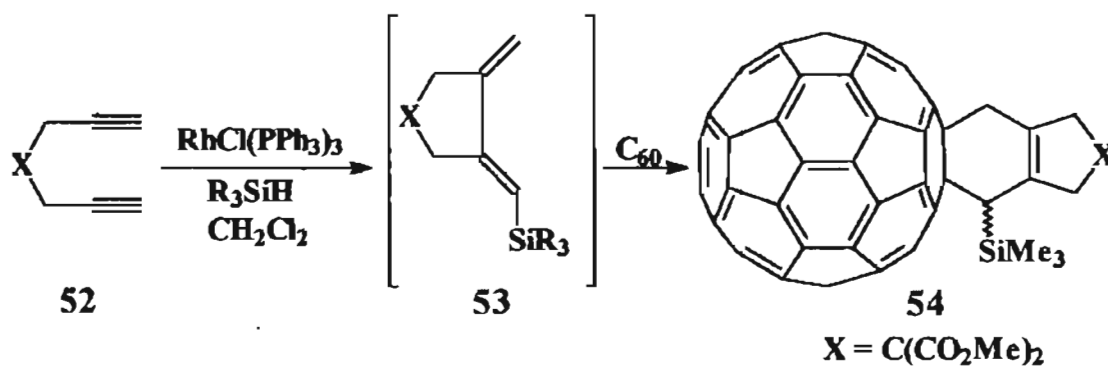
Scheme 15a





Scheme 15b

Very recently, a rhodium catalysed three component coupling of hepta-1,6-diyne **52**, hydrosilane and  $\text{C}_{60}$  has been reported (Scheme 16).<sup>35</sup>

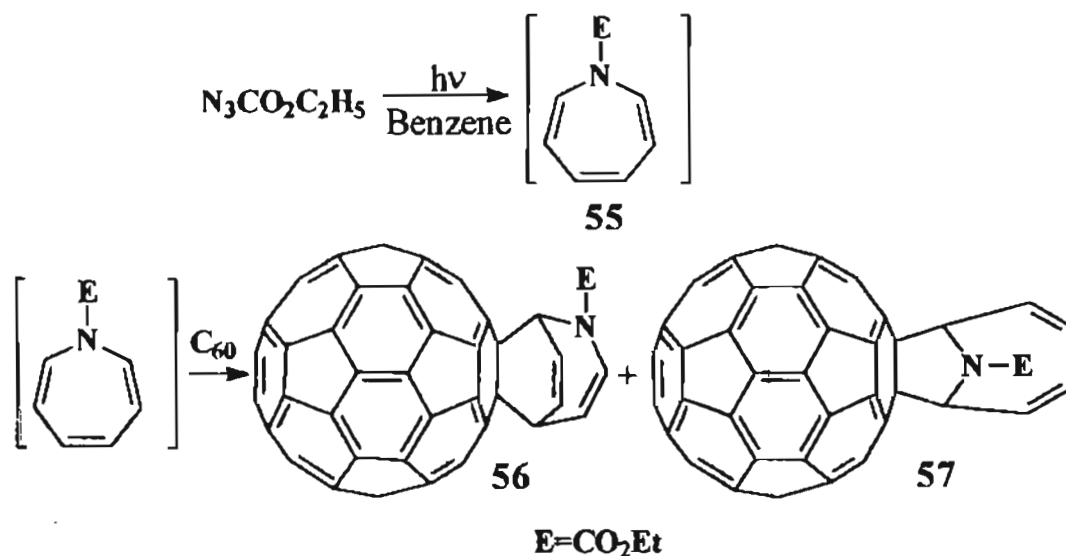


Scheme 16

### [6+2] Cycloaddition reaction of [60] fullerene

Only one reaction of this type is known. The photochemical reaction between  $\text{C}_{60}$  and N-ethoxycarbonyl azepine **55**, generated

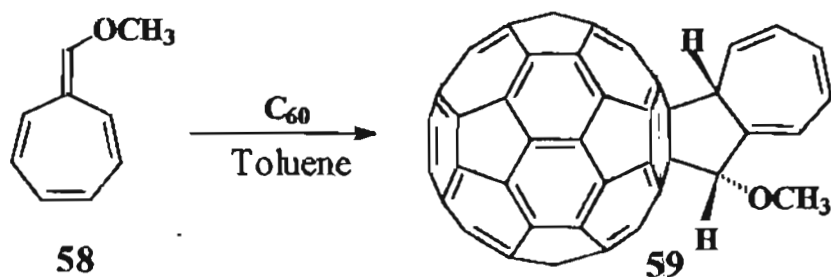
*in situ* by light induced decomposition of ethylazidoformate in benzene, produces two photo adducts **56** and **57** in the ratio 4:1, by [2+4] and [2+6] cycloaddition reactions (Scheme 17).<sup>36</sup>



Scheme 17

### [8+2] Cycloaddition reaction of [60] fullerene

Treatment of 8-methoxy heptafulvene **58** with C<sub>60</sub> at room temperature produced a tetrahydroazulenofullerene **59** (Scheme 18).<sup>37</sup>

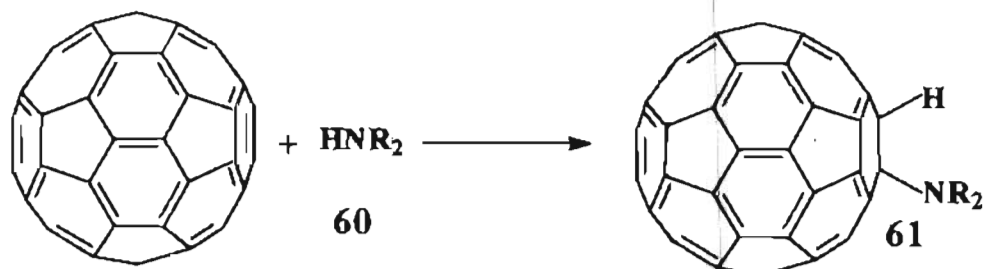


Scheme 18

### 1.1.3 NUCLEOPHILIC ADDITION REACTIONS OF [60] FULLERENE

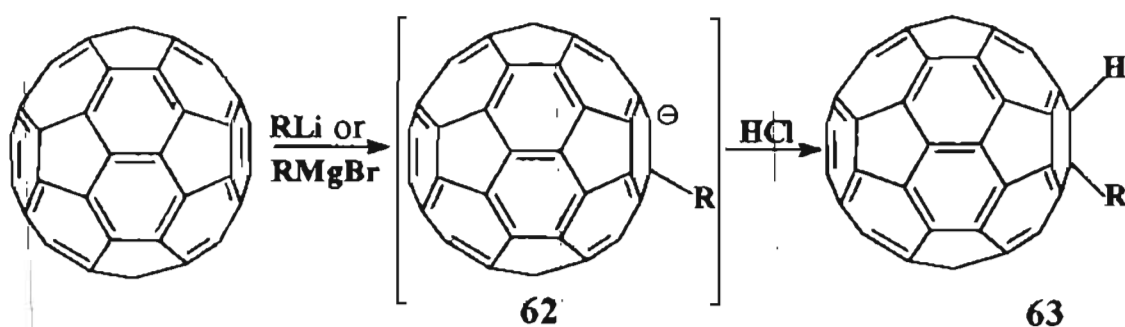
The strong electrophilic character of [60] fullerene makes it very reactive towards nucleophiles. Nucleophilic addition has been carried out with both neutral and charged species. For example, methylamine,

ethylamine, propylamine and morpholine have been added to  $C_{60}$  leading to 1,2 addition products (Scheme 19).<sup>38</sup>



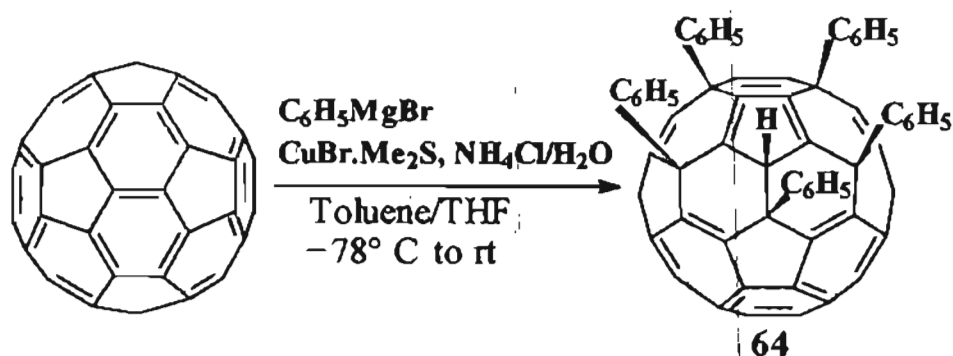
Scheme 19

$C_{60}$  has been reported to undergo alkylation with organolithium and magnesium compounds (Scheme 20).<sup>39</sup>



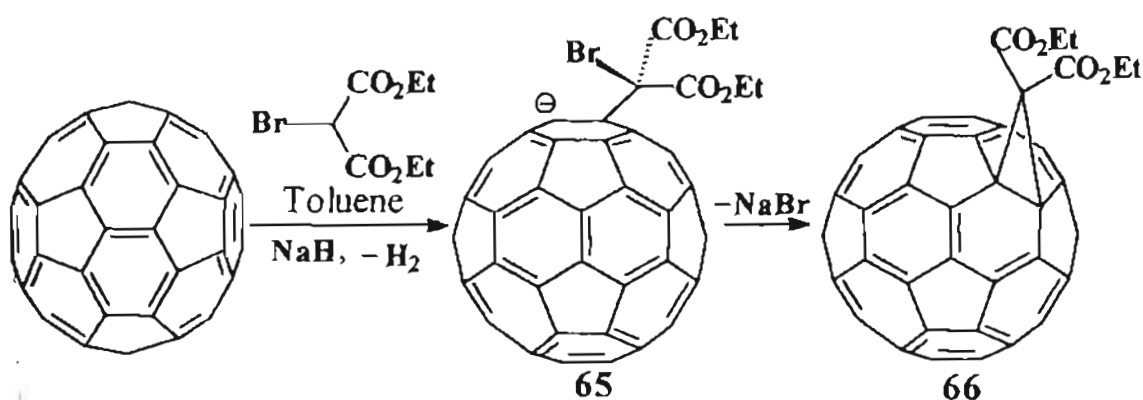
Scheme 20

Nakamura *et al.* have found that organocopper reagents react with  $C_{60}$  in a five fold fashion leading to a penta phenylated fullerene adduct 64 (Scheme 21).<sup>40</sup>



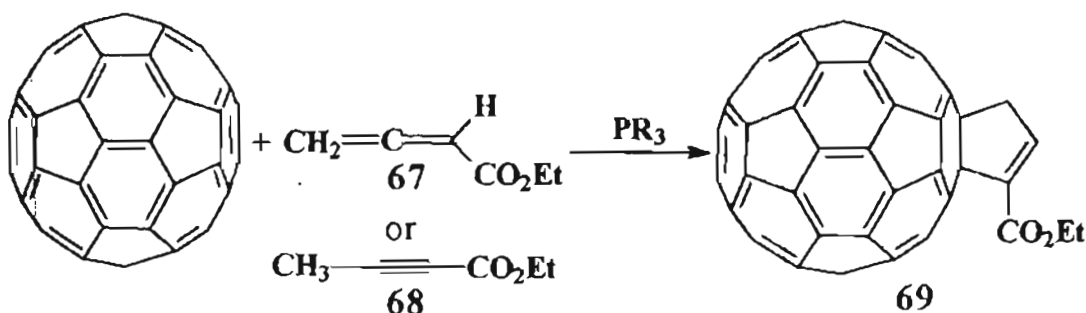
Scheme 21

The stabilization of intermediate  $\text{RC}_{60}^-$  to form dihydrofullerene derivatives can also be achieved by intramolecular nucleophilic substitution ( $\text{S}_{\text{Ni}}$ ) if R contains a leaving group. This reaction is called Bingel reaction and is one of the most widely studied reactions in fullerene chemistry (Scheme 22).<sup>41</sup>



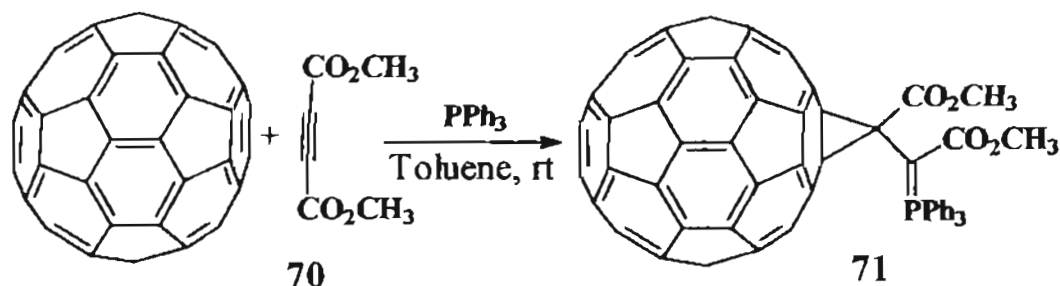
Scheme 22

Shu and O'Donovan have independently reported that phosphine catalysed reaction of buta-2, 3-dienoates **67** and but-2-ynoates **68** leads to cyclopentene annulated fullerene **69** (Scheme 23).<sup>42,43</sup>



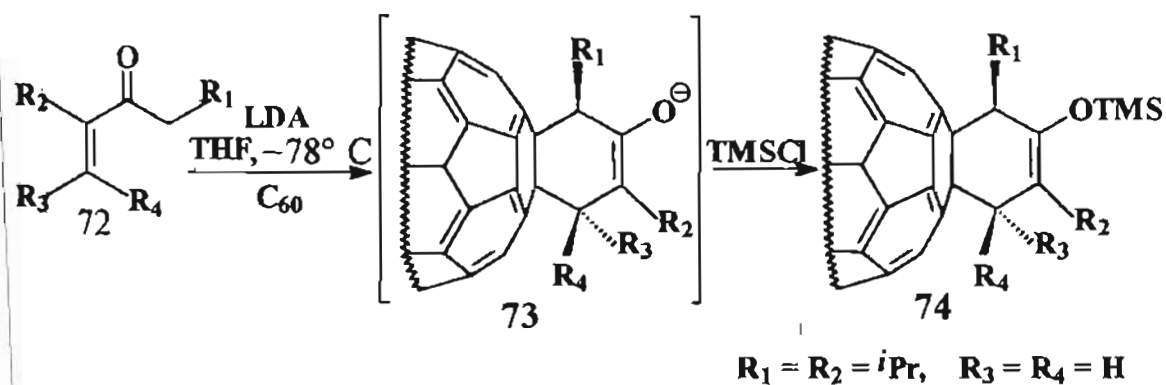
Scheme 23

A unique method to introduce phosphorous substituents on [60] fullerene was discovered by Chuang *et al.* Treatment of  $\text{C}_{60}$  with triphenylphosphine and DMAD **70** in toluene at ambient temperature gave fullerene derivative **71** consisting of a phosphorous ylide and a cyclopropane ring on the fullerene moiety in good yield (Scheme 24).<sup>44</sup>



Scheme 24

Rubin *et al.* have demonstrated that sequential double Michael addition of dienolates derived from  $\alpha, \beta$ -unsaturated compounds 72 with  $C_{60}$  leads to sterically congested [60] fullerene derivatives 74 with defined stereochemistry (Scheme 25).<sup>45</sup>



Scheme 25

Other related reactions more relevant to the work presented in this thesis are discussed in chapter 2.

## PART 2

### CYCLOADDITION REACTIONS OF *o*-QUINONES

#### 1.2 GENERAL

Compounds with quinonoid skeleton are endowed with rich and fascinating chemistry. They are used as versatile intermediates in organic synthesis and in dye industry. Quinonoid compounds play important roles in electron transport, in respiratory and photosynthetic elements of biological systems as well as a number of redox processes in nature. A large number of natural products with quinonoid skeleton have been isolated and many are found to be biologically active.<sup>46</sup> A few are listed below (Figure 3).

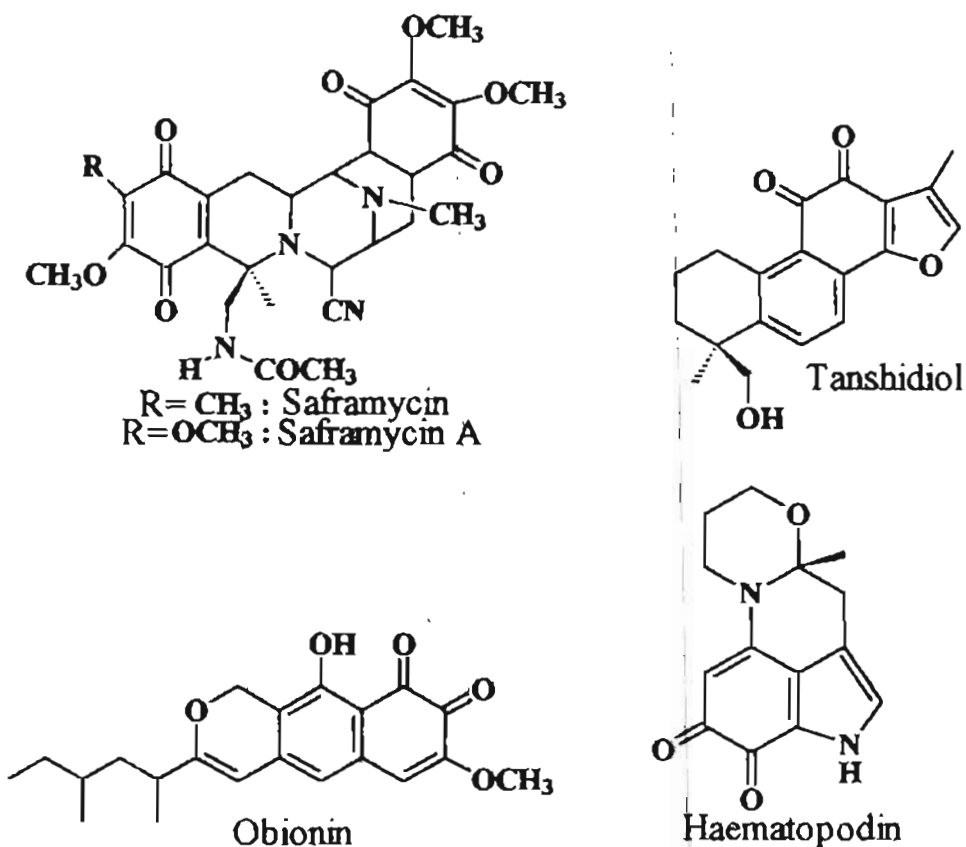


Figure 3

## 1.2.1 SYNTHESIS AND REACTIONS OF *o*-BENZOQUINONES

### Synthesis of *o*-quinones

*o*-Quinones can be prepared from catechols by oxidation with cerium (IV) sulphate in dilute acids<sup>47</sup>, Fremy's salt<sup>48</sup>, benzene seleninic anhydride<sup>49</sup>, iodosobenzene or iodoxy benzene.<sup>50</sup> The most commonly used method for the preparation of 1,2-benzoquinone involves oxidation of corresponding catechols with appropriate oxidizing agents such as Ag<sub>2</sub>O, Ag<sub>2</sub>CO<sub>3</sub>, FeCl<sub>3</sub>, NaIO<sub>4</sub><sup>51</sup>, MnO<sub>2</sub> or sodium hypochlorite in the presence of a phase transfer catalyst.<sup>52</sup>

### [4π+2π] Cycloaddition reactions of 1, 2-benzoquinones

*o*-Quinones can exhibit multiple reactivity profiles especially in cycloaddition reaction as they can participate as carbodiene, heterodiene, dienophile or heterodienophile (Figure 4).

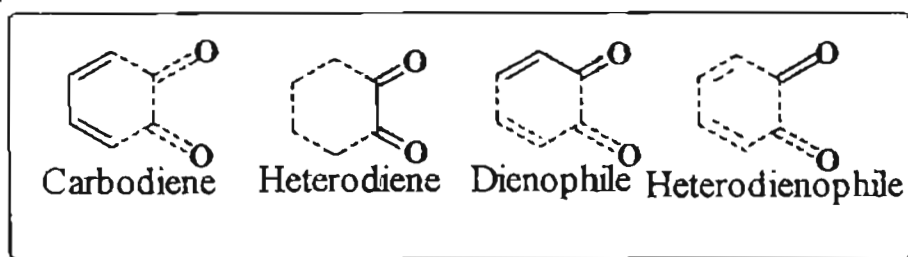
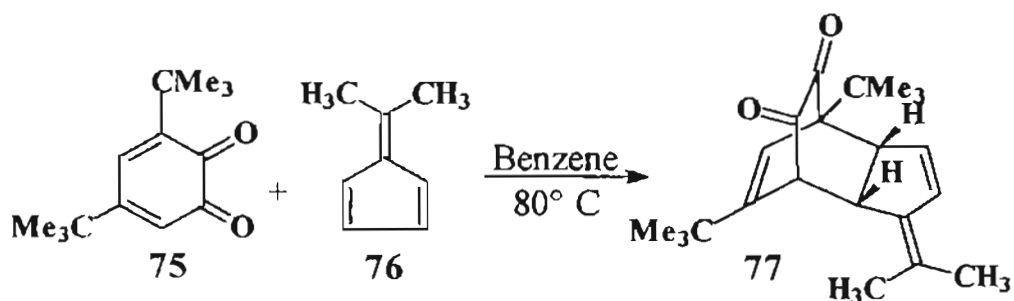


Figure 4

The different types of reactivity shown by 1,2-benzoquinones in [4π+2π] cycloaddition reactions are briefly outlined here.

### 1,2-Benzoquinone as carbodiene

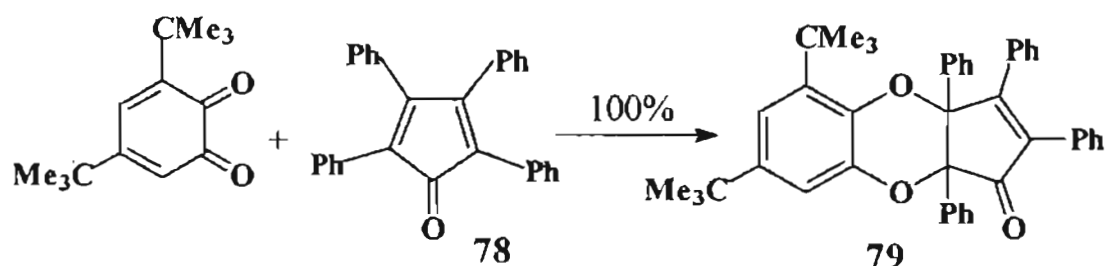
3,5-di-*tert*-butyl-1,2-benzoquinone **75** undergoes facile cycloaddition with pentafulvene **76** to afford bicyclo [2.2.2] octanedione **77** in 80% yield (Scheme 26).<sup>53</sup>



Scheme 26

### 1,2-Benzoquinone as heterodiene

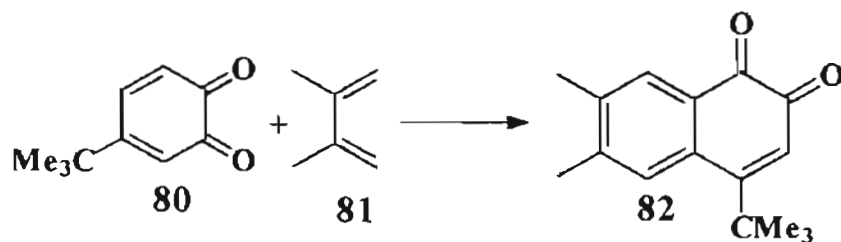
1,2-Benzoquinone has a highly activated heterodiene moiety and participates in facile Diels-Alder reaction with tetracyclone 78 leading to the formation of benzodioxin derivative 79 (Scheme 27).<sup>54</sup>



Scheme 27

### 1,2-Benzoquinone as dienophile

1,2-Benzoquinone 80 functions as an electron deficient dienophile in its reaction with 2,3-dimethyl butadiene 81 (Scheme 28).<sup>55</sup>

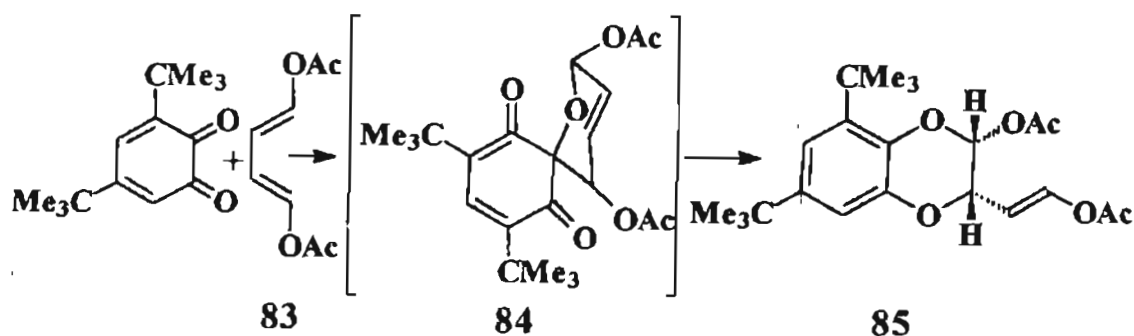


Scheme 28



### 1,2-Benzoquinone as heterodienophile

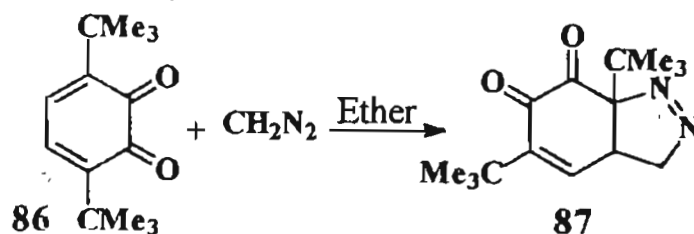
1,2-Benzoquinone can serve as a heterodienophile in cycloaddition reactions due to the presence of two activated carbonyl groups. Reaction of 3,5-di-*tert*-butyl-1,2-benzoquinone with 1,4-diacetoxy-1,3-butadiene **83** afforded benzodioxin derivative **85** (Scheme 29).<sup>56</sup>



Scheme 29

### Dipolar cycloaddition reactions of 1,2-benzoquinones

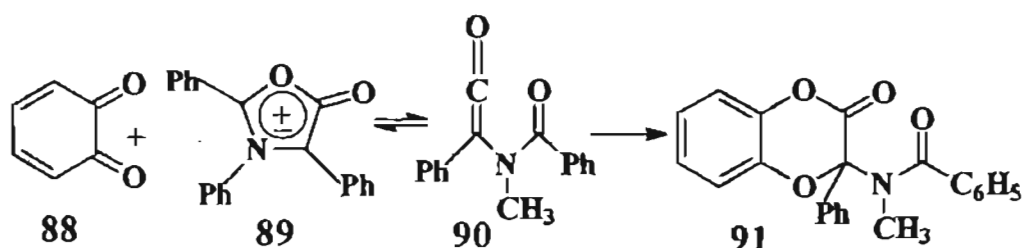
Dipolar cycloaddition reactions provide a powerful method for the synthesis of many nitrogen and oxygen heterocycles. *o*-Quinones exhibit dual reactivity in dipolar cycloaddition reactions as they react either as  $\text{C}=\text{C}$  or  $\text{C}=\text{O}$  dipolarophiles. The reaction of diazomethane with 3,6-di-*tert*-butyl-*o*-benzoquinone **86** afforded indazole **87** (Scheme 30).<sup>57</sup>



Scheme 30

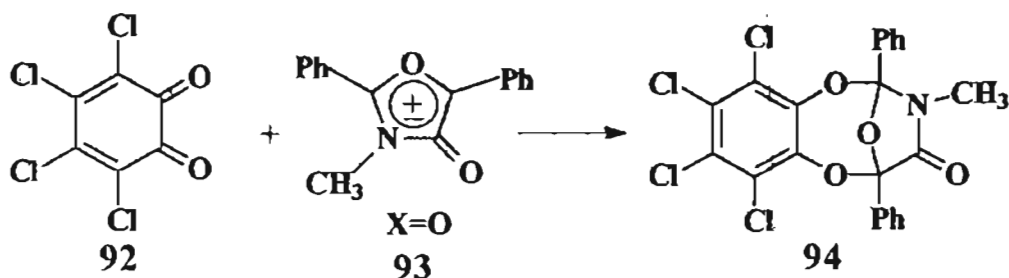
Mesoionic compounds have been extensively utilized as substrates in 1,3-dipolar cycloadditions. The anhydro-5-hydroxy-1,3-oxazoium

hydroxide or münchnone **89** reacts with unsubstituted 1,2-benzoquinone **88** affording the lactone **91**. Evidently, open chain ketene form **90** of the münchnone participates in this reaction (Scheme 31).<sup>58</sup>



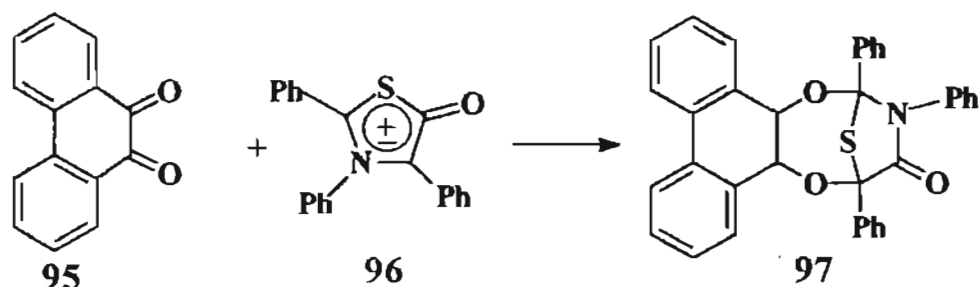
Scheme 31

Interestingly, 3-methyl-5-(4-nitrophenyl)-1,3-oxazolium-4-olate **93** undergoes [4+4] cycloaddition with *o*-chloranil **92** affording the heterocyclic system **94** (Scheme 32).<sup>59</sup>



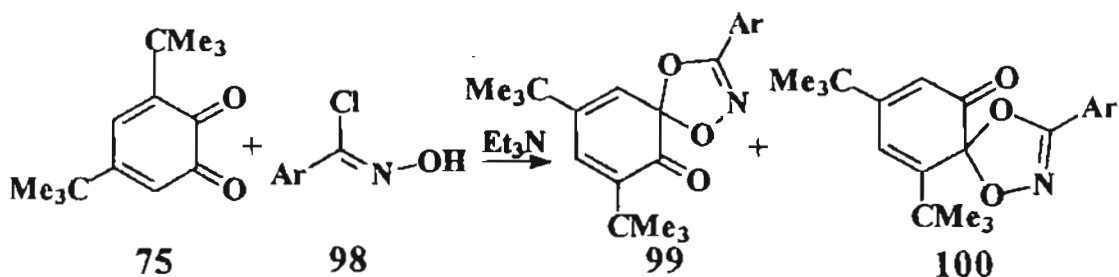
Scheme 32

Similarly thioisomünchnone **96** has been known to react with phenanthrenequinone **95** leading to **97** (Scheme 33).<sup>60</sup>



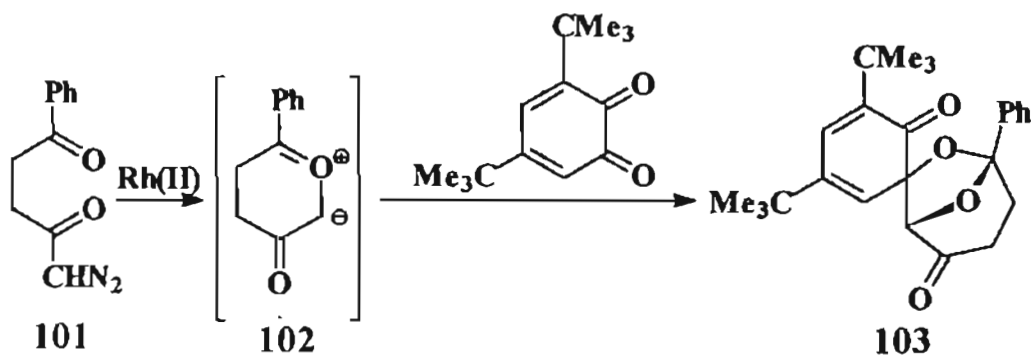
Scheme 33

A recent investigation from our laboratory has shown that aryl nitrile oxides undergo facile cycloaddition reaction with 1,2-benzoquinones. For example, reaction of 1,2-benzoquinone **75** with aryl nitrile oxide afforded a regioisomeric mixture of monospirodioxazoles **99** and **100** (Scheme 34).<sup>61</sup>



Scheme 34

Very recently it was shown that carbonyl ylide **102** undergoes facile [3+2] cycloaddition with 1,2-benzoquinones (Scheme 35).<sup>62</sup>



Scheme 35

### 1.3 1,3-DIPOLAR CYCLOADDITION REACTIONS: THEORETICAL CONSIDERATIONS

A 1,3-dipole is a three atom  $\pi$ -electron system with four  $\pi$ -electrons delocalised over three atoms. It is not possible to write structures for dipolar species without representing them as charged

species. However, this does not mean that the species are polar in nature since the charges are delocalized. 1,3-Dipolar species contain a heteroatom as the central atom which can be  $sp$  or  $sp^2$  hybridized. Dipoles containing  $sp$  hybridized heteroatom has a double bond orthogonal to the delocalized  $\pi$ -system; whereas dipoles with  $sp^2$  hybridized heteroatom does not have such a double bond. These are pictorially shown in figure 5.

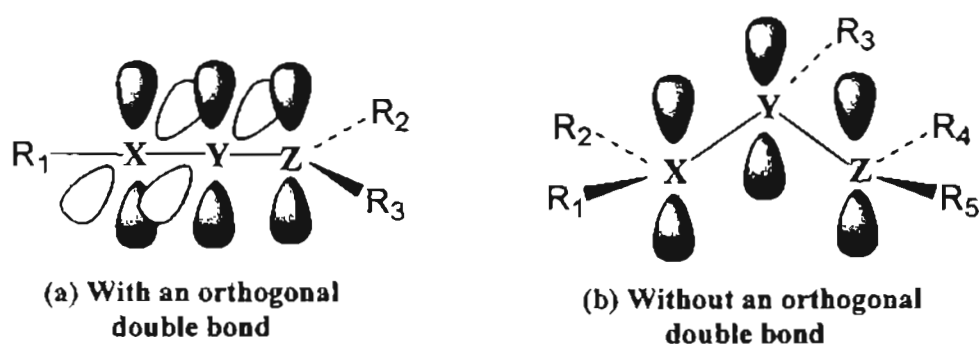


Figure 5

Nitrile ylide **104** (Figure 6) represents a typical example of the type (a), where the central atom is  $sp$  hybridized. These species are easily bent to permit cycloaddition reactions at the termini.<sup>69</sup> Carbonyl ylides **105** are of the type (b) where the central atom is  $sp^2$  hybridized (Figure 6).

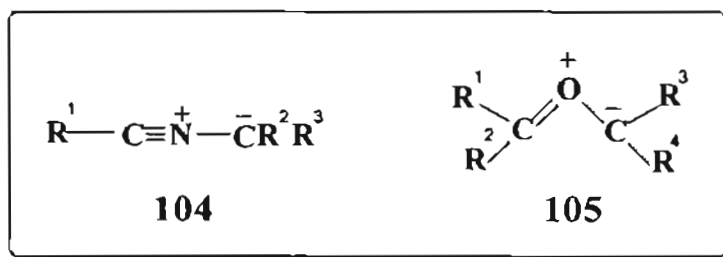


Figure 6

Compounds which can react with 1,3-dipoles are called dipolarophiles. Common dipolarophiles contain groups such as C=C, C=N, C=O, C=S, C≡C and C≡N.

### 1.3.1 REACTIVITY OF 1,3-DIPOLES

1,3-Dipolar cycloadditions are single step, four centered, concerted reactions in which two new  $\sigma$  bonds are formed simultaneously. These reactions are susceptible to electronic and steric influences, which affect the nature of the transition state. 1,3-Dipolar cycloaddition reactions proceed through a transition state, in which there is an interaction between the  $4\pi$ -component of the dipole and the  $2\pi$ -component of the dipolarophile. This is a thermally allowed process on the basis of Woodward-Hoffmann rules.<sup>64</sup> Frontier orbital theory proposes that reaction through such a transition state is favored if there is an interaction between a filled  $\pi$ -orbital (HOMO) of one reactant and empty  $\pi^*$ -orbital (LUMO) of the other. The orbitals must be of the correct symmetry for a favorable interaction and it must be sterically feasible also. The interaction will be strong if the energy gap between the orbitals is small. Therefore the course of the 1,3-dipolar cycloaddition reaction is determined by the HOMO-LUMO interactions of the reactants. The HOMO-LUMO interactions of the dipole and the dipolarophile can be represented as shown in Figure 7.

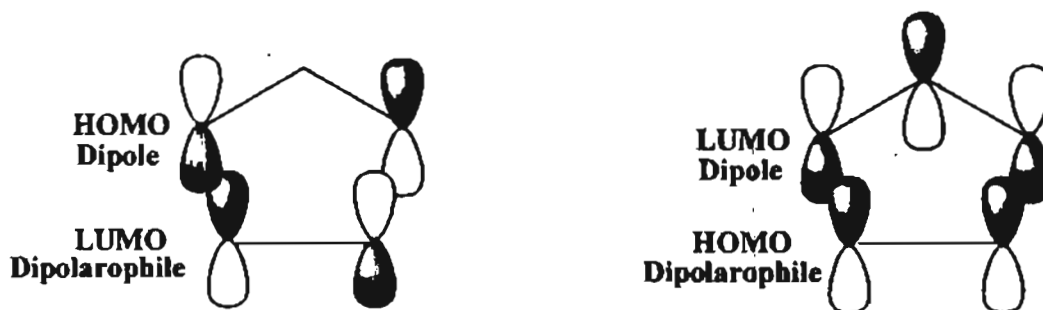
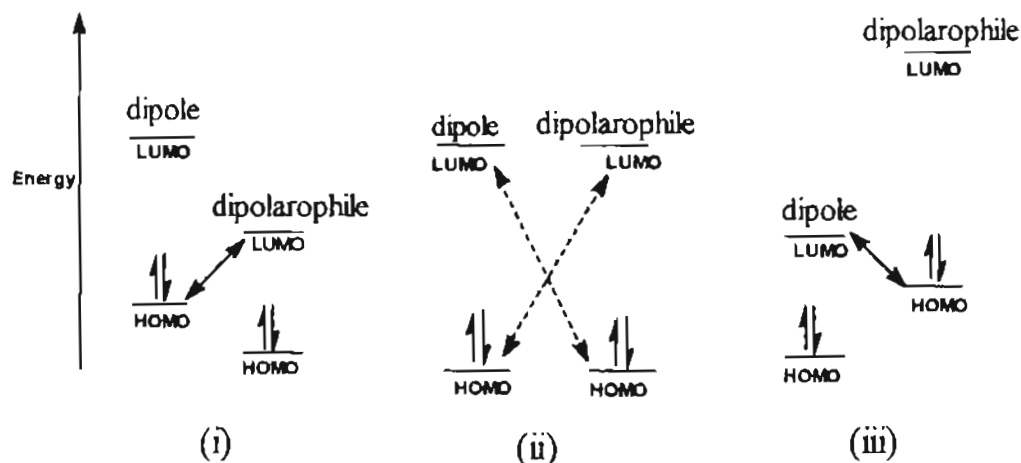


Figure 7

According to Sustmann's classification 1,3-dipolar cycloaddition reactions are of three types (Figure 8).



**Figure 8**

- (i) HOMO-controlled, in which the interaction of the dipole HOMO with dipolarophile LUMO is greatest.
- (ii) Both HOMO and LUMO controlled, which involves large interaction between both frontier orbitals.
- (iii) LUMO-controlled, in which the interaction of the dipole LUMO with the dipolarophile HOMO is greatest.

The substituents that raise the dipole HOMO energy or lower the dipolarophile LUMO energy will accelerate the HOMO controlled reactions. Substituents that lower the dipole LUMO energy or raise the dipolarophile HOMO energy will accelerate the LUMO controlled reactions. HOMO, LUMO controlled reactions will be accelerated by an increase of either frontier orbital interaction. It has been estimated that dipolarophiles with conjugative electron-withdrawing groups have lower energy LUMO values and hence the predominant interaction in a 1,3-dipolar cycloaddition reaction will be of the type (i). Conversely electron

rich dipolarophiles like enol ethers and enamines have high energy LUMO values and the predominant interaction will be of the type (iii).

#### 1.4 STATEMENT OF THE PROBLEM

It is clear from the literature survey that although a variety of dipoles and nucleophiles have been added to  $C_{60}$ , there are a number of reactions that remain unexplored. In order to find new methodologies for the functionalization of [60] fullerene, we have undertaken a study of the reaction of  $C_{60}$  with carbonyl ylides and allenamides and the first phase of the investigations was concerned with these reactions.

Very little information is available on the dipolar cycloaddition reactions of 1,2 dicarbonyl compounds such as isatins. Therefore in the second phase of the work, a study of the dipolar cycloaddition reactions of nitrile ylides and carbonyl ylides with isatins was undertaken with a view to synthesize oxindole fused heterocycles.

During the course of the investigations on cycloaddition reactions of *o*-benzoquinones, we encountered a facile synthesis of highly substituted tropolone derivatives. It was obligatory to study this reaction in some detail and the results are presented in the final phase of this thesis.

#### 1.5 REFERENCES

1. Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R.E. *Nature* **1985**, *318*, 162.
2. Taylor, R.; Walton, D. R. M. *Nature* **1993**, *24*, 363.
3. Hirsch, A. *The Chemistry of Fullerenes*; George Thieme Verlag: Stuttgart; 1994, Chapters 3 and 4, pages 56 and 79.

4. Taylor, R. *Lecture notes on fullerene chemistry*; Imperial college press: 1999, Chapters 8 and 9, pages 114 and 137.
5. Fullagar, W. K.; Gentle, I. R.; Heath, G. A.; White, J. W. *J. Chem. Soc., Chem. Commun.* **1993**, 525.
6. Bausch, J. W.; Prakash, G. K. S.; Tse, D. S.; Lorents, D. C.; Bae, Y. K.; Malhotra, R. *J. Am. Chem. Soc.* **1991**, *113*, 3205.
7. Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.
8. Ohsawa, Y.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 781.
9. Fhou, F.; Jehoulet, C.; Bard, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 11004.
10. Vasella, A.; Uhlmann, P.; Waldraff, C. A. A.; Diederich, F.; Thilgen C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1388.
11. Isaacs, L.; Diederich, F. *Helv. Chem. Acta.* **1993**, *76*, 2454.
12. Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 1605.
13. Wilson, S. R.; Kaprinidis, N.; Wu, Y.; Schuster, D. I. *J. Am. Chem. Soc.* **1993**, *115*, 8495.
14. Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 11024.
15. Hoke II, S. H.; Molstad, J.; Dilattato, D.; Jay, M. J.; Carlson, D.; Kahr, B.; Cooks, R. G. *J. Org. Chem.* **1992**, *57*, 5069.
16. Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *Chem. Lett.* **1992**, 2333.
17. Matsui, S.; Kinbara, K.; Saigo, K. *Tetrahedron Lett.* **1999**, *40*, 899 and references cited therein.



18. Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78.
19. Illescas, B. M.; Martin, N.; Seoane, C.; Orti, E.; Viruela, P. M.; Viruela, R.; Hoz, A. D. L. *J. Org. Chem.* **1997**, *62*, 7585.
20. Ohno, M.; Koide, N.; Sato, H.; Eguchi, S. *Tetrahedron* **1997**, *53*, 9075.
21. Tome, A. C.; Enes, R. F.; Cavaleiro, J. A. S.; Elguero, J. *Tetrahedron Lett.* **1997**, *38*, 2557.
22. Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344.
23. Gügel, A.; Kraus, A.; Spickermann, J.; Belik, P.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 559.
24. Gonzalez, B.; Herrera, A.; Illescas, B.; Martin, N.; Martinez, R.; Moreno, F.; Sanchez, L.; Sanches, A. *J. Org. Chem.* **1998**, *63*, 6807.
25. Foote, C. S.; Zhang, X. *J. Org. Chem.* **1994**, *59*, 5235.
26. Ohno, M.; Kojima, S.; Shirakawa, Y.; Eguchi, S. *Tetrahedron Lett.* **1995**, *36*, 6899.
27. Martin, N.; Martinez-Grau, A.; Sanchez, L.; Seoane, C.; Torres, M. *J. Org. Chem.* **1998**, *63*, 8074.
28. Rubin, Y.; Anderson, J. L.; An, Y.Z. *J. Org. Chem.* **1993**, *58*, 4779.
29. Ohno, M.; Kojima, S.; Shirakawa, Y.; Eguchi, S. *Tetrahedron Lett.* **1996**, *37*, 9211.
30. Ohno, M.; Kojima, S.; Eguchi, S. *J. Chem. Soc., Chem. Commun.* **1995**, 565.
31. Bidell, W.; Douthwaite, R. E.; Green, M. L. H.; Stephens, A. H. H.; Turner, J. F. C. *J. Chem. Soc., Chem. Commun.* **1994**, 1641.

32. Takeshita, H.; Liu, J. F.; Kato, N.; Mori, A.; Isobe, R. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1433.
33. Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1296.
34. Schlueter, J. A.; Seaman, J. M.; Taha, S.; Cohen, H.; Lykke, K. R.; Wang, H. H.; Williams, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 972.
35. Muraoka, T.; Asaji, H.; Yamamoto, Y.; Matsuda, I.; Itoh, K. *Chem. Commun.* **2000**, 199.
36. Bants, M. R. *J. Chem. Soc., Chem. Commun.* **1995**, 1171.
37. Beer, E.; Feuerer, M.; Knorr, A.; Mirlach, A.; Daub, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1087.
38. (i) Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1308. (ii) Shedari, S.; Govindaraj, A.; Nagarajan, R.; Pradeep, T.; Rao, C. N. R. *Tetrahedron Lett.* **1992**, *23*, 2069.
39. (i) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766. (ii) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697.
40. Sawamura, M.; Iikura, H.; Nakamura, E. *J. Am. Chem. Soc.* **1996**, *118*, 12850.
41. Bingel, C. *Chem. Ber.* **1993**, *126*, 1957.
42. Shu, L. H.; Sun, W. Q.; Zang, D. W.; Wu, S. H.; Wu, H. M.; Xu, J. F.; Lao, X. F. *Chem. Commun.* **1997**, 79.
43. O'Donovan, B. F.; Hitchcock, P. B.; Meidine, M. F.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Chem. Commun.* **1997**, 81.
44. Chuang, S. C.; Santhosh, K. C.; Lin, C. H.; Wang, S. L.; Cheng, C. H. *J. Org. Chem.* **1994**, *64*, 6664.

45. Ganapathi, P. S.; Friedman, S. H.; Kenyon, G. L.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 2954.
46. (i) Thomson, R. H. *Naturally occurring quinones, Recent Advances*; Chapman and Hall: New York, 1987. (ii) Patai, S.; Rappoport, Z. *The Chemistry of Quinonoid compounds*; John Wiley and Sons: New York, 1998, Vol 2.
47. Ho, T. L.; Hall, T. W.; Wong, C. M. *Synthesis* **1973**, 206.
48. Zimmer, H.; Laukin, D. C.; Horgan, S. W. *Chem. Rev.* **1971**, *71*, 229.
49. Barton, D. H. R.; Brewster, A. G.; Ley, S. V.; Rosenfeld, M. N. *J. Chem. Soc., Chem. Commun.* **1976**, 985.
50. Barton, D. H. R.; Godfrey, C. R. A.; Morzycki, J. E. *Tetrahedron Lett.* **1982**, *23*, 957.
51. Takata, T.; Tajima, R.; Ando, W. *J. Org. Chem.* **1983**, *48*, 4764.
52. Ishii, F.; Kishi, K. *Synthesis* **1980**, 706.
53. Nair, V.; Kumar, S.; Rath, N. P.; Morton, G. O. *Chem. Lett.* **1995**, 383.
54. Nair, V.; Mathew, B.; Radhakrishnan, K. V.; Rath, N. P. *Tetrahedron* **1999**, *55*, 11017.
55. Nair, V.; Kumar, S. *J. Chem. Soc., Perkin Trans. 1* **1996**, 443
56. Nair, V.; Kumar, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1341.
57. Kommissarova, N. L.; Belostotskaya, I. S.; Voleva, V. B.; Dzhurayan, E. V.; Novikova, I. A.; Ershov, V. V. *Izv. Akad. Nauk USSR. Ser. Khim. (Eng. Transl)* **1981**, 2360.
58. Friedrichsen, W.; Schwarz, I. *Tetrahedron Lett.* **1997**, *18*, 3581.
59. Friedrichsen, W.; Schroer, W. D. *Liebigs. Ann. Chem.* **1980**, 1850.

60. Friedrichsen, W.; Willy.; Schroer, W. D. *Naturforsch B. Anorg. Chem. Org. Chem. (German)*. **1981**, *36*, 609.
61. Nair, V.; Radhakrishnan, K. V.; Nair, A. G.; Bhadbhade, M. M. *Tetrahedron Lett.* **1996**, *37*, 5623.
62. Nair, V.; Sheela, K. C.; Radhakrishnan, K. V.; Rath, N. P. *Tetrahedron Lett.* **1998**, *39*, 5627.
63. Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 6397.
64. (i) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. (ii) Gilchrist, T. L.; Storr, R. C. *Organic Reactions and Orbital Symmetry*, Cambridge University Press, Cambridge, 1979.

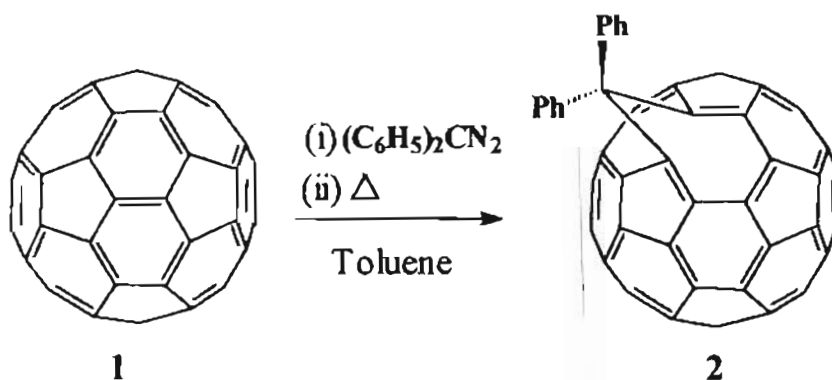
## CHAPTER 2

# REACTIONS OF CARBONYL YLIDES AND ALLENAMIDES WITH [60] FULLERENE

### 2.1 INTRODUCTION

The fullerenes were observed for the first time in 1985<sup>1</sup> and isolated in bulk in 1990.<sup>2</sup> Since then many research groups have been engaged in developing practical applications of this novel material.<sup>3</sup> The interesting properties of fullerenes make them potentially useful in a broad spectrum of science and technology ranging from nonlinear optical materials to superconductors. Also in the biological field, the fullerenes have a strong impact as it was discovered that functionalized fullerenes can be used in photodynamic therapy<sup>4</sup> or as inhibitors of the HIV-1 protease.<sup>5,6</sup> Naturally it was of great importance to make synthetically modified fullerenes for physicochemical as well as biological applications. Conceptually 1,3-dipolar cycloaddition reactions provide a useful method for synthesizing heterocycle fused organofullerenes.

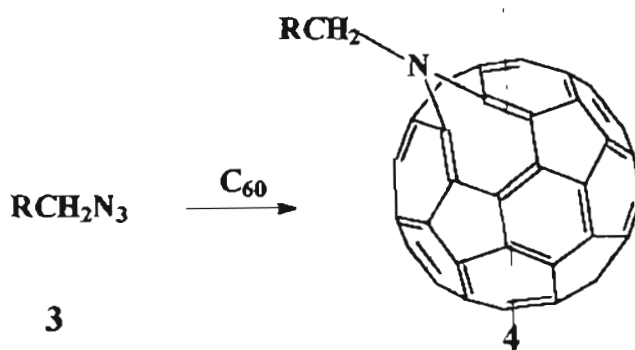
The [6,6] double bonds in C<sub>60</sub> are dipolarophilic in nature, which enables the molecule to undergo a variety of dipolar cycloadditions leading to a range of heterocycle fused fullerenes.<sup>7</sup> The first example of a dipolar cycloaddition reaction to [60] fullerene **1** is its reaction with diphenyldiazomethane to produce a methanofullerene **2** (Scheme 1).<sup>8</sup>



Scheme 1

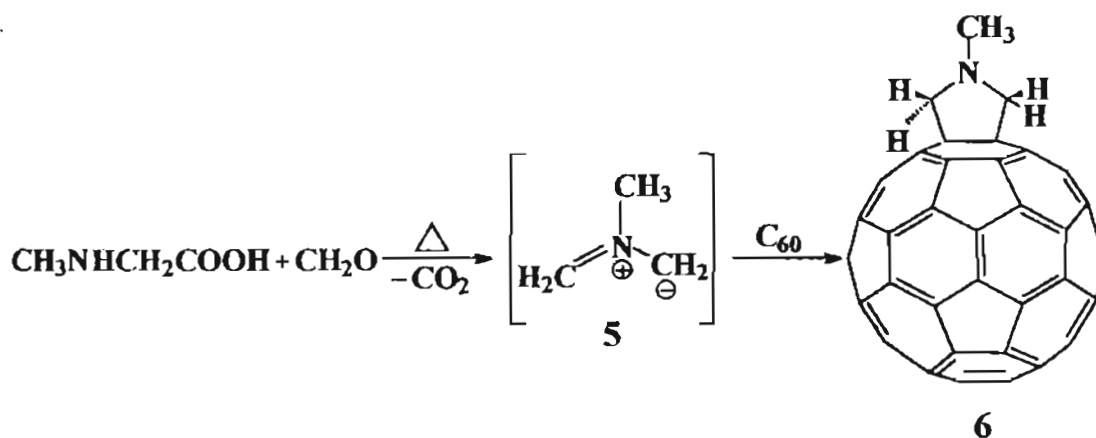
Subsequent to this finding, a number of diazoalkanes,<sup>9-18</sup> diazoamides<sup>19</sup>, and diazoesters,<sup>9, 20</sup> have been found to react with [60] fullerene to produce methanofullerenes.

Organic azides **3** are known to serve as 1,3-dipoles and these have been shown to undergo [2+3] cycloaddition reactions to [60] fullerene, leading to aza-bridged fullerenes **4** (Scheme 2).<sup>21</sup>



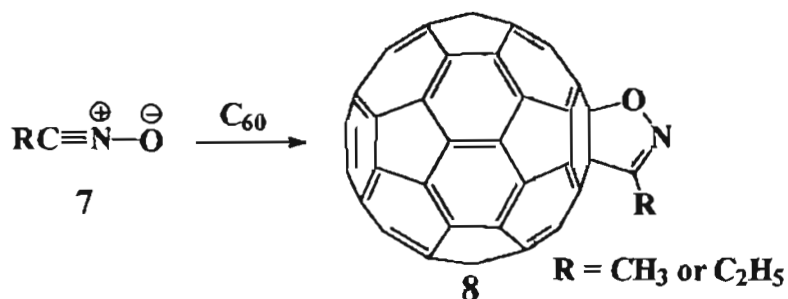
Scheme 2

Azomethine ylides **5**, of general formula  $(\text{R}_1\text{R}_2)\text{C}=\text{N}^+(\text{R}_3)\text{C}^-(\text{R}_4\text{R}_5)$ , represent one of the most reactive and versatile 1,3-dipoles. Of all the 1,3-dipolar reactions of  $\text{C}_{60}$ , azomethine ylide addition accounts for generating the maximum number of compounds called fulleropyrrolidines **6** (Scheme 3).<sup>22,23</sup>



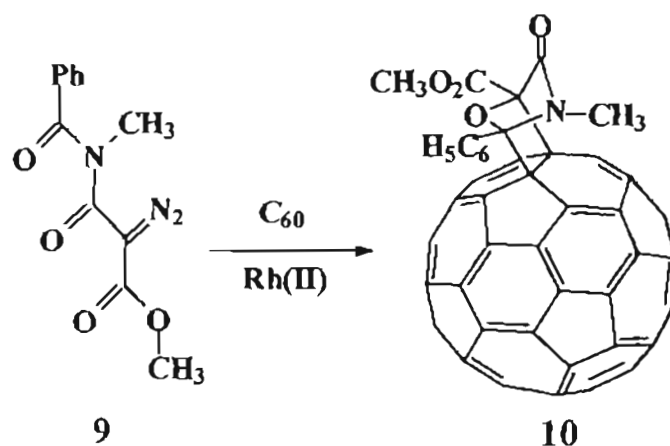
Scheme 3

Meier *et al.* have found that nitrile oxides undergo facile cycloaddition with  $\text{C}_{60}$  to give isoxazoline derivatives **8** (Scheme 4).<sup>24</sup>



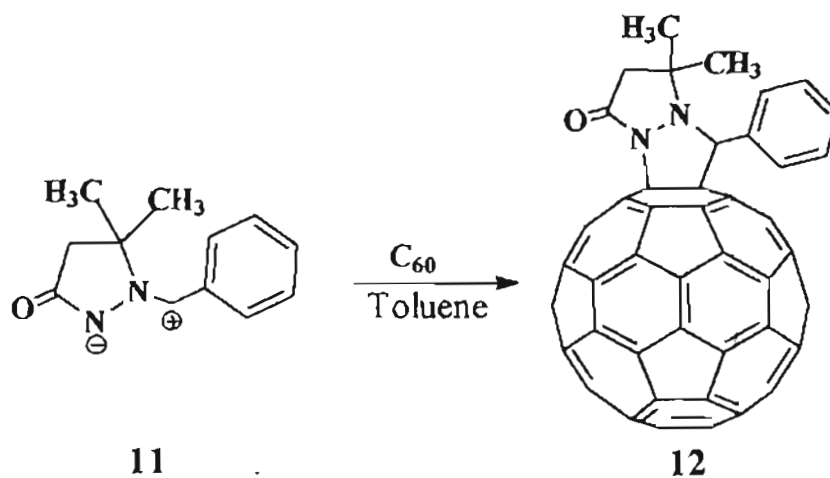
Scheme 4

Cycloaddition of mesoionic compounds with multiple bonds has been utilized for the preparation of numerous functionalised monocyclic and ring annulated heterocycles. Wudl and Padwa have reported that isomünchnone precursors such as **9**, in presence of Rh(II) acetate, readily react with [60] fullerene under very mild conditions affording novel heterocycle fused organofullerenes **10** (Scheme 5).<sup>25</sup>



Scheme 5

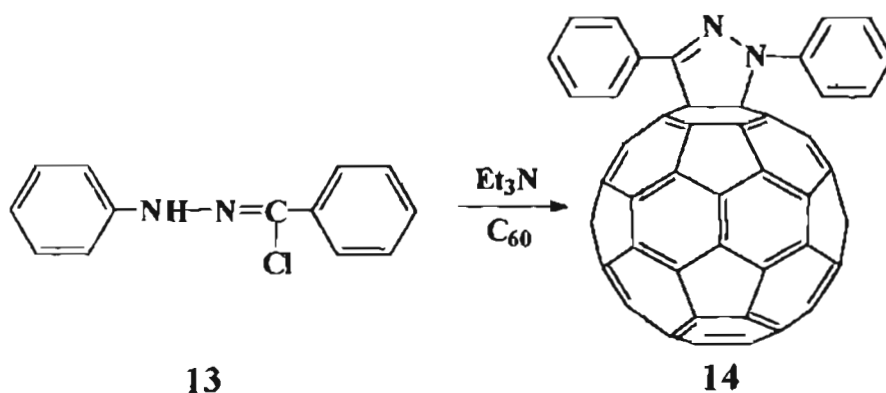
It has been reported that pyrazolinium ylide 11 undergoes 1,3-dipolar cycloaddition with  $C_{60}$  leading to novel heterocycle fullerene derivatives 12 (Scheme 6).<sup>26</sup>



Scheme 6

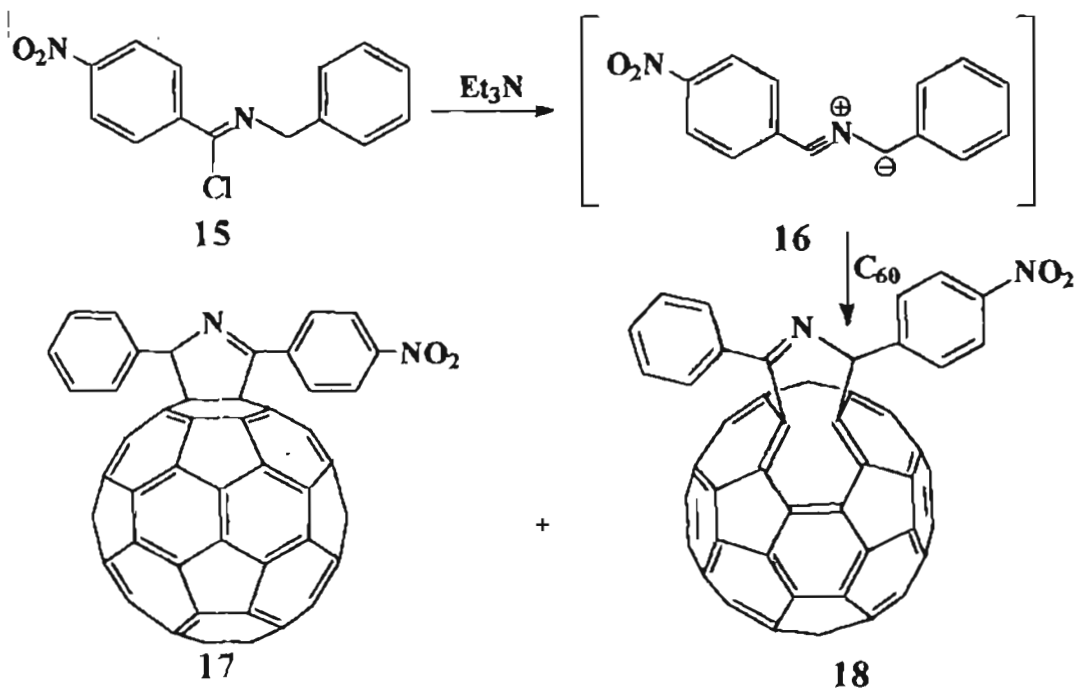
Yoshida *et al.* have found that nitrile imine adds to  $C_{60}$ . Thus 1,3-diphenyl nitrile imine, generated *in situ* from benzhydrazidoyl chloride 13, reacts with  $C_{60}$  leading to pyrazoline fused fullerene 14 (Scheme 7).<sup>27</sup>





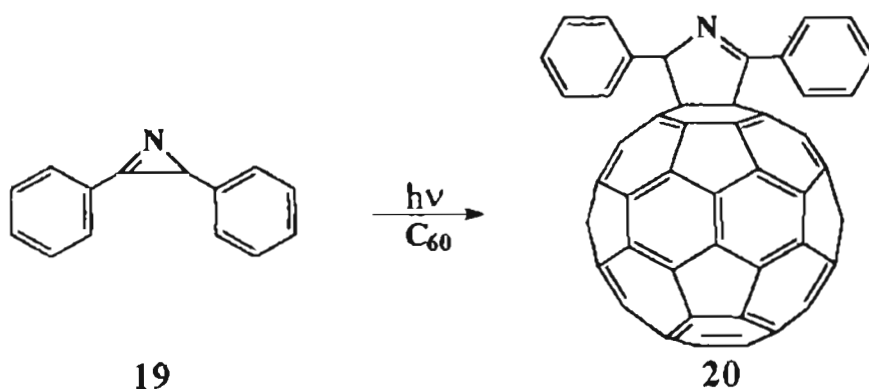
Scheme 7

A closely related dipole, nitrile ylide, has also been shown to react with C<sub>60</sub> leading to novel pyrrolinofullerenes. Nitrile ylide 16 generated from benzimidoyl chloride 15 reacts smoothly with [60] fullerene leading to the pyrrolinofullerene 17 and its ring opened isomer 18 (Scheme 8).<sup>28</sup>



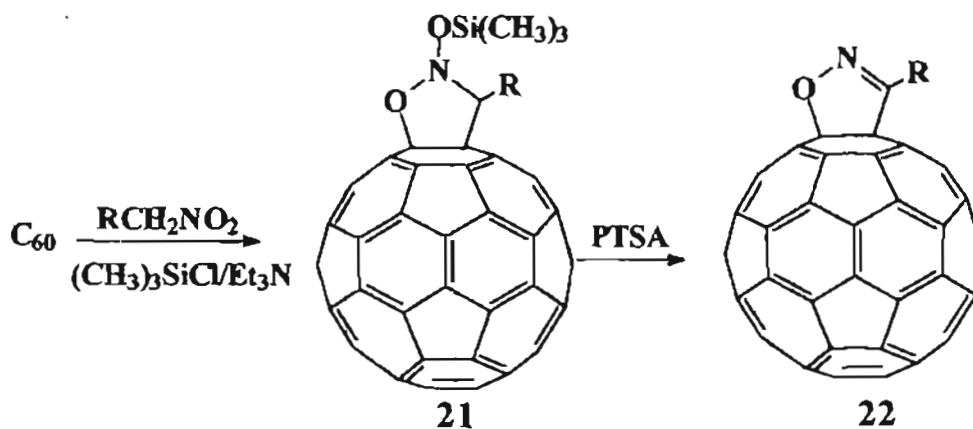
Scheme 8

Similarly, the azirine **19** reacts with [60] fullerene under photochemical conditions to afford pyrrolinofullerene **20** (Scheme 9).<sup>29</sup>



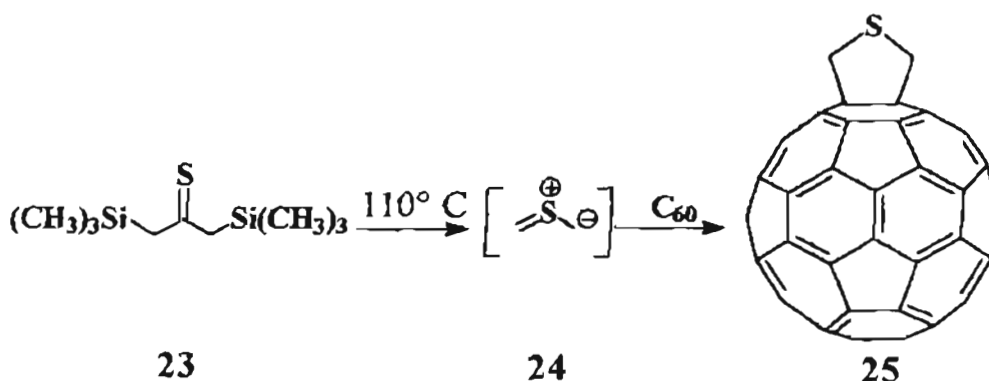
**Scheme 9**

Eguchi *et al.* have found that nitrones undergo facile 1,3-dipolar cycloaddition with C<sub>60</sub> leading to isoxazoline fused fullerenes **22** (Scheme 10).<sup>30</sup>



**Scheme 10**

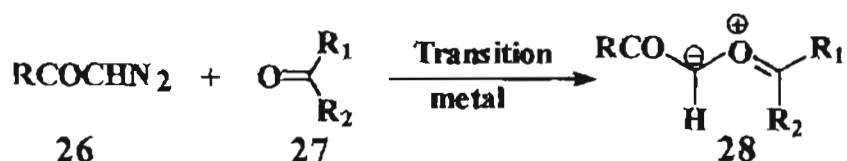
Recently thiocarbonyl ylide **24** has also been utilized for dipolar cycloaddition reaction with [60] fullerene (Scheme 11).<sup>31</sup>



Scheme 11

### 2.1.1 GENERATION AND REACTIONS OF CARBONYL YLIDES

Carbonyl ylides can be generated by a number of methods. Commonly used pathways for carbonyl ylide generation include thermolysis or photolysis of epoxides having electron withdrawing groups,<sup>32,33</sup> extrusion of nitrogen from 1,3,4-oxadiazolines,<sup>34-36</sup> and removal of carbon dioxide from 1,3-dioxolane-4-ones.<sup>37</sup> The transition metal catalyzed decomposition of an  $\alpha$ -diazo ketone **26** in the presence of a carbonyl functionality **27** provides the simplest and the easiest route to these dipoles **28** (Scheme 12).<sup>38-42</sup>

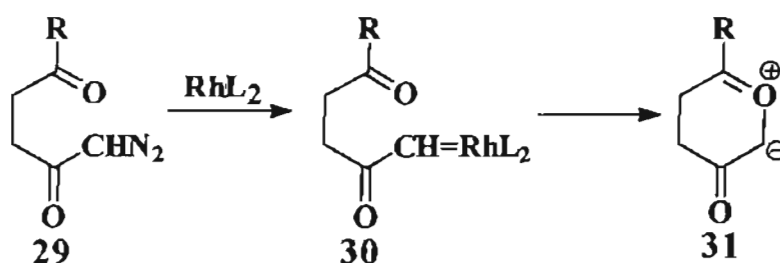


Scheme 12

Among all the catalysts developed for carbene addition to  $\pi$  bonds, rhodium (II) carboxylates are the most effective for bimolecular reactions that employ diazo carbonyl compounds.<sup>43</sup> In general, the reactions can be

carried out under mild conditions, often at 10°C, and the products are obtained in high yields.<sup>44, 45</sup>

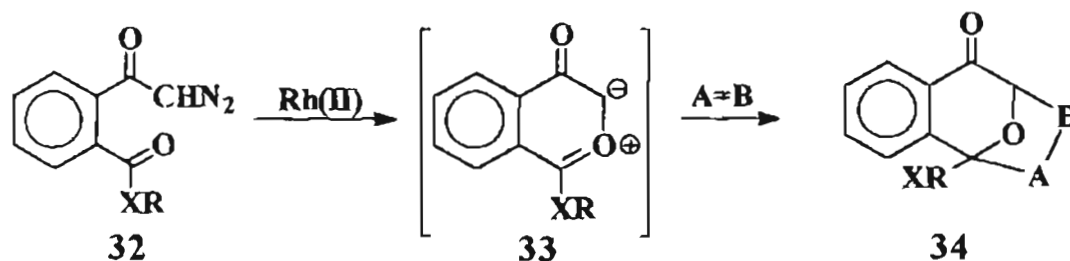
The rhodium (II) catalyzed decomposition of diazo carbonyl compounds is believed to involve a metallo-carbenoid intermediate **30** which retains the highly electrophilic properties associated with free carbenes.<sup>46,47</sup> Therefore, in an appropriate acyclic substrate, such an intermediate can be intercepted intramolecularly by the nonbonding electrons on the neighbouring carbonyl group to effect overall cyclization (Scheme 13).



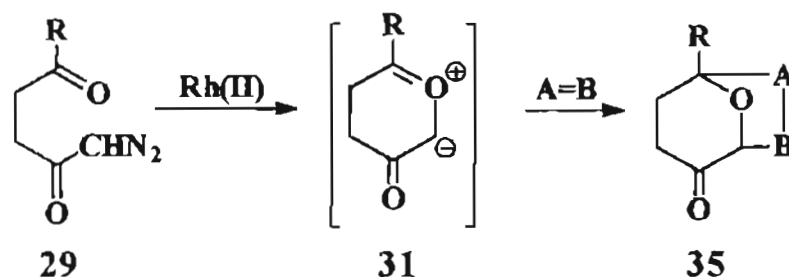
Scheme 13

The two types of diazo ketones, which can undergo tandem cyclization-cycloaddition chemistry,<sup>48</sup> are shown here. First one involves systems in which the diazo ketone and the remote carbonyl are attached in a 1,2-fashion on a benzene ring **32** (Scheme 14).<sup>49</sup> This arrangement provides interatomic distances and bond angles that are ideal for dipole formation and the second system involves the flexible 1-diazo-2,5-pentanedione backbone.<sup>50,51</sup> With this system, the ylide **31** was formed by reaction of the less nucleophilic keto carbonyl on the rhodium carbenoid center. The tether utilized corresponds to a simple dimethylene chain, which introduces a

conformational flexibility not available to the more rigid benzo systems (Scheme 15).



Scheme 14

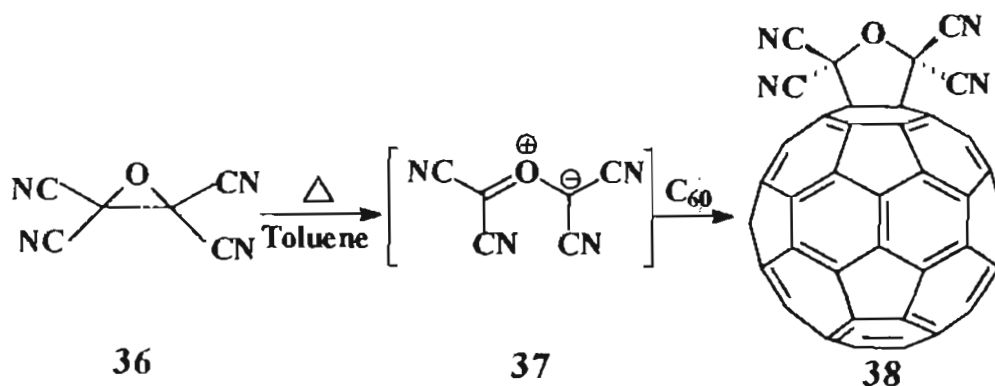


Scheme 15

The carbonyl ylides, generated by the tandem intramolecular carbenoid-carbonyl cyclizations are known to react with both external and internal dipolarophiles including acetylenic and olefinic dipolarophiles, such as dimethyl acetylenedicarboxylate (DMAD) and *N*-phenylmaleimide.<sup>51</sup>

### 2.1.2 REACTION OF CARBONYL YLIDE WITH [60] FULLERENE

There is only an isolated report on the dipolar cycloaddition reaction of carbonyl ylide with [60] fullerene. This involves addition of TCNE oxide 36, *via* the carbonyl ylide 37, to [60] fullerene (Scheme 16).<sup>52</sup>



Scheme 16

### 2.1.3 THE PRESENT WORK

It is noteworthy that although a large variety of reactions of carbonyl ylides with electron deficient dipolarophiles are known, there has been no work on the addition of cyclic carbonyl ylides with [60] fullerene. Against the literature background presented above and in the context of our general interest in the functionalization reactions of C<sub>60</sub>, it was of interest to undertake an investigation of the dipolar cycloaddition reactions of carbonyl ylides with [60] fullerene; such reactions were anticipated to afford novel furanofullerenes. The results of our investigations form the core of this chapter. The  $\alpha$ -diazo ketones selected for our investigations are shown here (Figures 1, 2 and 3).

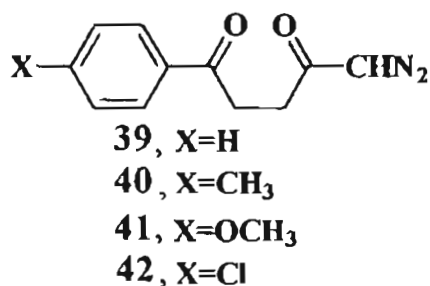


Figure 1

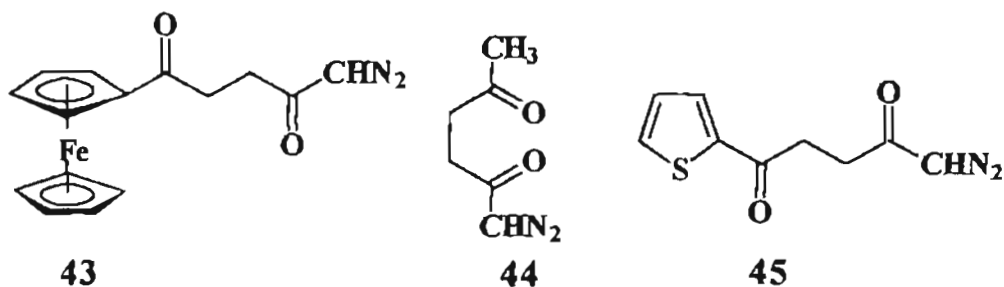


Figure 2

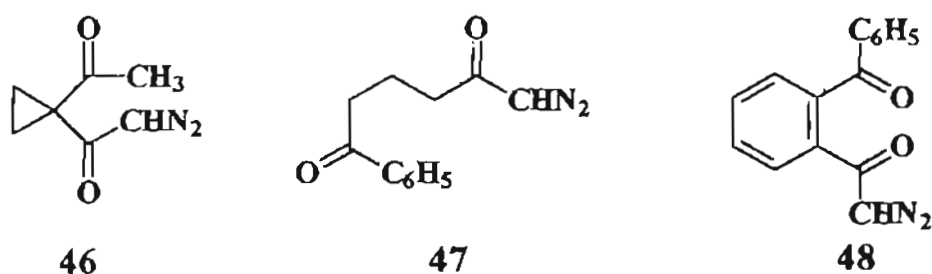
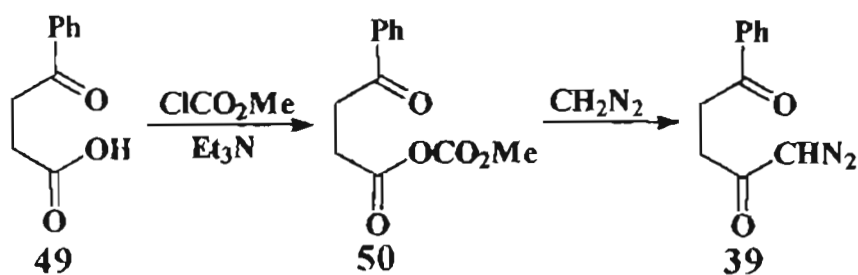


Figure 3

## 2.2 RESULTS AND DISCUSSION

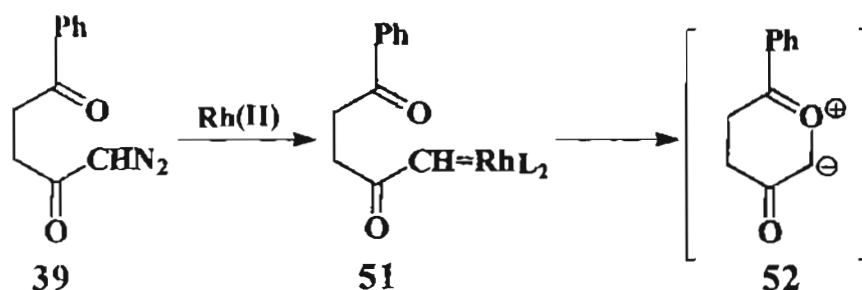
### 2.2.1 CYCLOADDITION REACTIONS OF CARBONYL YLIDES WITH [60] FULLERENE

The diazoketones required for our investigations were conveniently prepared from the corresponding carboxylic acids by a known procedure (Scheme 17).<sup>51</sup>



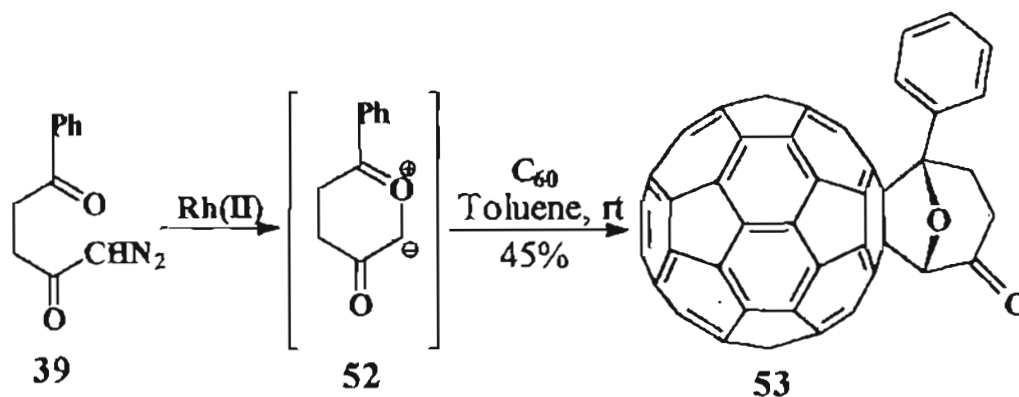
Scheme 17

Our preliminary investigations were focused on the dipolar cycloaddition reaction of carbonyl ylide dipole **52** generated from 3-benzoyl propionic acid as shown in scheme 18.



Scheme 18

The experiment was performed by the addition of the diazoketone **39** to a solution of C<sub>60</sub> in toluene in the presence of Rh (II) acetate. The 1,3-dipolar cycloaddition reaction of the carbonyl ylide with [60] fullerene occurred smoothly to afford the product **53** (Scheme 19).



Scheme 19

The product was purified by chromatography on silica gel column and it was characterized by spectroscopic analysis. The IR spectrum of **53** showed the carbonyl absorption band at 1732 cm<sup>-1</sup> and in its <sup>1</sup>H NMR



spectrum (Figure 4) the characteristic bridgehead proton resonated at  $\delta$  6.05 as a singlet. In the  $^{13}\text{C}$  NMR spectrum (Figure 5) the characteristic  $sp^3$  carbons at the [6,6] junction on the [60] fullerene resonated at  $\delta$  75.24 and 79.43. The two bridgehead carbons resonated at  $\delta$  92.26 and 92.15. The signal at  $\delta$  92.15 is due to the bridgehead methine carbon. These assignments were confirmed by DEPT studies. In the DEPT-135 spectrum of **53** (Figure 6) peaks at  $\delta$  92.26, 79.43 and 75.24 disappeared. The mass spectrum showing a molecular ion peak at 894 and the HRMS data supported the assigned structure.

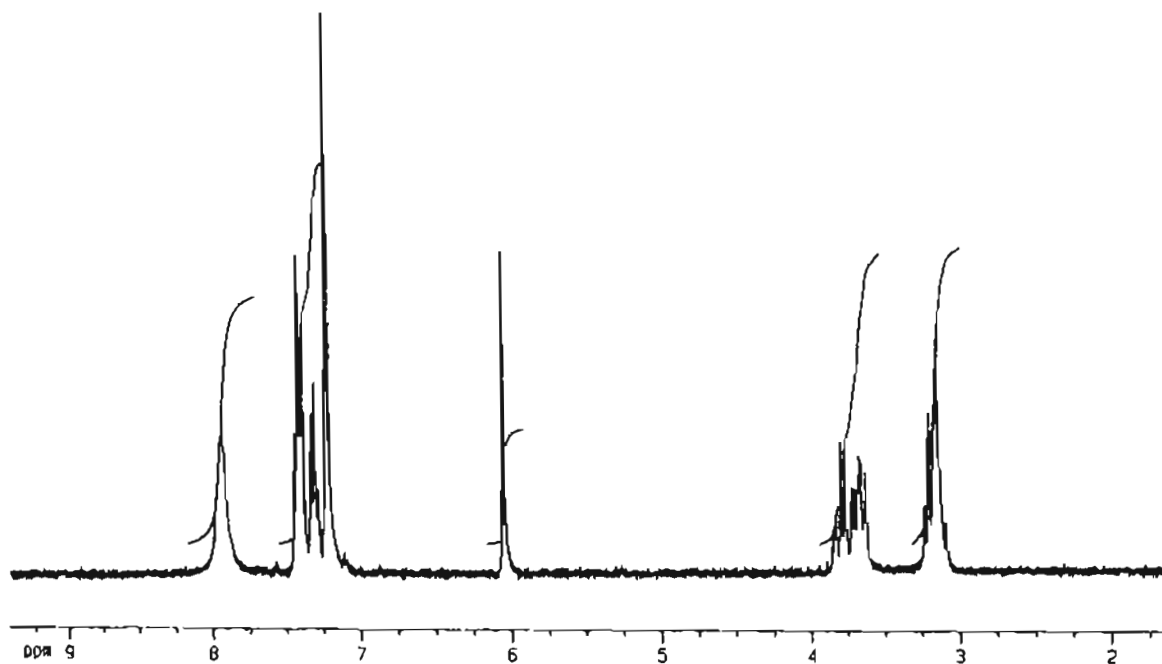


Figure 4.  $^1\text{H}$  NMR spectrum of cycloadduct **53**

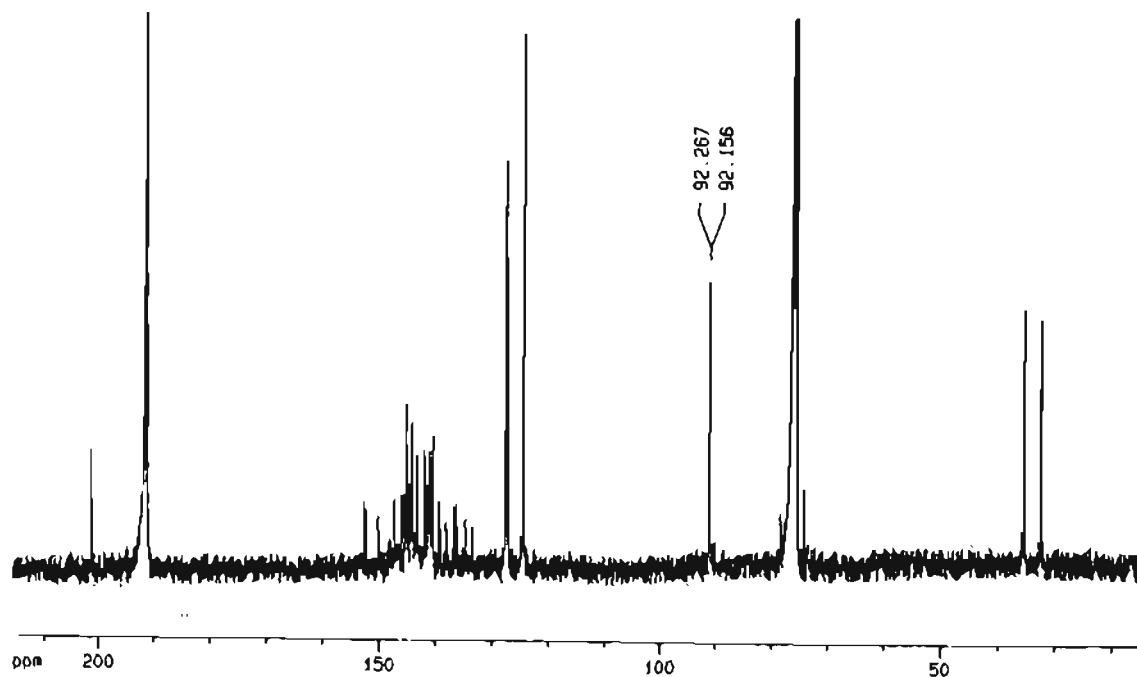


Figure 5.  $^{13}\text{C}$  NMR spectrum of cycloadduct 53

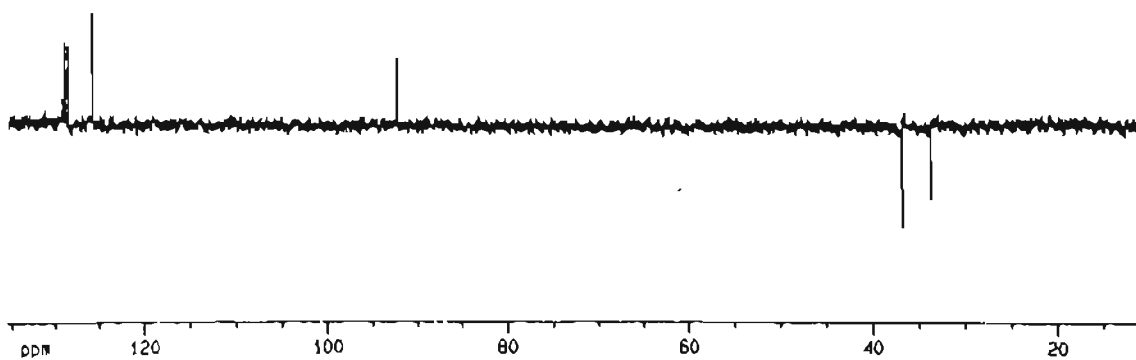
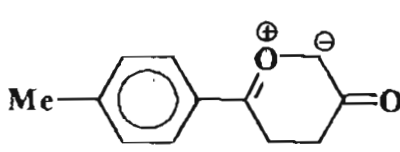
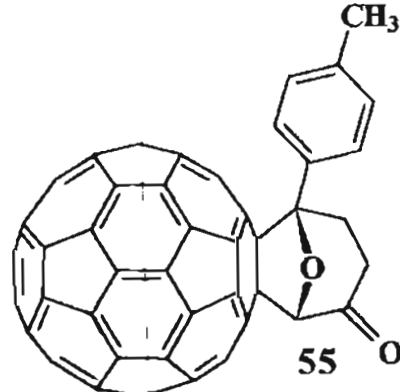
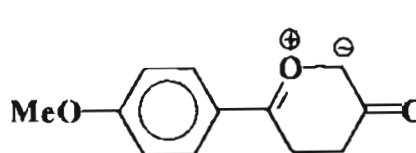
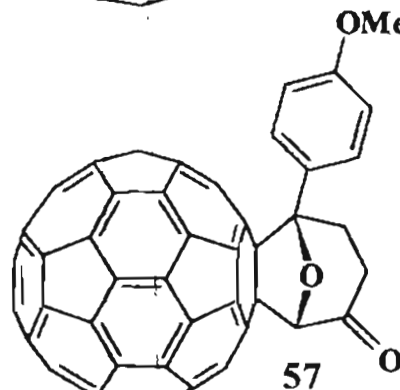
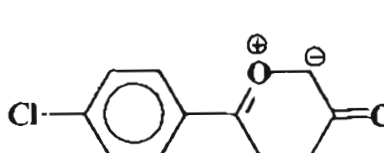
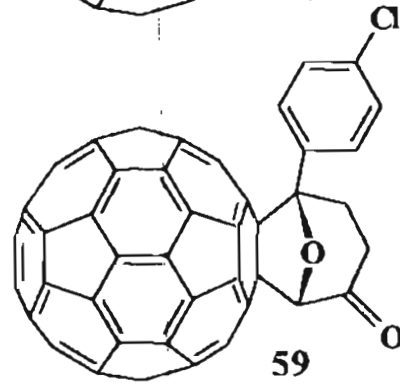


Figure 6. DEPT-135 spectrum of cycloadduct 53

The experiments were repeated with carbonyl ylides **54**, **56** and **58** derived from diazoketones **40**, **41** and **42** which were synthesized from

3-(4-toluoyl) propionic acid, 3-(4-anisoyl) propionic acid and 3-(4-chloro benzoyl) propionic acid. The results are shown in Table 1.

**Table 1.** Cycloaddition of Carbonyl Ylides **54**, **56** and **58** with [60] Fullerene

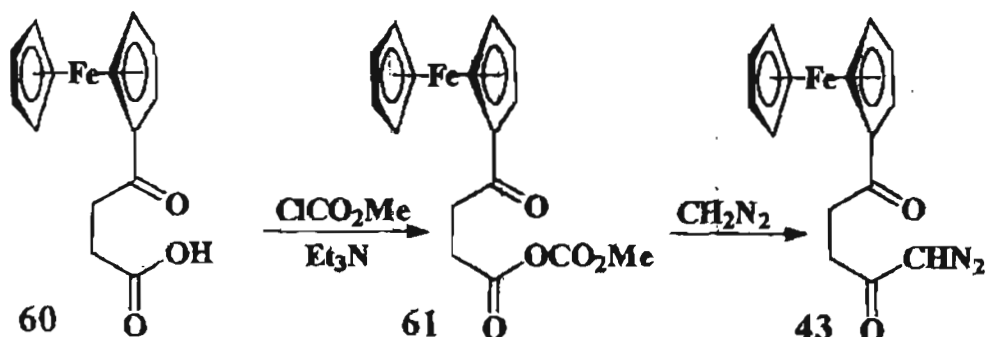
| Carbonyl Ylide   | Adduct  | Yield <sup>a(b)</sup> |
|--|---|-----------------------|
|  <p><b>54</b></p>  |  <p><b>55</b></p>  | 48 (87)               |
|  <p><b>56</b></p> |  <p><b>57</b></p> | 31 (43)               |
|  <p><b>58</b></p> |  <p><b>59</b></p> | 39 (79)               |

a. Isolated yield, b. Based on recovered C<sub>60</sub>

The cycloadducts were characterized by spectroscopic methods. All these compounds showed one carbonyl absorption each in the IR spectrum and they showed typical proton and carbon signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Satisfactory HRMS data was also obtained for all the cycloadducts.

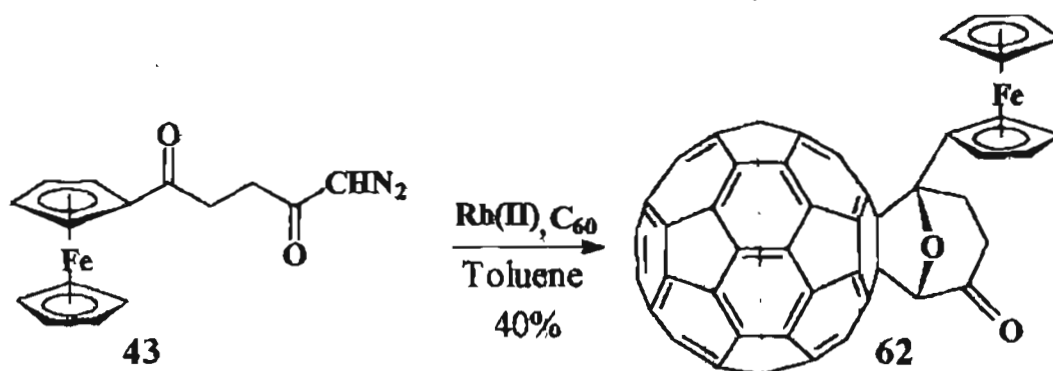
Materials containing two different covalently linked redox centers are very interesting from the vantage point of applications in molecular electronics.<sup>53</sup> Steady state fluorescence and time resolved flash photolytic investigations carried out on fulleropyrrolidine bridged ferrocene diads have shown that electron transfer occurs from the ferrocene donor to the fullerene acceptor. Only very few methods are available for the construction of such systems. The combination of these two electroactive species,  $\text{C}_{60}$  and ferrocene, in a single unit **62** can be achieved by the carbonyl ylide addition methodology.

The diazoketone required for this experiment was synthesized from 3-ferrocenoyl propionic acid **60**, which was prepared by the reaction of succinic anhydride and ferrocene in presence of anhydrous aluminium chloride. Treating the acid **60** with methyl chloroformate and triethylamine under the standard conditions afforded the mixed anhydride **61**. This was treated with excess diazomethane to afford the diazoketone **43** (Scheme 20).



Scheme 20

A solution of [60] fullerene in toluene on treatment with 43 in presence of  $\text{Rh}_2(\text{OAc})_4$  afforded the cycloadduct 62 in 40% yield (Scheme 21).

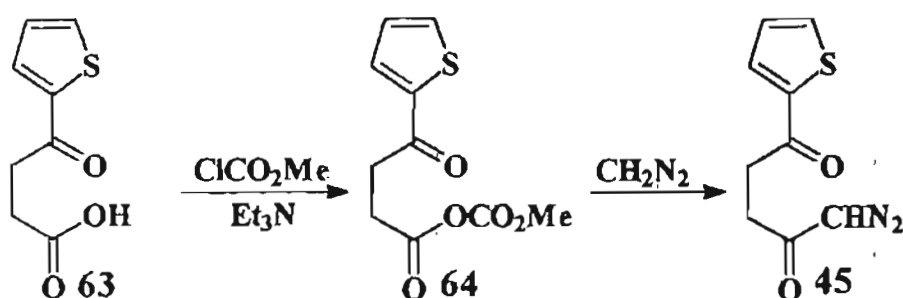


Scheme 21

The IR spectrum of 62 showed a band at  $1725\text{ cm}^{-1}$  indicating the presence of the carbonyl group. In the  $^1\text{H}$  NMR spectrum, the bridgehead proton resonated at  $\delta$  5.94 as a singlet. In the  $^{13}\text{C}$  NMR spectrum of 62 the characteristic  $sp^3$  carbons on the fullerene cage resonated at  $\delta$  75.23 and

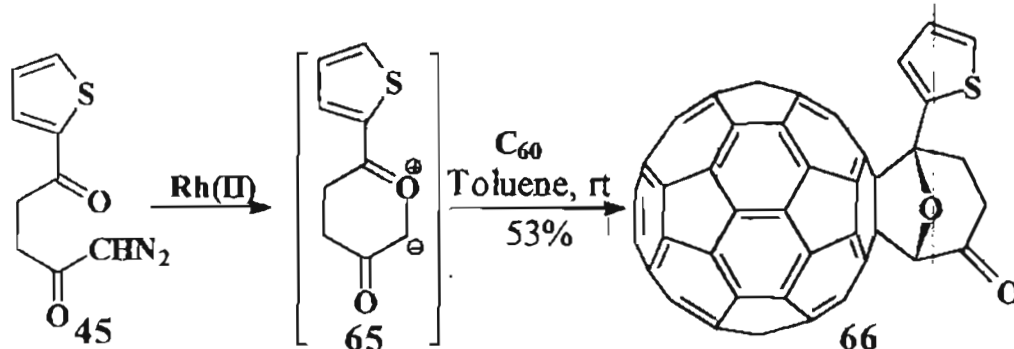
80.01. The carbonyl carbon was discernible at  $\delta$  202.56. Signals due to the ferrocene moiety were observable at  $\delta$  65-75.

Subsequently, 3-(2-thenoyl) propionic acid **63** was converted to the corresponding diazo ketone **45** by the usual procedure (Scheme 22).



Scheme 22

This diazo ketone on treatment with [60] fullerene in presence of  $\text{Rh}_2(\text{OAc})_4$  in toluene under the standard conditions afforded the fullerene derivative **66** in 53 % yield (Scheme 23).

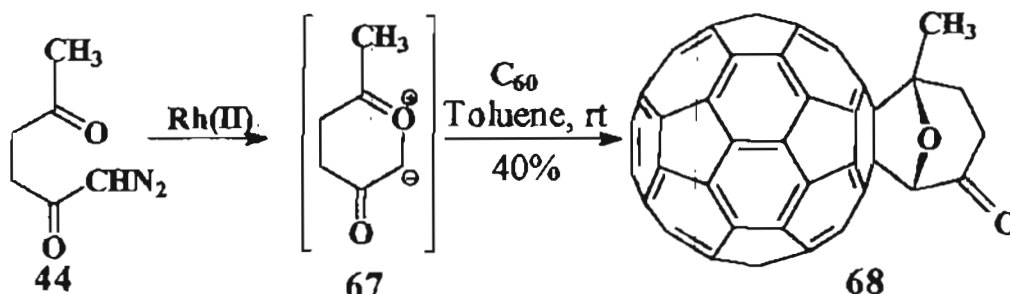


Scheme 23

The product **66** was characterized by spectral analysis. IR spectrum showed a typical carbonyl absorption at  $1725 \text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum the bridgehead proton resonated at  $\delta$  5.98 as a singlet. In the  $^{13}\text{C}$

NMR spectrum, the carbonyl carbon was discernible at  $\delta$  200.41. Other signals were also in agreement with the proposed structure.

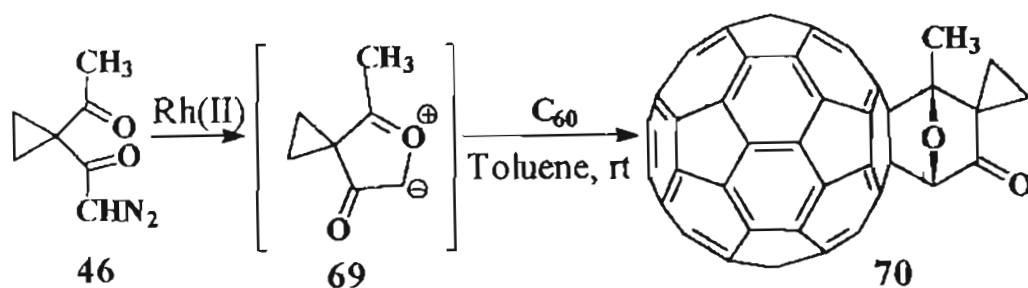
Similarly, the diazo ketone **44** obtained from levulinic acid was allowed to react with [60] fullerene under Rh (II) catalysis to afford the furanofullerene **68** in 40 % yield (Scheme 24).



**Scheme 24**

The product **68** was also characterized by spectroscopic analysis. IR spectrum showed the carbonyl absorption at  $1732\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum, the bridgehead and the methyl protons were observable at  $\delta$  5.77 and 2.25 as singlets. The  $^{13}\text{C}$  NMR spectrum of **68** showed signal for the carbonyl carbon at  $\delta$  201.12.

As a follow up of the investigations described above, it was of interest to study the cycloaddition of the five membered carbonyl ylide <sup>51</sup> **69** with  $\text{C}_{60}$ . Thus when diazo ketone **46** was treated with [60] fullerene in presence of Rh (II) acetate, in dry toluene under an atmosphere of argon at ambient temperature, the cycloadduct **70** was obtained in 54 % yield. The yield based on recovered  $\text{C}_{60}$  was 92% (Scheme 25).

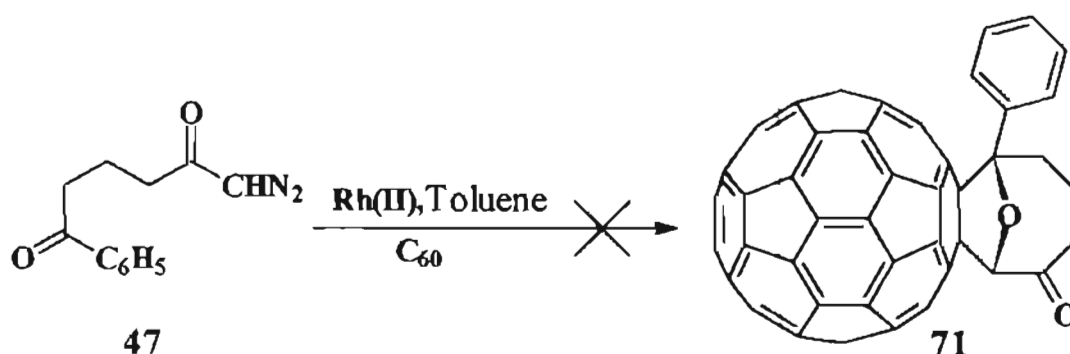


Scheme 25

The product was separated by chromatography on silica gel column and characterized by spectroscopic analysis. The IR spectrum of **70** showed the carbonyl absorption band at  $1745\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum of the same, the bridgehead methine proton resonated at  $\delta$  5.96 as a singlet. Protons of the cyclopropyl group were discernible at  $\delta$  1.35-1.99. Methyl group on the oxabicyclic system resonated at  $\delta$  2.13 as a singlet. In the  $^{13}\text{C}$  NMR spectrum, typical  $\text{C}_{60}$  carbons resonated between  $\delta$  139.00 and 154.00;  $sp^3$  carbons at the [6,6] junction on the fullerene moiety were observable at  $\delta$  74.61 and 80.02. The spirocarbon and the carbonyl carbon of **70** showed signals at  $\delta$  39.38 and 208.21. All these assignments were confirmed by DEPT-135 NMR analysis.

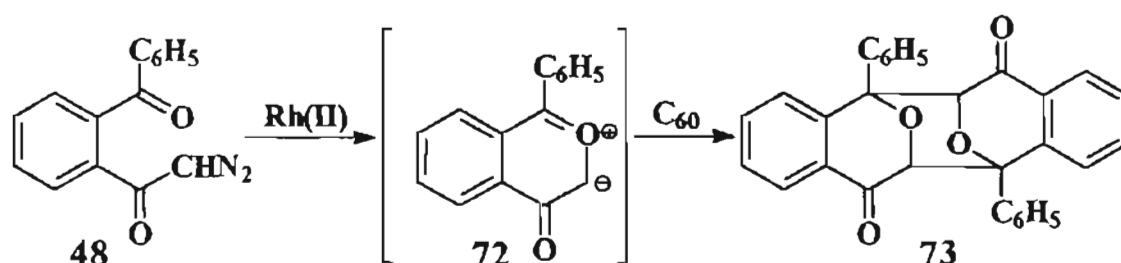
Subsequently we attempted the reaction of a seven membered carbonyl ylide<sup>51</sup> derived from the diazo ketone **47** with [60] fullerene under the experimental conditions described earlier. No reaction was observed in this case and (Scheme 26) and most of the  $\text{C}_{60}$  was recovered as such. The reason for the failure of this reaction is not clear. However it may be surmised that extending the tether to three methylene groups sufficiently retards the rate of intramolecular cyclization to form the carbonyl ylide and its subsequent cycloaddition.





Scheme 26

Attempted reaction between the diazo ketone 48 and [60] fullerene in the presence of Rh (II) acetate also did not succeed; a dimer 73 derived from head to tail coupling of the transient carbonyl ylide dipole 72, along with the unreacted  $C_{60}$ , was isolated from the reaction mixture (Scheme 27). The product 73 was characterized by spectroscopic analysis.



Scheme 27

## 2.2.2 CYCLIC VOLTAMETRY OF CARBONYL YLIDE- [60] FULLERENE ADDUCTS

Theoretical calculations have shown that  $C_{60}$  is an electronegative system and it was further shown that the lowest unoccupied molecular orbitals (LUMO) of  $C_{60}$  have low energy and are triply degenerate. The electrophilic nature of [60] fullerene have been proved experimentally by

cyclic voltammetry studies.<sup>54</sup>  $C_{60}$  is reducible up to the hexa anion,  $C_{60}^{6-}$ . The reduction has been found to be reversible also. For any applications it was of fundamental importance to verify the extent to which the characteristic fullerene properties are retained in the derivatives. Saturation of a double bond in  $C_{60}$  causes partial loss of conjugation in the extended  $\pi$ -system. Due to this effect, four reduction peaks for the  $C_{60}$  moiety in organofullerenes have been detected so far in the accessible potential range.

The electrochemical properties of compounds **53**, **62**, and **66** were studied by cyclic voltammetry (CV) at room temperature. Cycloadduct **62** showed a cyclic voltammogram, (Figure 8), with four reduction waves at potentials shifted to more negative values compared to the parent  $C_{60}$  (Figure 7).

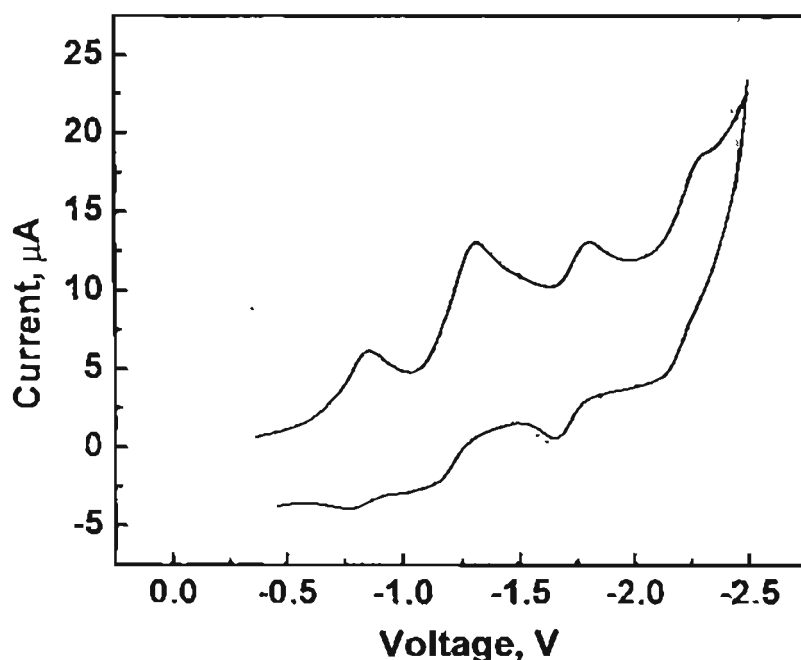
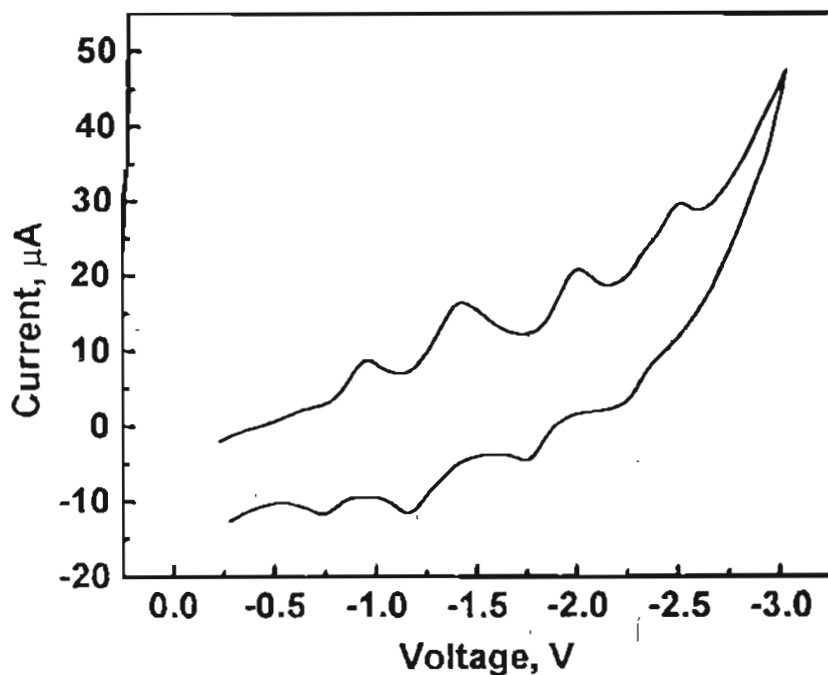


Figure 7. Cyclic Voltammogram of  $C_{60}$



**Figure 8.** Cyclic Voltammogram of **62**

This is due to the saturation of a double bond in the cage. This indicates that the electrophilicity of the cycloadduct is slightly less than that of [60] fullerene itself. The reduction potentials estimated by the position of reduction peaks for compounds **53**, **62** and **66** are given in Table 2 together with those measured for  $\text{C}_{60}$  under identical conditions.

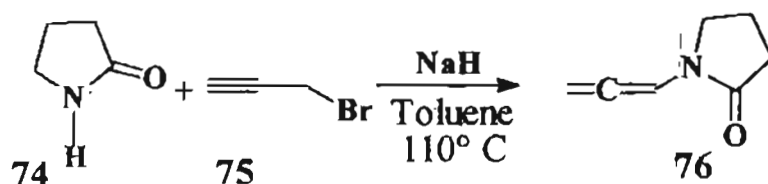
**Table 2.** Reduction Potential of C<sub>60</sub> Adducts **53**, **62**, **66** and C<sub>60</sub>.

| Compound        | E <sub>red</sub> <sup>1</sup> | E <sub>red</sub> <sup>2</sup> | E <sub>red</sub> <sup>3</sup> | E <sub>red</sub> <sup>4</sup> |
|-----------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| C <sub>60</sub> | -0.852                        | -1.308                        | -1.799                        | -2.294                        |
| <b>53</b>       | -0.932                        | -1.352                        | -1.891                        | -2.394                        |
| <b>66</b>       | -0.942                        | -1.381                        | -1.963                        | -2.451                        |
| <b>62</b>       | -0.949                        | -1.423                        | -1.993                        | -2.470                        |

**Experimental Conditions:** V vs Ag<sup>+</sup>/Ag; Glassy carbon electrode as working electrode; Bu<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> (0.1M) as supporting electrolyte; Scan rate 100 mv/s; Toluene/Acetonitrile (5:1) as solvent.

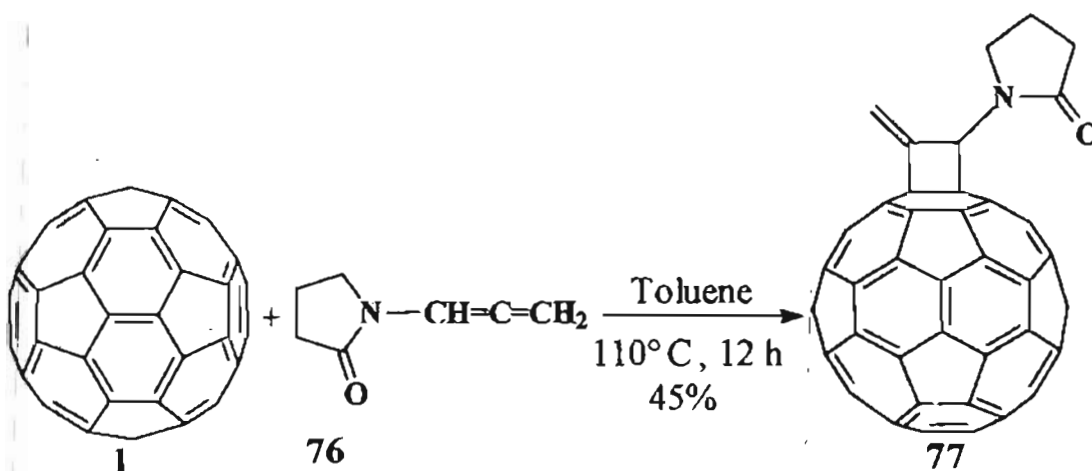
### 2.2.3 REACTIONS OF ALLENAMIDES WITH [60] FULLERENE

Five and six membered ring annulated [60] fullerenes can be prepared by a number of methods. However four membered ring annulated fullerenes<sup>55</sup> are less common. The most widely used method for their preparation is the [2+2] photochemical cycloaddition reaction. The reaction of benzyne and ketenes are also known to give cyclobutane fused [60] fullerene derivatives. Allenyl groups attached to nitrogen atom can, in principle, add to C<sub>60</sub> leading to cyclobutane annulated fullerenes. Allenes of the type **76** can be prepared by the reaction of the corresponding cyclic amide **74** with propargyl bromide **75** in presence of sodium hydride (Scheme 28).<sup>56</sup>



Scheme 28

Our studies were initiated with the reaction of 76 with [60] fullerene. Thus, heating a solution of allene 76 and C<sub>60</sub> in toluene under refluxing conditions, afforded the cyclobutane annulated fullerene 77 (Scheme 29).



Scheme 29

The product was purified by chromatography on silica gel column and characterized by spectroscopic analysis. IR spectrum of 77 showed a typical band for amide group at 1687cm<sup>-1</sup>. In the <sup>1</sup>H NMR spectrum (Figure 9), the exocyclic methylene hydrogens resonated as two broad triplets at δ 5.93 and δ 6.29. The proton on the cyclobutane ring also resonated at δ 7.00 as a broad triplet. In the <sup>13</sup>C NMR spectrum of 77 (Figure 10), the characteristic signals for the amide carbonyl and the exocyclic double bond were discernible at δ 175.24 and 115.38 respectively. The two sp<sup>3</sup> carbons of the [6,6] fused fullerene resonated at δ 73.08 and 74.46. The three

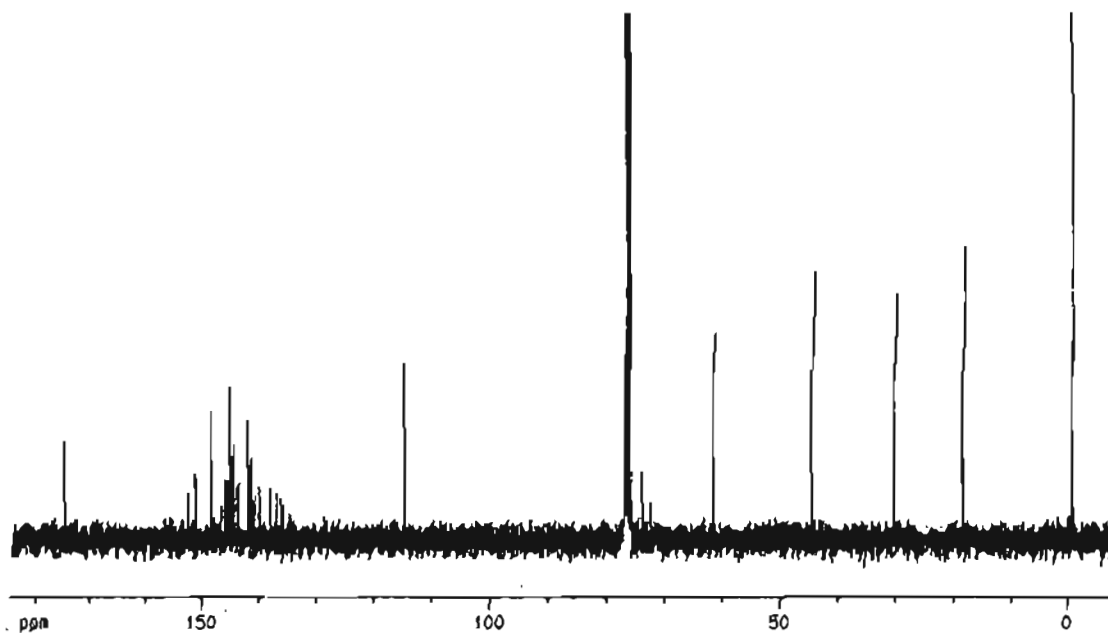


Figure 10.  $^{13}\text{C}$  NMR spectrum of compound 77

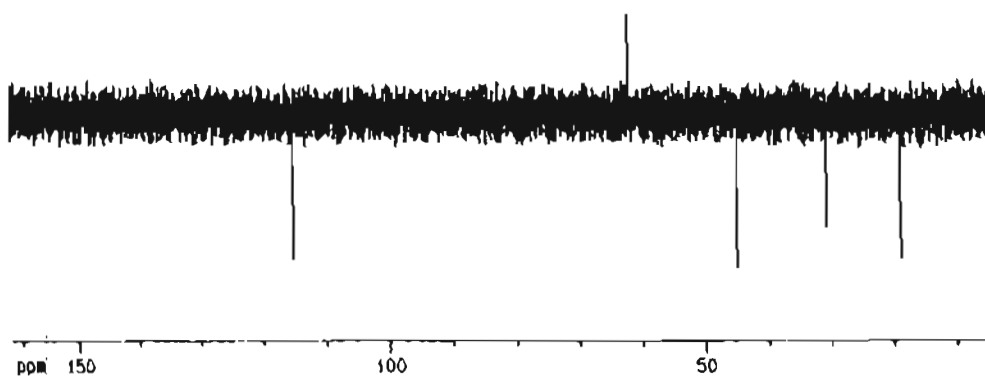
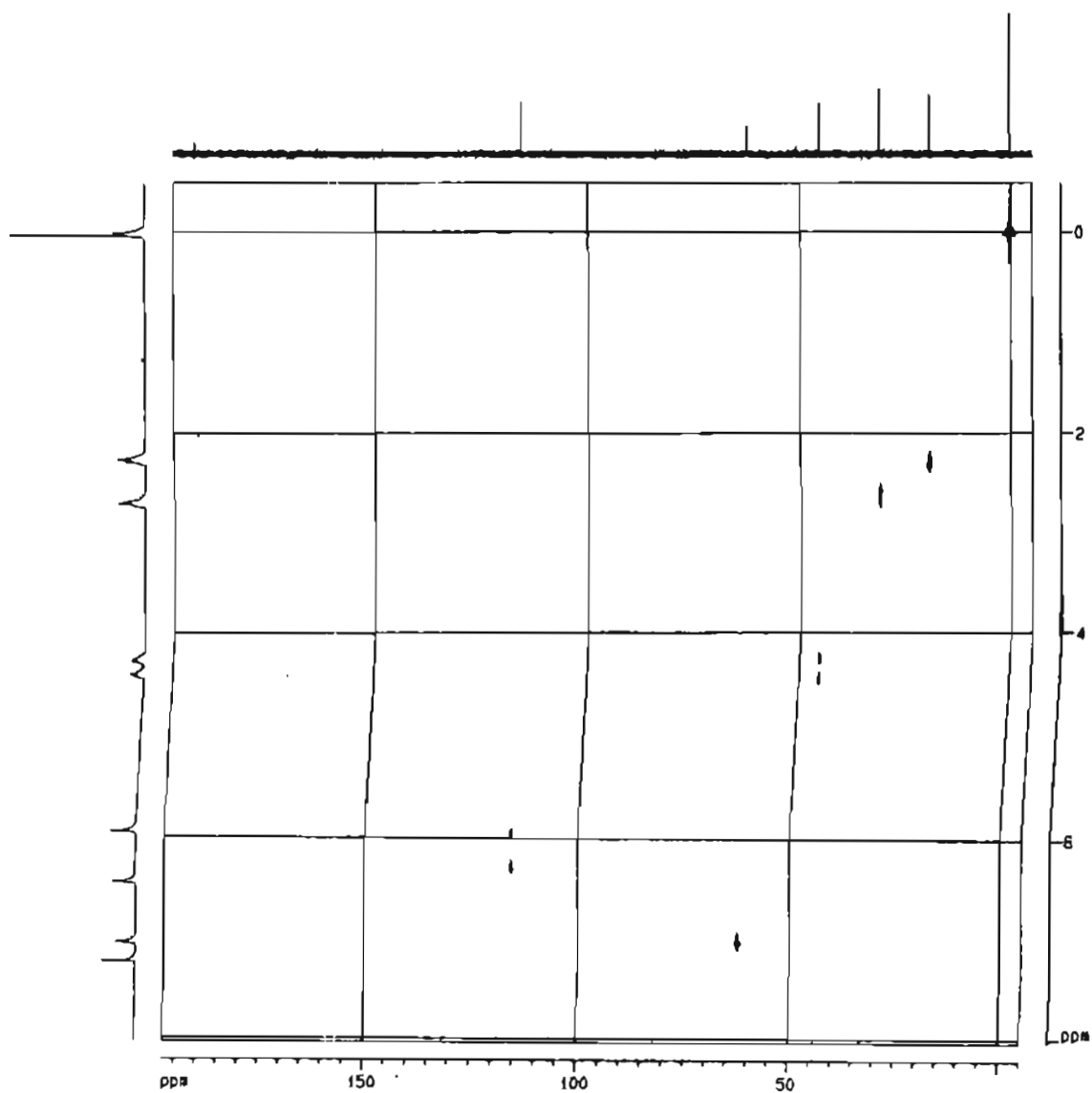
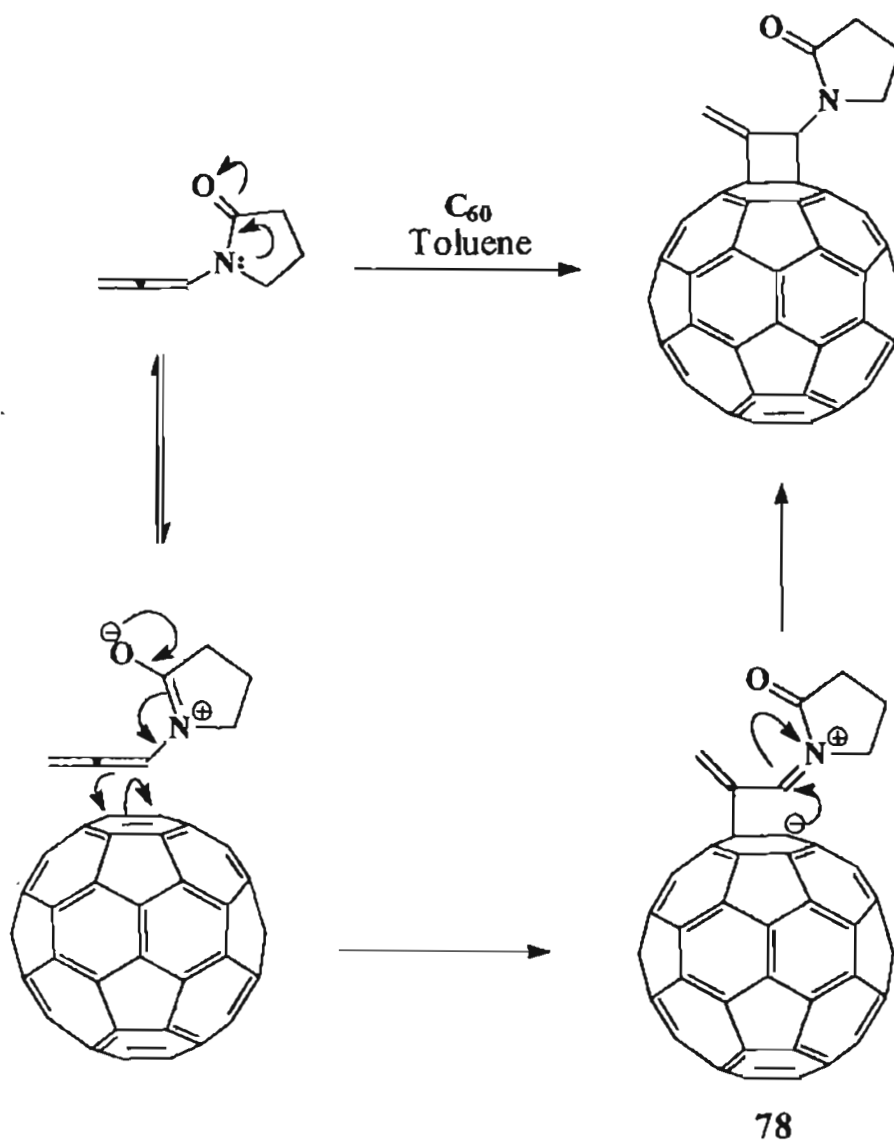


Figure 11. DEPT-135 NMR spectrum of compound 77



**Figure 12.** 2D-HETEROCOSY spectrum of compound 77

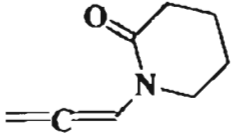
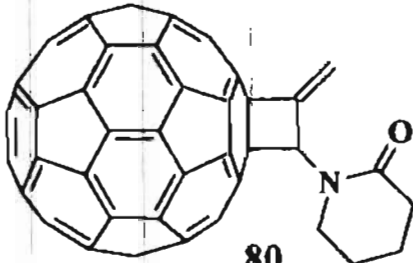
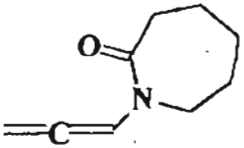
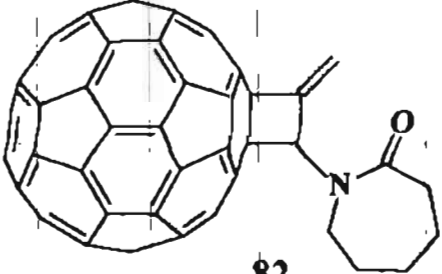
A mechanistic rationalization as outlined in the following scheme may be invoked for the annulation (Scheme 30).

**Scheme 30**

It is conceivable that the electron deficient fullerene cage can stabilize the negative charge, thereby facilitating the intramolecular attack on the iminium moiety. The experiments were repeated with two other allenes 79 and 81 and in these cases also the reaction proceeded smoothly to afford the cycloadducts. The results are summarized in table 3.



Table 3. Cycloaddition of Allenes **79** and **81** with [60] Fullerene.

| Allene  | C <sub>60</sub> Derivative   | Yield <sup>a(b)</sup> |
|---|--|-----------------------|
| <br><b>79</b>  | <br><b>80</b>  | 34(48)                |
| <br><b>81</b> | <br><b>82</b> | 28(38)                |

(a) Isolated yield, (b) Yield based on recovered C<sub>60</sub>

The product **80** was fully characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HRMS analysis. Cyclobutane derivative **82** was characterized by IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR analysis. It showed a very weak signal for molecular ion in the mass spectrum.

## 2.3 EXPERIMENTAL

All the reactions were carried out in oven dried glassware under an atmosphere of argon, unless otherwise mentioned. The IR spectra were recorded on Bomem MB series FT-IR spectrophotometer, using potassium bromide pellets. NMR spectra were recorded on Bruker-300 MHz FT-NMR spectrometer using  $\text{CDCl}_3\text{-CS}_2$  (1:2) mixture as solvent for fullerene adducts. For other samples  $\text{CDCl}_3$  was used as the solvent. The chemical shifts are given in the  $\delta$  scale with tetramethylsilane as internal standard. Elemental analysis were carried out using Perkin-Elmer 2400 CHN analyzer. High resolution mass spectra were obtained in EI mode on a Kratos MS50 instrument. Solvents used for experiments (toluene, benzene, ether and methanol) were distilled and dried according to the literature procedures.

### 2.3.1 SYNTHESIS OF DIAZO KETONES: TYPICAL EXPERIMENTAL PROCEDURE

The preparation of 1-diazo-5-phenyl-2, 5-pentanedione **39** from 3-benzoyl propionic acid described below is illustrative of the general procedure for the synthesis of  $\alpha$ -diazo ketones. The  $\gamma$ -keto acids required for the synthesis of diazoketones were either purchased or prepared by the literature procedure.  $\gamma$ -Keto acids required for the synthesis of diazoketones **40**, **41** and **42** were prepared by procedures similar to the one reported for the synthesis of 3-benzoyl propionic acid.<sup>57</sup> 3-Ferrocenoyl propionic acid **60** was prepared by the known procedure.<sup>58</sup> 3-(2-Thienoyl) propionic acid was prepared by the Friedel-Crafts reaction of thiophene and succinic anhydride using anhydrous  $\text{AlCl}_3$ .

***1-Diazo-5-phenyl-2, 5-pentanedione 39***

To a solution of 3-benzoyl propionic acid (1.78 g,  $9.88 \times 10^{-3}$  mol) in 50 mL dry ether was added methylchloroformate (0.99 g,  $10.5 \times 10^{-3}$  mol) and triethylamine (1.07 g,  $10.5 \times 10^{-3}$  mol). The resulting white suspension was stirred at room temperature under argon for two hours. The precipitated triethylamine hydrochloride was removed by filtration and the resulting pale yellow solution was immediately treated with freshly prepared diazomethane ( $25 \times 10^{-3}$  mol, in 20 mL ether) at  $0^\circ$  C. The reaction mixture was maintained at  $0^\circ$  C for 8 hours and then warmed to room temperature and stirred overnight. The solvent was removed and the resulting yellow oil was chromatographed on a silica gel column using hexane-ethyl acetate mixture (80:20) to afford 1-diazo-5-phenyl-2, 5-pentanedione **39** (1.36 g, 67%).

Yellow solid; recrystallized from hexane-dichloromethane.

mp : 55-56 $^\circ$  C  
IR (KBr)  $\nu_{\max}$  : 755, 1360, 1645, 1690, 2110, 2920, 3100  $\text{cm}^{-1}$ .  
 $^1\text{H NMR}$  :  $\delta$  2.65 (t, 2H), 3.25 (t, 2H), 5.30 (s, 1H), 7.30-7.50 (m, 3H), 7.80-8.00 (m, 2H).

***1-Diazo-5- (4-methyl phenyl)-2,5-pentanedione 40***

To a solution of 3-(4-toluoyl) propionic acid (1.5 g,  $7.81 \times 10^{-3}$  mol) in 50 mL dry ether, was added methylchloroformate (0.775 g,  $8.20 \times 10^{-3}$  mol) and triethylamine (0.836 g,  $8.20 \times 10^{-3}$  mol). The reaction mixture was stirred for two hours and filtered. The filtrate was treated with freshly prepared diazomethane ( $25 \times 10^{-3}$  mol, in 20 mL ether) at  $0^\circ\text{C}$ . The reaction conditions described previously were maintained and the resulting crude product was

chromatographed on a silica gel column using hexane-ethyl acetate mixture (80:20) as eluent to afford **40** (0.360 g, 21%).

Yellow solid; recrystallized from hexane-dichloromethane.

|                       |   |  |
|-----------------------|---|--|
| mp                    | : | 67-69° C   |
| IR (KBr) $\nu_{\max}$ | : | 1389, 1601, 1638, 1670, 2100, 2912, 3093 $\text{cm}^{-1}$ .  |
| $^1\text{H}$ NMR      | : | $\delta$ 2.40 (s, 3H), 2.74 (br s, 2H), 3.32 (t, 2H, $J = 6.25$ Hz), 5.39 (br s, 1H), 7.23 (d, 2H, $J = 7.92$ Hz), 7.86 (d, 2H, $J = 8.1$ Hz). |
| $^{13}\text{C}$ NMR   | : | $\delta$ 21.70, 33.08, 34.36, 54.62, 128.23, 129.30, 134.15, 143.92, 193.40, 197.74.   |

#### ***1-Diazo-5-(4-methoxy phenyl)-2, 5-pentanedione 41***

To a solution of 3-(4-anisoyl) propionic acid (2g,  $9.6 \times 10^{-3}$  mol) in 50 mL dry ether was added methylchloroformate (0.953 g,  $10 \times 10^{-3}$  mol) and triethylamine (1.028 g,  $10 \times 10^{-3}$  mol). The reaction mixture was stirred for two hours and filtered. The filtrate was treated with freshly prepared diazomethane ( $25 \times 10^{-3}$  mol, in 20 mL ether) at 0°C. The reaction conditions described previously were maintained and the resulting crude product was chromatographed on a silica gel column using hexane-ethyl acetate mixture (80:20) as eluent to afford **41** (0.248 g, 11%).

Yellow solid; recrystallized from hexane-dichloromethane.

|                       |   |   |
|-----------------------|---|---|
| mp                    | : | 53-55° C  |
| IR (KBr) $\nu_{\max}$ | : | 827, 1170, 1245, 1382, 1601, 1632, 1682, 2106, 3087 $\text{cm}^{-1}$ .  |
| $^1\text{H}$ NMR      | : | $\delta$ 2.73 (br s, 2H), 3.29 (t, 2H, $J = 5.83$ Hz), 3.85 (s, 3H), 5.37 (br s, 1H), 6.90 (d, 2H, $J = 8.09$ Hz), 7.94 (d, 2H, $J = 8.03$ Hz). |

$^{13}\text{C}$  NMR :  $\delta$  32.71, 34.18, 54.47, 55.24, 113.64, 129.61, 130.23, 163.49, 193.29, 196.42.

***1-Diazo-5- (4-chloro phenyl) -2,5-pentanedione 42***

To a solution of 3-(4-chlorophenyl) propionic acid (1 g,  $4.7 \times 10^{-3}$  mol) in 40 mL dry ether was added methylchloroformate (0.466 g,  $4.93 \times 10^{-3}$  mol) and triethylamine (0.503 g,  $4.93 \times 10^{-3}$  mol). The reaction mixture was stirred for two hours and filtered. The filtrate was treated with freshly prepared diazomethane ( $20 \times 10^{-3}$  mol, in 20 mL ether) at  $0^\circ\text{C}$ . The reaction conditions described previously were maintained and the resulting crude product was chromatographed on a silica gel column using hexane-ethyl acetate mixture (80:20) to afford **42** (0.530 g, 47%).

Yellow solid; recrystallized from hexane-dichloromethane.

mp : 68-70 $^\circ\text{C}$   
IR (KBr)  $\nu_{\text{max}}$  : 781, 1009, 1109, 1350, 1389, 1588, 1639, 1672, 2112, 3092  $\text{cm}^{-1}$ .  
 $^1\text{H}$  NMR :  $\delta$  2.76 (br s, 2H), 3.33 (t, 2H,  $J = 6.32$  Hz), 5.37 (br s, 1H), 7.43 (d, 2H,  $J = 8.38$  Hz), 7.91 (d, 2H,  $J = 8.37$  Hz).  
 $^{13}\text{C}$  NMR :  $\delta$  32.94, 34.11, 54.55, 128.87, 129.42, 134.79, 139.66, 192.87, 196.84.

***1-Diazo-5- (ferrocenyl)-2,5-pentanedione 43***

To a solution of ferrocenoyl propionic acid (0.20 g,  $6.99 \times 10^{-4}$  mol) in 25 mL dry ether was added methylchloroformate (0.069 g,  $7.34 \times 10^{-4}$  mol) and triethylamine (0.075 g,  $7.34 \times 10^{-4}$  mol). The reaction mixture was stirred for two hours and filtered. The filtrate was treated with freshly prepared

diazomethane ( $10 \times 10^{-3}$  mol, in 10 mL ether) at  $0^\circ\text{C}$ . The reaction conditions described previously were maintained and the resulting crude product was chromatographed on a silica gel column using hexane-ethyl acetate mixture (70:30) to afford **43** (0.051 g, 23%).

Red colored solid; recrystallized from hexane-dichloromethane.

mp : 83-85° C

IR (KBr)  $\nu_{\text{max}}$  : 479, 824, 1062, 1261, 1314, 1374, 1460, 1666, 2103, 2906, 3091  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  2.68 (br s, 2H), 3.11 (t, 2H,  $J = 6.37$  Hz), 4.23 (s, 5H), 4.48 (br s, 2H), 4.78 (br s, 2H), 5.39 (br s, 1H).

$^{13}\text{C}$  NMR :  $\delta$  33.51, 33.66, 54.19, 68.75, 69.51, 71.72, 77.91, 193.09, 201.70.

#### ***1-Diazo-5- (thienyl)-2,5-pentanedione 45***

To a solution of 3-(2-thienyl) propionic acid (0.60 g,  $3.25 \times 10^{-3}$  mol) in 30 mL dry ether was added methylchloroformate (0.323 g,  $3.42 \times 10^{-3}$  mol) and triethylamine (0.348 g,  $3.42 \times 10^{-3}$  mol). The reaction mixture was stirred for two hours and filtered. The filtrate was treated with freshly prepared diazomethane ( $15 \times 10^{-3}$  mol, in 20 mL ether) at  $0^\circ\text{C}$ . The reaction conditions described previously were maintained and the resulting crude product was chromatographed on a silica gel column using hexane-ethyl acetate mixture (70:30) to afford **45** (0.185 g, 27%).

Yellow solid; recrystallized from hexane-dichloromethane.

mp : 56-58° C

IR (KBr)  $\nu_{\text{max}}$  : 741, 857, 1042, 1125, 1243, 1321, 1365, 1621, 1663, 2106, 3108  $\text{cm}^{-1}$ .

- $^1\text{H NMR}$  :  $\delta$  2.75 (br s, 2H), 3.29 (t, 2H,  $J = 6.48$  Hz), 5.37 (br s, 1H), 7.12 (t, 1H,  $J = 4.22$  Hz), 7.63 (d, 1H,  $J = 4.44$  Hz), 7.76 (d, 1H,  $J = 3$  Hz).
- $^{13}\text{C NMR}$  : 33.69, 34.18, 54.62, 128.08, 132.00, 133.58, 143.65, 191.00, 192.93.

### 2.3.2 GENERAL PROCEDURE FOR THE Rh (II) CATALYSED CYCLOADDITION REACTION OF 1-DIAZO ALKANEDIONES WITH [60] FULLERENE

$\text{C}_{60}$  was completely dissolved in dry toluene by sonication. To this solution a catalytic amount (0.002 g) of  $\text{Rh}_2(\text{OAc})_4$  was added and dry oxygen free argon was passed through it. The diazo ketone in toluene, (10-15 mL), taken in a pressure equalizing funnel, was slowly added to the  $\text{C}_{60}$  solution with constant stirring, at the rate of five to six drops in a minute. After the addition was complete, the reaction mixture was allowed to stir for another 30 minutes. The solvent was then removed under reduced pressure and the contents were charged on a silica gel (100-200 mesh) column and eluted with toluene: hexane mixture (1:4). The unreacted  $\text{C}_{60}$  was eluted first and then eluting with toluene: hexane mixture (1:1) afforded the product. The product was dissolved in dry carbon disulfide (2 mL) and dry methanol was added dropwise to it till the product got precipitated completely. The supernatant liquid was decanted off to obtain the product, which was then washed three times with dry methanol and dried in a vacuum oven at  $60^\circ\text{C}$  and the products were identified on the basis of their spectral data.

**5'-(Phenyl)-fullereno-C<sub>60</sub>- [1', 9': 6,7][8] oxabicyclo [3.2.1] octan-2'-one (53)**

C<sub>60</sub> 1 (0.036 g, 5×10<sup>-5</sup> mol) dissolved in 36 mL dry toluene was treated with 1-diazo-5-phenyl-2, 5-pentanedione **39** (0.0101 g, 5×10<sup>-5</sup> mol) in 10 mL toluene in presence of a catalytic amount of Rh<sub>2</sub>(OAc)<sub>4</sub>, over a period of 90 minutes. Chromatography of the product on silica gel column using hexane-toluene mixtures afforded the product **53** as a black solid (0.0201 g, 45%, 86% based on recovered C<sub>60</sub>).

IR (KBr)  $\nu_{\max}$  : 525, 691, 751, 883, 1029, 1062, 1215, 1434, 1732, 2859, 2959, 3058 cm<sup>-1</sup>.

<sup>1</sup>H NMR :  $\delta$  3.08-3.23 (m, 2H), 3.62-3.85 (m, 2H), 6.05 (s, 1H), 7.24-7.40 (m, 3H), 7.94 (br s, 2H).

<sup>13</sup>C NMR :  $\delta$  33.62, 36.52, 75.24, 79.43, 92.15, 92.26, 125.52, 128.27, 128.66, 134.44, 135.68, 137.15, 139.05, 140.08, 140.25, 140.35, 141.40, 141.58, 141.67, 141.87, 141.90, 142.00, 142.02, 142.18, 142.26, 142.30, 142.61, 142.72, 142.87, 143.03, 143.15, 144.06, 144.24, 144.38, 144.49, 145.00, 145.17, 145.25, 145.43, 145.51, 145.61, 145.71, 145.81, 145.92, 146.05, 146.13, 146.30, 146.41, 146.57, 147.08, 147.18, 149.19, 151.11, 153.26, 153.71, 202.23.

DEPT-135 :  $\delta$  33.62, 36.52: Negative;  $\delta$  92.26, 125.52, 128.27, 128.66: Positive.

HRMS Calcd. for C<sub>71</sub>H<sub>10</sub>O<sub>2</sub>: 894.0680. Found: 894.0676.



***5'-(4-Methyl phenyl)-fullereno-C<sub>60</sub> [1', 9': 6,7][8] oxabicyclo [3.2.1] octan-2'-one 55***

C<sub>60</sub> **1** (0.036 g, 5×10<sup>-5</sup> mol) dissolved in 36 mL dry toluene was treated with diazo ketone **40** (0.011 g, 5×10<sup>-5</sup> mol) in 10 mL toluene in presence of a catalytic amount of Rh<sub>2</sub>(OAc)<sub>4</sub>, over a period of 90 minutes. Chromatography of the crude product on silica gel column using hexane-toluene mixtures afforded the product **55** as a black solid (0.022 g, 48%, 87% based on recovered C<sub>60</sub>).

IR (KBr)  $\nu_{\max}$  : 814, 1226, 1438, 1738, 2918, 2955 cm<sup>-1</sup>.

<sup>1</sup>H NMR :  $\delta$  2.35 (s, 3H), 3.08-3.22 (m, 2H), 3.60-3.84 (m, 2H), 6.03 (s, 1H), 7.20 (d, 2H, *J* = 7.6 Hz), 7.81 (br s, 2H).

<sup>13</sup>C NMR :  $\delta$  21.26, 33.58, 36.74, 75.18, 79.39, 92.03, 92.20, 125.38, 129.30, 135.64, 137.53, 137.75, 138.50, 139.05, 140.00, 140.18, 140.24, 140.29, 141.25, 141.29, 141.48, 141.57, 141.62, 141.82, 141.89, 141.96, 142.08, 142.10, 142.16, 142.22, 142.53, 142.60, 142.65, 142.95, 143.06, 143.96, 144.14, 144.17, 144.31, 144.41, 144.92, 145.06, 145.14, 145.29, 145.35, 145.43, 145.50, 145.68, 145.70, 145.82, 145.96, 146.03, 146.21, 146.37, 146.55, 146.97, 147.05, 148.20, 151.16, 153.16, 201.58.

HRMS Calcd. for C<sub>71</sub>H<sub>10</sub>O<sub>2</sub> : 908.0837. Found : 908.0805

***5'-(4-Methoxy phenyl) -fullereno-C<sub>60</sub>- [1', 9': 6,7][8] oxabicyclo [3.2.1] octan-2'-one 57***

C<sub>60</sub> **1** (0.072 g, 1×10<sup>-4</sup> mol) dissolved in 72 mL dry toluene was treated with diazo ketone **41** (0.023 g, 1×10<sup>-4</sup> mol) in 10 mL toluene in presence of a catalytic amount of Rh<sub>2</sub>(OAc)<sub>4</sub>, over a period of 90 minutes. Chromatography of the crude product on silica gel column using hexane-toluene mixtures afforded the product **57** as a black solid (0.021 g, 31%, 43% based on recovered C<sub>60</sub>).

IR (KBr)  $\nu_{\text{max}}$  : 525, 817, 1029, 1248, 1507, 1613, 1725 cm<sup>-1</sup>.

<sup>1</sup>H NMR :  $\delta$  3.12-3.30 (m, 2H), 3.66-3.82 (m, 2H), 3.86 (s, 3H), 6.09 (s, 1H), 6.98 (d, 2H,  $J = 9\text{Hz}$ ), 7.90 (br s, 2H).

<sup>13</sup>C NMR :  $\delta$  33.54, 36.67, 54.84, 75.09, 78.30, 91.98, 92.08, 113.79, 126.67, 133.52, 134.18, 137.52, 139.11, 140.10, 140.22, 141.25, 141.31, 141.46, 141.52, 141.58, 141.78, 141.86, 141.92, 142.00, 142.05, 142.12, 142.49, 142.57, 142.60, 142.89, 143.04, 143.92, 144.10, 144.13, 144.31, 144.35, 144.86, 144.89, 145.02, 145.05, 145.11, 145.16, 145.31, 145.78, 145.92, 145.99, 146.16, 146.34, 146.45, 146.95, 147.01, 148.09, 151.13, 153.39, 153.69, 159.07, 201.60.

HRMS Calcd. for C<sub>72</sub>H<sub>12</sub>O<sub>3</sub>: 924.0786. Found: 924.0774.

***5'-(4-Chloro phenyl)-fullereno- $C_{60}$ -[1', 9': 6,7][8] oxa bicyclo [3.2.1] octan-2'-one 59***

$C_{60}$  **1** (0.072 g,  $1 \times 10^{-4}$  mol) dissolved in 72 mL dry toluene was treated with diazo ketone **42** (0.024 g,  $1 \times 10^{-4}$  mol) in 10 mL toluene in presence of a catalytic amount of  $Rh_2(OAc)_4$ , over a period of 90 minutes. Chromatography of the crude product on silica gel column using hexane-toluene mixtures afforded the product **59** as a black solid (0.036 g, 39%, 79% based on recovered  $C_{60}$ ).

IR (KBr)  $\nu_{max}$  : 865, 1066, 1091, 1419, 1729  $cm^{-1}$ .

$^1H$  NMR :  $\delta$  3.09-3.26 (m 2H), 3.65-3.88 (m, 2H), 6.06 (s, 1H), 7.41-7.43 (d, 2H,  $J = 8.29$  Hz), 7.93 (br s, 2H).

$^{13}C$  NMR :  $\delta$  33.63, 36.82, 75.29, 79.30, 91.92, 92.214, 127.06, 128.99, 134.68, 137.35, 137.64, 139.39, 140.13, 140.29, 140.50, 141.54, 141.66, 141.77, 141.81, 141.97, 142.14, 142.28, 142.37, 142.41, 142.78, 142.85, 142.89, 143.15, 143.29, 143.41, 144.41, 144.25, 144.37, 144.51, 144.59, 145.06, 145.10, 145.23, 145.30, 145.38, 145.57, 145.76, 145.89, 145.91, 145.98, 146.05, 146.20, 146.28, 146.42, 147.21, 148.18, 150.89, 152.90, 153.62, 201.17.

HRMS Calcd. for  $C_{71}H_9O_2Cl$ : 928.02911 : Found: 928.02829.

***5'-(Ferrocenyl)-fullereno- $C_{60}$ -[1', 9': 6,7][8] oxa bicyclo [3.2.1] octan-2'-one 62***

$C_{60}$  **1** (0.072 g,  $1 \times 10^{-4}$  mol) dissolved in 72 mL dry toluene was treated with diazo ketone **43** (0.031 g,  $1 \times 10^{-4}$  mol) in 15 mL toluene in

presence of a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$ , over a period of 120 minutes. Chromatography of the crude product on silica gel column using hexane-toluene mixtures afforded the product **62** as a black solid (0.041 g, 40%, 85% based on recovered  $\text{C}_{60}$ ).

IR (KBr)  $\nu_{\text{max}}$  : 811, 1023, 1122, 1420, 1593, 1725, 2846, 2925, 3403  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  3.21-3.45 (m, 2H), 3.64-3.81 (m, 2H), 4.21 (s, 2H), 4.33 (s, 1H), 4.36 (s, 5H), 4.74 (s, 1H), 5.94 (s, 1H).

$^{13}\text{C}$  NMR :  $\delta$  33.32, 35.10, 67.14, 67.79, 68.08, 68.62, 69.29, 75.23, 80.01, 91.42, 91.66, 92.19, 133.74, 135.68, 136.38, 137.53, 139.25, 139.92, 140.02, 140.11, 141.29, 141.44, 141.51, 141.71, 141.79, 141.92, 141.99, 142.01, 142.06, 142.12, 142.42, 142.53, 142.57, 142.87, 142.95, 143.09, 143.95, 144.04, 144.28, 144.35, 144.37, 144.81, 144.88, 144.94, 145.01, 145.07, 145.34, 145.58, 145.64, 145.79, 145.87, 145.92, 146.07, 146.16, 146.34, 146.39, 146.97, 148.33, 151.02, 153.50, 154.09, 202.56.

HRMS Calcd. for  $\text{C}_{75}\text{H}_{14}\text{FeO}_2$ : 1002.0343. Found: 1002.0331.

***5'-(2-Thienyl)-fullereno- $\text{C}_{60}$ - [1', 9': 6,7][8] oxabicyclo [3.2.1] octan-2'-one 66***

$\text{C}_{60}$  **1** (0.050 g,  $6.94 \times 10^{-5}$  mol) dissolved in 50 mL dry toluene was treated with diazo ketone **45** (0.015 g,  $7.21 \times 10^{-5}$  mol) in 10 mL toluene in presence of a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$ , over a period of 90 minutes. Chromatography of the crude product on silica gel column using hexane-

toluene mixtures afforded the product **66** as a black solid (0.033 g, 53%, 82% based on recovered C<sub>60</sub>).

IR (KBr)  $\nu_{\max}$  : 525, 698, 890, 1420, 1513, 1725 cm<sup>-1</sup>.

<sup>1</sup>H NMR :  $\delta$  3.13-3.32 (m, 2H), 3.54-3.61 (m, 1H), 3.74-3.83 (m, 1H), 5.98 (s, 1H), 7.02 (dd, 1H,  $J_1 = 5.0$  Hz,  $J_2 = 3.6$  Hz), 7.30 (dd, 1H,  $J_1 = 5.1$  Hz,  $J_2 = 1.1$  Hz), 7.37 (dd, 1H,  $J_1 = 3.5$  Hz,  $J_2 = 1.1$  Hz).

<sup>13</sup>C NMR :  $\delta$  33.57, 37.68, 74.78, 79.54, 91.76, 92.17, 124.94, 125.53, 127.09, 134.63, 135.73, 136.97, 137.55, 139.08, 140.11, 140.16, 140.25, 141.31, 141.44, 141.47, 141.52, 141.74, 141.94, 142.10, 142.20, 142.32, 142.63, 142.66, 142.95, 143.09, 143.96, 144.06, 144.13, 144.35, 144.40, 144.54, 144.84, 144.98, 145.04, 145.16, 145.25, 145.38, 145.61, 145.70, 145.84, 145.94, 146.01, 146.10, 146.20, 146.23, 146.30, 146.42, 147.01, 147.08, 147.77, 150.43, 152.56, 153.22, 200.41.

HRMS Calcd. for C<sub>69</sub>H<sub>8</sub>O<sub>2</sub>S: 900.02508. Found: 900.02489.

***5'-(Methyl)-fullereno-C<sub>60</sub> [1', 9': 6,7][8] oxabicyclo [3.2.1] octan-2'-one***  
**68**

C<sub>60</sub> **1** (0.072 g, 1×10<sup>-4</sup> mol) dissolved in 72 mL dry toluene was treated with diazo ketone **44** (0.014 g, 1×10<sup>-4</sup> mol) in 15 mL toluene in presence of a catalytic amount of Rh<sub>2</sub>(OAc)<sub>4</sub>, over a period of 120 minutes. Chromatography of the crude product on silica gel column using hexane-

toluene mixtures afforded the product **68** as a black solid (0.033 g, 40%, 87% based on recovered C<sub>60</sub>).

IR (KBr)  $\nu_{\max}$  : 864, 1220, 1395, 1457, 1501, 1539, 1645, 1732, 2850, 2942 cm<sup>-1</sup>.

<sup>1</sup>H NMR :  $\delta$  2.25 (s, 3H), 2.88-3.10 (m, 3H), 3.50-3.66 (m, 1H), 5.77 (s, 1H).

<sup>13</sup>C NMR :  $\delta$  27.23, 33.66, 37.14, 75.62, 78.13, 89.64, 92.15, 134.93, 135.53, 136.77, 137.51, 139.70, 140.17, 140.30, 141.46, 141.58, 141.63, 141.85, 141.89, 141.93, 142.04, 142.05, 142.12, 142.57, 142.64, 142.68, 142.85, 142.95, 143.12, 143.94, 144.14, 144.34, 144.40, 144.43, 144.64, 144.86, 145.04, 145.09, 145.19, 145.36, 145.46, 145.51, 145.62, 145.77, 145.87, 145.95, 146.05, 146.16, 146.34, 146.95, 147.04, 148.62, 151.49, 153.24, 153.49, 201.12.

HRMS Calcd. for C<sub>66</sub> H<sub>8</sub> O<sub>2</sub>: 832.05243; Found: 832.05146.

***4'-(Methyl)-3'-spiro[cyclopropane-1] fullereno-C<sub>60</sub>-[1', 9'-5, 6][7] oxabicyclo [2,2,1] heptan-2'-one 70***

C<sub>60</sub> **1** (0.072 g, 1×10<sup>-4</sup> mol) dissolved in 72 mL dry toluene was treated with diazo ketone **46** (0.015 g, 1×10<sup>-4</sup> mol) in 15 mL toluene in presence of a catalytic amount of Rh<sub>2</sub>(OAc)<sub>4</sub>, over a period of 120 minutes. Chromatography of the crude product on silica gel column using hexane-toluene mixtures afforded the product **70** as a black solid (0.045 g, 54%, 92% based on recovered C<sub>60</sub>).

IR (KBr)  $\nu_{\max}$  : 525, 824, 1016, 1381, 1507, 1745  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  1.35-1.45 (m, 2H), 1.70-1.75 (m, 1H), 1.93-1.99 (m, 1H), 2.13 (s, 3H), 5.96 (s, 1H).

$^{13}\text{C}$  NMR :  $\delta$  15.55, 15.65, 16.77, 39.38, 74.61, 80.02, 90.57, 93.24, 139.85, 139.89, 139.98, 140.33, 139.85, 139.89, 139.98, 140.33, 141.53, 141.73, 141.82, 141.89, 141.94, 142.05, 142.18, 142.51, 142.62, 142.65, 142.95, 143.03, 144.06, 144.16, 144.24, 144.54, 144.66, 145.19, 145.25, 145.31, 145.47, 145.51, 145.56, 145.69, 145.80, 145.92, 145.95, 145.98, 146.18, 146.27, 146.95, 147.05, 149.21, 150.40, 151.47, 153.08, 208.21.

DEPT-135 : 16.77, 90.54: Positive; 15.56, 15.68: Negative.

HRMS Calcd. for  $\text{C}_{67}\text{H}_8\text{O}_2$ : 844.05243. Found: 844.05060.

***Dimerized product 73***

mp : 146-148° C

IR (KBr)  $\nu_{\max}$  : 3089, 2878, 1751, 1701, 1589, 1334, 1222, 1147, 1060, 973, 768  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  8.06-8.03 (m, 2H), 7.89-7.86 (m, 2H), 7.35-7.25 (m, 3H), 7.18-7.16 (m, 2H), 4.23 (s, 1H).

$^{13}\text{C}$  NMR :  $\delta$  197.82, 142.63, 135.75, 133.06, 128.87, 128.66, 127.72, 123.66, 96.22, 59.57.

Analysis Calcd. for  $\text{C}_{30}\text{H}_{20}\text{O}_4$ : C, 81.07; H, 4.54. Found: C, 80.54; H, 4.43.

### 2.3.3 GENERAL PROCEDURE FOR THE REACTION OF ALLENAMIDES WITH [60] FULLERENE

To a solution of  $C_{60}$  (1 equivalent) in dry toluene (1 mL/mg) was added the appropriate allenamide (1.3 equivalents) in toluene. The reaction mixture was thoroughly deoxygenated using argon. The reaction mixture was then heated to reflux under an atmosphere of argon for 12 hours. The solvent was removed under reduced pressure and the contents were charged on a silica gel column and eluted with toluene. The unreacted  $C_{60}$  was eluted first and then eluting with toluene-ethyl acetate mixture (9:1) afforded the product.

#### *Cyclobutane derivative 77*

$C_{60}$  **1** (0.036 g,  $5 \times 10^{-5}$  mol) was dissolved in 36 mL toluene and to this solution allenamide **76** (0.0080 g,  $6.50 \times 10^{-5}$  mol) in 2 mL toluene was added. The reaction mixture was refluxed for 12 hours under an atmosphere of argon. Purification according to the standard procedure afforded the product **77** (0.019 g, 45%, 60% based on recovered  $C_{60}$ ).

IR (KBr)  $\nu_{\max}$  : 915, 1273, 1395, 1511, 1687, 2885, 2976  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  2.23-2.33 (m, 2H), 2.58-2.64 (m, 2H), 4.19-4.30 (m, 1H), 4.37-4.45 (m, 1H), 5.93 (t, 1H,  $J = 2.09$  Hz), 6.29 (t, 1H,  $J = 2.13$  Hz), 7.00 (br s, 1H).

$^{13}\text{C}$  NMR :  $\delta$  19.16, 30.93, 45.19, 62.35, 73.08, 74.46, 115.38, 136.51, 136.82, 137.59, 138.75, 140.49, 140.53, 140.61, 140.77, 141.37, 141.80, 141.84, 141.94, 141.97, 142.04, 142.28, 142.31, 142.35, 142.61, 142.68, 142.72, 142.77, 142.88, 144.17, 144.24,



**Cyclobutane derivative 83**

$C_{60}$  **1** (0.095 g,  $1.31 \times 10^{-4}$  mol) was dissolved in 95 mL toluene and to this solution allenamide **81** (0.025 g,  $1.7 \times 10^{-4}$  mol) in 2 mL toluene was added. The reaction mixture was refluxed for 12 hours under an atmosphere of argon. Purification according to the standard procedure afforded the product **82** (0.032 g, 28%, 38% based on recovered  $C_{60}$ )

IR (KBr)  $\nu_{\max}$  : 519, 1410, 1507, 1553, 1653, 2925  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  1.87-2.19 (m, 6H), 2.84-2.86 (m, 2H), 4.11-4.19 (m, 1H), 4.62-4.69 (m, 1H), 6.04 (s, 1H), 6.40 (s, 1H), 7.45 (s, 1H).

$^{13}\text{C}$  NMR :  $\delta$  37.68, 47.22, 66.60, 73.10, 74.83, 115.00, 136.72, 137.78, 138.82, 140.56, 140.69, 140.81, 141.42, 141.75, 141.87, 142.00, 142.10, 142.36, 142.41, 142.65, 142.71, 142.88, 144.27, 144.64, 145.03, 145.07, 145.14, 145.17, 145.26, 145.31, 145.45, 145.51, 145.77, 145.80, 145.85, 145.89, 145.91, 146.02, 146.55, 146.76, 146.82, 147.57, 147.66, 147.81, 149.66, 150.48, 151.82, 153.92, 176.49.

**2.4 REFERENCES**

1. Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
2. Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.
3. Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097.

4. Tokuyama, H.; Yamago, S.; Nakamura, E.; Shiraki, T.; Sugiura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7918.
5. Friedman, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506.
6. Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Castoro, J. A.; Wilkins, C.; Friedman, S. H.; DeCamp, D. L.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6510.
7. Hirsh, A. *The Chemistry of Fullerenes*; George Thieme Verlag: Stuttgart; 1994, 79.
8. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186.
9. Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157.
10. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7300.
11. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *114*, 7301.
12. Shi, S.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656.
13. Smith III, A. B.; Strongin, R. M.; Brard, L.; Frust, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829.
14. Prato, M.; Suzuki, T.; Wudl, F.; Lucchini, V.; Maggini, M. *J. Am. Chem. Soc.* **1993**, *115*, 7876.
15. Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479.

16. Prato, M.; Biacco, A.; Maggini, M.; Scorrano, G.; Toniolo, C.; Wudl, F. *J. Org. Chem.* **1993**, *58*, 5578.
17. Wooley, L.; Hawker, C. J.; Frechet, J. M. J.; Wudl, F.; Srdanov, G.; Shi, S.; Li, Q.; Kao, M. *J. Am. Chem. Soc.* **1993**, *115*, 9836.
18. Isaacs, L.; Diederich, F. *Helv. Chem. Acta.* **1993**, *76*, 2454.
19. Skiebe, A.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1994**, 335.
20. Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chem. Acta.* **1993**, *76*, 1231.
21. Prato, M.; Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148.
22. Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
23. Wu, S. H.; Sun, W. Q.; Zhang, D. W.; Shu, L. H.; Wu, H. M.; Xu, J. F.; Lao, X. F. *J. Chem. Soc., Perkin. Trans. I* **1998**, 1733.
24. Meier, M. S.; Poplawska, M. *J. Org. Chem.* **1993**, *58*, 4524.
25. Gonzales, R.; Knight, B. W.; Wudl, F.; Semones, M. A.; Padwa, A. *J. Org. Chem.* **1994**, *59*, 7949.
26. Niclas, H. J.; Duczek, W. *Tetrahedron Lett.* **1995**, *36*, 2457.
27. Matsubara, Y.; Tada, H.; Nagese, S.; Yoshida, Z. *J. Org. Chem.* **1995**, *60*, 5372.
28. Ovcharenko, A. A.; Chertkov, V. A.; Karchava, A. V.; Yurovskaya, M. A. *Tetrahedron Lett.* **1997**, *38*, 6933.
29. Averdung, J.; Albrecht, E.; Lauterwein, J.; Luftmann, H.; Mattay, J.; Mohn, H.; Müller, W. H.; Meer, H-U. *Chem. Ber.* **1994**, *127*, 787.
30. Ohno, M.; Yoshiro, A.; Eguchi, S. *Synlett* **1996**, 815.

31. Ishida, H.; Ohno, M. *Tetrahedron Lett.* **1999**, *40*, 1543.
32. (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572.  
(b) Griffin, G. W.; Padwa, A. in *Photochemistry of Heterocyclic Compounds*; Buchart, O., Ed.; Wiley: New York, 1976; Chapter 2.
33. Das, P. K.; Griffin, G. W. *J. Photochem.* **1985**, *27*, 317.
34. Bèkhazi, M.; Smith, P. J.; Warkentin, J. *Can. J. Chem.* **1984**, *62*, 1646.
35. Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 4260.
36. Hoffmann, R. W.; Luthardt, H. *J. Chem. Ber.* **1968**, *101*, 3861.
37. (a) Keus, D.; Kaminski, M.; Warkentin, J. *J. Org. Chem.* **1984**, *49*, 343. (b) Bèkhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1983**, *105*, 1289. (c) Bèkhazi, M.; Warkentin, J. *Can. J. Chem.* **1983**, *61*, 619.
38. Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348.
39. Maas, G. *Top. Curr. Res.* **1987**, *137*, 75.
40. Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.
41. Wulff, W. D. in *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ed.; Pergamon Press: New York, 1990, Vol. 5.
42. For a review, see Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. in *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley Interscience: New York, 1978; Part 2, Chapter 18.
43. Paulissen, R.; Reimlinger, E.; Hayez, E.; Hubert, A. J.; Teyssié, P. *Tetrahedron Lett.* **1973**, *14*, 2233.
44. Padwa, A.; Austin, D. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1797.

45. (a) Paulissen, R.; Reimlinger, E.; Hayez, E.; Hubert, A. J.; Teyssie, P. *Tetrahedron Lett.* **1974**, *15*, 607. (b) Petinoit, N.; Noels, A. F.; Anciaux, A. J.; Hubert, A. J.; Teyssié, P. in *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum: New York, 1979; Vol. 3, p 421. (c) Hubert, A. J.; Noels, A. F.; Anciaux, A. J.; Teyssié, P. *Synthesis* **1976**, 600.
46. Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348.
47. (a) Hubert, A. J.; Noels, A. F.; Anciaux, A. J.; Teyssié, P. *J. Chem. Soc., Chem. Commun.* **1980**, 765. (b) Anciaux, A. J.; Hubert, A. F.; Noels, N.; Petiniot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695.
48. Padwa, A. *Acc. Chem. Res.* **1991**, *24*, 22.
49. (a) Ibata, T.; Toyoda, J.; Sawada, M.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1266. (b) Ibata, T.; Toyoda, J. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2489. (c) Veda, K.; Ibata, T.; Takebayashi, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2779.
50. Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Org. Chem.* **1988**, *53*, 2875.
51. (a) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100. (b) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223.
52. Jagerovic, N.; Elguero, J.; Abagnac, J. L.; *J. Chem. Soc., Perkin Trans. 1* **1996**, 499.
53. Lehn, J.-M. *Angew. Chem., Int. Ed. Eng.* **1990**, *29*, 1304.
54. Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519.
55. (a) Prato, M.; Maggini, M.; Scorrano, G. *J. Org. Chem.* **1993**, *58*, 3613.

- (b) Yamago, S.; Takeichi, A.; Nakamura, E. *J. Am. Chem. Soc.* **1994**, *116*, 1123.
- (c) Mehta, G.; Viswanath, M. B. *Tetrahedron Lett.* **1995**, *36*, 5631.
56. (a) Broggin, G.; Bruche, L.; Zecchi, G. *J. Chem. Soc., Perkin Trans. 1* **1990**, 533.
- (b) Wei, L.-L.; Xiong, H.; Douglas, C.J.; Hsung, R. P. *Tetrahedron Lett.* **1999**, *40*, 6903.
- (c) Horino, Y.; Kimura, M.; Wakamiya, Y.; Okajima, T.; Tamaru, Y. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 121.
57. Vogel, A. I.; *Text Book of Practical Organic Chemistry*; Fourth Edition, ELBS: 1978, pp 778.
58. Graham, P. J.; Lindsey, R. V.; Parshall, G. W.; Peterson, M. L. *J. Am. Chem. Soc.* **1957**, *79*, 3416.

# CHAPTER 3

## DIPOLAR CYCLOADDITION REACTIONS OF NITRILE YLIDES AND CARBONYL YLIDES WITH 1,2-DIONES

### 3.1 GENERATION AND REACTIONS OF NITRILE YLIDES

#### 3.1.1 INTRODUCTION

The name nitrile ylide was conceived by Huisgen while developing the concept of 1,3-dipolar cycloadditions.<sup>1</sup> It has a triad of atoms (C-N-C), that has a  $\pi$ -system of four electrons and three ligands linked to the carbon atoms. It is possible to write three electronic arrangements with a linear C-N-C framework; they are the 2-azonia -1-allenide **1**, the 2-azonia-1-propynide **2**, and the 2-azapropene -1,3-diyl **3** (Figure 1).

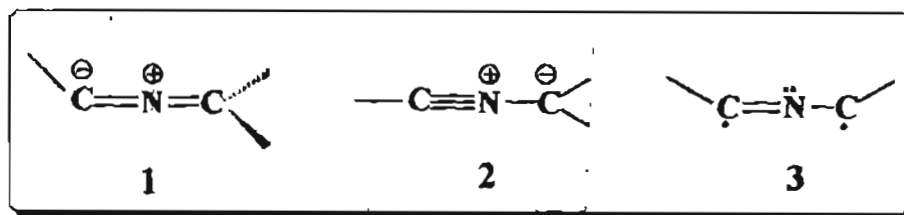


Figure 1

Nitrile ylides are isomeric with isocyanides and isoelectronic with nitrous oxide. Nitrile ylides, along with nitrile imines, oxides, sulfides,

and selenides, belong to the general category of *nitrilium betaines* and can be represented by the structural type 4 (Figure 2).

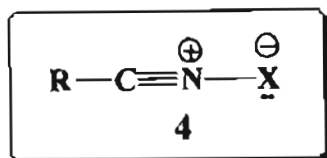
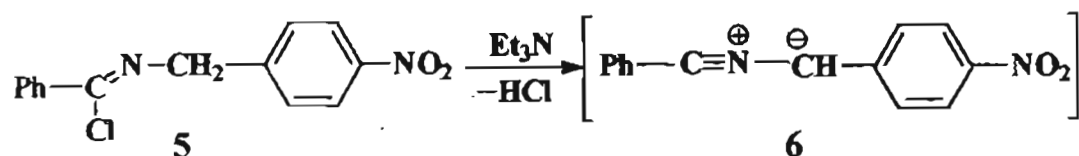


Figure 2

Chemistry of nitrile ylides has received the attention of organic chemists both from synthetic and theoretical standpoints and a number of methods have been developed for the generation of nitrile ylides.

### 3.1.2 GENERATION OF NITRILE YLIDES

The very first nitrile ylide, named benzonitrilio *p*-nitrophenylmethanide 6, was prepared from *N*-(*p*-nitrobenzyl) benzimidoylchloride 5 in presence of triethylamine at room temperature (Scheme 1).<sup>2</sup>



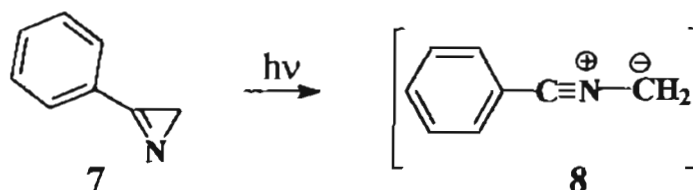
Scheme 1

Since imidoyl chlorides can be easily prepared from *N*-monoalkylated carboxamides and chlorides like  $\text{SOCl}_2$ ,  $\text{PCl}_5$ ,  $\text{COCl}_2$ , the base catalysed elimination of hydrogen chloride from imidoyl chlorides represents a general method for the *in situ* preparation of nitrile ylides.

The photochemical ring opening reaction of easily accessible 2*H*-azirine system represents the most versatile route to nitrile ylides. An illustrative example is the irradiation of 3-phenyl 2*H*-azirine 7 with a high pressure mercury lamp in solvents like benzene, cyclohexane or

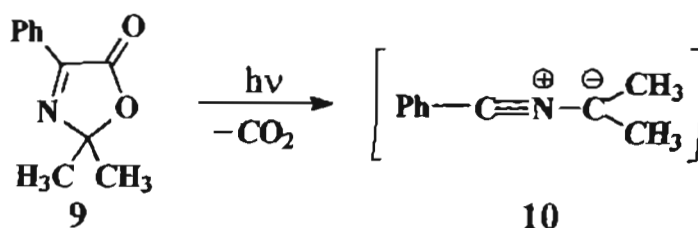


acetonitrile at room temperature, resulting in the efficient formation of nitrile ylide **8** (Scheme 2).<sup>3,4</sup>



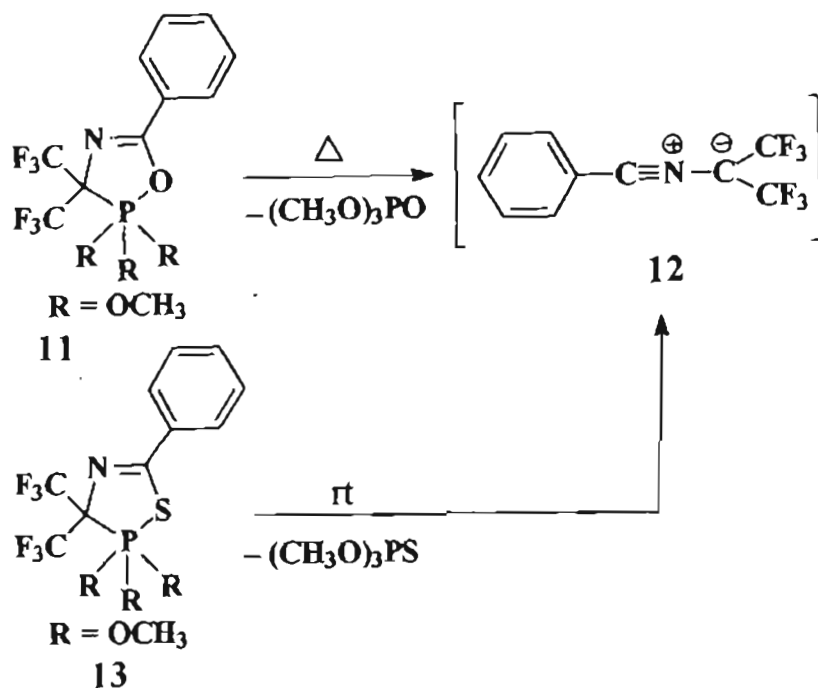
Scheme 2

In addition to the two methods described above, nitrile ylides can be generated by a number of other pathways. It has been reported that carbon dioxide extrusion from oxazolin-5-ones produces nitrile ylides. Thus irradiation of 2,2-dimethyl-4-phenyl-3-oxazolin-5-one **9** results in the loss of  $\text{CO}_2$  leading to the nitrile ylide **10** (Scheme 3).<sup>5</sup>



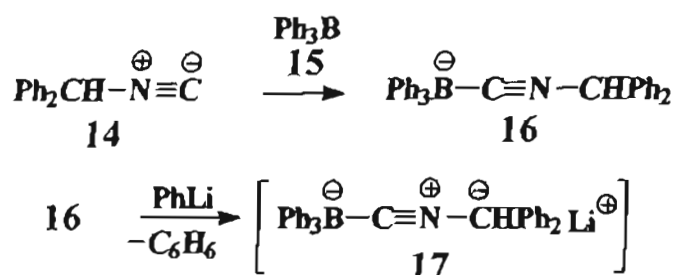
Scheme 3

Alkyl phosphate and thiophosphate extrusion from oxazaphosphole **11** and thiazaphosphole **13** also produces nitrile ylide **12** (Scheme 4).<sup>6</sup>



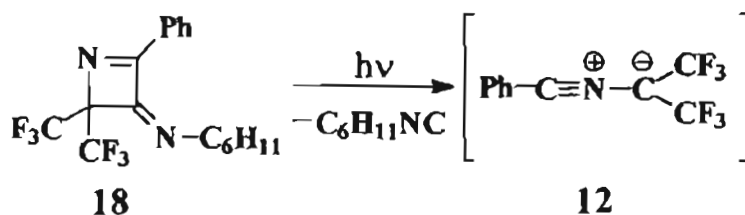
Scheme 4

It has been reported that addition of isocyanide 14 to triphenylborane 15 leads to nitrile ylide 17 (Scheme 5).<sup>7</sup>

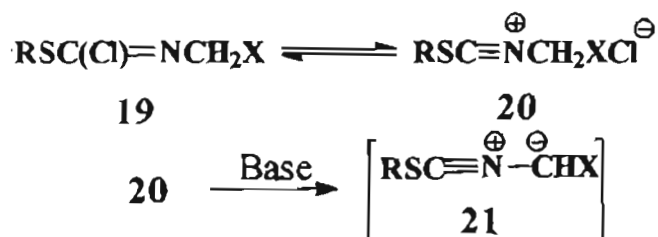


Scheme 5

Isocyanide extrusion from 3-imino-1-azetines 18 (Scheme 6)<sup>8</sup> and base mediated reactions of iminochlorosulphides 19 (Scheme 7)<sup>9</sup> are also known to produce nitrile ylides 12 and 21 respectively.

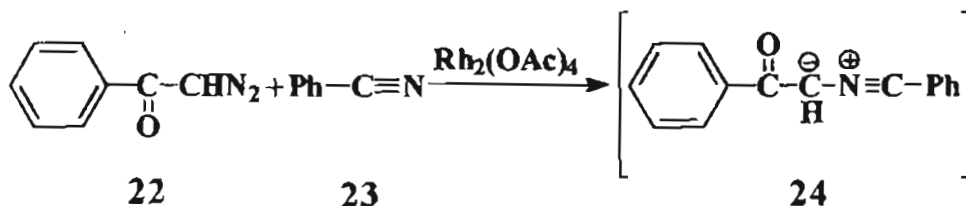


Scheme 6



Scheme 7

$\text{Rh}_2(\text{OAc})_4$  catalyzed reaction of  $\alpha$ -diazocarbonyl compound **22** with benzonitrile **23** produces acyl substituted nitrile ylide **24** (Scheme 8).<sup>10</sup>



Scheme 8

### 3.1.3 [2+3] CYCLOADDITION REACTIONS OF NITRILE YLIDES

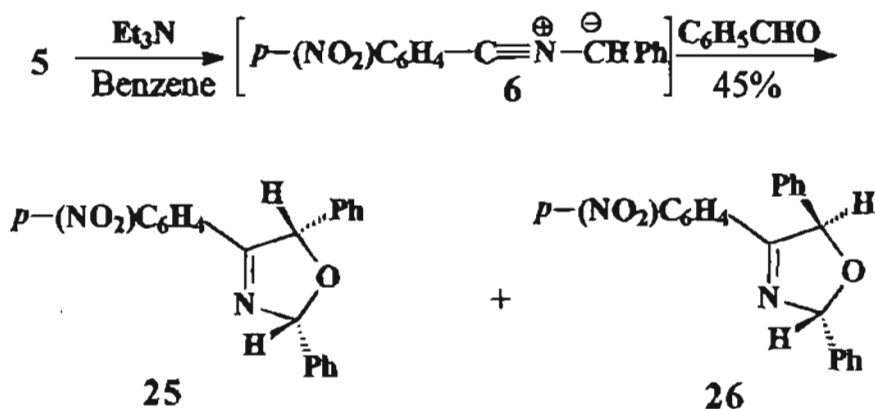
#### Reactions of Activated Alkenes, Allenes and Acetylenes

Activated alkenes, acetylenes, and allenes carrying electron acceptor groups react efficiently with nitrile ylides in a [2+3] manner. Thus acenaphthylene,<sup>2</sup> norbornene,<sup>11</sup> styrene,<sup>12</sup> vinyl pyridine,<sup>13</sup> acrylates,<sup>14</sup> acrylonitriles,<sup>15</sup> fumaric and maleic acid derivatives,<sup>16</sup> vinyl phosphonium bromides<sup>17</sup> and vinyl sulphones<sup>18</sup> undergo dipolar

cycloaddition reactions with nitrile ylides generated by various methods. Methyl allene carboxylates, dimethyl allene 1,3 dicarboxylates, phenyl acetylene, acetylene dicarboxylates and propiolates also react with nitrile ylides in a [2+3] manner.<sup>19</sup>

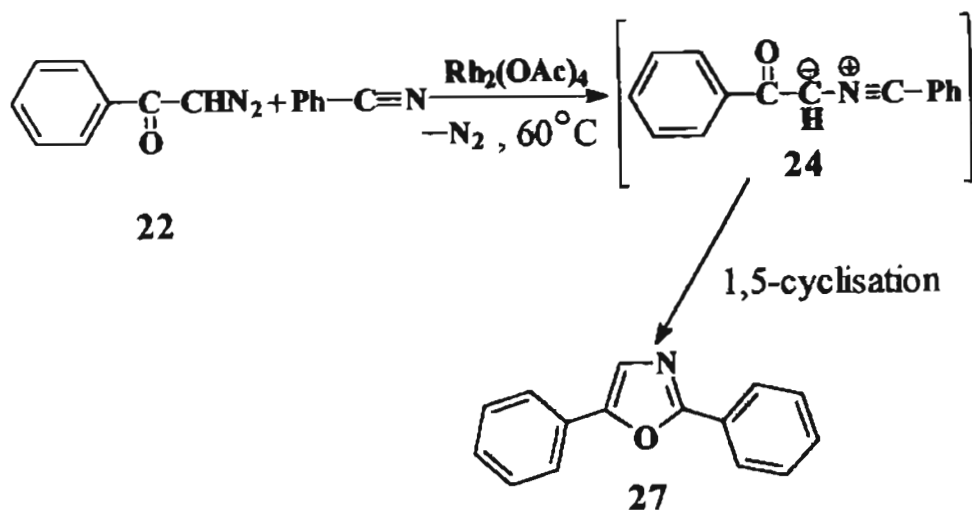
### Reaction of Nitrile Ylides with Carbonyl Compounds

Huisgen and co-workers have observed that aldehydes exhibit pronounced reactivity towards nitrile ylides. Treatment of imidoyl chloride **5** with benzaldehyde in presence of triethylamine in benzene resulted in the formation of *cis* and *trans* 3-oxazolines **25** and **26** (Scheme 9).<sup>20</sup>



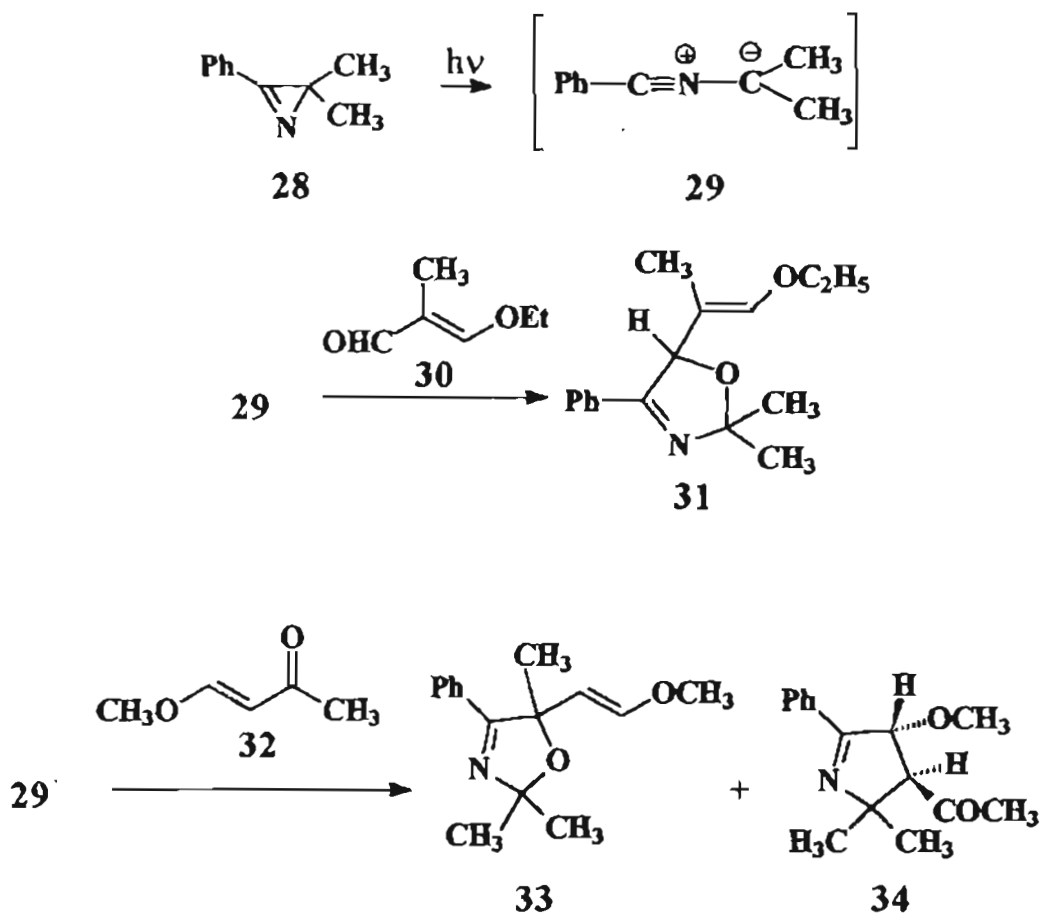
Scheme 9

Ketones like benzophenone,<sup>21</sup> diethylmesoxalate,<sup>20</sup> and ethyl pyruvate<sup>22</sup> have also been found to react with nitrile ylides, leading to oxazoline derivatives. Iyata *et al.* have shown that nitrile ylide **24** generated by the decomposition of  $\alpha$ -diazoketone **22** in presence of  $\text{Rh}_2(\text{OAc})_4$  in benzonitrile, undergoes intramolecular cyclisation leading to oxazole derivative **27** (Scheme 10).<sup>10</sup>



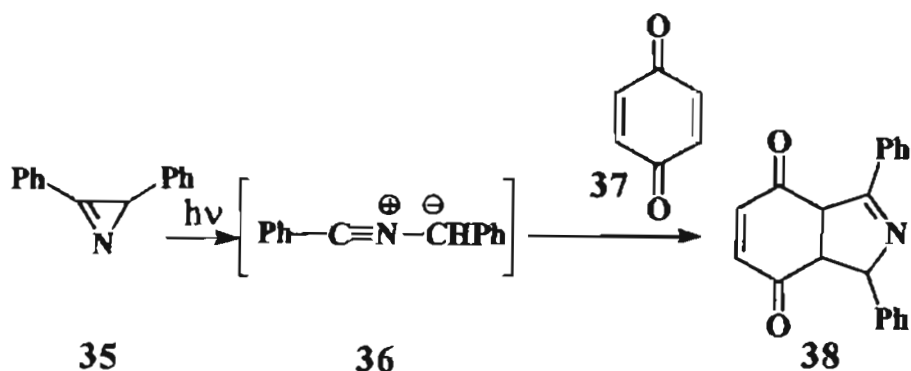
Scheme 10

$\alpha,\beta$ -Unsaturated aldehydes, ketones and 1,4-quinones undergo [2+3] cycloaddition reactions with nitrile ylides across the carbon-carbon and carbon-oxygen double bonds. Irradiation of 2H-azirine 28 in presence of  $\beta$ -ethoxy methacrolien 30 afforded the carbonyl addition product 31 exclusively. However, reaction of 29 with  $\beta$ -methoxy vinyl methyl ketone 32 led to the formation of both carbonyl and carbon-carbon double bond addition products 33 and 34 (Scheme 11).<sup>23</sup>



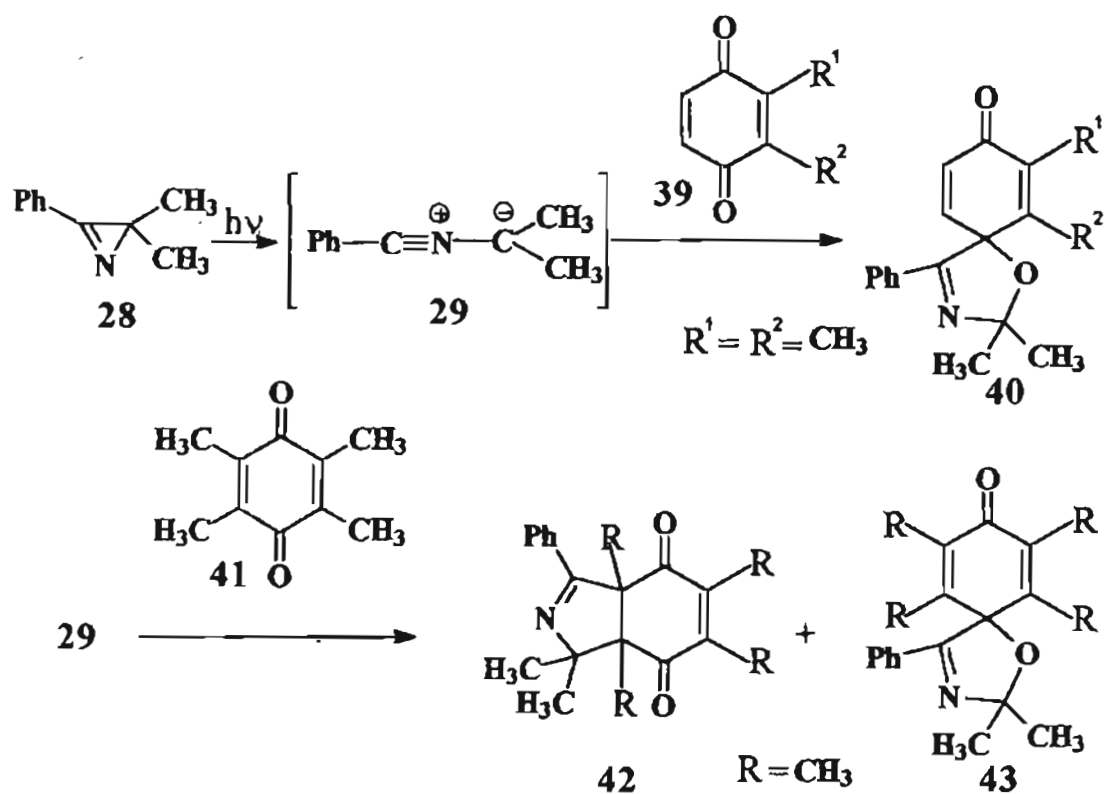
Scheme 11

Reaction of nitrile ylide with 2-cycloalkenones<sup>23</sup> and diethyl chelidonate<sup>24</sup> afforded exclusively the product resulting from addition to the carbon-carbon double bond. In the reaction of 1,4-quinones with nitrile ylides, the [2+3] cycloaddition occurs across the carbon-carbon double bond and the carbonyl group. Irradiation of 2,3-diphenyl 2H-azirine 35 in presence of 1,4-benzoquinone afforded a product 38 which is formed by the [2+3] addition across the carbon-carbon double bond (Scheme 12).<sup>25</sup>



Scheme 12

Irradiation of 2H-azirine 28 in presence of 2,3-dimethyl and tetramethyl 1,4-benzoquinone resulted in the formation of the carbonyl as well as the carbon-carbon double bond addition products 40, 42 and 43 (Scheme 13).<sup>23</sup>

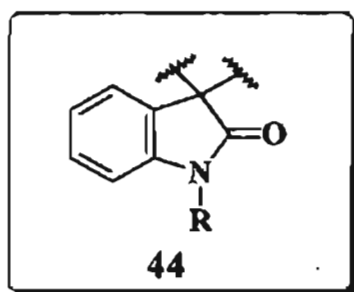


Scheme 13

## 3.2 CYCLOADDITION REACTIONS OF ISATINS

### 3.2.1 INTRODUCTION

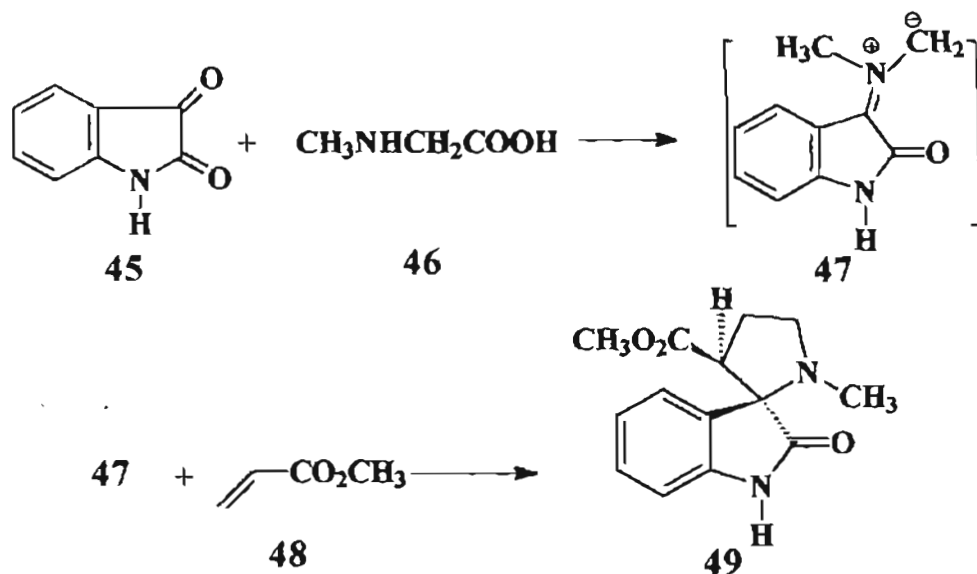
Isatin and its derivatives have interesting biological activities<sup>26-30</sup> and have been widely used as precursors of many natural products. It may be noted that the spirooxindole skeleton **44** (Figure 3) is common to many naturally occurring alkaloids with significant biological activity.



**Figure 3**

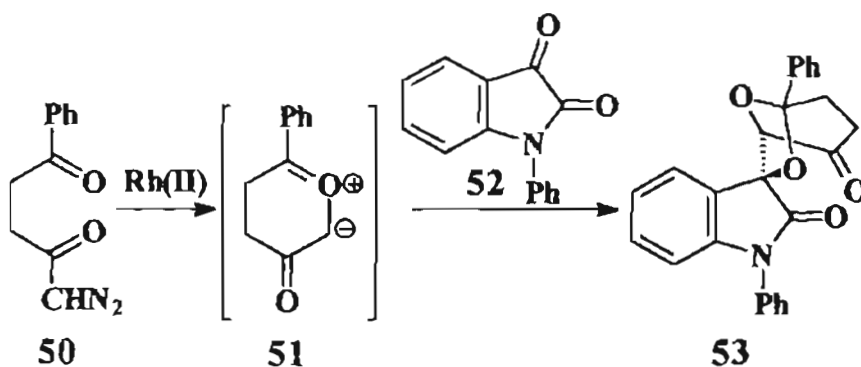
Conceptually, 1,3-dipolar cycloaddition reactions involving isatins can lead to oxindole fused heterocycles. There have been many reports of isatin derived dipoles taking part in cycloaddition reactions with various dipolarophiles. An illustrative example is the [2+3] cycloaddition of dipole **47**, generated from isatin **45** and sarcosine **46**, with methyl acrylate **48** (Scheme 14).<sup>31</sup>





Scheme 14

Very recently, studies in our own laboratory have shown that isatin **52** participates as dipolarophile in cycloaddition reaction with carbonyl ylide **51** to afford novel spirooxindole **53** (Scheme 15).<sup>32</sup>



Scheme 15

Except for this work there has been no report of any cycloaddition in which isatin participates as a dipolarophile.

### 3.2.2 THE PRESENT WORK

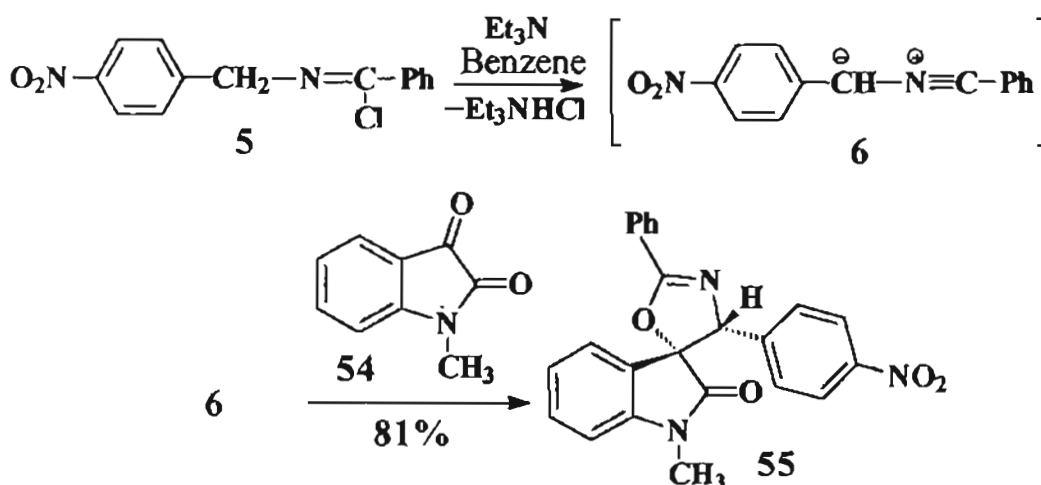
From the literature survey it is clear that there has been no report of dipolar cycloaddition of nitrile ylides with isatins and 1,2-benzoquinones. In the context of our general interest<sup>33, 34</sup> in the dipolar

cycloaddition reactions of 1,2-diones, an investigation was undertaken to gain insight into the reactivity of nitrile ylides towards various 1,2-dicarbonyl compounds such as isatins, acenaphthenequinone and phenanthrenequinone. The details of the investigations carried out are presented here.

### 3.3 RESULTS AND DISCUSSION

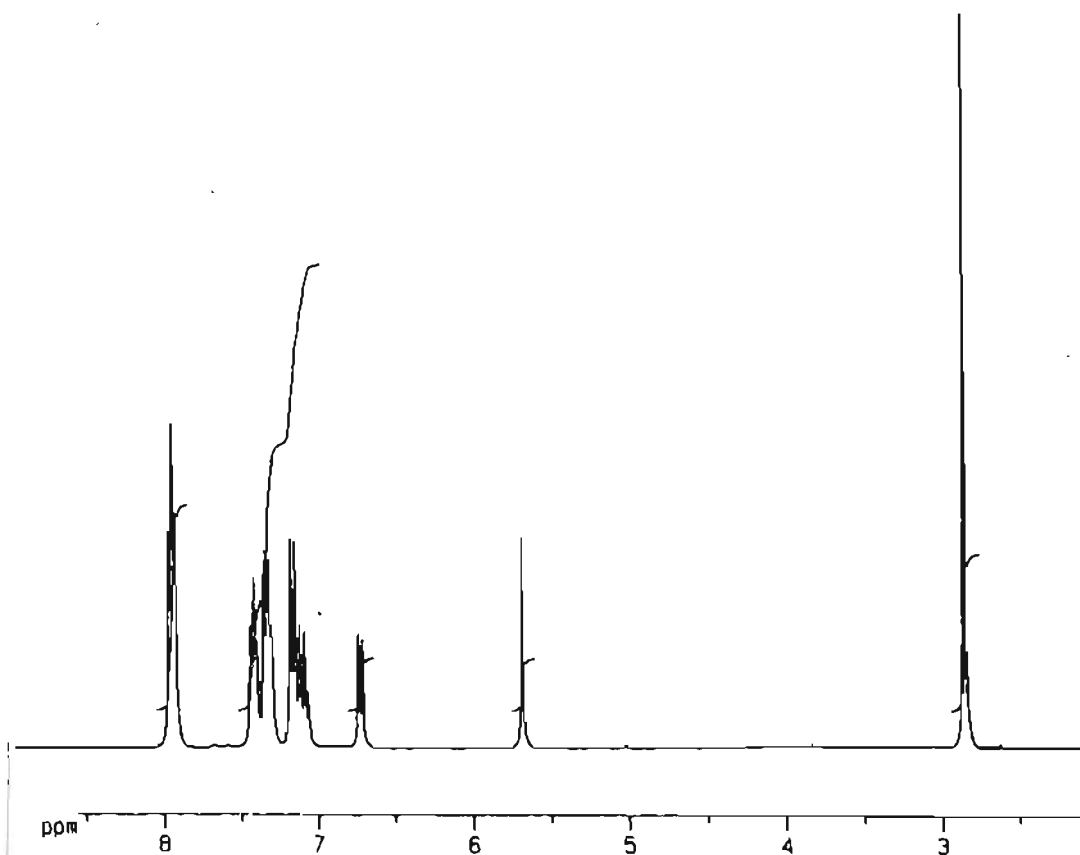
#### 3.3.1 CYCLOADDITION REACTIONS OF NITRILE YLIDES WITH ISATINS

Our studies were initiated with the reaction of nitrile ylide **6**, generated by the base catalyzed reaction of 4-nitro-N-benzyl benzimidoyl chloride **5**, and N-methyl isatin **54** in benzene at room temperature. The reaction proceeded smoothly to afford an oxazoline fused spirooxindole derivative **55** in 81% yield. As expected, the [2+3] addition occurred across the more electrophilic ketonic carbonyl (Scheme 16).



Scheme 16

The product was purified by chromatography on silica gel column, and characterized by spectroscopic analysis. The IR spectrum of **55** showed a band at  $1731\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum, the benzylic and methyl protons resonated as singlets at  $\delta$  5.79 and 2.91 respectively. In the  $^{13}\text{C}$  NMR spectrum of **55**, the amide carbonyl resonated at  $\delta$  171.45 whereas the spirocarbon was discernible at  $\delta$  87.01. The characteristic imine carbon of the oxazoline ring showed a signal at  $\delta$  165.17. These assignments were confirmed by DEPT-135 NMR analysis. In the DEPT-135 NMR spectrum of **55**, peak at  $\delta$  79.29 for the benzylic carbon was positive and the spirocarbon signal at  $\delta$  87.01 disappeared. Finally the structure assigned was confirmed unequivocally by single crystal X-ray analysis (Figures 4, 5, 6 and 7).



**Figure 4.**  $^1\text{H}$  NMR spectrum of **55**

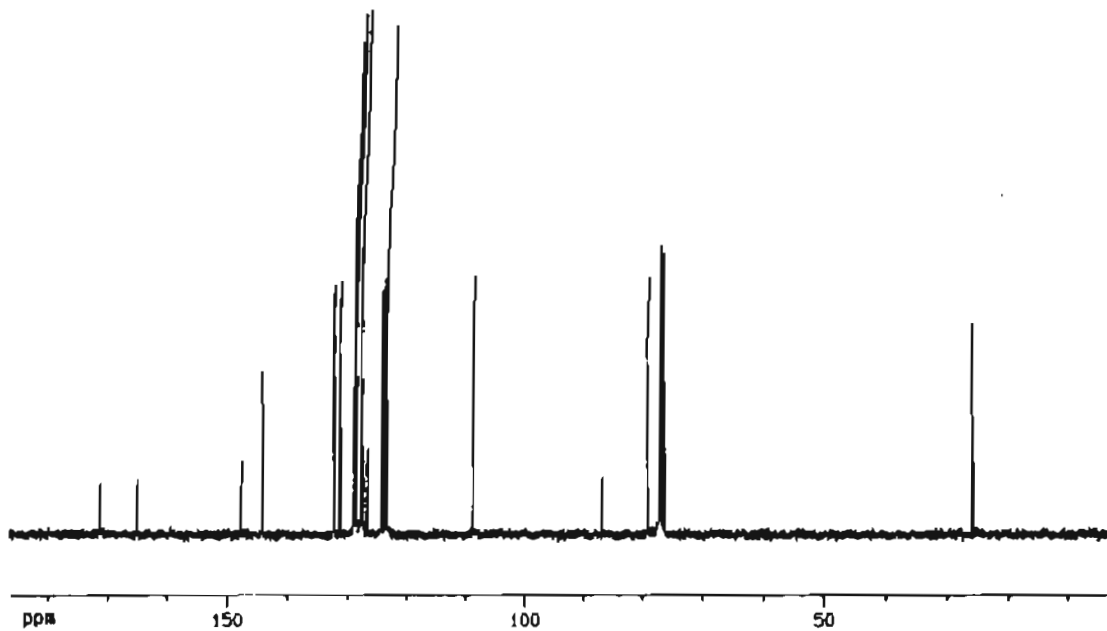


Figure 5.  $^{13}\text{C}$  NMR spectrum of 55

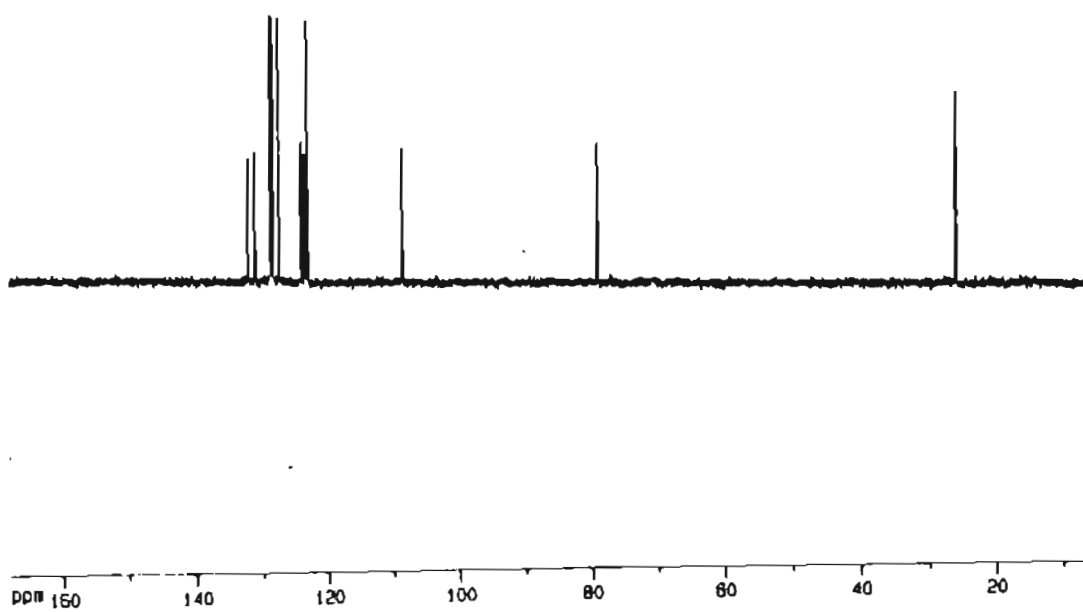
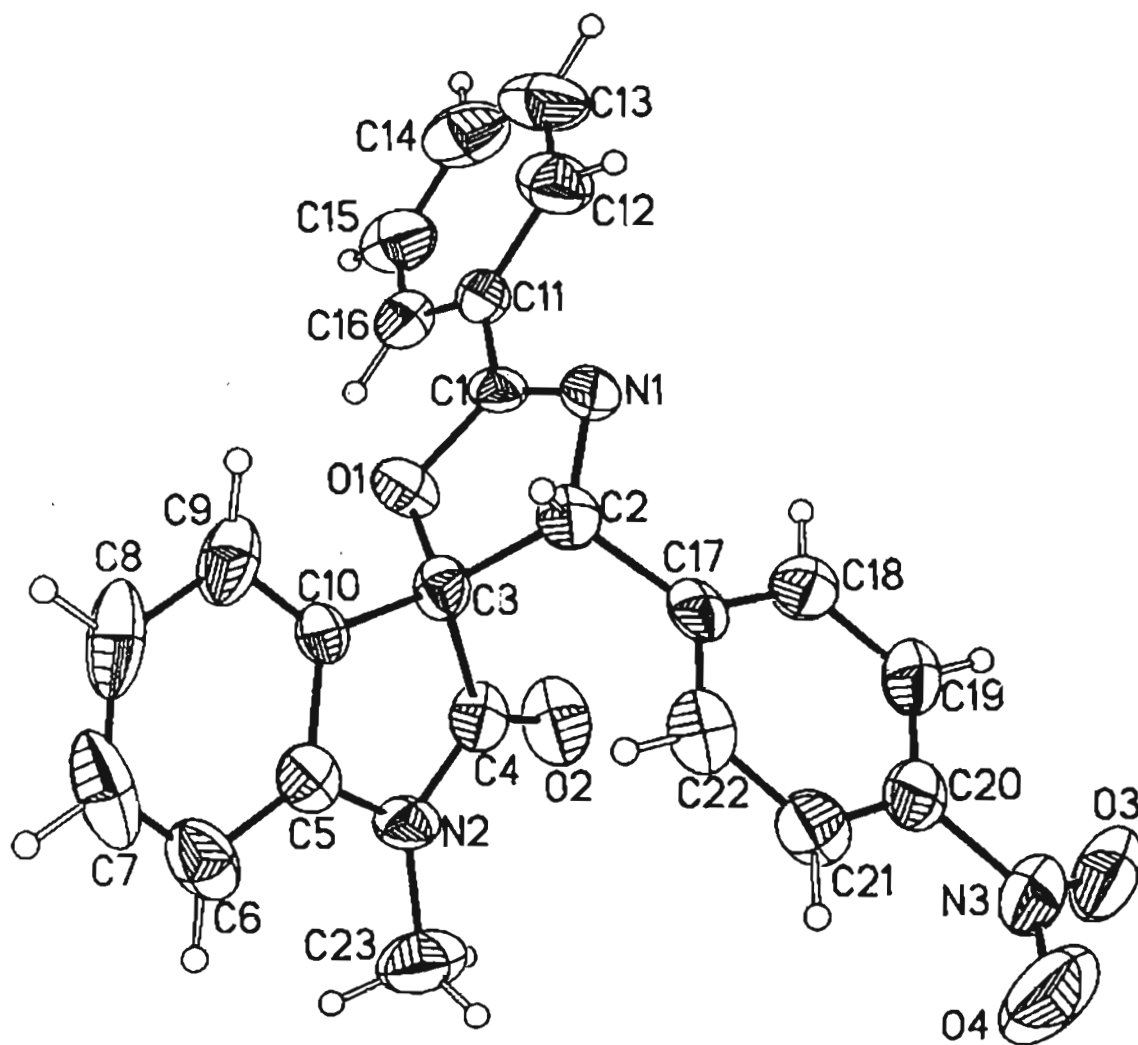


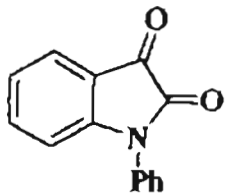
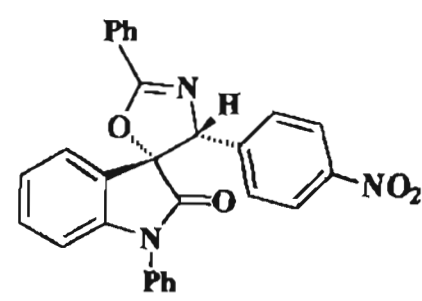
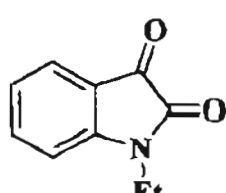
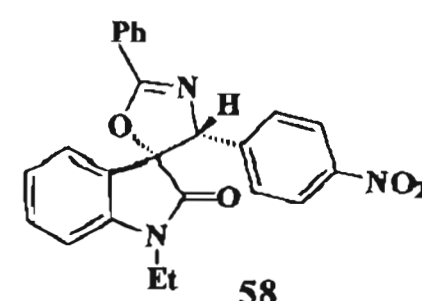
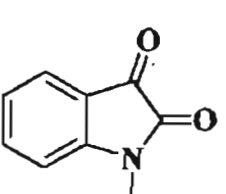
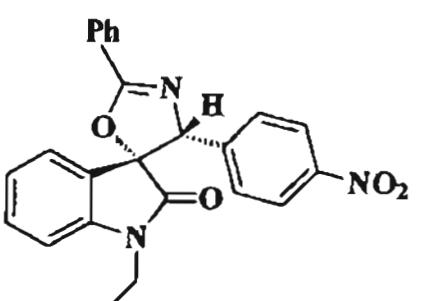
Figure 6. DEPT-135 NMR spectrum of 55



**Figure 7.** X-ray structure of **55**

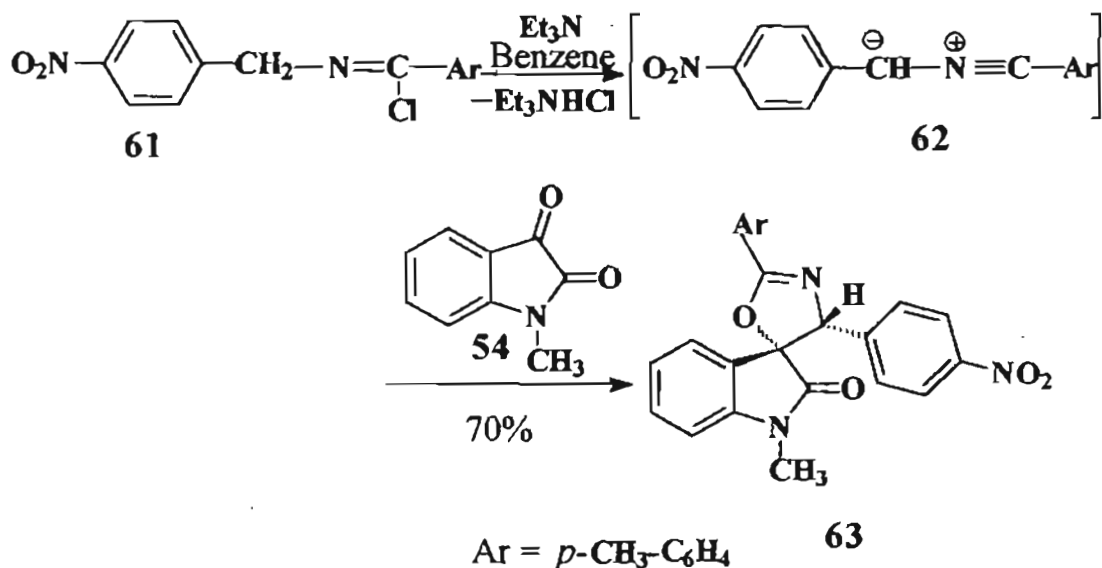
The reaction was extended to other isatins. In all cases, the reaction proceeded smoothly to afford the spirooxindoles. The results are summarized in table 1.

Table 1. [2+3] Cycloaddition Reactions of Nitrile Ylide 6 with Isatins.

| Entry | Isatin  | Product  | Yield(%) |
|-------|---|--|----------|
| 1     | <br>52   | <br>56   | 94       |
| 2     | <br>57  | <br>58  | 83       |
| 3     | <br>59 | <br>60 | 84       |

All the products were fully characterized by spectroscopic analysis.

Similarly, reaction of nitrile ylide **62** derived from 4-nitro-N-benzyl-(4-methyl)benzimidoyl chloride **61**, with N-methyl isatin **54** was carried out. In this case also the reaction proceeded smoothly to afford the spirooxindole **63** in 70% yield (Scheme 17).

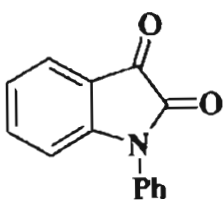
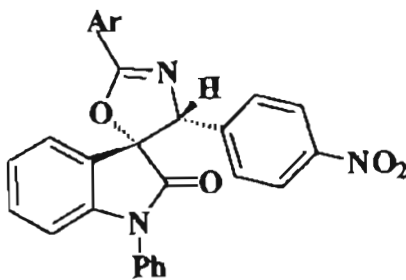
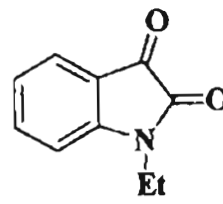
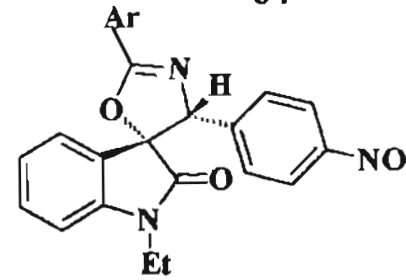
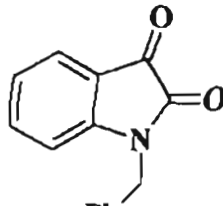
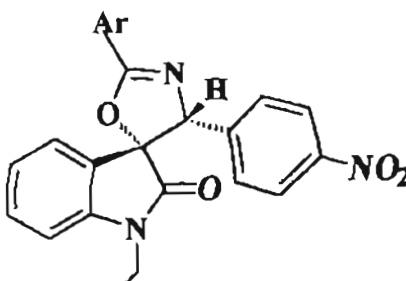


Scheme 17

The product was purified by chromatography on silica gel column and characterized by spectroscopic analysis. The IR spectrum of **63** showed a band at  $1725\text{ cm}^{-1}$  characteristic of the carbonyl group. In the  $^1\text{H}$  NMR spectrum, the benzylic and methyl protons on the oxindole moiety resonated as singlets at  $\delta$  5.77 and 2.91. The methyl group on the aromatic ring was discernible at  $\delta$  2.44. In the  $^{13}\text{C}$  NMR spectrum, the N-methyl and C-methyl carbons resonated at  $\delta$  26.04 and 21.76 respectively. The characteristic signal for the spiro carbon was visible at  $\delta$  86.91 and the benzylic carbon was discernible at  $\delta$  79.32. The carbonyl carbon of the oxindole moiety and the imine carbon of the oxazoline ring resonated at  $\delta$  171.53 and 165.29 respectively.

As in the earlier case, the reaction was repeated with different isatins and the products were obtained in high yields. The results are summarized in table 2.

Table 2. [2+3] Cycloaddition of Nitrile Ylide 62 with Isatins.

| Entry | Isatin  | Product  | Yield(%) |
|-------|---|--|----------|
| 1     | <br>52   | <br>64   | 90       |
| 2     | <br>57  | <br>65  | 89       |
| 3     | <br>59 | <br>66 | 63       |

$Ar = p\text{-CH}_3\text{-C}_6\text{H}_4$

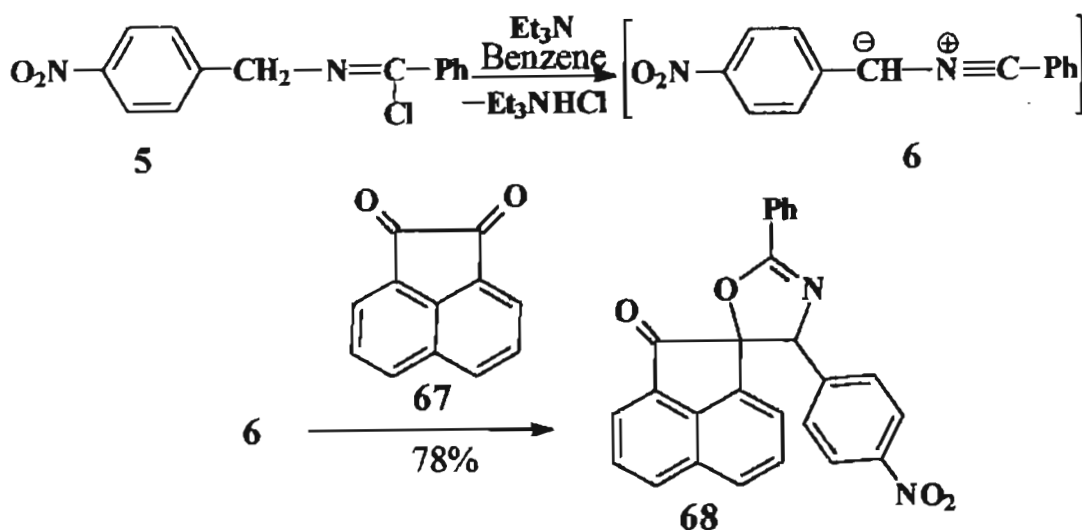
All the products were fully characterized by spectroscopic analysis.

### 3.3.2 REACTIONS OF NITRILE YLIDES WITH 1,2-QUINONES

In view of the encouraging results obtained with the nitrile ylides and isatins it was of interest to study the reaction of nitrile ylides with acenaphthenequinone and phenanthrenequinone. Thus when



acenaphthenequinone **67** was allowed to react with imidoyl chloride **5** in presence of triethylamine, a product was obtained in 78% yield, and this was identified as spirooxazoline **68** (Scheme 18).

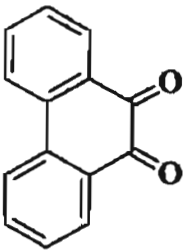
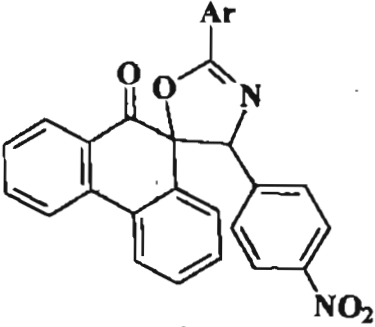
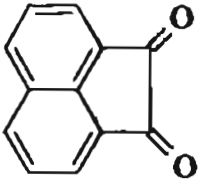
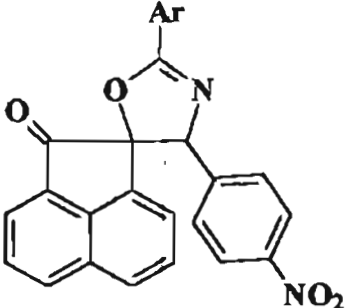
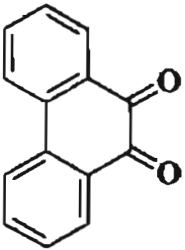
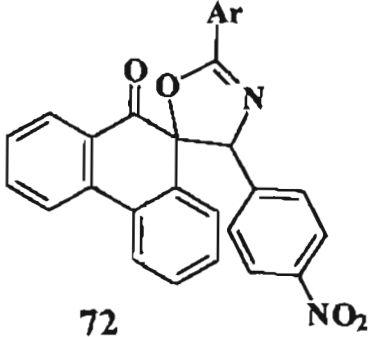


**Scheme 18**

The product was purified by chromatography on silica gel column, and characterized by spectroscopic analysis. The IR spectrum of **68** showed the carbonyl absorption at  $1726\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum, the benzylic proton resonated at  $\delta$  5.99 as a singlet. In the  $^{13}\text{C}$  NMR spectrum of **68** the spirocarbon and the imine carbon of the oxazoline ring resonated at  $\delta$  90.16 and 165.39 respectively. The signal due to the benzylic carbon was present at  $\delta$  79.68 and the carbonyl carbon was discernible at  $\delta$  197.58.

The reaction of **6** with phenanthrenequinone **69** was also performed as described above to afford the corresponding oxazoline derivative **70** in 48% yield. Subsequently, the nitrile ylide generated from 4-nitro-(N-benzyl)-4-methyl benzimidoylchloride **62** was also allowed to react with acenaphthenequinone and phenanthrenequinone. The results are summarized in table 3.

**Table 3.** [2+3] Cycloaddition Reactions of Nitrile ylides **6** and **62** with Phenanthrenequinone and Acenaphthenequinone.

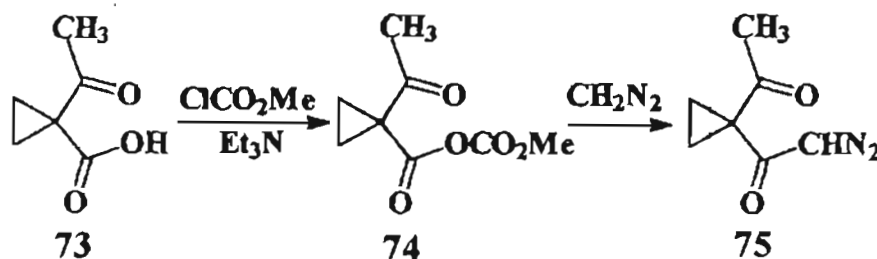
| Entry | Nitrile Ylide | Quinone   | Product   | Yield (%) |
|-------|---------------|---|---|-----------|
| 1     | 6             | <br>69   | <br>70<br>Ar = Ph   | 48        |
| 2     | 62            | <br>67 | <br>71<br>Ar = <i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>  | 83        |
| 3     | 62            | <br>69 | <br>72<br>Ar = <i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> | 54        |

All the products were fully characterized by spectroscopic analysis.

The reaction of nitrile ylide **6** with 3,5-di-*tert*-butyl *o*-benzoquinone was also attempted. Inexplicably the reaction failed and most of the *o*-benzoquinone was recovered as such.

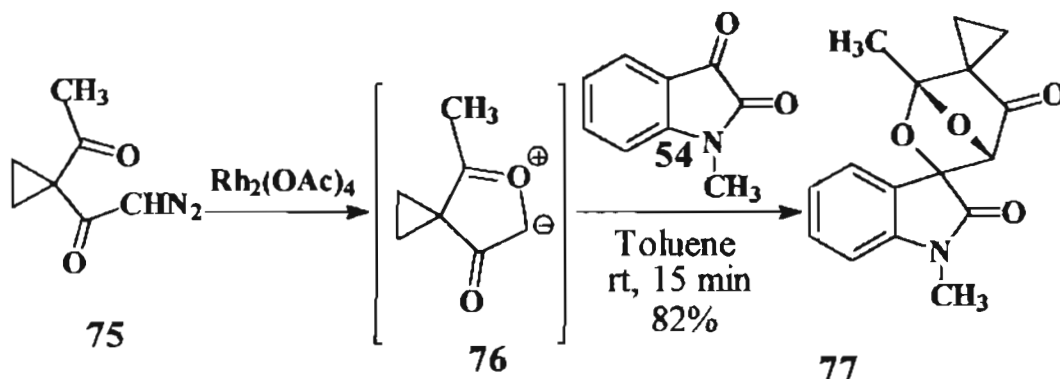
### 3.3.3 REACTIONS OF CYCLIC CARBONYL YLIDE WITH ISATINS

It has been recently observed in our laboratory that six membered carbonyl ylides undergo facile [2+3] cycloaddition reaction with isatins leading to highly oxygenated spirooxindoles.<sup>35</sup> As a logical extension of this work, it was of interest to undertake a study of the reaction of a five membered cyclic carbonyl ylide with isatins. The results of a limited study are presented here. The diazo ketone **75** required for the investigation was conveniently prepared from the corresponding carboxylic acid **73** by the known procedure (Scheme 19).<sup>36</sup>



Scheme 19

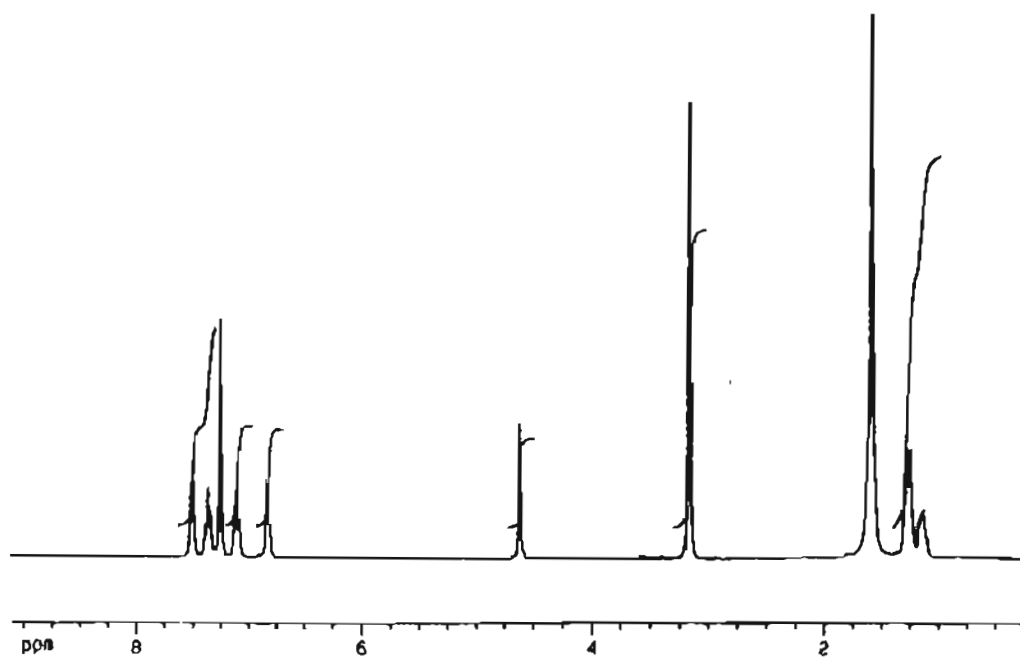
When a mixture of the diazo ketone **75** and *N*-methyl isatin was allowed to react in presence of a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$  at room temperature, the product **77** was obtained in 82% yield (Scheme 20).



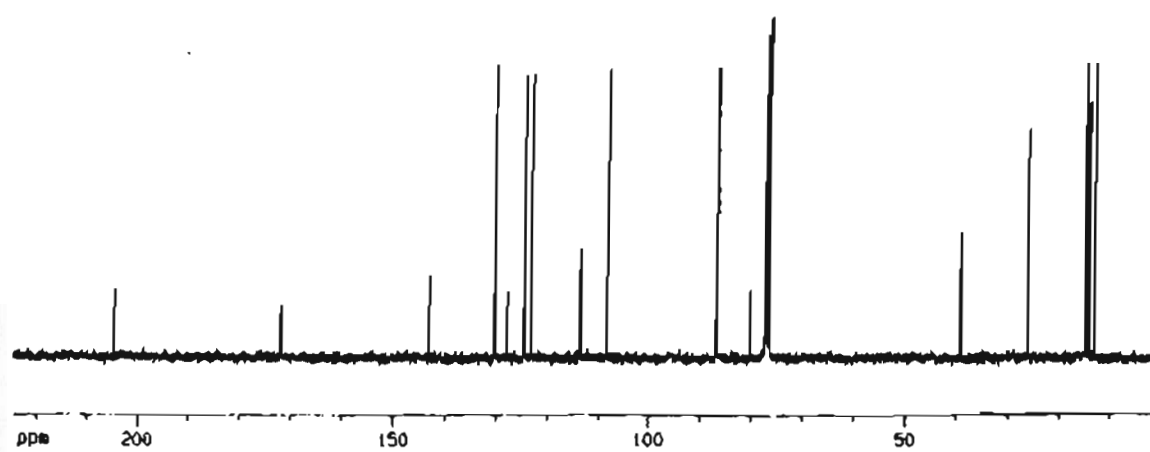
Scheme 20

The product was purified by column chromatography and characterized by spectroscopic analysis. The IR spectrum of **77** showed two carbonyl absorptions at  $1730\text{ cm}^{-1}$  and at  $1684\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum, (Figure 8), the bridgehead proton resonated at  $\delta$  4.62 as a singlet. The N-methyl protons and C-methyl protons resonated at  $\delta$  3.18 and 1.60.

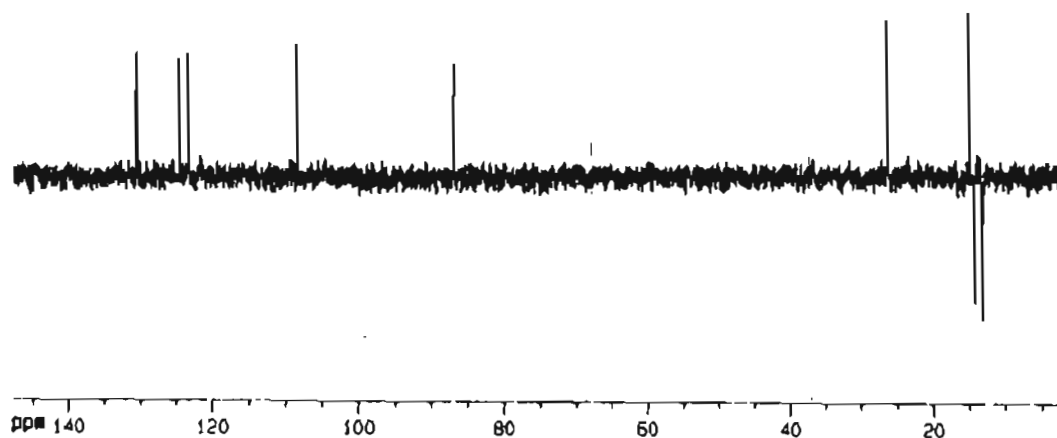
In the  $^{13}\text{C}$  NMR spectrum (Figure 9) of **77**, the spirocarbons of the oxindole ring and cyclopropyl ring resonated at  $\delta$  80.32 and 39.46 respectively. The methine carbon adjacent to the keto group resonated at  $\delta$  86.97 and the spirocarbon at the bridgehead position was discernible at  $\delta$  113.67. The lactam carbonyl and the keto carbonyl were discernible at  $\delta$  172.99 and 204.79. These assignments were confirmed by DEPT-135 NMR analysis (Figure 10).



**Figure 8.**  $^1\text{H}$  NMR spectrum of 77



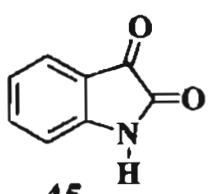
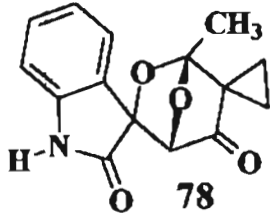
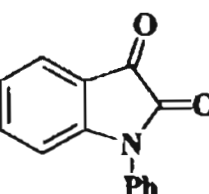
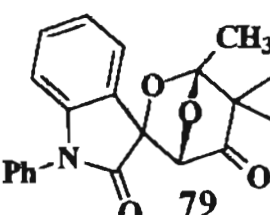
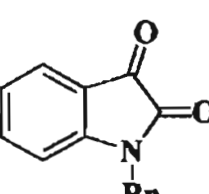
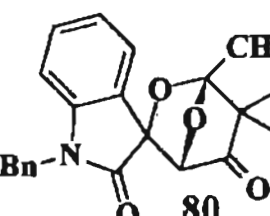
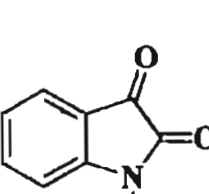
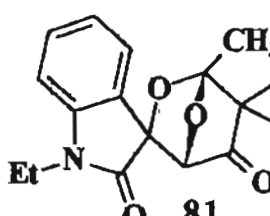
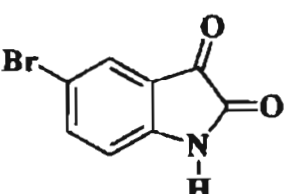
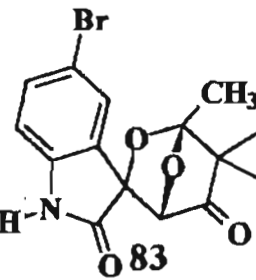
**Figure 9.**  $^{13}\text{C}$  NMR spectrum of 77



**Figure 10.** DEPT-135 NMR spectrum of **77**

*The reaction was extended to different isatins and in all cases the cycloaddition proceeded smoothly to afford spirooxindoles in good yields. The results are summarized in table 4.*

**Table 4.** Cycloaddition of Carbonyl Ylide **76** with Isatins.

| Entry | Isatin   | Product  | Yield (%) |
|-------|--|--|-----------|
| 1     | <br><b>45</b>   | <br><b>78</b>   | 52        |
| 2     | <br><b>52</b>   | <br><b>79</b>   | 77        |
| 3     | <br><b>59</b>  | <br><b>80</b>  | 80        |
| 4     | <br><b>57</b> | <br><b>81</b> | 78        |
| 5     | <br><b>82</b> | <br><b>83</b> | 86        |

All the products were fully characterized by spectroscopic analysis.

### 3.4 EXPERIMENTAL

All the reactions were carried out in oven dried glassware under an atmosphere of argon, unless otherwise mentioned. The IR spectra were recorded on Bomem MB series FT-IR spectrophotometer, using potassium bromide pellets. NMR spectra were recorded on Bruker-300 MHz FT-NMR spectrometer using  $\text{CDCl}_3$  as solvent. The chemical shifts are given in the  $\delta$  scale with tetramethylsilane as internal standard. Elemental analysis was carried out using Perkin-Elmer 2400 CHN analyzer. High-resolution mass spectra were obtained in EI mode on a Kratos MS50 instrument. Solvents used for the experiments (benzene, cyclohexane, and toluene) were distilled and dried according to the standard procedures. Starting materials required for the synthesis of imidoyl chlorides (4-nitro benzylamine hydrochloride, benzoyl chloride and toluoyl chloride) were purchased from Aldrich and used as such. Thionyl chloride was fractionally distilled over quinoline before use. Isatins required for the study were either purchased or synthesized according to the literature procedure.<sup>37</sup>

#### 3.4.1 SYNTHESIS OF IMIDOYL CHLORIDES

##### *4-Nitro-N-Benzyl Benzimidoyl Chloride 5*

The preparation of 4-nitro-N-benzyl benzimidoyl chloride **5** was carried out according to the known procedure.<sup>2</sup> 4-nitro benzylamine hydrochloride (12 g, 0.0638 mol) was dissolved in 84 mL of distilled water. To this benzoyl chloride (9.08 g, 0.0648 mol) and NaOH (43 mL, 3 molar solution) were added simultaneously. The reaction mixture was stirred for 30 minutes at 50° C and filtered. The solid obtained was washed and dried to afford 4-nitro-N-benzyl benzamide (8.9 g, 54%). This amide was then refluxed with freshly distilled thionyl chloride



(20.6 g, 0.1738 mol) for 30 minutes. A clear solution was obtained. Excess thionyl chloride was removed under reduced pressure and the solid obtained was recrystallized from rigorously dried cyclohexane under an atmosphere of argon to afford the imidoyl chloride **5** (6.6 g, 70%)

Pale yellow solid; recrystallized from dry cyclohexane.

- mp : 70-72° C
- IR (KBr)  $\nu_{\max}$  : 657, 689, 834, 858, 1027, 1106, 1345, 1511, 1603, 1636, 1657, 3065  $\text{cm}^{-1}$ .
- $^1\text{H}$  NMR :  $\delta$  4.97 (s, 2H), 7.40-7.52 (m, 3H), 7.59 (d, 2H,  $J = 8.43$  Hz), 8.06 (d, 2H,  $J = 7.15$  Hz), 8.20 (d, 2H,  $J = 8.5$  Hz)

#### ***4-Nitro N-Benzyl (4-Methyl) Benzimidoyl Chloride 61***

4-Nitro benzylamine hydrochloride (1 g,  $5.3 \times 10^{-3}$  mol) was treated with 4-toluoyl chloride (0.819 g,  $5.29 \times 10^{-3}$  mol) in presence of NaOH (4 mL, 3 molar solution) to afford 4-nitro-N-benzyl (4-methyl) benzamide (1g, 70%). This amide on refluxing with freshly distilled thionyl chloride (2.18 g, 0.0185 mol) afforded the imidoyl chloride **61** (0.630 g, 60%).

Pale yellow solid; recrystallised from dry cyclohexane.

- mp : 90-92° C
- IR (KBr)  $\nu_{\max}$  : 724, 858, 889, 1012, 1105, 1347, 1409, 1517, 1599, 1640, 1676  $\text{cm}^{-1}$ .
- $^1\text{H}$  NMR :  $\delta$  2.41 (s, 3H), 4.98 (s, 2H), 7.23 (d, 2H,  $J = 7.9$ Hz), 7.61 (d, 2H,  $J = 8.4$  Hz), 7.96 (d, 2H,  $J = 8.1$  Hz), 8.21 (d, 2H,  $J = 8.4$  Hz).
- $^{13}\text{C}$  NMR :  $\delta$  21.50, 56.59, 123.76, 123.88, 127.09, 128.30, 128.35, 129.16, 129.21, 129.30, 168.38.

### 3.4.2 GENERAL PROCEDURE FOR THE REACTION OF IMIDOYL CHLORIDES WITH ISATINS AND QUINONES

The preparation of the cycloadduct (**55**) from N-methyl isatin **54** and imidoyl chloride **5** is illustrative of the general procedure for the synthesis of spirooxazolines. N-methyl isatin (0.042 g,  $2.60 \times 10^{-4}$  mol) and imidoylchloride **5** (0.10 g,  $3.91 \times 10^{-4}$  mol) were taken in 2 mL rigorously dried benzene. To this, triethylamine (0.0434 g,  $4.30 \times 10^{-4}$  mol) was added and stirred for three hours under an atmosphere of argon at room temperature. The orange red reaction mixture turned colorless. It was then filtered through a celite pad using dichloromethane (50 mL) as eluent. Dichloromethane and benzene were removed on a rotary evaporator and the crude product was subjected to chromatography on silica gel column using hexane-ethyl acetate (85:15) as eluent to afford the cycloadduct **55** (0.084 g, 81%).

*(3R, 4'R)-1-Methyl-2'-(phenyl)-4'-(4-nitrophenyl) spiro [3H-indole-3, 5'(4'H)-oxazol]-2(1H)-one 55*

Colorless crystals; recrystallized from hexane-dichloromethane.

mp : 221-223° C

IR (KBr)  $\nu_{\max}$  : 689, 751, 854, 1020, 1088, 1338, 1513, 1607, 1657, 1731  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  2.91 (s, 3H), 5.79 (s, 1H), 6.85 (d, 1H,  $J = 7.8$  Hz), 7.22-7.31 (m, 3H), 7.43-7.58 (m, 5H), 8.07-8.12 (m, 4H).

$^{13}\text{C}$  NMR :  $\delta$  26.04, 79.29, 87.01, 108.78, 123.33, 123.78, 124.29, 126.63, 127.50, 127.71, 128.54, 128.96, 131.29, 132.29, 144.16, 147.76, 165.17, 171.45.

Anal. Calcd. for  $C_{23}H_{17}N_3O_4$ : C, 69.17; H, 4.29; N, 10.52. Found: C, 69.16; H, 4.51; N, 10.40.

**Crystal data for 55:**  $C_{23}H_{17}N_3O_4$ . M. 399.40, orthorhombic, space group pbca, unit cell dimensions  $a = 16.0787$  (3) Å,  $\alpha = 90^\circ$ ;  $b = 12.2058$  (3) Å,  $\beta = 90^\circ$ ;  $c = 19.8996$  (4) Å,  $\gamma = 90^\circ$ , R indices (all data)  $RI = 0.1753$ ,  $wR2 = 0.2670$ , volume,  $Z = 3905.4$  (1) Å<sup>3</sup>, 8,  $D_{\text{calc}} = 1.359$  Mg/m<sup>3</sup>, absorption coefficient =  $0.095$  mm<sup>-1</sup>,  $\lambda = 0.71073$  Å, reflections collected 64797.

***(3R,4'R)-1-Phenyl-2'-(phenyl)-4'-(4-nitrophenyl)spiro[3H-indole-3,5'(4'H)-oxazol]-2(1H)-one 56***

N-phenyl isatin **52** (0.025 g,  $1.12 \times 10^{-4}$  mol) and imidoylchloride **5** (0.046 g,  $1.68 \times 10^{-4}$  mol), taken in 2 mL benzene was stirred with triethylamine (0.0186g,  $1.84 \times 10^{-4}$  mol) for three hours. Chromatography of the crude product on silica gel column using hexane-ethyl acetate (85:15) as eluent afforded the cycloadduct **56** (0.0485 g, 94%).

Pale yellow crystals; recrystallized from hexane-dichloromethane.

mp : 201-203° C  
 IR (KBr)  $\nu_{\text{max}}$  : 745, 993, 1081, 1346, 1511, 1614, 1651, 1726 cm<sup>-1</sup>.  
<sup>1</sup>H NMR :  $\delta$  5.86 (s, 1H), 6.82 (d, 1H,  $J = 7.83$  Hz), 6.90 (d, 2H,  $J = 7.19$  Hz), 7.25-7.65 (m, 11H), 8.11-8.16 (m, 4H).  
<sup>13</sup>C NMR :  $\delta$  80.17, 87.22, 110.09, 123.39, 124.22, 124.53, 125.88, 126.60, 127.13, 127.87, 128.43, 128.57, 129.01, 129.70, 131.12, 132.34, 133.15, 144.03, 147.81, 165.36, 170.78.

Anal. Calcd. for  $C_{28}H_{19}N_3O_4$ : C, 72.88; H, 4.15; N, 9.11. Found: C, 72.74; H, 4.37; N, 8.84.

**(3*R*, 4'*R*)-1-Ethyl-2'-(phenyl)-4'-(4-nitrophenyl) spiro [3*H*-indole-3, 5'(4'*H*)-oxazol]-2(1*H*)-one 58**

N-ethyl isatin **57** (0.030 g,  $1.71 \times 10^{-4}$  mol) and imidoylchloride **5** (0.070 g,  $2.57 \times 10^{-4}$  mol), taken in 2 mL benzene, was stirred with triethylamine (0.0285 g,  $2.82 \times 10^{-4}$  mol) for three hours. Chromatography of the crude product on silica gel column using hexane-ethyl acetate (80:20) as eluent afforded the cycloadduct **58** (0.059 g, 83%).

Colorless crystals; recrystallized from hexane-ethyl acetate.

mp : 84-86° C

IR (KBr)  $\nu_{\max}$  : 691, 751, 844, 1023, 1202, 1341, 1467, 1520, 1613, 1650, 1725  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  0.87-0.95 (m, 3H), 3.25-3.32 (m, 1H), 3.55-3.62 (m, 1H), 5.77 (s, 1H), 6.85 (d, 1H,  $J = 7.7$  Hz), 7.18-7.32 (m, 3H), 7.41-7.58 (m, 6H), 8.08-8.11 (m, 3H).

$^{13}\text{C}$  NMR : 12.24, 34.54, 79.57, 87.05, 108.77, 123.24, 123.53, 124.46, 126.66, 127.61, 127.87, 128.54, 128.98, 131.19, 132.28, 143.24, 144.05, 147.75, 165.33, 171.01.

Anal. Calcd. for  $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_4$  : C, 69.72; H, 4.63; N, 10.16. Found C, 69.74; H, 5.18; N, 9.89.

**(3*R*,4'*R*)-1-Benzyl-2'-(phenyl)-4'-(4-nitrophenyl)spiro[3*H*-indole-3,5'(4'*H*)-oxazol]-2(1*H*)-one 60**

N-benzyl isatin **59** (0.046 g,  $1.94 \times 10^{-4}$  mol) and imidoylchloride **5** (0.080 g,  $2.91 \times 10^{-4}$  mol), taken in 2 mL benzene, was stirred with triethylamine (0.032 g,  $3.21 \times 10^{-4}$  mol) for three hours. Chromatography of the crude product on silica gel column using hexane-ethyl acetate (80:20) as eluent afforded the cycloadduct **60** (0.077 g, 84%).

Pale yellow crystals; recrystallized from hexane-dichloromethane.

mp : 168-170° C

IR (KBr)  $\nu_{\max}$  : 692, 753, 848, 1021, 1172, 1349, 1522, 1604, 1647, 1732  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  4.23 (d, 1H,  $J = 15.3$  Hz), 4.88 (d, 1H,  $J = 15.3$  Hz), 5.79 (s, 1H), 6.75-6.80 (m, 3H), 7.11-7.59 (m, 11H), 8.02 (d, 2H,  $J = 8.4$  Hz), 8.10 (d, 2H,  $J = 7.2$  Hz).

$^{13}\text{C}$  NMR :  $\delta$  43.98, 79.53, 87.14, 109.63, 123.42, 123.74, 124.47, 126.66, 127.03, 127.43, 128.02, 128.14, 128.58, 128.63, 128.99, 131.27, 132.34, 134.85, 143.55, 143.63, 147.82, 165.44, 171.58.

Anal. Calcd. for  $\text{C}_{29}\text{H}_{21}\text{N}_3\text{O}_4$ : C, 73.25; H, 4.45; N, 8.84. Found: C, 73.12; H, 4.52; N, 8.63.

***(3R,4'R)-1-Methyl-2'-(4-methylphenyl)-4'-(4-nitrophenyl)spiro[3H-indole-3,5'(4'H)-oxazol]-2(1H)-one 63***

N-methyl isatin **54** (0.024 g,  $1.49 \times 10^{-4}$  mol) and imidoylchloride **61** (0.064 g,  $2.23 \times 10^{-4}$  mol), taken in 2 mL benzene, was stirred with triethylamine (0.024 g,  $2.45 \times 10^{-4}$  mol) for three hours. Chromatography of the product on silica gel column using hexane-ethyl acetate (85:15) as eluent afforded the cycloadduct **63** (0.043 g, 70%).

Pale yellow crystals; recrystallized from hexane-dichloromethane.

mp : 213-215° C

IR (KBr)  $\nu_{\max}$  : 685, 744, 764, 830, 996, 1076, 1235, 1348, 1467, 1520, 1613, 1646, 1725  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  2.44 (s, 3H), 2.91 (s, 3H), 5.77 (s, 1H), 6.84 (d, 1H,  $J = 7.7$  Hz), 7.19-7.57 (m, 7H), 7.96 (d, 2H,  $J = 7.8$  Hz), 8.10 (d, 2H,  $J = 8.4$  Hz).

$^{13}\text{C}$  NMR :  $\delta$  21.76, 26.04, 79.32, 86.91, 108.74, 123.32, 123.76, 123.85, 124.29, 127.65, 127.74, 128.96, 129.27, 131.23, 142.78, 144.16, 144.31, 147.75, 165.29, 171.53.

HRMS: Calcd. for  $\text{C}_{29}\text{H}_{19}\text{N}_3\text{O}_4$ : 413.13756. Found: 413.13752.

**(3*R*, 4'*R*)-1-Phenyl-2'-(4-methylphenyl)-4'-(4-nitrophenyl) spiro[3*H*-indole-3,5'(4'*H*)-oxazol]-2(1*H*)-one 64**

N-phenyl isatin **52** (0.025 g,  $1.12 \times 10^{-4}$  mol) and imidoylchloride **61** (0.048 g,  $1.68 \times 10^{-4}$  mol), taken in 2 mL benzene, was stirred with triethylamine (0.019 g,  $1.84 \times 10^{-4}$  mol) for three hours. Chromatography of the crude product on silica gel column using hexane-ethyl acetate (85:15) as eluent afforded the cycloadduct **64** (0.048 g, 90%).

Pale yellow crystals; recrystallized from hexane-dichloromethane.

mp : 105-107° C

IR (KBr)  $\nu_{\text{max}}$  : 699, 750, 1080, 1344, 1514, 1608, 1651, 1740  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  2.45 (s, 3H), 5.85 (s, 1H), 6.82 (d, 1H,  $J = 7.8$  Hz), 6.90 (d, 1H,  $J = 7.7$  Hz), 7.25-7.44 (m, 10H), 7.64 (d, 1H,  $J = 7.1$  Hz), 8.00 (d, 2H,  $J = 7.90$ ), 8.14 (d, 2H,  $J = 8.4$  Hz).

$^{13}\text{C}$  NMR :  $\delta$  21.77, 80.23, 87.14, 110.09, 123.41, 123.83, 124.22, 124.55, 125.91, 127.29, 127.90, 128.43, 129.02, 129.30, 129.72, 129.86, 131.08, 133.20, 142.87, 144.05, 144.19, 147.82, 165.52, 170.89.

***(3R, 4'R)-1-Ethyl-2'-(4-methylphenyl)-4'-(4-nitrophenyl) spiro[3H-indole-3,5'(4'H)-oxazol]-2(1H)-one 65***

N-ethyl isatin **57** (0.030 g,  $1.71 \times 10^{-4}$  mol) and imidoylchloride **61** (0.074 g,  $2.57 \times 10^{-4}$  mol), taken in 2 mL benzene, was stirred with triethylamine (0.028 g,  $2.82 \times 10^{-4}$  mol) for three hours. Chromatography of the crude product on silica gel column using hexane-ethyl acetate (80:20) as eluent afforded the cycloadduct **65** (0.065 g, 89%).

Pale yellow crystals; recrystallized from hexane-ethyl acetate.

mp : 186-188° C

IR (KBr, : 685, 744, 830, 1009, 1082, 1175, 1208, 1467, 1513, 1606, 1646, 1725  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  0.87-0.91 (m, 3H), 2.44 (s, 3H), 3.24-3.31 (m, 1H), 3.55-3.62 (m, 1H), 5.75 (s, 1H), 6.84 (d, 1H,  $J = 7.79$  Hz), 7.17-7.57 (m, 5H), 7.97 (d, 2H,  $J = 8.03$  Hz), 8.09 (d, 2H,  $J = 8.48$  Hz).

$^{13}\text{C}$  NMR :  $\delta$  12.26, 21.75, 34.54, 79.60, 86.95, 108.73, 123.24, 123.51, 123.89, 124.46, 127.74, 127.89, 128.97, 129.25, 131.13, 142.77, 143.22, 144.22, 147.73, 165.45, 171.09.

***(3R, 4'R)-1-Benzyl-2'-(4-methylphenyl)-4'-(4-nitrophenyl) spiro[3H-indole-3,5'(4'H)-oxazol]-2(1H)-one 66***

N-benzyl isatin **59** (0.044 g,  $1.85 \times 10^{-4}$  mol) and imidoylchloride **61** (0.080 g,  $2.78 \times 10^{-4}$  mol), taken in 2 mL benzene, was stirred with triethylamine (0.030 g,  $3.05 \times 10^{-4}$  mol) for three hours. Chromatography of the crude product on silica gel column using hexane-ethyl acetate (80:20) as eluent afforded the cycloadduct **66** (0.057 g, 63%).

Pale yellow crystals; recrystallized from hexane-dichloromethane.

|                     |   |  |
|---------------------|---|--|
| mp                  | : | 192-194° C   |
| IR                  | : | 696, 751, 847, 1074, 1174, 1349, 1518, 1607, 1650, 1733 cm <sup>-1</sup> .   |
| <sup>1</sup> H NMR  | : | δ 2.44 (s, 3H), 4.23 (d, 1H, <i>J</i> = 15.0 Hz), 4.89 (d, 1H, <i>J</i> = 15.3 Hz), 5.79 (s, 1H), 6.78 (br s, 3H), 7.14-7.39 (m, 9H), 7.59 (d, 1H, <i>J</i> = 7.02 Hz), 7.98-8.05 (m, 4H). |
| <sup>13</sup> C NMR | : | δ 21.72, 43.95, 79.49, 87.05, 109.63, 123.42, 123.75, 124.44, 127.08, 127.41, 127.95, 128.15, 128.59, 128.91, 129.29, 131.22, 134.87, 142.94, 143.54, 143.72, 147.75, 165.61, 171.72.      |

HRMS Calcd. for C<sub>30</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>: 489.168857. Found: 489.16675

### ***Cycloadduct 68***

Acenaphthenequinone **67** (0.030 g, 1.64×10<sup>-4</sup> mol) and imidoylchloride **5** (0.067 g, 2.47×10<sup>-4</sup> mol), taken in 2 mL benzene, was stirred with triethylamine (0.027 g, 2.71×10<sup>-4</sup>) for four hours. Chromatography of the crude product on silica gel column using hexane-ethyl acetate (80:20) as eluent afforded the cycloadduct **68** (0.054 g, 78%).

Colorless crystals; recrystallized from hexane-dichloromethane.

|                           |   |   |
|---------------------------|---|---|
| mp                        | : | 204-205° C  |
| IR (KBr) ν <sub>max</sub> | : | 780, 830, 1017, 1272, 1340, 1521, 1651, 1726 cm <sup>-1</sup> .   |
| <sup>1</sup> H NMR        | : | δ 5.99 (s, 1H), 7.13 (d, 2H, <i>J</i> = 8.5 Hz), 7.26-8.28 (m, 11 H), 7.97 (d, 2H, <i>J</i> = 8.6 Hz).  |
| <sup>13</sup> C NMR       | : | δ 79.68, 90.16, 120.73, 121.99, 122.57, 123.37, 126.69, 127.89, 128.44, 128.59, 128.97, 129.02, 129.23, 130.49, 130.70, 131.98, 132.28, 132.47, 137.22, 142.04, 144.30, 147.57, 165.39, 197.58. |



HRMS Calcd. for  $C_{26}H_{16}N_2O_4$ : 420.1110. Found: 420.1112.

***(3R,4'R)-2'-(phenyl)-4'-(4-nitrophenyl)spiro[oxazole-5(4H),9'(10'H)-phenanthren]-10'-one 70***

Phenanthrenequinone **69** (0.030 g,  $1.44 \times 10^{-4}$  mol) and imidoylchloride **5** (0.059 g,  $2.16 \times 10^{-4}$  mol), taken in 2 mL benzene, was stirred with triethylamine (0.024 g,  $2.37 \times 10^{-4}$  mol) for four hours. Chromatography of the crude product on silica gel column using hexane-ethyl acetate (70:30) as eluent afforded the cycloadduct **70** (0.031 g, 48%).

Colorless crystals; recrystallized from hexane-dichloromethane.

mp : 196-198° C

IR (KBr)  $\nu_{\max}$  : 694, 751, 834, 916, 994, 1096, 1334, 1449, 1517, 1599, 1654, 1707  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  5.63 (s, 1H), 6.76 (d, 2H,  $J = 8.5$  Hz), 7.03-7.25 (m, 3H), 7.53-7.81 (m, 9H), 8.14 (d, 1H,  $J = 7.6$  Hz), 8.25 (d, 2H,  $J = 7.0$  Hz).

$^{13}\text{C}$  NMR :  $\delta$  78.60, 92.58, 122.44, 123.27, 123.97, 126.24, 126.38, 127.74, 128.23, 128.59, 128.66, 128.94, 129.00, 129.07, 130.15, 132.41, 133.43, 135.53, 137.67, 144.10, 147.17, 165.86, 195.34.

Anal. Calcd. for  $C_{28}H_{18}N_2O_4$ : C, 75.33; H, 4.06; N, 6.27. Found: C, 75.84; H, 4.20; N, 5.97.

***Cycloadduct 71***

Acenaphthenequinone **67** (0.033 g,  $1.81 \times 10^{-4}$  mol) and imidoylchloride **61** (0.078 g,  $2.71 \times 10^{-4}$  mol), taken in 2 mL benzene, was stirred with triethylamine (0.030 g,  $2.97 \times 10^{-4}$  mol) for three hours. Chromatography of the crude product on silica gel column using

hexane-ethyl acetate (70:30) as eluent afforded the cycloadduct **71** (0.065 g, 83%).

Colorless crystals; recrystallized from hexane-dichloromethane.

mp : 185-187° C

IR (KBr)  $\nu_{\max}$  : 785, 829, 1014, 1073, 1272, 1348, 1520, 1601, 1645, 1726  $\text{cm}^{-1}$ .

$^1\text{H NMR}$  :  $\delta$  2.44 (s, 3H), 5.97 (s, 1H), 7.12 (d, 2H,  $J = 8.4$  Hz), 7.28 (d, 2H,  $J = 7.8$  Hz) 7.70-8.17 (m, 10H).

$^{13}\text{C NMR}$  :  $\delta$  21.73, 79.73, 90.10, 120.70, 122.50, 123.34, 123.97, 126.62, 127.93, 128.96, 129.22, 129.30, 130.50, 130.79, 131.93, 137.38, 142.02, 142.76, 144.48, 147.59, 165.50, 197.65.

Anal. Calcd. for  $\text{C}_{27}\text{H}_{18}\text{N}_2\text{O}_4$ : C, 74.64; H, 4.18; N, 6.45. Found: C, 74.73; H, 4.36; N, 6.48.

**(3*R*, 4'*R*)-2'-(4-Methylphenyl)-4'-(4-nitrophenyl) spiro[oxazole-5(4*H*), 9'(10'*H*)-phenanthren]-10'-one 72**

Phenanthrenequinone **69** (0.030 g,  $1.44 \times 10^{-4}$  mol) and imidoylchloride **61** (0.062 g,  $2.16 \times 10^{-4}$  mol), taken in 2 mL benzene, was stirred with triethylamine (0.024 g,  $2.37 \times 10^{-4}$  mol) for three hours. Chromatography of the crude product on silica gel column using hexane-ethyl acetate (70:30) as eluent afforded the cycloadduct **72** (0.036 g, 54%).

Colorless crystals; recrystallized from hexane-dichloromethane.

mp : 204-206° C

IR (KBr)  $\nu_{\max}$  : 718, 744, 830, 1089, 1268, 1341, 1454, 1513, 1593, 1646, 1706  $\text{cm}^{-1}$ .

|                     |   |
|---------------------|---|
| $^1\text{H}$ NMR    | : $\delta$ 2.49 (s, 3H), 5.61 (s, 1H), 6.76 (d, 2H, $J = 8.5$ Hz), 7.03-7.18 (m, 3H), 7.35 (d, 2H, $J = 7.9$ Hz), 7.51-7.59 (m, 2H), 7.74-7.80 (m, 4H), 8.12-8.15 (m, 3H).                            |
| $^{13}\text{C}$ NMR | : 21.82, 78.69, 92.60, 122.2, 123.35, 123.67, 124.04, 126.33, 127.90, 128.34, 128.65, 128.73, 129.01, 129.08, 129.12, 129.48, 130.22, 133.62, 135.55, 137.78, 143.06, 144.34, 147.22, 166.06, 195.53. |

HRMS Calcd. for  $\text{C}_{29}\text{H}_{20}\text{N}_2\text{O}_4$ : 460.14231. Found: 460.1420.

### 3.4.3 TYPICAL EXPERIMENTAL PROCEDURE FOR THE CYCLOADDITION OF CARBONYL YLIDE WITH ISATINS

The experimental details given here for the synthesis of the cycloadduct **77** is illustrative of the general procedure for the synthesis of cycloadducts **78**, **79**, **80**, **81** and **83**. The diazo ketone **75** (0.102 g,  $6.7 \times 10^{-4}$  mol) taken in 2 mL of rigorously dried toluene was stirred with a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$  (0.002 g) for 1 minute under an atmosphere of argon. To this, N-methylisatin **54** (0.098 g,  $6.1 \times 10^{-4}$  mol) was added and stirred for 30 minutes at room temperature. The orange red reaction mixture turned colorless. The solvent was then removed under reduced pressure and the contents were charged on a silica gel column and eluted with hexane-ethyl acetate mixture (80:20) to afford the cycloadduct **77** (0.142 g, 82%).

#### *Cycloadduct 77*

Colorless crystals; recrystallized from hexane-dichloromethane.

|                             |  |
|-----------------------------|--|
| mp                          | : 158-160° C   |
| IR (KBr) $\nu_{\text{max}}$ | : 988, 1147, 1475, 1611, 1684, 1730, 3007 $\text{cm}^{-1}$ .   |
| $^1\text{H}$ NMR            | : $\delta$ 1.11-1.18 (m, 1H), 1.25-1.31 (m, 3H), 1.60 (s, 3H), 3.18 (s, 3H), 4.62 (s, 1H), 6.83 (d, 1H, $J = 7.0$ Hz), 7.11 (t, 1H, $J = 7.3$ Hz), 7.37 (t, $J = 7.3$ Hz), 7.51 (d, 2H, $J = 7.1$ Hz). |

$^{13}\text{C}$  NMR :  $\delta$  13.48, 14.51, 15.19, 26.45, 39.46, 80.32, 86.97, 108.32, 113.67, 123.36, 124.65, 128.00, 130.47, 143.19, 172.99, 204.79.

HRMS Calcd. for  $\text{C}_{16}\text{H}_{15}\text{N}_1\text{O}_4$ : 285.100. Found: 285.0989.

### ***Cycloadduct 78***

The diazo ketone **75** (0.059 g,  $3.89 \times 10^{-4}$  mol) taken in 2 mL of rigorously dried toluene was stirred with a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$  (0.002g) for 1 minute under an atmosphere of argon. To this, isatin **45** (0.052 g  $3.53 \times 10^{-4}$  mol) was added and stirred for 30 minutes at room temperature. Chromatographic purification of the crude product using hexane-ethyl acetate mixture (70:30) afforded the cycloadduct **78** (0.050 g, 52%).

Colorless crystals; recrystallized from hexane-ethyl acetate.

mp : 180-182° C

IR (KBr)  $\nu_{\text{max}}$  : 751, 812, 993, 1107, 1333, 1402, 1469, 1620, 1729, 1769, 3099, 3180  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR : 1.09-1.16 (m, 1H), 1.23-1.29 (m, 2H), 1.51-1.55 (m, 1H), 1.59 (s, 3H), 4.63 (s, 1H), 6.85 (d, 1H,  $J = 7.71$  Hz), 7.05 (t, 1H,  $J = 7.34$  Hz), 7.28 (t, 1H,  $J = 7.7$  Hz), 7.46 (d, 1H,  $J = 7.31$  Hz), 8.30 (br s, 1H).

$^{13}\text{C}$  NMR : 13.45, 14.53, 15.15, 39.49, 80.60, 87.15, 110.21, 113.71, 123.26, 125.01, 128.41, 130.39, 140.27, 173.84, 204.86.

HRMS Calcd. for  $\text{C}_{15}\text{H}_{13}\text{NO}_4$ : 271.084. Found: 271.08499.

### ***Cycloadduct 79***

The diazo ketone **75** (0.112 g,  $7.4 \times 10^{-4}$  mol) taken in 2 mL toluene was treated with N-phenylisatin (0.15 g,  $6.7 \times 10^{-4}$  mol) in presence of

$\text{Rh}_2(\text{OAc})_4$ . Chromatographic purification of the crude product using hexane-ethyl acetate mixture (80:20) afforded the cycloadduct **79** (0.179 g, 77%).

Colorless crystals; recrystallized from hexane-dichloromethane.

mp : 139-141° C

IR (KBr)  $\nu_{\text{max}}$  : 761, 833, 985, 1109, 1209, 1327, 1406, 1503, 1613, 1729, 1770, 3071  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR : 1.09-1.16 (m, 1H), 1.24-1.31 (m, 2H), 1.53-1.58 (m, 1H), 1.62 (s, 3H), 4.73 (s, 1H), 6.84 (d, 1H,  $J = 7.8$  Hz), 7.10-7.58 (m, 8H).

$^{13}\text{C}$  NMR : 13.69, 14.61, 15.32, 39.53, 80.51, 87.25, 105.50, 109.80, 113.94, 123.92, 125.11, 126.27, 127.81, 128.23, 129.57, 130.44, 133.86, 143.20, 171.48, 204.53.

HRMS Calcd. for  $\text{C}_{21}\text{H}_{17}\text{N}_1\text{O}_4$ : 347.1157. Found: 347.1159.

### ***Cycloadduct 80***

The diazo ketone **75** (0.085 g,  $5.56 \times 10^{-4}$  mol) taken in 2 mL toluene was treated with *N*-benzylisatin (0.120 g,  $5.06 \times 10^{-4}$  mol) in presence of  $\text{Rh}_2(\text{OAc})_4$ . Chromatographic purification of the crude product using hexane-ethyl acetate mixture (80:20) afforded the cycloadduct **80** (0.146 g, 80%).

Colorless crystals; recrystallized from hexane-dichloromethane.

mp : 63-65° C

IR (KBr)  $\nu_{\text{max}}$  : 755, 836, 994, 1145, 1355, 1472, 1615, 1729, 1763, 3071  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  1.12-1.19 (m, 1H), 1.24-1.30 (m, 3H), 1.59 (m, 3H), 4.61 (s, 1H), 4.76 (d, 1H,  $J = 15.6$  Hz), 4.92 (d,

1H,  $J=15.6$  Hz), 6.67 (d, 1H,  $J=7.7$  Hz), 7.03 (t, 1H,  $J=7.3$  Hz), 7.18-7.31 (m, 1H), 7.49 (d, 1H,  $J=7.34$  Hz).

$^{13}\text{C}$  NMR : 13.49, 14.51, 15.18, 39.45, 44.05, 80.36, 87.11, 109.40, 113.78, 123.32, 124.65, 127.24, 127.70, 127.93, 128.79, 130.32, 135.03, 142.19, 172.05, 204.63.

Anal. Calcd. for:  $\text{C}_{22}\text{H}_{19}\text{N}_1\text{O}_4$ : C, 72.99; H, 5.42; N, 3.64. Found: C, 73.11; H, 5.29; N, 3.87.

### *Cycloadduct 81*

The diazo ketone **75** (0.041 g,  $2.70 \times 10^{-4}$  mol) taken in 2 mL toluene was treated with N-ethylsatin (0.043 g,  $2.45 \times 10^{-4}$  mol) in presence of  $\text{Rh}_2(\text{OAc})_4$ . Chromatographic purification of the crude product using hexane-ethyl acetate mixture (80:20) afforded the cycloadduct **81** (0.057 g, 78%).

Colorless crystals; recrystallized from hexane-ethyl acetate.

mp : 168-170° C

IR (KBr)  $\nu_{\text{max}}$  : 685, 751, 837, 983, 1096, 1222, 1348, 1374, 1467, 1613, 1719, 1765  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  1.13-1.17 (m, 1H), 1.24-1.29 (m, 6H), 1.59 (s, 3H), 3.63-3.68 (m, 1H), 3.76-3.81 (m, 1H), 4.58 (s, 1H), 6.83 (d, 1H,  $J=7.7$  Hz), 7.07 (t, 1H,  $J=7.4$  Hz), 7.33 (t, 1H,  $J=7.7$  Hz), 7.49 (d, 1H,  $J=7.3$  Hz).

$^{13}\text{C}$  NMR :  $\delta$  12.55, 13.52, 14.57, 15.28, 35.14, 39.52, 80.40, 87.0, 108.51, 113.71, 123.22, 124.94, 128.27, 130.47, 142.32, 171.64, 204.77.

HRMS Calcd. for  $\text{C}_{17}\text{H}_{17}\text{NO}_4$ : 299.1157. Found: 299.1151

**Cycloadduct 83**

The diazo ketone **75** (0.066 g,  $4.38 \times 10^{-4}$  mol) taken in 2 mL toluene was treated with 5-bromoisatin **82** (0.90 g,  $3.98 \times 10^{-4}$  mol) in presence of  $\text{Rh}_2(\text{OAc})_4$ . Chromatographic purification of the crude product using hexane-ethyl acetate mixture (70:30) afforded the cycloadduct **83** (0.119 g, 86%).

Colorless crystals; recrystallized from hexane-ethyl acetate.

mp : 234-235° C

IR (KBr)  $\nu_{\text{max}}$  : 813, 994, 1122, 1218, 1330, 1450, 1621, 1730, 1773, 3184  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR : 1.12-1.13 (m, 1H), 1.25-1.28 (m, 3H), 1.59 (s, 3H), 4.59 (s, 1H), 6.77 (d, 1H,  $J = 8.1$  Hz), 7.35-7.49 (m, 2H), 10.38 (s, 1H).

$^{13}\text{C}$  NMR : 12.91, 14.08, 14.76, 39.04, 80.22, 86.52, 111.71, 113.38, 114.59, 127.30, 130.02, 132.65, 140.36, 172.84, 204.13.

Anal. Calcd. for  $\text{C}_{15}\text{H}_{13}\text{N}_1\text{O}_4\text{Br}$ : C, 51.45; H, 3.45; N, 4.00. Found C, 51.00, H, 3.51, N, 3.46.

**3.5 REFERENCES**

- 1 Hansen, H.-J.; Heimgartner, H. in *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1; pp. 177-290.
- 2 Huisgen, R.; Stangl, H.; Sturm, H. J.; Raab, R.; Bunge, K. *Chem. Ber.* **1972**, *105*, 1258.

- 3 Uebelhart, P.; Gilgen, P.; Schmid, H. in *Organic Photochemical Synthesis*; Srinivasan, R., Ed.; Wiley: New York, 1976; Vol. 2; p.72.
- 4 Padwa, A. and Wetmore, S. I. in *Organic Photochemical Synthesis*; Srinivasan, R., Ed.; Wiley: New York, 1976; Vol. 2; p. 87.
- 5 Padwa, A.; Wetmore, S. I. *J. Am. Chem. Soc.* **1974**, *96*, 2414.
- 6 (a) Burger, K.; Fehn, J. *Angew. Chem., Int. Ed. Eng.* **1971**, *10*, 728.  
(b) Burger, K.; Fehn, J. *Angew. Chem., Int. Ed. Eng.* **1971**, *10*, 729.  
(c) Burger, K.; Fehn, J. *Chem. Ber.* **1972**, *105*, 3814.  
(d) Burger, K.; Fehn, J. *Angew. Chem., Int. Ed. Eng.* **1972**, *11*, 47.  
(e) Burger, K.; Fehn, J.; Muller, E. *Chem. Ber.* **1973**, *106*, 1.  
(f) Burger, K.; Einhellig, K.; Roth, W.-D.; Daltrozzo, E. *Chem. Ber.* **1977**, *110*, 605.
- 7 Hesse, G.; Witte, H.; Bittner, G. *Liebigs. Ann. Chem.* **1965**, 687, 9.
- 8 Burger, K.; Albanbauer, J.; Manz, F. *Chem. Ber.* **1974**, *107*, 1823.
- 9 Berree, F.; Marchand, E.; Morel, G. *Tetrahedron Lett.* **1992**, *33*, 6155.
- 10 Ibata, T.; Fukushima, K. *Chem. Lett.* **1992**, 2197.
- 11 Padwa, A.; Rasmussen, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 5912.
- 12 Huisgen, R.; Sustmann, R.; Bunge, K. *Tetrahedron Lett.* **1966**, 7 3603.
- 13 Pfoertner, K.-H.; Zell, R. *Helv. Chim. Acta.* **1980**, *63*, 645.
- 14 Steglich, W.; Gruber, P.; Heininger, H.-U.; Kneidl, F. *Chem. Ber.* **1971**, *104*, 3816.



- 15 Burger, K.; Albanbauer, J.; Manz, F. *Chem. Ber.* **1974**, *107*, 1823.
- 16 Padwa, A.; Dharan, M.; Smolanoff, J.; Wetmore, S. I. *J. Am. Chem. Soc.* **1973**, *95*, 1954.
- 17 Gakis, N.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta.* **1974**, *57*, 1403.
- 18 Widmer, U.; Gakis, N.; Arnet, B.; Heimgartner, H.; Schmid, H. *Chimia*, **1976**, *30*, 453.
- 19 Hansen, H.-J.; Heimgartner, H. in *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A. Ed.; Wiley: New York, 1984; Vol. 1; pp. 241-245.
- 20 Bunge, K.; Huisgen, R.; Raab, R.; Stangl, H. *Chem. Ber.* **1972**, *105*, 1279.
- 21 Bittner, G.; Witte, H.; Hesse, G.; *Liebigs. Ann. Chem.* **1968**, 713, 1.
- 22 Claus, P.; Gilgen, P.; Hansen, H.-J.; Heimgartner, H.; Jackson, B.; Schmid, H. *Helv. Chim. Acta.* **1974**, *57*, 2173.
- 23 Hansen, H.-J.; Heimgartner, H. in *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 1; pp. 260-263.
- 24 Pfoertner, K.-H.; Zell, R. *Helv. Chim. Acta.* **1980**, *63*, 645.
- 25 Gilgen, P.; Jackson, B.; Hansen, H.-J.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta.* **1974**, *57*, 2634.
- 26 *The Alkaloids: Chemistry and Biology*; Cordell, G. A., Ed: Academic, San Diego, 1998; vol. 5.
- 27 Cui, C.-B.; Kakeya, H.; Osada, H. *Tetrahedron* **1996**, *52*, 12651.
- 28 James, M. N. G.; Williams, G. J. B. *Can. J. Chem.* **1972**, *50*, 2407.

- 29 Jossang, A.; Jossang, P.; Hadi, H. A.; Sevenent, T. Bodo, B. *J. Org. Chem.* **1991**, *56*, 6527.
- 30 Xue, J.; Zhang, Y.; Wang, X-l.; Fun, H. K.; Xu, J.-H. *Org. Lett.* **2000**, *2*, 2583 and references cited therein.
- 31 Coulter, T.; Grigg, R.; Malone, J. F.; Sridharan, V. *Tetrahedron Lett.* **1991**, *32*, 5417.
- 32 Nair, V.; Sheela, K. C.; Sethumadhavan, D.; Bindu, S.; Rath, N. P.; Eigendorf, G. K. *Synlett* **2001**, 0000.
- 33 Nair, V.; Sheela, K. C.; Radhakrishnan, K. V.; Rath, N. P. *Tetrahedron Lett.* **1998**, *39*, 5627.
- 34 Nair, V.; Sheela, K. C.; Radhakrishnan, K. V.; Rath, N. P. *Tetrahedron* **1999**, *55*, 14199.
- 35 Sheela, K. C. Ph.D. Thesis, Cochin University of Science and Technology, **2000**.
- 36 Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223.
- 37 Garden, S. J.; Torres, J. C.; Silva, L. E.; Pinto, A. C. *Synth. Commun.* **1998**, *28*, 1679.

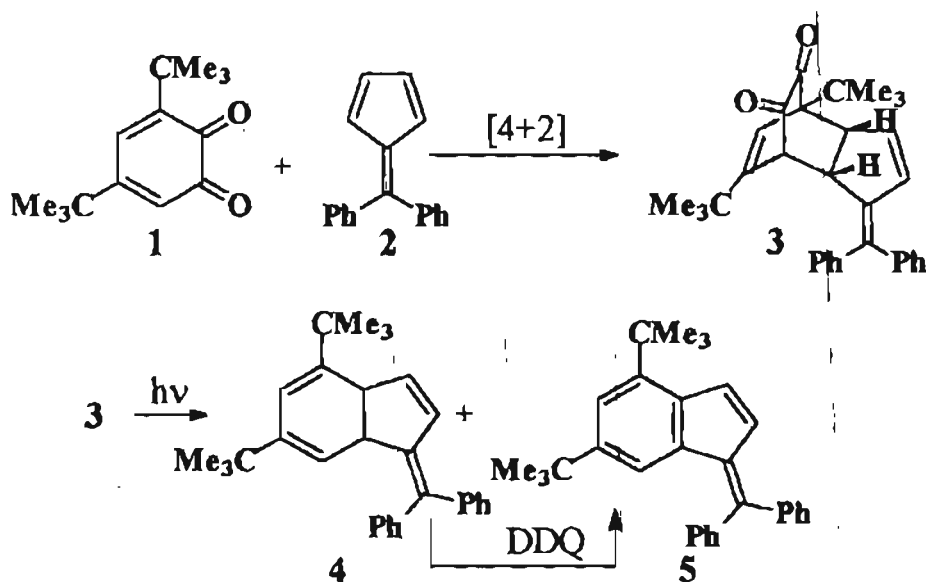
## CHAPTER 4

# A FACILE ONE POT SYNTHESIS OF TROPOLONE DERIVATIVES BY THE LEWIS ACID CATALYZED REACTION OF *o*-BENZOQUINONES AND ARYLACETYLENES

### 4.1 INTRODUCTION

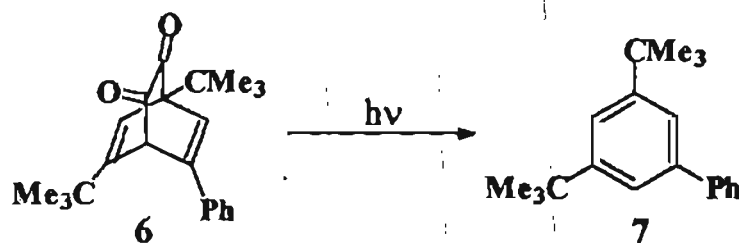
As described in the introductory chapter, quinones have been the subject of extensive investigations at least partly due to the potential offered by them in the synthesis of natural products.<sup>1</sup> Much of the interest has centered around *p*-quinones which are excellent dienophiles in Diels-Alder reactions. In contrast, the reactivity profile of *o*-quinones has received less attention, presumably due to the instability and inaccessibility of these compounds, and much of the work on the cycloadditions of *o*-quinones has involved the readily available and stable *o*-chloranil and *o*-bromanil. As part of the systematic investigation of the cycloadditions of *o*-quinones, a detailed study of their Diels-Alder reaction with various dienophiles was carried out in our laboratories.<sup>2</sup> It has been shown that fulvenes undergo facile [4+2] cycloaddition reactions with *o*-benzoquinones to afford novel

bicyclo [2.2.2] octene diones.<sup>3</sup> These bicyclic systems can be decarbonylated and aromatized efficiently to the corresponding benzofulvene derivatives. An illustrative example is the cycloaddition of 3,5-di-*tert*-butyl *o*-benzoquinone 1 with diphenyl fulvene 2 to the tricyclic compound 3 and its transformation to 5 (Scheme 1).<sup>4</sup>



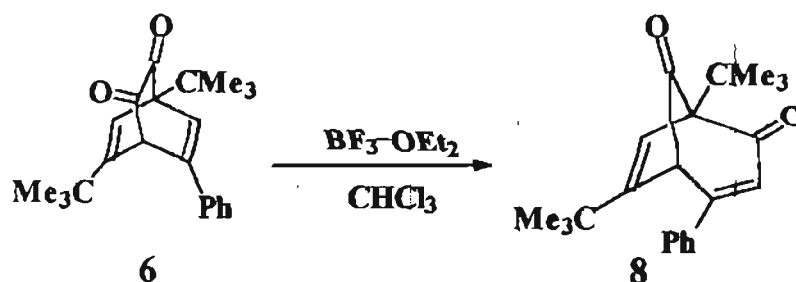
Scheme 1

Similarly, bicyclic dione 6 obtained by the cycloaddition of *o*-benzoquinone 1 and phenylacetylene also underwent photolytic double decarbonylation to afford the biphenyl derivative 7 (Scheme 2).<sup>4</sup>



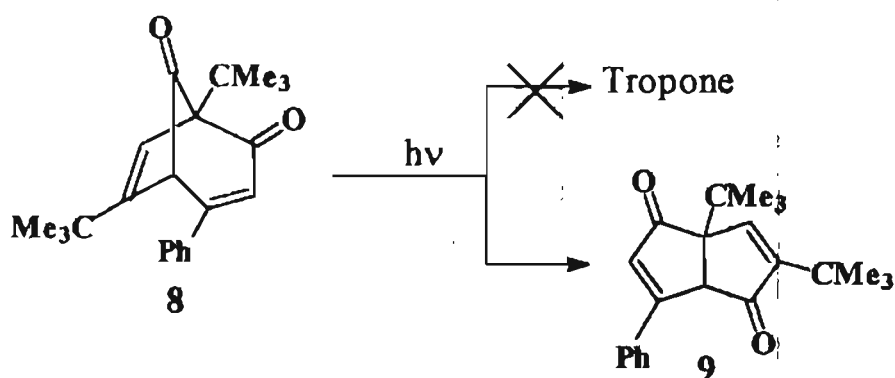
Scheme 2

In a related reaction, it was found that the bicyclo [2.2.2] octenedione **6** rearranged smoothly on refluxing with  $\text{BF}_3\text{-OEt}_2$  in chloroform to afford the bicyclo [3.2.1] octenedione **8** (Scheme 3).<sup>5</sup>



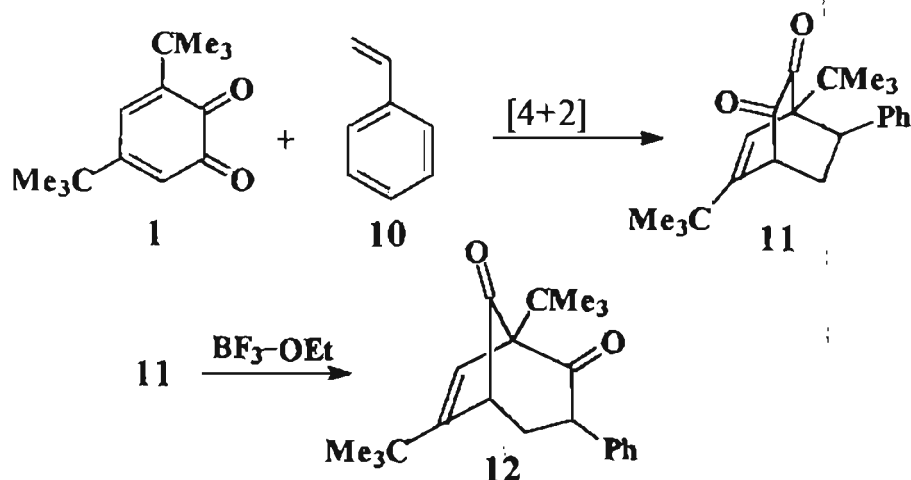
Scheme 3

As a follow up of this reaction, attempts were made to photodecarbonylate the [3.2.1] adduct **8** to produce a tropone derivative. However this reaction did not occur; instead a bicyclo [3.3.0] system **9** resulted (Scheme 4).<sup>6</sup>



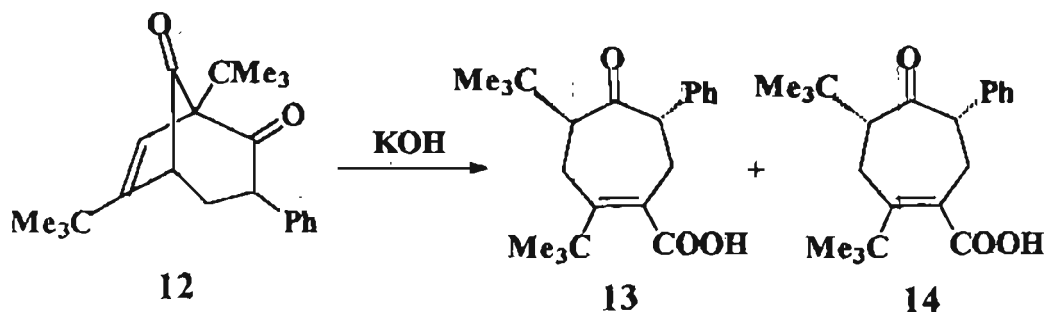
Scheme 4

The bicyclo adduct **11** synthesized from 3,5-di-*tert*-butyl *o*-benzoquinone and styrene **10**, on treatment with  $\text{BF}_3\text{-OEt}_2$  afforded the [3.2.1] adduct **12** (Scheme 5).<sup>7</sup>



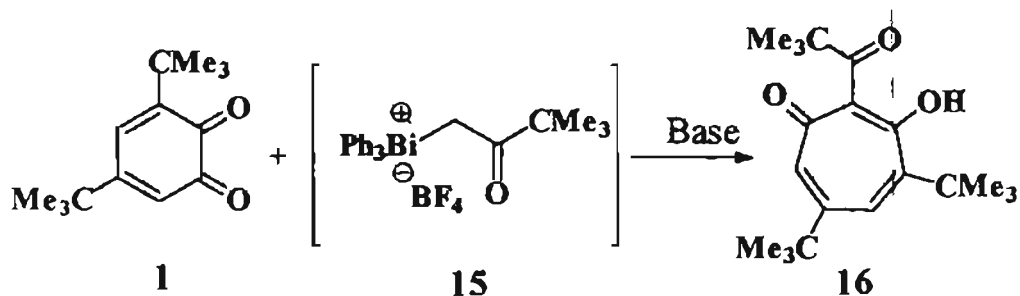
Scheme 5

This bicycloadduct 12 on treatment with potassium hydroxide afforded ketoacids 13 and 14 as a mixture of isomers (Scheme 6).<sup>8</sup>



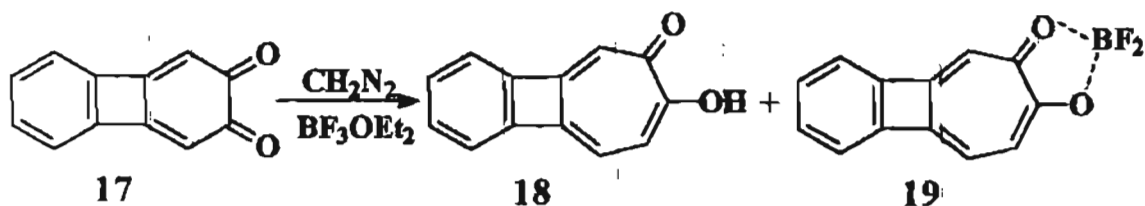
Scheme 6

Very recently Suzuki *et al.* have found that the reaction of bismuthonium ylide 15 with 1,2-benzoquinone leads to tropolone 16 (Scheme 7).<sup>9</sup>



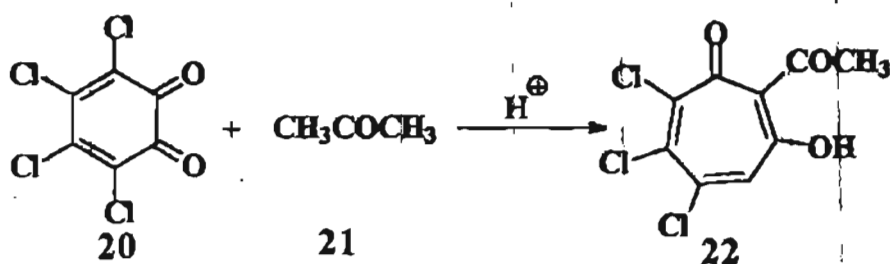
Scheme 7

Ebin *et al.* have found that biphenylene-2,3-quinone **17** reacts with diazomethane in presence of  $\text{BF}_3\text{-OEt}_2$  to afford tropolone derivatives **18** and **19** (Scheme 8).<sup>10</sup>



Scheme 8

Kogler *et al.* have reported a facile synthesis of acetyl tropolone **22** from *o*-chloranil **20** (Scheme 9).<sup>11</sup>



Scheme 9

#### 4.1.1 THE PRESENT WORK

Synthesis, characterization and reactions of stable charged species like aromatic cation radical **23**, radical **24**, and anion **25** (Figure 1) have been of considerable interest recently.

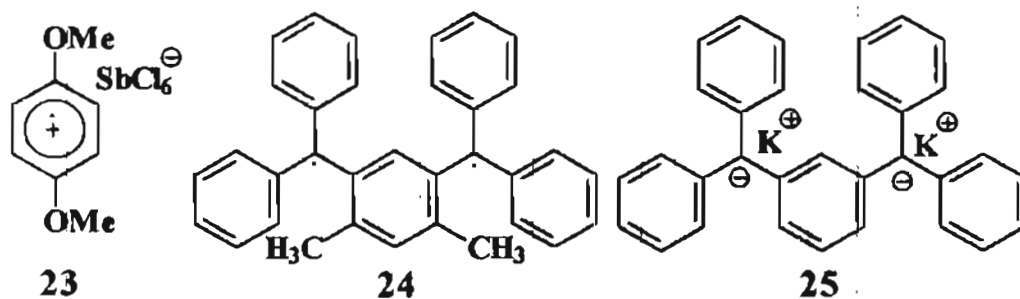


Figure 1

Stable cation radicals relate directly to the contemporary interest in organic materials for molecular devices like electrical and photoconductors, sensors, optical switches etc.<sup>12</sup> Development of organic polyradicals and anions is also of current interest from the standpoint of basic research as well as practical applications.<sup>13</sup> Because of our general interest in the cycloaddition chemistry of *o*-benzoquinones and, intrigued by the possibility of the synthesis of polyarylated compounds of the type 26 and 27 (Figure 2) by utilizing the Diels-Alder cycloaddition, decarbonylation protocol (cf. Schemes 1 and 2), some work was undertaken.

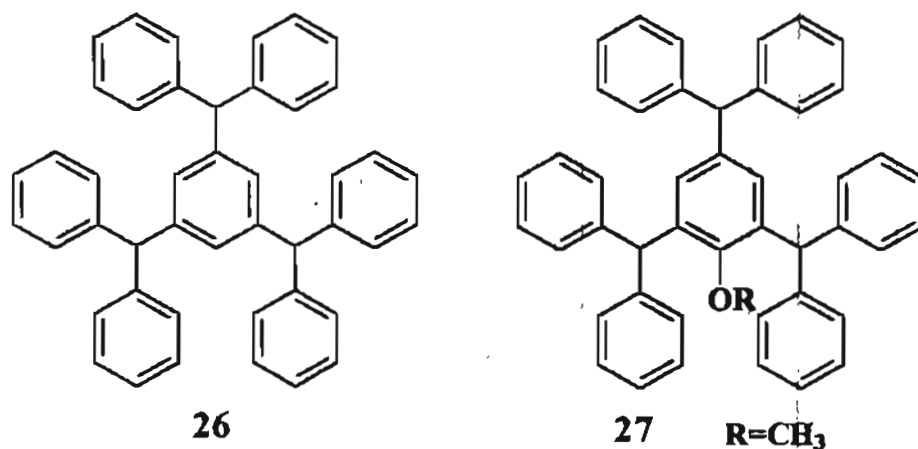


Figure 2



The proposed synthetic route involves the [4+2] cycloaddition of quinones of the type **28** (Figure 3) with arylacetylene **29** and subsequent photodecarbonylation (Scheme 10).

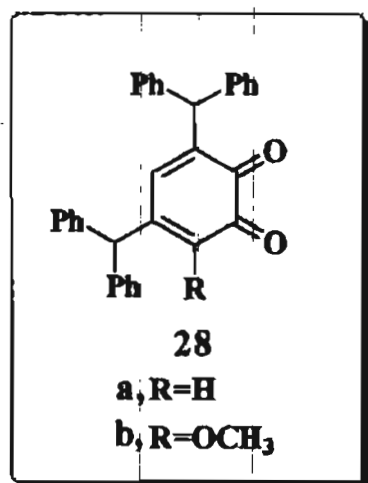
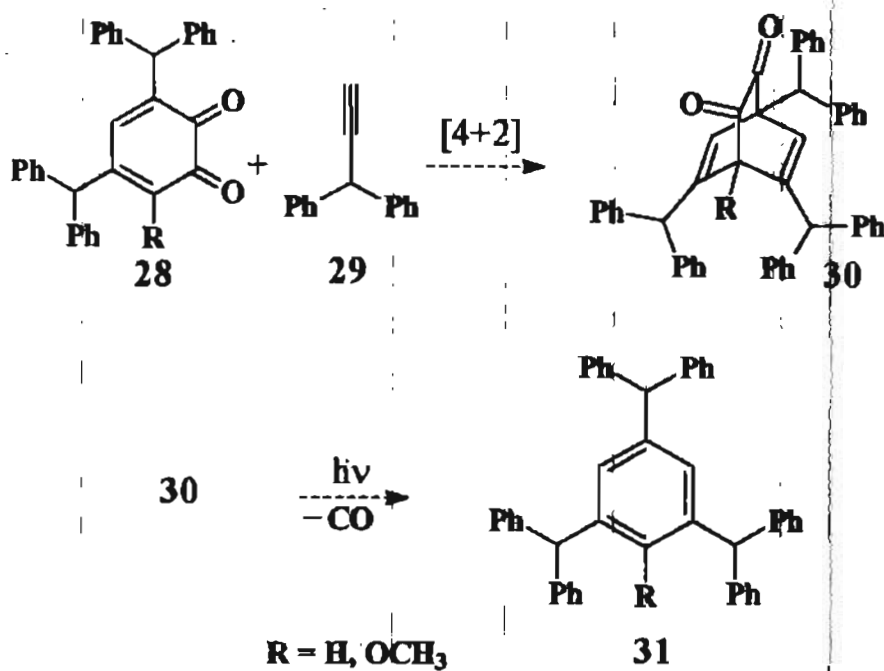
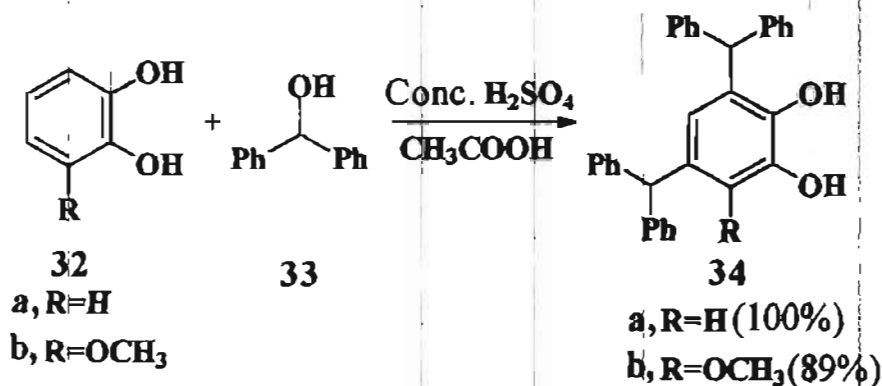


Figure 3



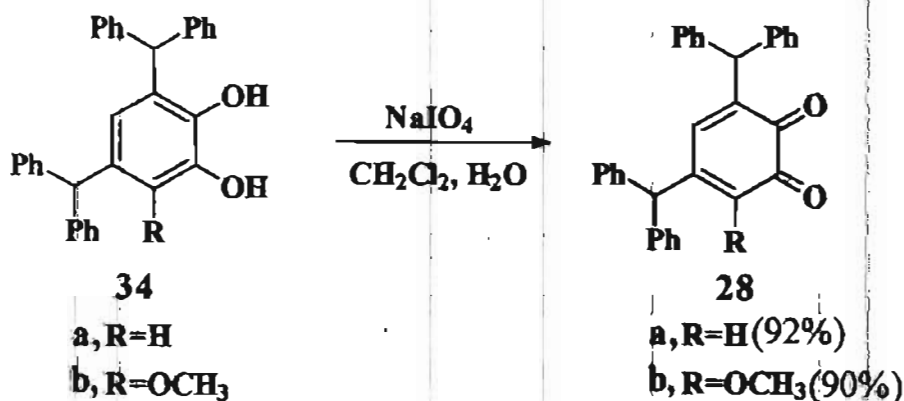
Scheme 10

The *o*-benzoquinones required for the study were conveniently synthesized by a method developed earlier in our laboratory. Treating the corresponding catechol **32** with benzhydrol **33** in presence of conc. sulfuric acid afforded the substituted catechol **34** (Scheme 11).<sup>14</sup>



Scheme 11

The catechols **34a** and **34b** on oxidation with NaIO<sub>4</sub> afforded the corresponding *o*-benzoquinones in excellent yields (Scheme 12).



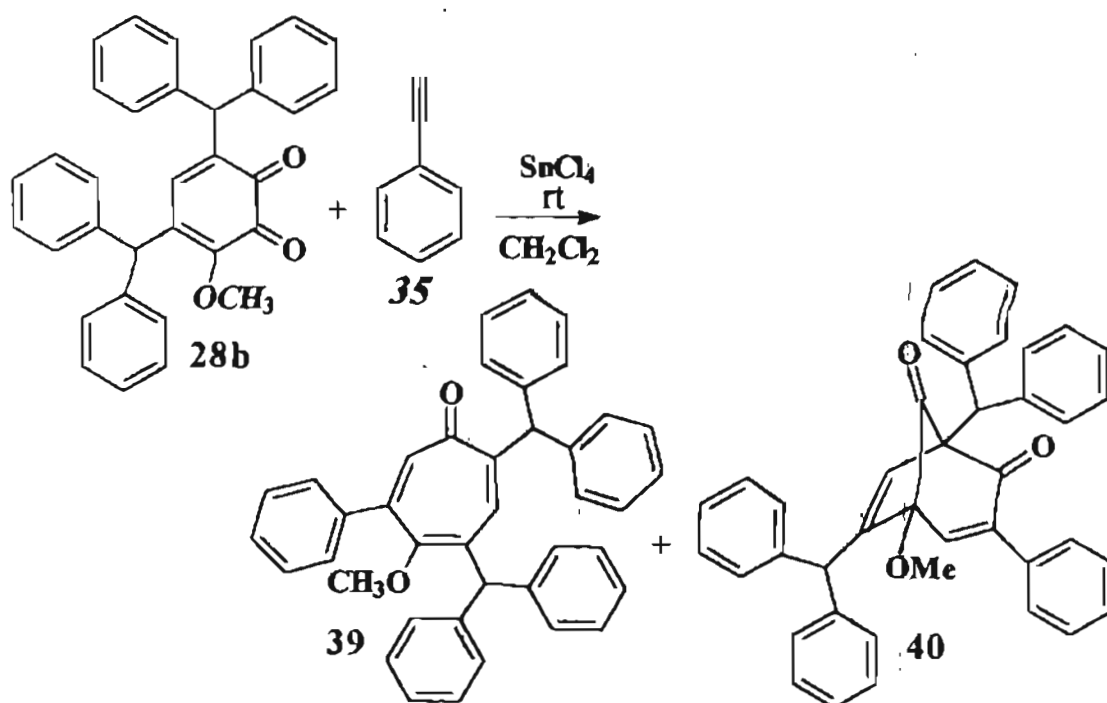
Scheme 12

A prototype experiment involved an attempt at the cycloaddition of quinone **28b** and phenylacetylene **35**. In this reaction, it was found that in addition to the expected [4+2] adducts **36** and **37**, which were obtained in

we decided to explore this reaction further. It should be emphasized that tropones and tropolones have aroused considerable interest as non-benzenoid aromatic compounds.<sup>15-24</sup> Also, the tropolone ring<sub>1</sub> has attracted attention due to its presence in a number of natural products. In this context, naturally it was of considerable interest to test the feasibility of the reaction and we extended the study further with other quinones and *p*-tolylaethylene also. The details of the investigations carried out are presented here.

## 4.2 RESULTS AND DISCUSSION

The present work was initiated by allowing the quinone **28b** to react with phenylacetylene **35** under Lewis acid mediation. It was found that the tropolone derivative **39** was formed in 60% yield along with the [3.2.1] adduct **40** in 18% yield (Scheme 14).



Scheme 14

The products were separated by column chromatography and characterized by spectroscopic analysis. The IR spectrum of **39** showed a very weak carbonyl absorption band at  $1686\text{ cm}^{-1}$  indicating that the carbonyl character of the C=O bond is attenuated due to the resonance contribution of the polarized structure **41** (Figure 5).

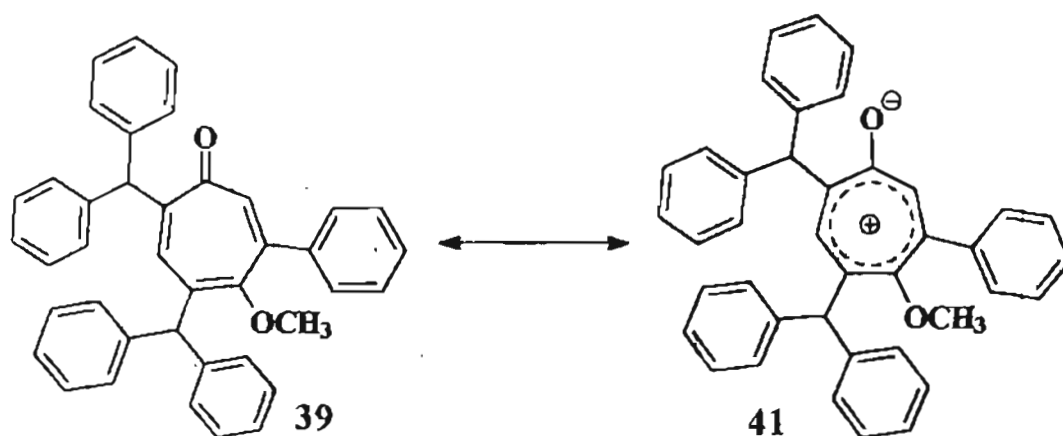


Figure 5

In the  $^1\text{H}$  NMR spectrum (Figure 6), the methoxy protons resonated at  $\delta$  2.99 as a singlet. The benzylic protons were discernible at  $\delta$  5.93 and 6.10 as singlets. The signals due to protons on the tropolone ring were also visible as singlets at  $\delta$  6.95 and 7.07. In the  $^{13}\text{C}$  NMR spectrum (Figure 7) of **39**, benzylic carbons resonated at  $\delta$  51.23 and 52.52. The methoxy carbon showed a signal at  $\delta$  59.94 and the carbonyl carbon at  $\delta$  184.52. Finally, the structure assigned was confirmed unequivocally by single crystal X-ray analysis (Figure 8).

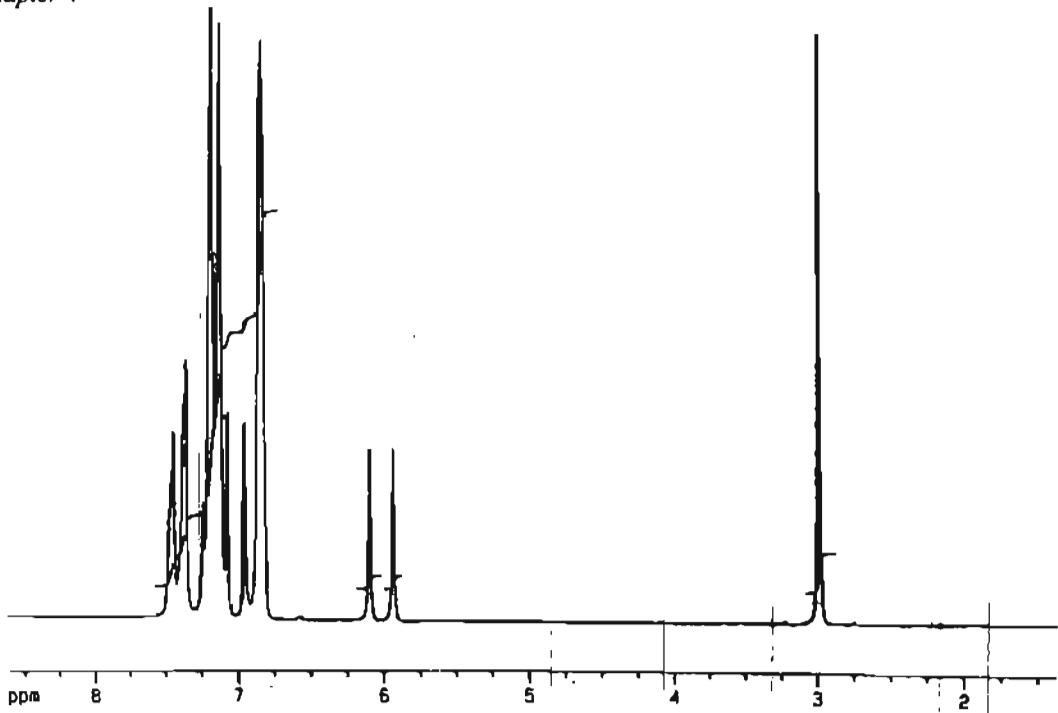


Figure 6.  $^1\text{H}$  NMR spectrum of 39

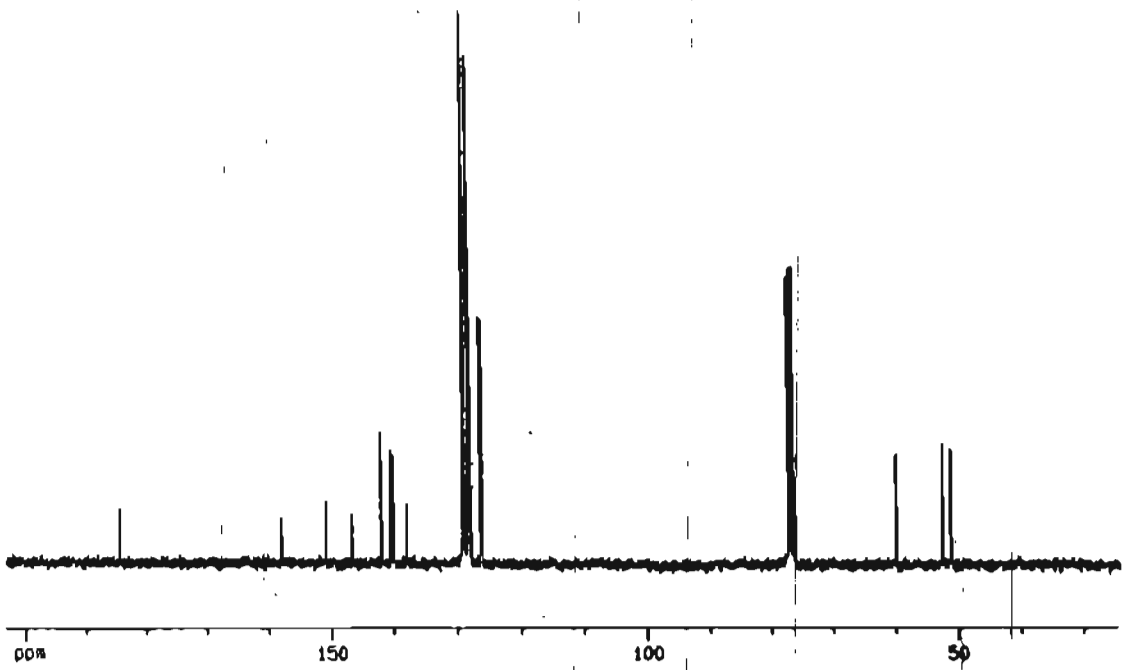


Figure 7.  $^{13}\text{C}$  NMR spectrum of 39

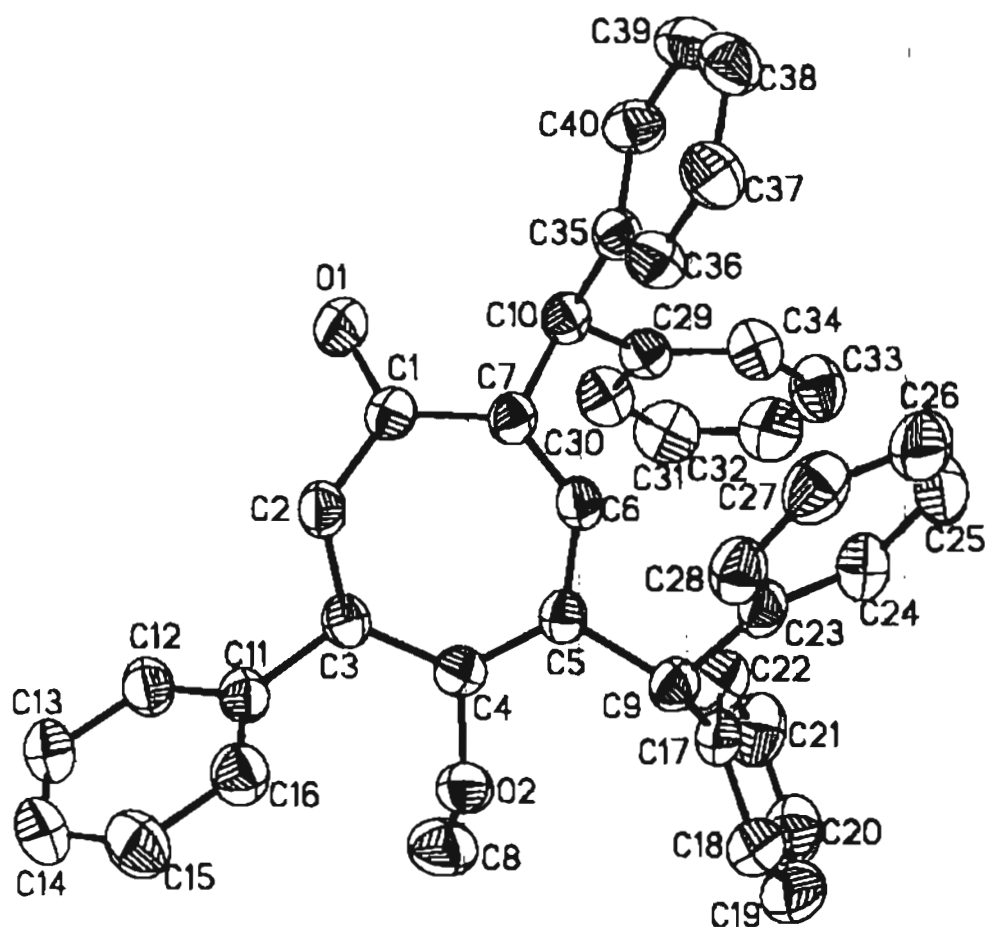
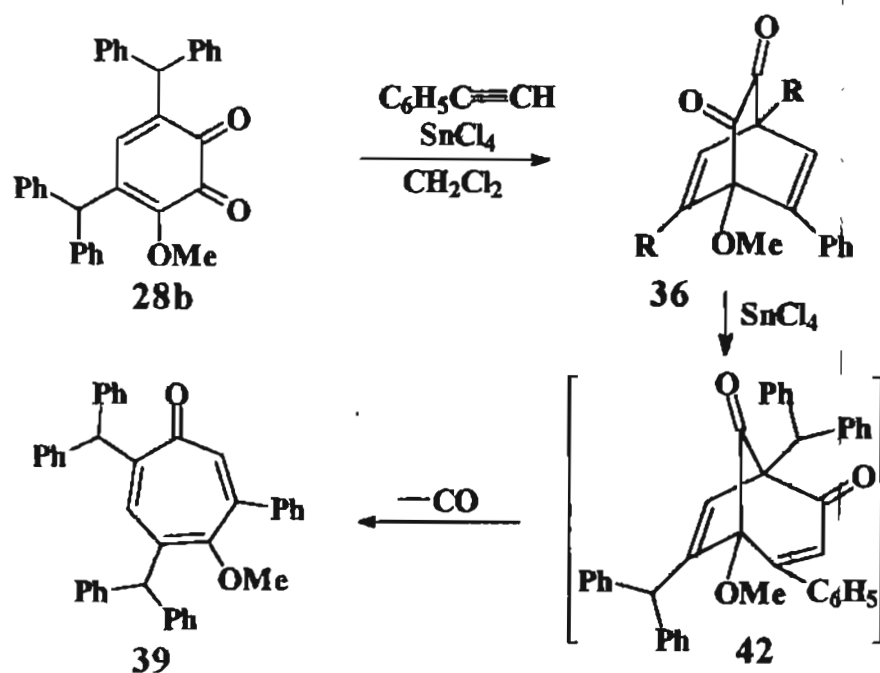


Figure 8. X-ray structure of 39

The structure of the product 40 was also elucidated by spectroscopic analysis. IR spectrum showed two bands at 1669 and 1781  $\text{cm}^{-1}$  corresponding to the  $\alpha, \beta$ -unsaturated and bridging carbonyl groups. In the  $^1\text{H}$  NMR spectrum, the methoxy protons resonated at  $\delta$  3.54 as a singlet. Benzylic protons of 40 were observed at  $\delta$  4.67 and 4.97. The olefinic protons showed signals at  $\delta$  5.72 and 6.41. In the  $^{13}\text{C}$  NMR spectrum, the signal due to the methoxy carbon was seen at  $\delta$  55.53. The benzylic carbons

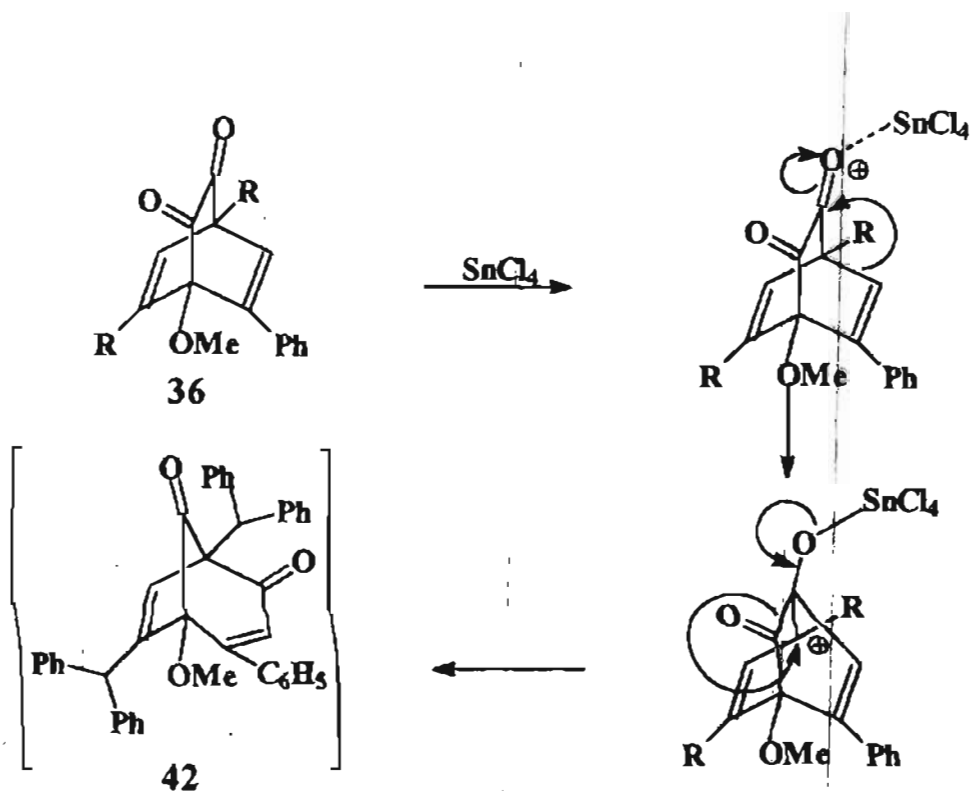
resonated at  $\delta$  49.29 and 53.61, and the quaternary carbons at the bridgehead positions were discernible at  $\delta$  64.69 and 99.29. The signals due to  $\alpha,\beta$ -unsaturated carbonyl carbon and the bridgehead carbonyl carbon were visible at  $\delta$  188.54 and 198.00 respectively.

The mechanistic details of the formation of **39** are not clearly understood. However, a rationalization along the following lines may be invoked. It is reasonable to assume that the initial reaction will be a [4+2] cycloaddition between the *o*-benzoquinone and phenylacetylene, catalyzed by  $\text{SnCl}_4$ , leading to the [2.2.2] adduct **36**. This can undergo a Lewis acid mediated rearrangement leading to the [3.2.1] adduct **42**. Such transformations have ample precedence in the literature.<sup>5</sup> Conceivably this bicyclo system spontaneously eliminates a molecule of carbon monoxide to afford the tropolone derivative **39** (Scheme 15).



Scheme 15

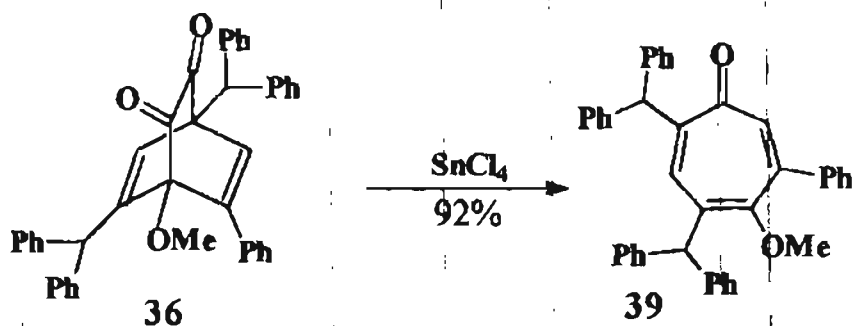
The mechanism for the conversion of **36** to **42** can be depicted as follows (Scheme 16).



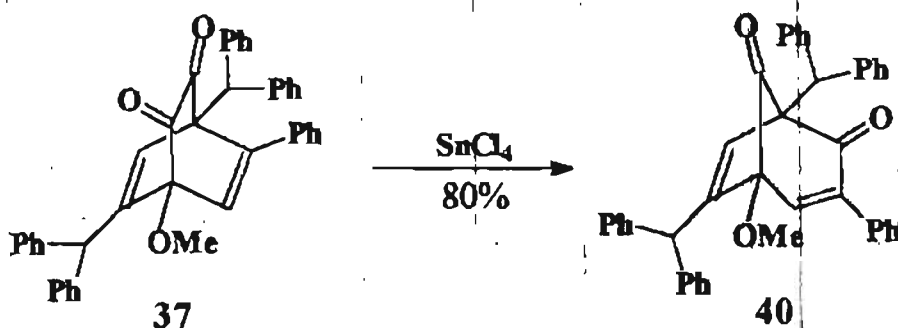
**Scheme 16**

In order to adduce some evidence for the mechanistic pathway suggested above, the following experiments were performed. Bicycloadducts **36** and **37** were treated with  $\text{SnCl}_4$  under identical conditions. It was found that the [2.2.2] adduct **36** produced only the tropolone **39** whereas **37** was transformed to the [3.2.1] adduct **40** exclusively (Schemes 17 and 18).



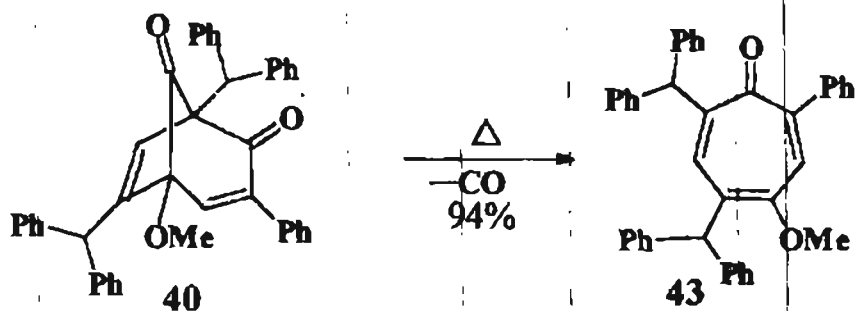


Scheme 17



Scheme 18

It is evident from this experiment that the precursor for the tropolone 39 is the bicyclo adduct 36. The [3.2.1] adduct 40, on heating above its melting point, lost one molecule of carbon monoxide to afford another tropolone derivative 43 which is isomeric with 39 (Scheme 19).

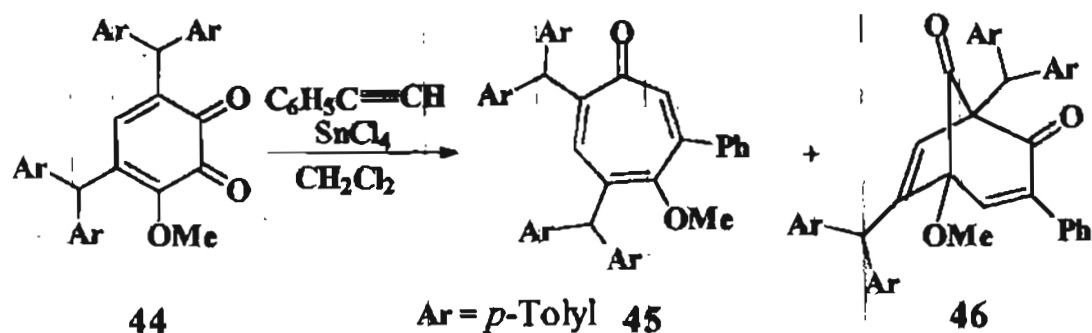


Scheme 19

From these experiments, it can be reasonably concluded that compound **39** was formed from the bicyclosystem **42**, which could not be isolated. The ease of decarbonylation of **42** *vis a vis* **40** may be attributed to the release of steric strain in the former.

The reaction was extended to two other quinones and phenyl acetylene and the results are discussed in the following passages.

Thus, the quinone **44** was allowed to react with phenylacetylene in presence of  $\text{SnCl}_4$  under the conditions described earlier. The reaction proceeded smoothly to afford the products **45** and **46** in 58 % and 12 % yields respectively (Scheme 20).

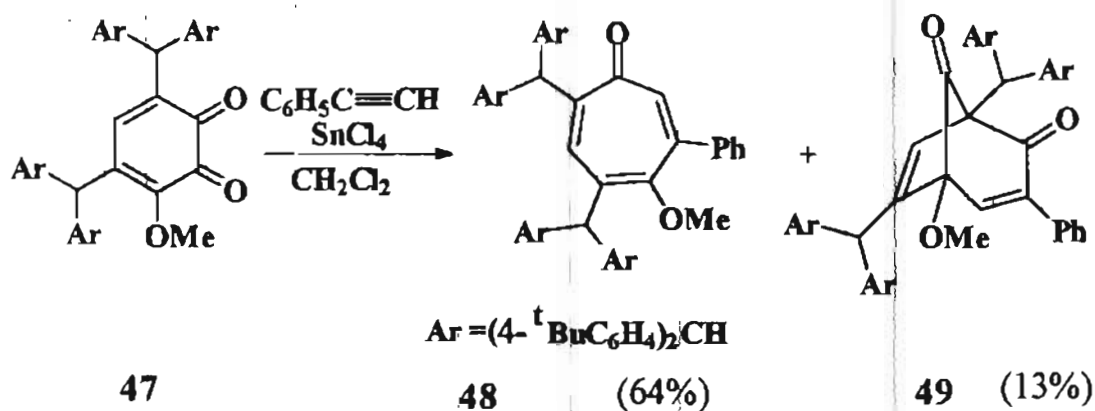


Scheme 20

The products were separated by column chromatography and characterized by spectroscopic analysis. The IR spectrum of **45** showed a very weak carbonyl absorption at  $1683\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum, the methoxy protons resonated at  $\delta$  2.97 as a singlet. The benzylic protons resonated at  $\delta$  5.83 and 6.00 as singlets. The  $^{13}\text{C}$  NMR spectrum of **45** showed the methoxy carbon at  $\delta$  59.94. The benzylic carbons were observable at  $\delta$  50.52 and 51.89 and the carbonyl carbon signal was visible at  $\delta$  184.68.

The bicycloadduct **46** was also characterized by spectroscopic analysis. IR spectrum showed two carbonyl absorptions at 1680 and 1781  $\text{cm}^{-1}$  due to the enone and bridging carbonyl groups respectively. In the  $^1\text{H}$  NMR spectrum, the methoxy protons resonated at  $\delta$  3.54 as a singlet. The benzylic protons were discernible at  $\delta$  4.60 and 4.88 as singlets. In the  $^{13}\text{C}$  NMR spectrum, the four methyl carbons on the aromatic ring resonated at  $\delta$  21.06 and 21.25. The two benzylic carbons, the methoxy carbon and the two quaternary carbons resonated at  $\delta$  48.58, 52.65, 55.60, 64.73 and 99.42 respectively. The enone and the bridging carbonyls were discernible at  $\delta$  188.83 and 198.11 respectively.

The reaction of quinone **47** with phenylacetylene also proceeded in a similar way affording the tropolone derivative **48** and the bicycloadduct **49** (Scheme 21).

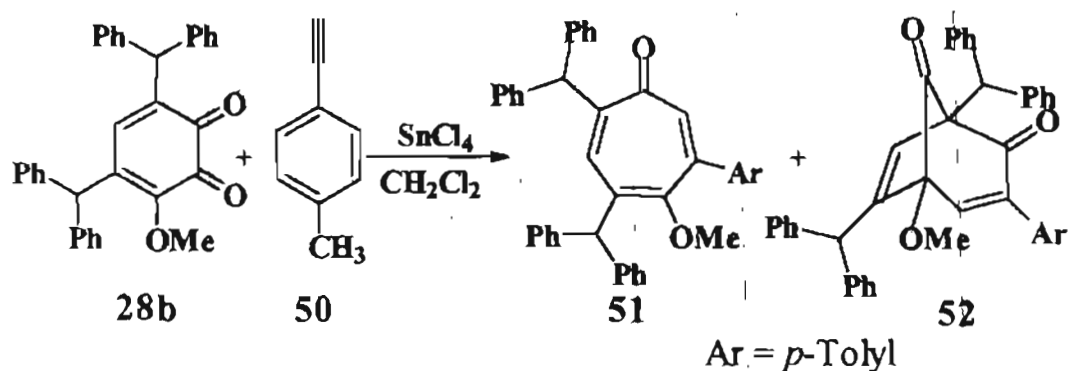


Scheme 21

As usual, the structure of the product **48** was established from its spectroscopic data. The  $^1\text{H}$  NMR spectrum showed two signals at  $\delta$  1.27 and 1.31 for the *t*-butyl hydrogens. The methoxy and benzylic protons were

seen at  $\delta$  3.02, 5.89 and 5.98 respectively. In the  $^{13}\text{C}$  NMR spectrum of **48** the *t*-butyl carbons resonated between  $\delta$  26.00 and 35.00. The benzylic carbons were observable at  $\delta$  50.50 and 51.65. The methoxy and carbonyl carbons resonated at  $\delta$  60.07 and 184.19. The [3.2.1] adduct **49** was also characterized by spectroscopic analysis.

Subsequently we carried out the reaction of *o*-benzoquinone **28b** and *p*-tolylacetylene **50** under Lewis acid catalysis. This reaction also afforded the tropolone derivative **51** and the bicyclo [3.2.1] adduct **52** in 61 % and 14 % yields respectively (Scheme 22).



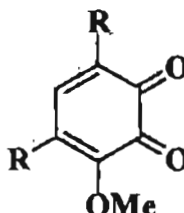
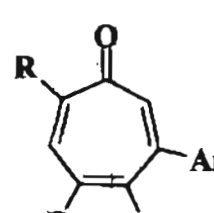
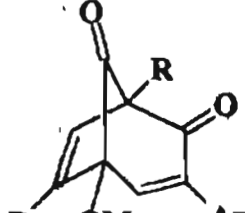
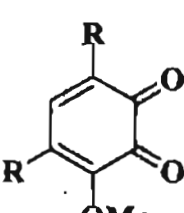
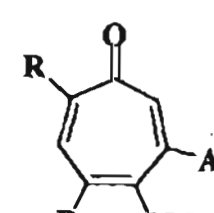
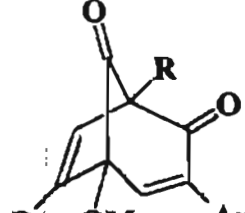
**Scheme 22**

The products were separated and purified by column chromatography and identified by spectroscopic analysis. The IR spectrum of **51** showed a weak band at  $1689\text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum, the methyl and methoxy groups were discernible at  $\delta$  2.38 and 2.99. Benzylic protons of **51** resonated at  $\delta$  5.93 and 6.09. The protons on the tropolone ring were observable at  $\delta$  6.93 and 7.06. In the  $^{13}\text{C}$  NMR spectrum, the methyl and methoxy carbons resonated at  $\delta$  21.32 and 60.01.

The benzylic carbons showed signals at  $\delta$  51.36 and 52.63. The [3.2.1] adduct **52** was also characterized by spectroscopic analysis.

The reaction of *p*-tolylacetylene was extended to quinones **44** and **47** also. In these cases also the reaction proceeded smoothly to afford the corresponding tropolones and the bicycloadducts. The results are summarized in Table 1.

**Table 1.** Reaction of Quinones **44** and **47** with *p*-Tolylacetylene.

| Quinones   | Products   |  | Yield*% |
|--|--|--|---------|
|  | Tropolone  | [3,2,1] adduct   |         |
| <br>$R = (p\text{-CH}_3\text{C}_6\text{H}_5)_2\text{CH}$<br><b>44</b> | <br><b>53</b> | <br>$\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_5$<br><b>54</b> | 57(13)  |
| <br>$R = (p\text{-ButC}_6\text{H}_5)_2\text{CH}$<br><b>47</b>         | <br><b>55</b> | <br>$\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_5$<br><b>56</b> | 60(18)  |

\* Yield of the [3.2.1] adduct is given in brackets

All the products (**53-56**) were characterized by spectroscopic analysis.

### 4.3 EXPERIMENTAL

General information about the experiments is given in section 3.4 (Chapter 3). Arylacetylenes (phenylacetylene and *p*-tolylacetylene) and SnCl<sub>4</sub> (1M solution in heptane) required for the reactions were purchased from Aldrich and used as such.

#### 4.3.1 EXPERIMENTAL PROCEDURE FOR THE THERMAL REACTION BETWEEN *o*-QUINONE AND PHENYLACETYLENE

*o*-Benzoquinone **28b** (0.25 g,  $5.3 \times 10^{-4}$  mol) and phenylacetylene (0.108 g,  $1.06 \times 10^{-4}$  mol) were taken in a Schlenk tube. The Schlenk tube was evacuated and filled with argon. It was then heated at 90° C for 8 h. The crude product was then subjected to chromatography on silica gel column using hexane-ethyl acetate mixture (90:10). Cycloadduct **36** (0.0609 g, 20%) was eluted first. Further elution afforded the cycloadduct **37** (0.018 g, 6%) and the dimeric product **38** (0.164 g, 46%).

##### *Bicycloadduct 36*

Orange crystals; recrystallized from hexane-dichloromethane.

mp : 195-197° C

IR (KBr)  $\nu_{\max}$  : 694, 932, 1031, 1238, 1445, 1492, 1741, 2948, 3020, 3067 cm<sup>-1</sup>.

<sup>1</sup>H NMR :  $\delta$  3.15 (s, 3H), 5.13 (s, 1H), 5.40 (s, 1H), 5.76 (s, 1H), 6.36 (s, 1H), 6.86-6.91 (m, 4H), 7.13-7.34 (m, 21H).

<sup>13</sup>C NMR :  $\delta$  48.25, 50.59, 57.03, 60.58, 89.80, 126.53, 126.67, 128.18, 128.40, 128.51, 128.63, 129.14, 129.57, 129.80, 129.94, 134.97, 140.03, 140.28, 140.77, 141.27, 143.89, 149.04, 178.05, 182.19.

Anal. Calcd. for C<sub>41</sub>H<sub>32</sub>O<sub>3</sub>: C, 85.99; H, 5.63. Found: C, 85.39; H, 5.75.

***Bicycloadduct 37***

Pale orange crystals; recrystallized from hexane-dichloromethane.

- mp : 177-179° C
- IR (KBr)  $\nu_{\max}$  : 697, 745, 1025, 1276, 1447, 1490, 1746, 3023  $\text{cm}^{-1}$ .
- $^1\text{H}$  NMR :  $\delta$  3.44 (s, 1H), 5.19 (s, 1H), 5.31 (s, 1H), 6.26 (s, 1H),  
6.49 (s, 1H), 6.66-6.69 (m, 2H), 6.76-6.79 (m, 2H),  
6.86-7.40 (m, 21H).
- $^{13}\text{C}$  NMR :  $\delta$  47.21, 50.42, 54.38, 63.59, 86.54, 125.75, 126.34,  
126.53, 126.69, 127.49, 127.84, 128.27, 128.33, 128.74,  
128.90, 129.31, 130.66, 136.87, 139.56, 140.27, 140.86,  
141.45, 145.90, 147.05, 179.77, 181.24.

Anal. Calcd. for  $\text{C}_{41}\text{H}_{32}\text{O}_3$ : C, 85.99; H, 5.63. Found: C, 86.45; H, 5.78.

***Dimeric Product 38***

Yellow crystals; recrystallized from hexane-dichloromethane.

- mp : 188-190° C
- IR (KBr)  $\nu_{\max}$  : 695, 744, 1034, 1097, 1246, 1314, 1445, 1488, 1691,  
1759, 3026, 3065  $\text{cm}^{-1}$ .
- $^1\text{H}$  NMR :  $\delta$  2.78 (s, 3H), 2.87 (s, 3H), 4.83 (s, 1H), 5.27 (s, 1H),  
5.71 (s, 1H), 5.74 (s, 3H), 6.21 (s, 1H), 6.73-6.77 (m,  
5H), 6.87-7.37 (m, 35H).

$^{13}\text{C}$  NMR  $\delta$  48.12, 49.79, 49.88, 52.39, 57.48, 59.67, 81.59, 97.52, 124.29, 125.99, 126.12, 126.55, 126.80, 127.12, 127.88, 127.92, 128.06, 128.44, 128.67, 128.83, 128.96, 129.07, 130.03, 130.73, 131.31, 135.26, 135.74, 138.06, 139.33, 141.32, 142.18, 143.18, 143.34, 143.62, 145.52, 145.58, 147.90, 181.29, 181.88.

Anal. Calcd. for  $\text{C}_{66}\text{H}_{52}\text{O}_6$ : C, 84.23; H, 5.57. Found C, 84.04; H, 5.61.

### 4.3.2 TYPICAL EXPERIMENTAL PROCEDURE FOR THE SYNTHESIS OF THE TROPOLONE DERIVATIVES AND THE BICYCLO [3.2.1] ADDUCTS

The general procedure for the synthesis of tropolone derivatives and bicycloadducts is exemplified by the synthesis of **39** and **40**. To a stirred mixture of *o*-benzoquinone **28b** (0.20 g,  $4.25 \times 10^{-4}$  mol) and phenylacetylene (0.052 g,  $5.10 \times 10^{-4}$  mol) in dry dichloromethane (2 mL) was added  $\text{SnCl}_4$  (0.851 mL, 1 molar solution of  $\text{SnCl}_4$  in heptane) and stirred for two hours under an atmosphere of argon at room temperature. After that the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane ( $2 \times 10$  mL). The organic extract was concentrated and the crude product subjected to column chromatography on silica gel using hexane-ethyl acetate mixture (90:10) to afford the tropolone derivative **39** (0.139 g, 60%,) and the [3.2.1] adduct **40** (0.044 g, 18%).

#### *4-Methoxy-3-phenyl-5, 7-bis (diphenyl methyl) 2,4,6-cycloheptatriene-1-one 39*

Pale yellow crystals; recrystallized from hexane-dichloromethane.

mp : 200-202° C



|                       |   |
|-----------------------|---|
| IR (KBr) $\nu_{\max}$ | : 689, 752, 989, 1151, 1201, 1439, 1489, 1551, 1686, 2930, 3030 $\text{cm}^{-1}$ .  |
| $^1\text{H}$ NMR      | : $\delta$ 2.99 (s, 3H), 5.93 (s, 1H), 6.10 (s, 1H), 6.84-6.85 (m, 5H), 6.95 (s, 1H), 7.07 (s, 1H), 7.13-7.45 (m, 20H)  |
| $^{13}\text{C}$ NMR   | : $\delta$ 51.23, 52.52, 59.94, 126.22, 126.49, 128.06, 128.18, 128.43, 129.00, 129.13, 129.20, 138.11, 140.09, 140.26, 140.66, 142.15, 142.24, 146.81, 150.99, 158.12, 184.52. |

Anal. Calcd. for  $\text{C}_{40}\text{H}_{32}\text{O}_2$ : C, 88.20; H, 5.92. Found C, 88.28; H, 6.04.

**Crystal data for 39:**  $\text{C}_{40}\text{H}_{32}\text{O}_2$ . M. 544.66, Triclinic, space group P-1, unit cell dimensions  $a = 10.2641(1) \text{ \AA}$ ,  $\alpha = 108.907(1)^\circ$ ;  $b = 10.6112(1) \text{ \AA}$ ,  $\beta = 90.290(1)^\circ$ ;  $c = 14.3475(2) \text{ \AA}$ ,  $\gamma = 95.119(1)^\circ$ , R indices (all data)  $R_1 = 0.0805$ ,  $wR_2 = 0.1411$ , volume,  $Z = 1471.48(3) \text{ \AA}^3$ , 2,  $D_{\text{calc}} = 1.229 \text{ Mg/m}^3$ , absorption coefficient =  $0.074 \text{ mm}^{-1}$ ,  $\lambda = 0.71073 \text{ \AA}$ , reflections collected 27852.

***1,6-Bis (diphenyl methyl)-5-methoxy-3-phenyl-bicyclo [3.2.1] oct-3, 6-diene-2, 8-dione 40***

Colorless crystals; recrystallized from hexane-dichloromethane.

|                       |  |
|-----------------------|--|
| mp                    | : 132-134°C  |
| IR (KBr) $\nu_{\max}$ | : 1032, 1151, 1238, 1438, 1494, 1669, 1781, 2949 $\text{cm}^{-1}$ .  |
| $^1\text{H}$ NMR      | : $\delta$ 3.54 (s, 3H), 4.67 (s, 1H), 4.97 (s, 1H), 5.72 (s, 1H), 6.41 (s, 1H), 6.80-6.87 (m, 4H), 6.96-6.98 (m, 8H), 7.05-7.13 (m, 4H), 7.21-7.24 (m, 9H). |
| $^{13}\text{C}$ NMR   | : $\delta$ 49.29, 53.61, 55.53, 64.69, 99.29, 126.09, 126.45,  |

126.68, 126.99, 127.38, 127.73, 127.93, 128.27,  
128.43, 128.77, 128.96, 129.32, 129.81, 130.86,  
137.49, 137.58, 138.57, 139.31, 139.53, 140.42,  
147.40, 165.25, 188.54, 198.00.

Anal. Calcd. for  $C_{41}H_{32}O_3$ : C, 85.99; H, 5.63. Found: C, 86.26; H, 6.38.

***4-Methoxy-2-phenyl-5, 7-bis (diphenyl methyl) 2,4,6-cycloheptatriene-1-one 43***

Bicycloadduct **40** (0.110 g,  $2.01 \times 10^{-4}$  mol) was taken in a Schlenk tube under an atmosphere of argon. It was then heated at  $150^\circ\text{C}$  for 30 minutes. The product obtained was subjected to column chromatography on silica gel using hexane-ethyl acetate mixture (90:10) to afford the product **43** (0.099 g, 94%).

Pale yellow crystals; recrystallized from hexane-ethyl acetate.

mp : 152-154 $^\circ\text{C}$

IR (KBr)  $\nu_{\text{max}}$  : 738, 1026, 1092, 1152, 1208, 1441, 1487, 1571, 1613,  
1697, 3024, 3061  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR : 3.82 (s, 3H), 5.17 (s, 1H), 6.17 (s, 1H), 6.51-6.53 (m,  
4H), 6.78 (s, 1H), 6.84-6.86 (m, 4H), 6.93-6.96 (d, 1H,  
 $J = 6.76$  Hz), 7.09-7.30 (m, 16 H).

$^{13}\text{C}$  NMR :  $\delta$  51.60, 56.66, 59.00, 126.42, 126.53, 127.67, 127.93,  
128.17, 128.26, 128.44, 129.32, 138.86, 139.64, 140.35,  
141.77, 141.98, 142.24, 144.95, 151.22, 161.86, 180.68.

Anal. Calcd. for  $C_{40}H_{32}O_2$ : C, 88.20; H, 5.92. Found: C, 88.48; H, 5.92.

***5-Methoxy-3-phenyl-5,7-bis (di-4-methylphenyl methyl) 2,4,6-cycloheptatriene-1-one 45 and 1,6-Bis (di-4-methylphenyl methyl)-5-methoxy-3-phenyl-bicyclo [3.2.1] oct-3, 6-diene-2, 8-dione 46***

To a stirred mixture of *o*-benzoquinone **44** (0.160 g,  $3.04 \times 10^{-4}$  mol) and phenylacetylene (0.037 g,  $3.65 \times 10^{-4}$  mol) in dry dichloromethane (2 mL) was added SnCl<sub>4</sub> (0.608 mL, 1 molar solution of SnCl<sub>4</sub> in heptane) and stirred for two hours under an atmosphere of argon at room temperature. The reaction mixture was worked up by the procedure described previously. The crude product was subjected to column chromatography on silica gel using hexane-ethyl acetate mixture (90:10) to afford the tropolone derivative **45** (0.106 g, 58%) and the [3.2.1] adduct **46** (0.023 g, 12%).

***Tropolone Derivative 45***

Colorless yellow crystals; recrystallized from hexane-ethyl acetate.

mp : 189-191° C

$\nu_{\text{max}}$  (KBr) : 764, 805, 996, 1153, 1242, 1370, 1445, 1510, 1576, 1613, 1683, 2921, 3020 cm<sup>-1</sup>.

<sup>1</sup>H NMR :  $\delta$  2.29 (s, 6H), 2.33 (s, 6H), 2.97 (s, 3H), 5.83 (s, 1H), 6.00 (s, 1H), 6.72-6.76 (m, 8H), 6.92-7.00 (m, 8H), 7.04 (s, 1H), 7.25 (s, 1H), 7.36-7.45 (m, 5H).

<sup>13</sup>C NMR :  $\delta$  21.02, 50.52, 51.89, 59.94, 128.00, 128.14, 128.79, 129.01, 129.07, 135.38, 135.76, 138.55, 139.42, 139.49, 140.13, 140.23, 140.49, 146.77, 151.31, 157.82, 184.68.

Anal. Calcd. for C<sub>44</sub>H<sub>40</sub>O<sub>2</sub>: C; 87.96; H; 6.71. Found: C; 88.05, H, 6.69.

***Bicyclic adduct 46***

Colorless crystals; recrystallized from hexane-dichloromethane.

|                       |   |   |
|-----------------------|---|---|
| mp                    | : | 177-179°C   |
| IR (KBr) $\nu_{\max}$ | : | 746, 1151, 1259, 1438, 1510, 1680, 1781, 2937 $\text{cm}^{-1}$ .  |
| $^1\text{H}$ NMR      | : | $\delta$ 2.19 (s, 3H), 2.28 (s, 3H), 2.35 (s, 3H), 3.54 (s, 3H),<br>4.60 (s, 1H), 4.88 (s, 1H), 5.71 (s, 1H), 6.39 (s, 1H),<br>6.67-6.88 (m, 10H), 6.99-7.09 (m, 11H).  |
| $^{13}\text{C}$ NMR   | : | $\delta$ 21.06, 21.25, 48.58, 52.65, 55.60, 64.73, 99.42,<br>126.41, 126.51, 127.90, 128.46, 128.57, 128.90, 128.95,<br>129.20, 129.51, 129.68, 130.00, 135.36, 135.86, 136.02,<br>136.35, 136.60, 136.73, 136.97, 137.39, 137.77, 137.80,<br>147.48, 165.53, 188.83, 198.11. |

**4-Methoxy-3-phenyl-5, 7-bis (di-4'-butylphenyl methyl) 2,4,6-cycloheptatriene-1-one 48 and 1,6-Bis (di-4'-butylphenyl methyl)-5-methoxy-3-phenyl-bicyclo [3.2.1] oct-3, 6-diene-2, 8-dione 49**

To a stirred mixture of *o*-benzoquinone 47 (0.20 g,  $2.88 \times 10^{-4}$  mol) and phenylacetylene (0.035 g,  $3.453 \times 10^{-4}$  mol) in dry dichloromethane (2 mL) was added  $\text{SnCl}_4$  (0.6 mL, 1 molar solution of  $\text{SnCl}_4$  in heptane) and stirred for two hours under an atmosphere of argon at room temperature. The reaction mixture was worked up as described previously. The crude product was subjected to column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) to afford the tropolone derivative 48 (0.121 g, 55%) and the [3.2.1] adduct 49 (0.039 g, 17%).

#### ***Tropolone Derivative 48***

Pale yellow crystals; recrystallized from hexane-ethyl acetate.

|    |   |           |
|----|---|-----------|
| mp | : | 130-132°C |
|----|---|-----------|

IR (KBr)  $\nu_{\max}$  : 575, 699, 821, 997, 1018, 1155, 1268, 1364, 1508, 1582, 1614, 1686, 2867, 2961  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  1.27 (m, 18H), 1.31 (m, 18H), 3.02 (s, 3H), 5.89 (s, 1H), 5.98 (s, 1H), 6.70-6.74 (m, 8H), 6.90 (s, 1H), 7.07 (s, 1H), 7.16-7.42 (m, 13H).

$^{13}\text{C}$  NMR :  $\delta$  26.92, 31.44, 34.32, 34.40, 50.50, 51.65, 60.07, 125.01, 125.25, 128.03, 128.14, 128.93, 129.03, 129.09, 139.28, 139.43, 140.44, 141.07, 146.75, 148.68, 149.17, 151.29, 157.85, 184.19.

***Bicycloadduct 49***

Colorless crystals; recrystallized from hexane-dichloromethane.

mp : 194-196° C

IR (KBr)  $\nu_{\max}$  : 820, 1138, 1257, 1432, 1512, 1688, 1769, 2962  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  1.21 (s, 9H), 1.26 (s, 9H), 1.33 (s, 18H), 3.52 (s, 3H), 4.55 (s, 1H), 4.90 (s, 1H), 5.70 (s, 1H), 6.43 (s, 1H), 6.71-7.24 (m, 21H).

$^{13}\text{C}$  NMR :  $\delta$  31.27, 31.30, 31.38, 34.10, 34.35, 48.03, 52.88, 55.27, 64.93, 99.18, 124.30, 124.62, 124.84, 125.38, 126.20, 126.36, 127.57, 127.92, 128.42, 128.55, 129.38, 130.78, 136.05, 136.24, 136.39, 137.70, 137.77, 137.91, 147.08, 148.42, 149.01, 149.28, 149.63, 165.47, 188.47, 198.02.

**4-Methoxy-3-(4-methyl phenyl)-5, 7-bis (diphenyl methyl) 2,4,6-cycloheptatriene-1-one 51 and 1,6-Bis (diphenyl methyl)-5-methoxy-3- (4-methyl phenyl)-bicyclo [3.2.1] oct-3, 6-diene-2, 8-dione 52**

To a stirred mixture of *o*-benzoquinone **28b** (0.20 g,  $4.25 \times 10^{-4}$  mol) and *p*-tolylacetylene (0.059 g,  $5.10 \times 10^{-4}$  mol) in dry dichloromethane (2 mL) was added SnCl<sub>4</sub> (0.85 mL, 1M solution of SnCl<sub>4</sub> in heptane) and stirred under an atmosphere of argon for two hours at room temperature. The reaction mixture was worked up as usual. The crude product was subjected to column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) to afford the tropolone derivative **51** (0.145 g, 61%) and the [3.2.1] adduct **52** (0.035 g, 14%).

**Tropolone Derivative 51**

Pale yellow crystals; recrystallized from hexane-ethyl acetate.

|                       |   |  |
|-----------------------|---|--|
| mp                    | : | 160-162° C   |
| IR (KBr) $\nu_{\max}$ | : | 699, 743, 994, 1153, 1368, 1447, 1492, 1572, 1601, 1689, 2931, 3024 cm <sup>-1</sup> .   |
| <sup>1</sup> H NMR    | : | $\delta$ 2.38 (s, 3H), 2.99 (s, 3H), 5.93 (s, 1H), 6.09 (s, 1H), 6.84-6.87 (m, 8H), 6.93 (s, 1H), 7.06 (s, 1H), 7.12-7.36 (m, 16 H).   |
| <sup>13</sup> C NMR   | : | $\delta$ 21.32, 51.36, 52.63, 60.01, 126.32, 126.59, 128.29, 128.54, 128.90, 129.06, 129.27, 129.33, 137.36, 138.06, 138.25, 140.30, 140.59, 142.34, 142.42, 146.89, 151.00, 158.44, 184.71. |

HRMS Calcd for C<sub>41</sub>H<sub>34</sub>O<sub>2</sub>: 558.2558. Found: 558. 2553.

**Bicycloadduct 52**

Colorless crystals; recrystallized from hexane-dichloromethane.

|                       |   |  |
|-----------------------|---|--|
| mp                    | : | 167-169°C  |
| IR (KBr) $\nu_{\max}$ | : | 689, 1022, 1146, 1177, 1448, 1493, 1686, 1775, 2947, 3025 $\text{cm}^{-1}$ .   |
| $^1\text{H}$ NMR      | : | $\delta$ 2.24 (s, 3H), 3.53 (s, 3H), 4.71 (s, 1H), 4.96 (s, 1H), 5.71 (s, 1H), 6.39 (s, 1H), 6.80-6.97 (m, 13H), 7.22-7.24 (m, 11H).   |
| $^{13}\text{C}$ NMR   | : | $\delta$ 21.15, 49.18, 53.24, 55.32, 64.51, 99.22, 125.92, 126.02, 126.31, 126.55, 126.87, 127.26, 127.64, 128.15, 128.51, 128.64, 128.83, 129.21, 129.65, 130.77, 134.63, 137.30, 138.37, 138.44, 139.23, 139.62, 140.30, 147.11, 165.37, 188.51, 197.92. |

Anal. Calcd. for  $\text{C}_{42}\text{H}_{34}\text{O}_3$ : C, 85.98; H, 5.84. Found: C, 85.92; H, 6.04.

***4-Methoxy-3-(4-methyl phenyl)-5, 7-bis (di-4-methylphenyl methyl) 2,4,6-cycloheptatriene-1-one 53 and 1,6-Bis (di-4-methylphenyl methyl)-5-methoxy-3-(4-methyl phenyl)-bicyclo [3.2.1] oct-3, 6-diene-2, 8-dione 54***

To a stirred mixture of *o*-benzoquinone **44** (0.226 g,  $4.29 \times 10^{-4}$  mol) and *p*-tolylacetylene (0.059 g,  $5.15 \times 10^{-4}$  mol) in dry dichloromethane (2 mL) was added  $\text{SnCl}_4$  (0.85 mL, 1M solution of  $\text{SnCl}_4$  in heptane) and stirred under an atmosphere of argon for two hours at room temperature. The crude product was subjected to column chromatography on silica gel using hexane-ethyl acetate mixture (90:10) to afford the tropolone derivative **53** (0.137 g, 57%) and the [3.2.1] adduct **54** (0.036 g, 13%).

#### ***Tropolone Derivative 53***

Pale yellow crystals; recrystallized from hexane-ethyl acetate.

mp : 83-85° C

IR (KBr)  $\nu_{\max}$  : 766, 996, 1153, 1204, 1368, 1510, 1572, 1594, 1611, 2921, 3020  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  2.31 (s, 6H), 2.35 (s, 6H), 2.40 (s, 3H), 3.00 (s, 3H), 5.85 (s, 1H), 6.03 (s, 1H), 6.74-6.76 (m, 4H), 6.94-7.38 (m, 14H), 7.06 (s, 1H), 7.20 (s, 1H).

$^{13}\text{C}$  NMR :  $\delta$  21.10, 21.29, 50.62, 51.98, 59.98, 128.87, 129.08, 129.13, 129.16, 135.44, 135.82, 137.46, 138.09, 138.49, 139.58, 139.64, 140.16, 140.40, 146.83, 151.29, 158.11, 184.82.

Anal. Calcd for  $\text{C}_{45}\text{H}_{42}\text{O}_2$ : C, 87.91; H, 6.89. Found: C, 87.58, H, 7.15.

### ***Bicycloadduct 54***

Colorless crystals; recrystallized from hexane-dichloromethane.

mp : 120-122°C

IR (KBr)  $\nu_{\max}$  : 807, 1020, 1145, 1245, 1439, 1676, 1776, 2987  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR :  $\delta$  2.20 (s, 3H), 2.25 (s, 3H), 2.27 (s, 3H), 2.35 (s, 3H), 2.36 (s, 3H), 3.52 (s, 3H), 4.64 (s, 1H), 4.87 (s, 1H), 5.70 (s, 1H), 6.36 (s, 1H), 6.66 (d, 2H,  $J = 7.8$  Hz), 6.75-7.10 (m, 18 H).

$^{13}\text{C}$  NMR :  $\delta$  20.97, 21.11, 21.16, 21.27, 48.45, 52.23, 55.41, 64.53, 99.36, 125.98, 126.42, 128.31, 128.41, 128.51, 128.78, 128.83, 129.08, 129.39, 129.49, 130.66, 134.86, 135.24, 135.75, 135.92, 136.27, 136.54, 136.63, 137.13, 137.25, 137.66, 138.43, 147.15, 165.72, 188.83, 198.05.



**4-Methoxy-3- (4-methyl phenyl)-5, 7-bis (di-4<sup>t</sup>-butylphenyl methyl) 2,4,6-cycloheptatriene-1-one 55 and 1,6-Bis (di-4<sup>t</sup>-butylphenyl methyl)-5-methoxy-3- (4-methyl phenyl)-bicycle [3.2.1] oct-3, 6-diene-2, 8-dione 56**

To a stirred mixture of *o*-benzoquinone 47 (0.183 g,  $2.63 \times 10^{-4}$  mol) and *p*-tolylacetylene (0.037 g,  $3.16 \times 10^{-4}$  mol) in dry dichloromethane (2 mL) was added SnCl<sub>4</sub> (0.55 mL, 1M solution of SnCl<sub>4</sub> in heptane) and stirred under an atmosphere of argon for two hours at room temperature. The reaction mixture was worked up as usual and the crude product was subjected to column chromatography on silica gel using hexane-ethyl acetate mixture (95:5) to afford the tropolone derivative 55 (0.115 g, 56%) and the [3.2.1] adduct 56 (0.115 g, 18%).

#### ***Tropolone Derivative 55***

Pale yellow crystals; recrystallized from hexane-ethyl acetate.

mp : 115-117°C

IR (KBr)  $\nu_{\max}$  : 996, 1018, 1109, 1268, 1364, 1406, 1510, 1573, 1610, 1685, 2878, 2903 cm<sup>-1</sup>.

<sup>1</sup>H NMR :  $\delta$  1.26 (s, 18H), 1.31 (s, 18H), 2.37 (s, 3H), 3.02 (s, 3H), 5.88 (s, 1H), 5.98 (s, 1H), 6.90-6.74 (m, 7H), 6.87 (s, 1H), 7.05 (s, 1H), 7.15-7.35 (m, 13H).

<sup>13</sup>C NMR :  $\delta$  21.30, 31.46, 34.35, 34.43, 50.51, 51.64, 60.07, 125.02, 125.26, 128.78, 128.95, 129.05, 137.60, 137.99, 139.08, 139.33, 139.49, 140.94, 141.08, 147.04, 148.67, 149.16, 151.45, 158.06, 184.27.

HRMS Calcd for C<sub>57</sub>H<sub>66</sub>O<sub>2</sub>: 782.50628; Found: 782.50568

**Bicycloadduct 56**

Colorless crystals; recrystallized from hexane-dichloromethane.

mp : 203-205°C

IR (KBr)  $\nu_{\max}$  : 578, 825, 1149, 1269, 1363, 1510, 1692, 1770, 2867, 2961  $\text{cm}^{-1}$ . $^1\text{H NMR}$  :  $\delta$  1.21 (s, 9H), 1.26 (s, 9H), 1.30 (s, 9H), 1.33 (s, 9H), 2.23 (s, 3H), 3.49 (s, 3H), 4.58 (s, 1H), 4.89 (s, 1H), 5.69 (s, 1H), 6.43 (s, 1H), 6.72-6.74 (m, 4H), 6.83-6.97 (m, 8H), 7.13-7.23 (m, 8H). $^{13}\text{C NMR}$  :  $\delta$  21.19, 31.37, 31.40, 31.48, 34.18, 34.45, 48.15, 52.91, 55.27, 65.15, 99.34, 124.42, 124.57, 124.95, 125.48, 126.21, 126.36, 128.34, 128.53, 128.67, 129.51, 130.39, 135.09, 136.10, 136.48, 136.58, 137.84, 138.03, 146.98, 149.14, 149.41, 149.75, 165.76, 188.64, 198.53.**4.4 REFERENCES**

1. Carruthers, W. in *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press : New York, 1990.
2. Nair, V.; Kumar, S. *Synlett* **1996**, 1143.
3. Nair, V.; Kumar, S.; Anilkumar, G.; Nair, J. S. *Tetrahedron* **1995**, *51*, 9155.
4. Thomas, A.; Anilkumar, G.; Nair, V. *Tetrahedron* **1996**, *52*, 2481.
5. Nair, V.; Anilkumar, G.; Eigendorf, G. K.; Willard, P. G. *Tetrahedron Lett.* **1996**, *37*, 8271.

6. Nair, V.; Davis, M.; Anilkumar, G.; Rath, N. P. *Synlett* **2000**, 1139.
7. Nair, V.; Davis, M.; Treesa, P. M.; Anilkumar, G.; Vairamani, M.; Prabhakar, S.; Rath N. P. *Tetrahedron* **2000**, *56*, 3735.
8. Davis, M. Ph.D. Thesis, University of Kerala, **2000**.
9. Rahman, M. M.; Matano, Y.; Suzuki, H. *J. Chem. Soc., Perkin Trans. I* **1999**, 1533.
10. Sato, M.; Ebine, S.; Nishijima, K.; Tsunetsugu, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 766.
11. Kogler, H.; Fehlhaber, H.-W.; Luebe, K.; Dürckheimer, W. *Chem. Ber.* **1989**, *122*, 2205.
12. (a) Rathore, R.; Kumar, A. S.; Lindeman, S.V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847.  
(b) Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, P. A. Jr.; Reynolds, D. W.; Wirth, D. D.; Chiou, H. S.; Marsh, B. K. *Acc. Chem. Res.* **1987**, *20*, 371.  
(c) Kita, Y.; Tohma, H.; Hatanaka, K.; Takeda, T.; Fujita, S.; Mitoh, S.; Sakurai, H.; Oka, S. *J. Am. Chem. Soc.* **1994**, *116*, 3864.
13. (a) Rajca, A.; Rajca, S.; Desai, S. R.; Day, V.W. *J. Org. Chem.* **1997**, *62*, 6524.  
(b) Adam, W.; Mass, W. *J. Org. Chem.* **2000**, *65*, 7650.  
(c) Rajca, A.; *Chem. Rev.* **1994**, *94*, 871.
14. Nair, J. S. Ph.D. Thesis, University of Kerala. **1999**.
15. Silverton, J. V.; Kabuto, C.; Buk, K.T.; Cava, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 6708.
16. Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6713.

17. Boger, D. L.; Brotherton, C. E. *Tetrahedron* **1986**, *42*, 2777.
18. Nair, V.; Powell, D. W.; Suri, S. C. *Synth. Commun.* **1987**, *17*, 1897.
19. Suri, S. C.; Nair, V. *Synthesis* **1990**, 695.
20. Davies H. M. L.; Clark, T. J.; Kimmer, G. F. *J. Org. Chem.* **1991**, *56*, 6440 and references cited therein.
21. Lee, J. C.; Cho, S. Y.; Cha, J. K. *Tetrahedron Lett.* **1999**, *40*, 7675 and references cited therein.
22. Lee, J. C.; Jin, S.; Cha, J. K. *J. Org. Chem.* **1998**, *63*, 2804.
23. Eistert, B.; Klein, L. *Chem. Ber.* **1968**, *101*, 391.
24. Sato, M.; Tsunetsugu, J.; Ebine, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 638.

## SUMMARY

The thesis entitled "NOVEL CYCLOADDITION REACTIONS OF [60] FULLERENE, 1,2-DIONES AND RELATED CHEMISTRY" embodies the results of investigations carried out to gain some insight into the reactivity of [60] fullerene, isatins and 1,2-benzoquinones in cycloaddition reactions.

A general introduction to the cycloaddition and nucleophilic addition chemistry of [60] fullerene is presented in chapter 1. In addition, a brief overview of the Diels-Alder and dipolar cycloaddition reactions of 1,2-benzoquinones is presented in this chapter. A definition of the present research problems has also been incorporated.

The second chapter deals with the results of an investigation of the cycloaddition reactions of [60] fullerene with carbonyl ylides. It has been found that six and five membered cyclic carbonyl ylides undergo facile dipolar cycloaddition with  $C_{60}$ , under very mild conditions leading to novel organofullerenes. The products were characterized by spectroscopic analysis. Cyclic voltametry studies have shown that the  $C_{60}$  adducts are less electrophilic compared to the parent [60] fullerene. In another set of experiments it has been found that allenamides undergo facile cyclization with [60] fullerene leading to novel cyclobutane derivatives. It may be emphasized that, there are very few methods available for the synthesis of cyclobutane annulated fullerenes.

The third chapter contains the results of investigations aimed at studying the reactivity of nitrile ylides and carbonyl ylides towards 1,2-diones. It has been observed that nitrile ylides undergo facile 1,3-dipolar cycloaddition with isatins leading to oxindole fused spiro oxazolines. These reactions are chemoselective and the more electrophilic keto carbonyl participates as the dipolarophile. Reactions of acenaphthenequinone and phenanthrenequinone with nitrile ylides also afforded novel spiro oxazolines. Novel spiro oxindole derivatives were also formed by the reaction of a five membered cyclic carbonyl ylide with isatins.

The fourth and final chapter of the thesis deals with a facile one pot synthesis of highly substituted tropolone derivatives from *o*-benzoquinones. It has been found that SnCl<sub>4</sub> catalyses the Diels-Alder reaction of *o*-benzoquinone and arylacetylenes. The bicyclo [2.2.2] adduct formed, further rearranged to another bicyclo adduct which extruded a molecule of CO spontaneously to afford the tropolone derivative.

In conclusion we have uncovered some novel reactivity patterns of [60] fullerene, isatins and *o*-benzoquinones in cycloaddition reactions. It is especially noteworthy that this work has opened up efficient routes to the synthesis of novel organofullerenes, oxindole fused oxazolines and highly substituted tropolone derivatives.

## LIST OF PUBLICATIONS

1. Cycloaddition reactions of carbonyl ylides to [60] fullerene: Synthesis of novel C<sub>60</sub> derivatives. Nair, V.; **Sethumadhavan, D.**; Sheela, K. C.; Eigendorf, G. K. *Tetrahedron Lett.* **1999**, *40*, 5087.
2. Cycloaddition of Carbonyl Ylides to Isatins: Synthesis of Novel Spiro Oxindoles. Nair, V.; Sheela, K. C.; **Sethumadhavan, D.**; Bindu, S.; Rath, N. P.; Eigendorf, G. K. *Synlett* **2001**, 0000.
3. Cycloaddition reactions of carbonyl ylides to [60] fullerene: Synthesis of novel C<sub>60</sub> derivatives. Nair, V.; **Sethumadhavan, D.**; Sheela, K. C.; Eigendorf, G. K. (Communicated to *J. Org. Chem.*).
4. Reactions of allenamides with [60] fullerene: Formation of novel cyclobutane annulated fullerene derivatives. Nair, V.; **Sethumadhavan, D.**; Eigendorf, G. K. (Communicated to *Chem. Commun.*).
5. A facile synthesis of oxindole fused spiro oxazolines.  
Nair, V.; **Sethumadhavan, D.**; Sheela, K. C.; Smitha M. Nair.; Rath, N. P.; Eigendorf, G. K. (To be communicated to *Tetrahedron Lett.*).
6. A facile one pot synthesis of highly substituted tropolones by the Lewis acid catalysed reaction of *o*-benzoquinones and arylacetylenes.  
Nair, V.; **Sethumadhavan, D.**; Rath, N. P.; Eigendorf, G. K. (To be communicated to *J. Org. Chem.*).
7. Dipolar Cycloadditions of Carbonyl Ylides to 1,2-Diones: Synthesis of novel spiro oxabicycles. Nair, V.; Sheela, K. C.; **Sethumadhavan, D.**; Dhanya, R.; Rath, N. P.; Eigendorf, G. K. (To be communicated to *Tetrahedron*).