NOVEL [4π+2π]CYCLOADDITION REACTIONS OF *o*-QUINONES

THESIS SUBMITTED TO THE UNIVERSITY OF KERALA
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BY

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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me at the Organic Chemistry Division of the Regional Research Laboratory Trivandrum, under the supervision of ***Dr. G. VIJAY NAIR*** *and the same has not been submitted elsewhere for a degree.*

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE

Certified that the work described in this thesis entitled ***NOVEL [4π+2π]CYCLOADDITION REACTIONS OF o-QUINONES*** *has been carried out by* ***Mr. T. K. SASI KUMAR****, under my supervision and the same has not been submitted elsewhere for a degree.*

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G. VIJAY NAIR

THESIS SUPERVISOR

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I would like to express my gratitude to Dr. A. D. Damodaran, Director, RRL, Trivandrum for permitting me to utilise all the facilities during my stay at RRL, Trivandrum.

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Financial assistance from Regional Research Laboratory, Trivandrum, and the Department of Science and Technology, Govt. of India, is gratefully acknowledged.

Finally, I wish to express my sincere gratitude to my parents and other family members for their constant support.

Trivandrum
March, 1995

T. K. SASI KUMAR

CONTENTS

PREFACE

Quinones constitute a large and important class of organic compounds that are endowed with rich and fascinating chemistry. Quite often they serve as versatile intermediates in organic synthesis and in dye industry. They play a vital role in the respiratory and photosynthetic elements of biological systems as well as a number of redox processes in Nature.

In contrast to the well known reacitvity pattern of *p*-benzoquinones in [4+2]cycloadditions, the reactivity profile of *o*-benzoquinones in such reactions is not clearly understood. *p*-Benzoquinones can function only as dienophiles in [4+2]cycloaddition reactions, whereas *o*-benzoquinones can function as carbodienes, heterodienes and dienophiles. Although isolated examples of all the above kinds of reactions are known, it cannot be predicted with certainty which set of conditions or reactants will elicit a particular reactvity pattern. Threrefore a detailed investigation on the Diels-Alder reaction of *o*-quinones with various dienes have been carried out and the results obtained are presented in the thesis entitled **NOVEL [4π+2π] CYCLOADDITION REACTIONS OF *o*-QUINONES**. The thesis is di vided into four chapters. Relevent references are given at the end of each chapter.

A general introduction to the chemistry of *o*-quinones along with a qualitative study of the Diels-Alder reaction is presented in chapter 1. A definition of the present research problem has also been incorporated.

The second chapter deals with the cycloaddition reactions of *o*-quinones with acyclic dienes. A brief introduction to theoretical studies along with the results of MNDO calculations is also presented. General information on experimental procedure is given in this chapter.

The cycloaddition reactions of *o*-quinones with carbocyclic and hetero-cyclic dienes are discussed in the third chapter.

The last chapter deals with the cycloadditions of *o*-quinones with various substituted fulvenes.

A summary of the work is given towards the end of the thesis.

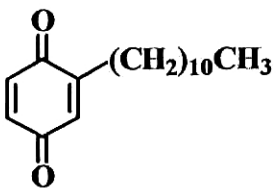
CHAPTER 1

AN INTRODUCTION TO THE CHEMISTRY OF *o*-BENZOQUINONES

1.1 GENERAL

Quinones constitute a large and important class of organic compounds that are endowed with rich and fascinating chemistry. Quite often they serve as versatile intermediates in organic synthesis and in dye industry. They play a vital role in electron transport in the respiratory and photosynthetic elements of biological systems as well as a number of redox processes in Nature.

A number of compounds containing 1,4- as well as 1,2-quinone moiety have been isolated from Nature and are found to be biologically active. eg. Embelin **1**, Rapanone **2**, Laurequinone **3**, Echinofuran **4**, Zonarone **5**, anthracyclic antibiotic Aranciamycinone **6**, Auramycinone **7**, Saframycin **8**, Conocurvone **9**, Hypericine **10**, Glutaminyl quinone **11**, Echlonoquinone **12**, Stypoldione **13**, Haloquinone **14**, Obionin **15**, Rosemariquinone **16**, Tanshinone **17**, Haematopodin **18**, Damirone **19**, Pyrroloquinolinequinone **20**, etc.[1,2]



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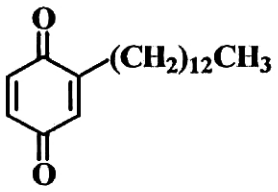

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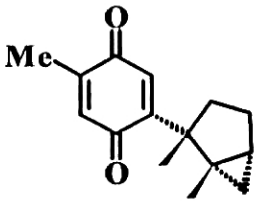

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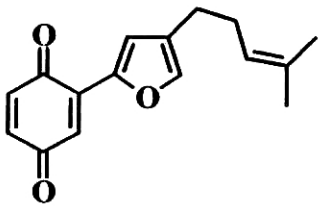

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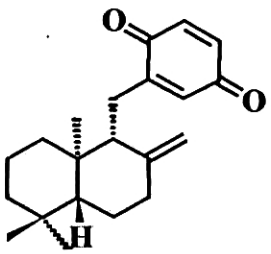

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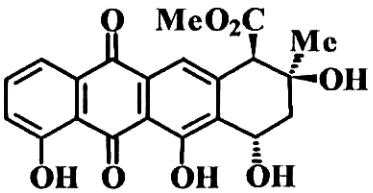

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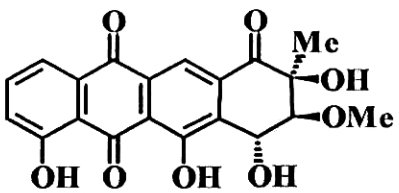

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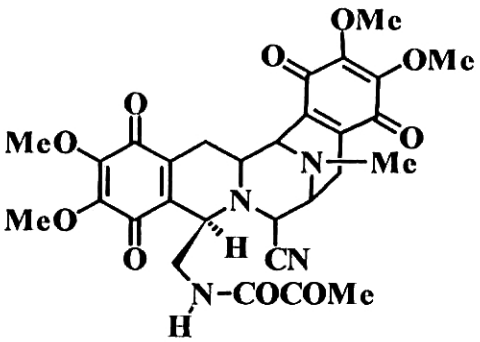

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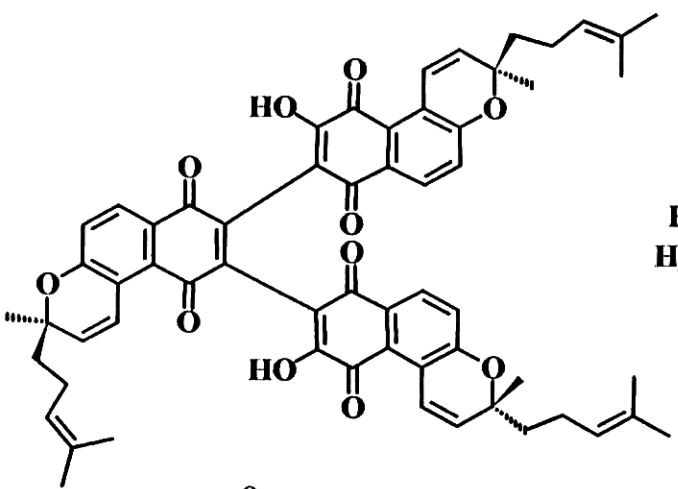

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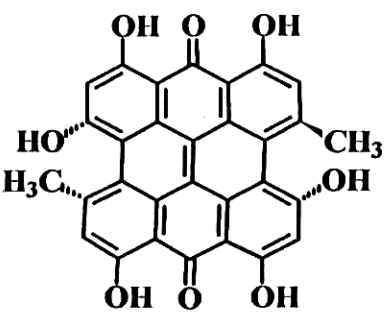

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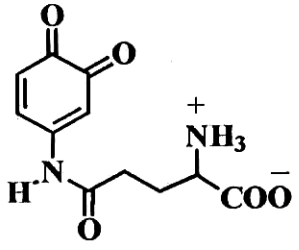

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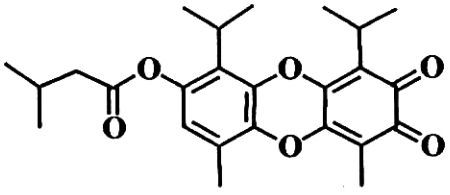

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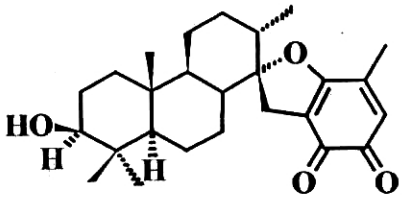

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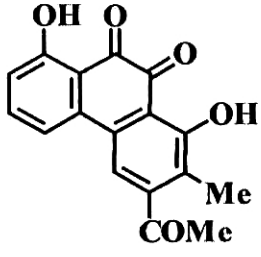

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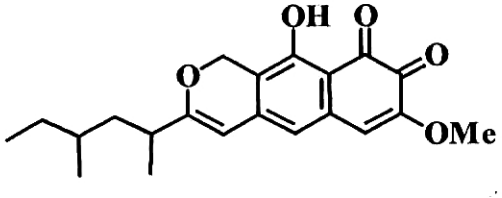

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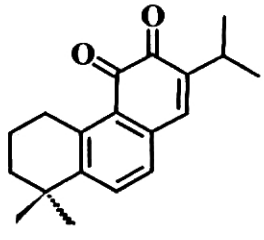

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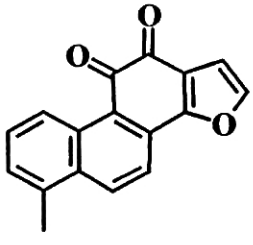

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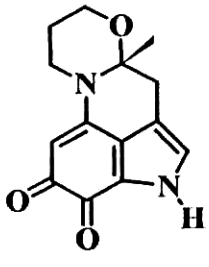

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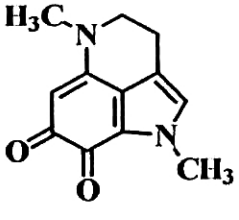

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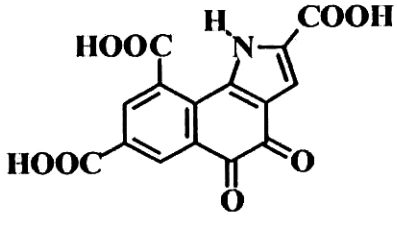

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Enormous amount of work has been done on the synthesis and reactions of quinones. Most of the work however is centered around *p*-quinones due to their stability and easy availability. In contrast, *o*-quinones have received only limited attention particularly in the area of cycloaddition.

1.2 Ortho Quinonoid Compounds

Mainly there are four types of ortho quinonoid compounds and these are represented by *o*-benzoquinone **21**, *o*-quinomethane **22**, *o*-quinodimethane **23**, and *o*-quinoneimine **24**.

21 **22** **23** **24**

o-Benzoquinone **21** is an isolable crystalline solid at low temperature, but it dimerizes readily and can act as both a carbo- and a heterodiene in cycloaddition reactions. *o*-Quinomethane **22** appears to be stable at -50 °C but trimerizes at -20 °C. *o*-Quinodimethane **23** is a reactive intermediate that dimerizes at -150 °C to give the Diels-Alder dimer. *o*-Quinoneimines **24** are more stable than *o*-quinodimethanes.[2]

Since the present work is focussed on the reactivity of *o*-benzoquinones, a discussion of their synthesis and properties is appropriate and it is given in Sections 1.3 and 1.4.

1.3 Synthesis of *o*-Benzoquinones

A number of oxidation procedures have been developed for the synthesis of quinones from aromatic hydrocarbons. Among the many metal salts used for oxidation, Ce(IV) salts give satisfactory results. Ammonium cerium(IV) sulfate in dilute acid gives quinones in higher yield than ammonium cerium(IV) nitrate (CAN).[3]

Anodic oxidation[2] with cerium sulfate or CAN as a mediator is reported to give improved yields than those obtained under stoichiometric conditions. Chromic acid oxidation generally gives poor results.[2]

Monohydric phenols can be converted to the quinones by treatment with Fremy's salt [$.ON(SO_3K)_2$].[4] It is suitable mainly for small scale experiments. Sometimes O_2-Salcomine system is also used for oxidation.[5] Benzene seleninic anhydride, $(PhSeO)_2O$, oxidizes phenols to the corresponding *o*-quinones in good yields and high product selectivities, even when the para position is unsubstituted.[6] Iodosobenzene (PhIO) and iodoxybenzene ($PhIO_2$) also oxidize phenols to *o*-quinones in good yields in the presence of a protic or a Lewis acid catalyst.[7]

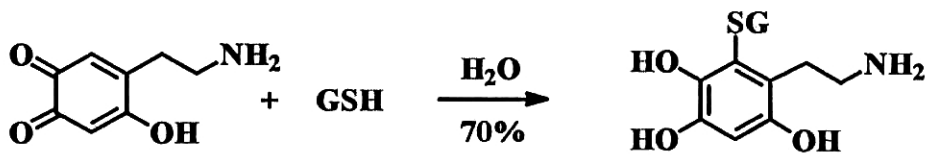
Conversion of hydroquinones and catechols to the corresponding quinones can be achieved by using a number of well-known oxidants such as Ag_2O, Ag_2CO_3, $FeCl_3$ etc. Sodium hypochlorite in the presence of phase transfer catalyst (PTC) oxidizes hydroquinones to the corresponding quinones in good yields.[8] Sodium periodate under PTC conditions gives excellent yields of quinones from a wide range of hydroquinones.[9] Nitric acid impregnated MnO_2 is suitable for the preparation of highly reactive quinones like 1,2-benzoquinone.[10] Corey-Kim reagent prepared from N-Chloro-

succinimide and dimethyl sulfide in presence of silver tetrafluoroborate can oxidize hydroquinones in high yields at low temperature.[11]

Indirect oxidation of phenol ethers and hydroquinone diethers *via* their quinone dialkyl acetals is realized by anodic oxidation in alkaline medium.[12] *o*-Quinone formation from the catechols can be accomplished by DDQ in refluxing dioxane.

1.4 General Reactions of *o*-Quinones

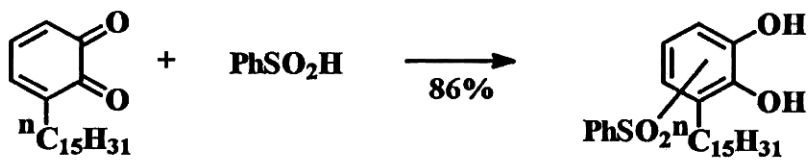
Addition of sulfur, nitrogen and oxygen nucleophiles to *o*-quinones has been studied extensively by various groups. Most of the work involved *p*-quinones, but *o*-quinones have also received some attention. eg. The addition of glutathione to 6-hydroxydopamine.[13]



25 26 27

G = HOOC CH_2 NH CO CH NH CO CH_2 CH_2 $CH(NH_2)$ COOH
CH_2 SH

Another interesting reaction of this type is the addition of benzenesulfinic acid to 3-pentadecyl-*o*-benzoquinone.[14]



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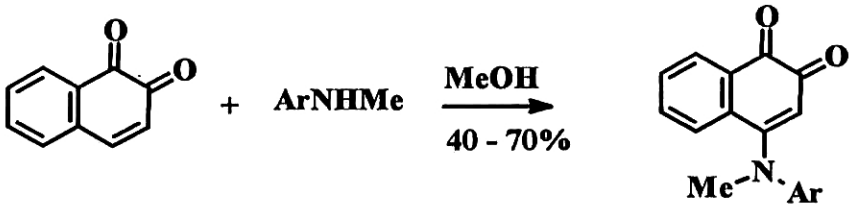
N-Substituted amines are reported to undergo nucleophilic addition at the 4-position of 1,2-naphthoquinone in 40-70% yields.[15]



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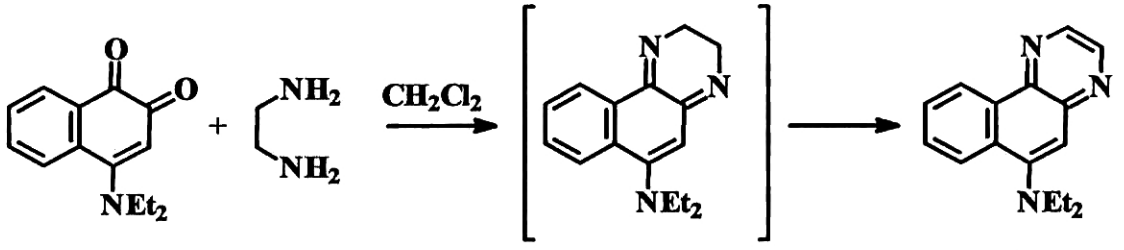
Many studies involving the addition of nitrogen nucleophiles to quinones have been reported in connection with the synthesis of novel dye stuffs and therapeutic agents. The addition of ethylenediamine to the naphthoquinone **34** under mild condition leading to the quinoxaline derivative **36** is an example.[16]



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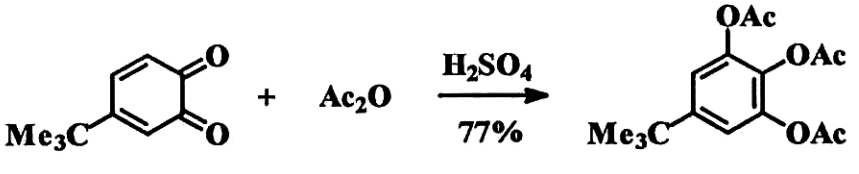
Another interesting reaction of *o*-quinones is the Thiele-Winter acetoxylation.[16]



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A few reports on the addition of halogens, hydrogen halides, azides, organometallics etc. have also appeared.[2]

1.5 Cycloaddition Reactions

The investigations documented in this thesis are primarily concerned with the [4π+2π] cycloadditions of *o*-quinones. In this context a description of the general characteristics of cycloaddition reactions is considered essential and therefore it is given here as background material.

The origin of cycloaddition chemistry can be traced to the dimerization of tetrachlorocyclopentadiene by Zincke[17] and the correct interpretation of the reaction and determination of the structure of the product by Diels and Alder.[18] This was followed by extensive investigation in this area by Diels and Alder.

Cycloadditions in general and Diels-Alder reactions in particular, are among the most important reactions of quinones. In recent years Diels-Alder reaction has been widely exploited for the facile synthesis of a number of quinonoid natural products.[19,20,21] In its simplest form, this reaction is the addition of an alkene to a conjugated diene to give a cyclohexene. It is termed as a [4π+2π]cycloaddition reaction, since it involves a 4π electron system and a 2π electron system.

Diels and Alder were already able to identify essential characteristics of a [4+2]cycloaddition.[22]

1. The addition reactions take a stereospecific course resulting in *cis* addition.
2. In the case of cyclic dienes the *endo* principle is often followed.
3. Unsymmetrically substituted reactants combine regiospecifically to

give the cycloadduct.

4. Electron releasing groups on the diene accelerate the reaction, while electron withdrawing groups on the diene retard it.

In most cases, the reaction takes place easily at ambient or slightly elevated temperatures. An important and preparatively useful extension of the cycloaddtion was the Lewis acid catalyzed reaction described by Yates and Eaton.[23] Lewis acid catalysis, while preserving or enhancing the stereospecificity of the reaction, accelerates the rate of addition by several powers of ten. Use of high pressure, aqueous medium, chiral catalysis etc represent other advances in this area.[24]

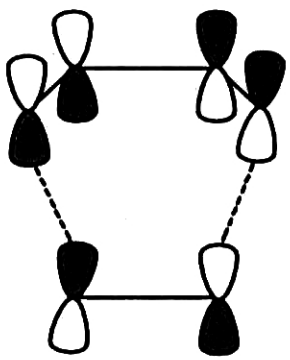
Most Diels-Alder reactions involve a diene carrying electron donating substituents (eg. alkyl, alkoxy etc.) and a dienophile bearing electron withdrawing substituents (eg. -CO, -CN etc.). But there is another smaller group of cycloaddition which involves the reaction between an electron rich dienophile and an electron deficient diene. These reactions, inverse electron demand Diels-Alder reactions as they are called, have recently found substantial use in organic synthesis. The essential requirement of the reaction, whether normal or the inverse electron demand variety is that the two components should have complementary electronic character.

A description of the fundamental process involved in Diels-Alder reaction using frontier orbital rationalization is presented in the following passage.

The concepts about the mechanism of Diels-Alder reaction were strongly influenced by the Woodward-Hoffmann rules.[22] Indeed, most [4+2] cycloadditions are best described in terms of a symmetry-allowed one step mechanism. The usefulness of the Diels-Alder reaction in synthesis arises from its versatility and its high regio- and stereoselectivity.[25] The

difference in reactivity of dienes and dienophiles towards Diels-Alder reaction can be explained by the principle of conservation of orbital symmetry.[26] The orbital symmetry rules apply only to concerted reactions, and are based on the principle that reaction takes place in such a way as to maintain maximum bonding throughout the course of the reaction.

The rate of a Diels-Alder reaction is determined largely by the degree of interaction between the highest occupied molecular orbital (HOMO) of one component and the lowest unoccupied molecular orbital (LUMO) of the other, and the smaller the energy separation between these orbitals the more readily the reaction proceeds. In a normal Diels-Alder reaction, ie., one between an electron rich diene and an electron deficient dienophile, the major interaction is that between the HOMO of the diene and the LUMO of the dienophile.[27] The simplest example of a Diels-Alder reaction is the formation of cyclohexene from butadiene and ethylene. Overlap of the frontier orbitals of the reactants are shown below. The dashed lines identify the bonding overlap which can develop as a prelude to the reaction (Figure 1).



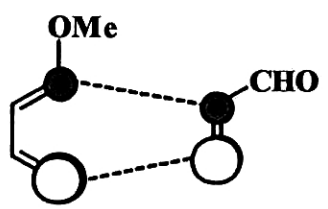
HOMO of Butadiene

LUMO of Ethylene

Figure 1

1.5.1 Regioselectivity in Diels-Alder Reaction

As already mentioned the value of the Diels-Alder reaction in synthesis is due in large measure to its high regio- and stereoselectivity. The reaction of an unsymmetrical diene with an unsymmetrical dienophile could, in principle, give rise to two regioisomeric products but in practice one product generally predominates. The regioselectivity can be explained by considering the coefficients of the frontier orbitals. For example, 1-methoxybutadiene gives the 'ortho' adduct rather than the 'meta' adduct with acrolein. One can explain the regioselectivity in terms of the coefficients of molecular orbitals of the monosubstituted diene and the monosubstituted dienophile. For 1-methoxybutadiene and acrolein the frontier orbitals are polarized as shown below (Figure 3).



HOMO **LUMO**
-0.85eV **0.0eV**

Figure 3

The size of the circle is roughly proportional to the size of the coefficient. The circles represent the lobes of the *p*-orbitals above the plane of the paper and the shaded and unshaded ones are of opposite signs. The important interaction in the methoxybutadiene-acrolein reaction will be that between the HOMO of the diene and the LUMO of the dienophile. The

molecular orbital with large coefficient will interact with the large coefficient of the other reactant. This large-large / small-small interaction will explain the observed regioselectivity. Secondary orbital interactions may also play a part, particularly when the primary interactions show little preference for one regioisomer over the other.

1.5.2 Stereochemistry of Diels-Alder Reaction

Another valuable feature of the Diels-Alder reaction is its high stereoselectivity, and it is probably this factor more than any other which has led to its widespread application in the synthesis of complex natural products. Upto four new chiral centres may be set up in the reaction between a diene and a dienophile, but it is frequently found that one of the several possible stereoisomers is formed predominantly or even exclusively. The stereochemistry of the main product can generally be predicted on the basis of two well known rules, the *cis* rule, which states that the relative stereochemistry of the substituent groups in the diene and dienophile is maintained in the product of cycloaddition, and the Alder *endo* rule, according to which the diene and the dienophile arrange themselves in parallel planes and the most stable transition state is that in which there is "maximum accumulation of double bonds" or the maximum possibility of overlap. The *cis* rule is very widely followed. The *endo* rule appears to be strictly obeyed only in the addition of cyclic dienes to cyclic dienophiles. For example, the reaction of maleic anhydride with cyclopentadiene gives the *endo* adduct exclusively. This can be explained in terms of secondary orbital overlap as shown in Figure 4.

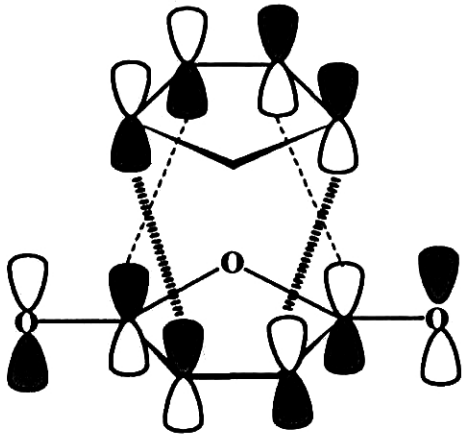


Figure 4

The *endo* rule applies only to the kinetic products of the reaction. It is very frequently found that the proportion of *endo* isomer is higher in the reactions catalyzed by Lewis acids. On the other hand, the reaction may become less selective at elevated temperatures.

1.6 Definition of the Problem

In contrast to the well-known reactivity pattern of *p*-benzoquinones in [4+2] cycloadditions, the reactivity profile of *o*-benzoquinones in such reactions is not clearly understood. *p*-Benzoquinones can function only as dienophiles in [4+2]cycloaddition reactions, whereas *o*-benzoquinones can function as carbodienes, heterodienes and dienophiles.

The following representations of *o*-benzoquinone emphasize its multiple reaction patterns (Figure 5).

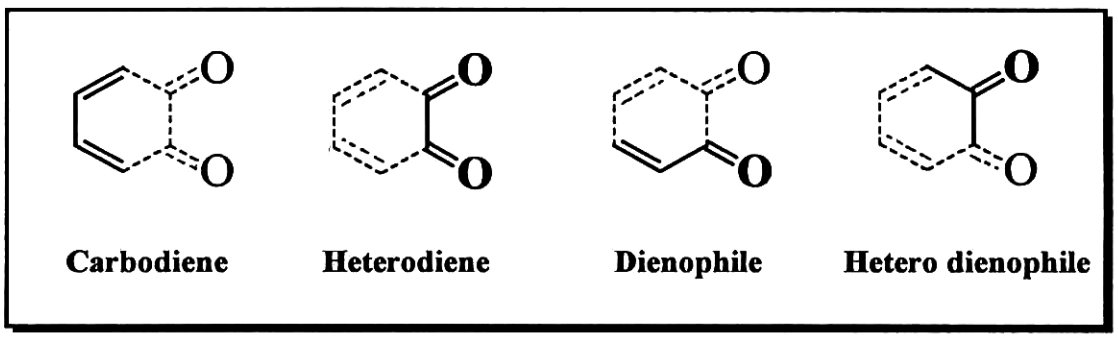
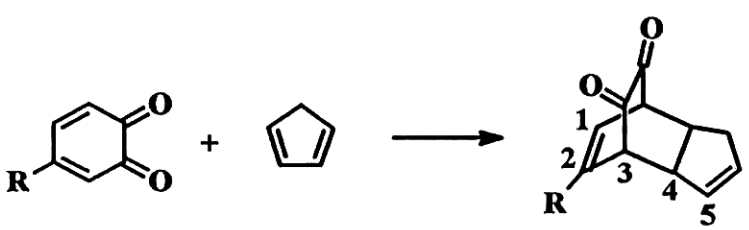


Figure 5

1.6.1 Cycloaddition Reactions of *o*-Benzoquinones

1.6.1a *o*-Quinone as Carbodiene[28]

In 1971 Ansell and coworkers reported the cycloaddition of a variety of *o*-quinones bearing alkyl, aryl, alkoxy and chloro substituents with cyclopentadiene. The products formed are 1,5-dienes and these are shown to undergo Cope rearrangement at high temperature.



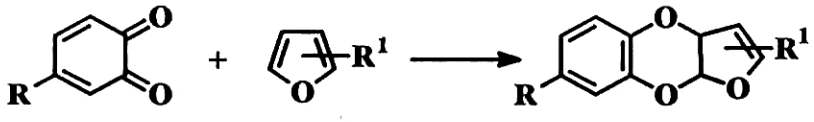
39 **40** **41**

R = Aryl, Alkoxy etc.

1,5-Diene
Cope rearrangement intermediate

1.6.1b *o*-Quinone as Heterodiene[29]

Horspool and coworkers studied the reactions of *o*-benzoquinones with furan and substituted furans. In these cases they obtained dihydrobenzodioxin derivatives in poor yields.

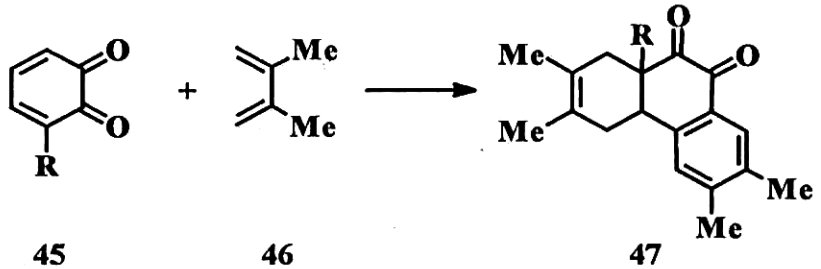


42 43 44

R = R^1 = Alkyl

1.6.1c *o*-Quinone as Dienophile[30]

o-Quinones substituted with an electron withdrawing group at 3-position react with 2,3-dimethyl-1,3-butadiene to give a 1: 2 adduct.

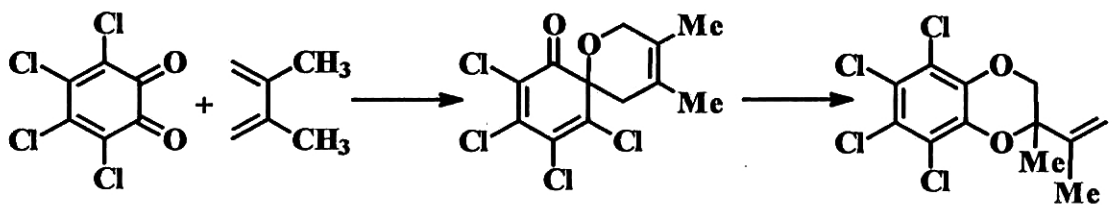


45 46 47

R = -CHO

1.6.1d *o*-Quinone as Heterodienophile[31]

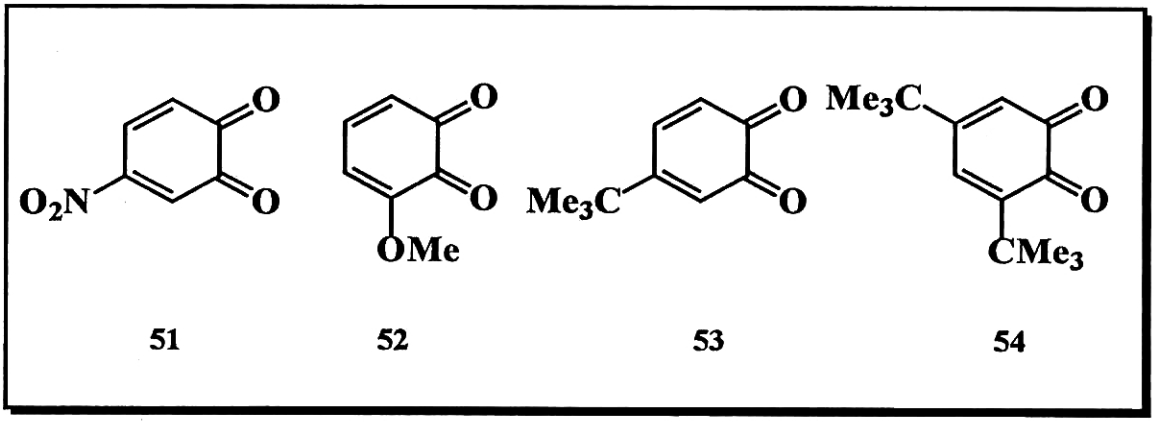
Tetrachloro-*o*-benzoquinone reacts with 2,3-dimethylbutadiene to give a spiro compound **49**, which is unstable at higher temperatures and undergoes Claisen rearrangement to afford the dihydrobenzodioxin **50**.



48 **46** **49** **50**

More details on the cycloaddition reactions of *o*-quinones with various dienes are given in the succeeding chapters.

It may be emphasized that, although isolated examples of all the four kinds of reactions are known, it cannot be predicted with certainty which set of conditions or reactants will elicit a particular reactivity pattern. We have therefore undertaken a systematic investigation of the [4+2]cycloaddition of a variety of substituted *o*-quinones with acyclic, carbocyclic and heterocyclic dienes. Very little information is available on the reactivity of such systems with *o*-quinones. Inorder to understand the influence of electronic and steric factors on the cycloaddition reactions, the following quinones were selected for our investigations.



51 52 53 54

The details of the work along with a theoretical study of the cycloaddition reactions of *o*-quinones are given in the following chapters.

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CHAPTER 2

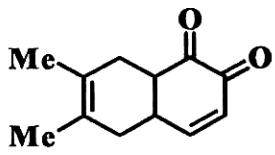
CYCLOADDITION REACTIONS OF *o*-QUINONES WITH ACYCLIC DIENES

2.1 INTRODUCTION

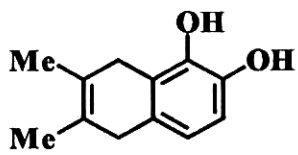
Diels-Alder reactions of acyclic dienes with *o*-benzoquinone and mono-, di-, and tri substituted *o*-benzoquinones have been studied by Ansell and co workers in 1971.[1] In these reactions the quinone always acts as a dienophile, with the addition occurring preferentially to the more electron deficient olefinic linkage. In some cases the adducts are labile and they readily undergo aromatization and therefore the primary products are not isolable.

Simple *o*-benzoquinones are unstable compounds and they undergo rapid dimerization. Therefore the cycloadditions with acyclic dienes are low

yielding reactions. Ansell and coworkers have used large excess of the diene in order to circumvent the dimerization. The reaction between *o*-benzoquinone and 2,3-dimethylbutadiene (25 molar excess) at room temperature was complete within 6 hours. The IR spectrum of the product initially isolated was consistent with the Diels-Alder adduct **1**. When this material was crystallized, aromatization occurred to give the dihydronaphthalene-1,2-diol **2** which underwent a symmetry allowed dehydrogenation at 100 °C (reduced pressure) to afford the naphthalene diol **3**.



1



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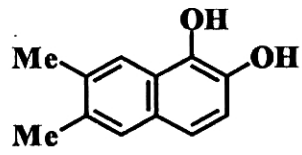
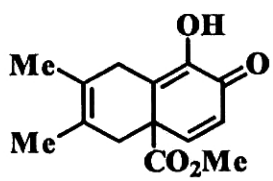


3

The reactions of monomethyl-, methoxy-, chloro-, and acetamido-*o*-benzoquinones were comparable to those of *o*-benzoquinone itself. In all cases addition occurred at the less hindered double bond.

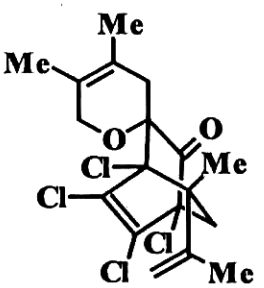
4-Methoxycarbonyl-*o*-benzoquinone was found to be too unstable to be isolated by the oxidation of the corresponding catechol. However it could be trapped as the adduct **4** in high yield by the oxidation of the catechol with silver oxide in the presence of 2,3-dimethylbutadiene.



4

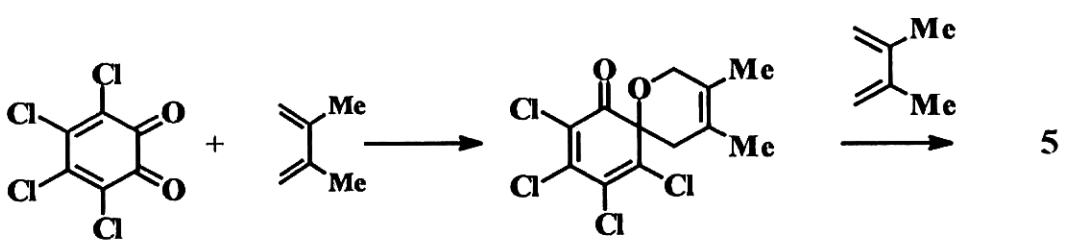
The reactions of 4-cyano-*o*-benzoquinone with dienes parallel those of 4-methoxycarbonyl-*o*-benzoquinone.

Of all the *o*-benzoquinones, *o*-chloranil and *o*-bromanil are the most thoroughly investigated because of their stability and easy availability. The reaction of excess 2,3-dimethylbutadiene with *o*-chloranil was shown by Horner and Merz[2] to give a 2:1 adduct, the structure of which was not established. Later Ansell and coworkers reexamined this problem and they have suggested the correct structure for the 2:1 adduct as **5**.[3]

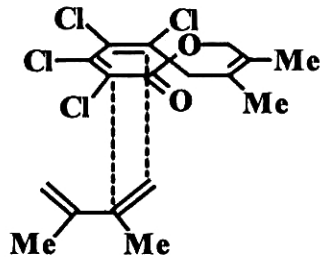


5

The primary adduct (1:1 adduct) can be isolated at 0 °C when one equivalent of 2,3-dimethylbutadiene is reacted with chloranil. This spiro-compound retains a reactive diene system that can undergo a second Diels-Alder reaction with 2,3-dimethylbutadiene. The overall reaction can be depicted by the following equation.



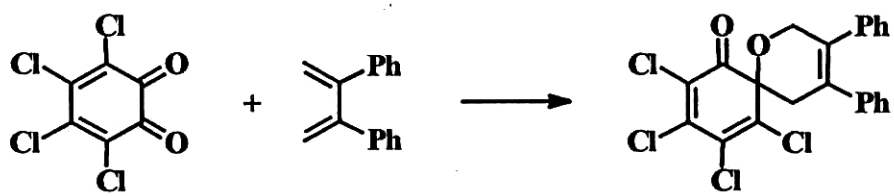
The formation of the adduct **5** results from the *endo* addition of 2,3-dimethylbutadiene to the cyclic diene. For this addition a transition state **6** has been proposed, which indeed is the preferred one.



6

It has been suggested that in *o*-chloranil and *o*-bromanil, it is the electron withdrawing effect of the halogen substituents which activates the carbonyl group towards the first cycloaddition, while the steric effect prevents addition to the C-C double bond.

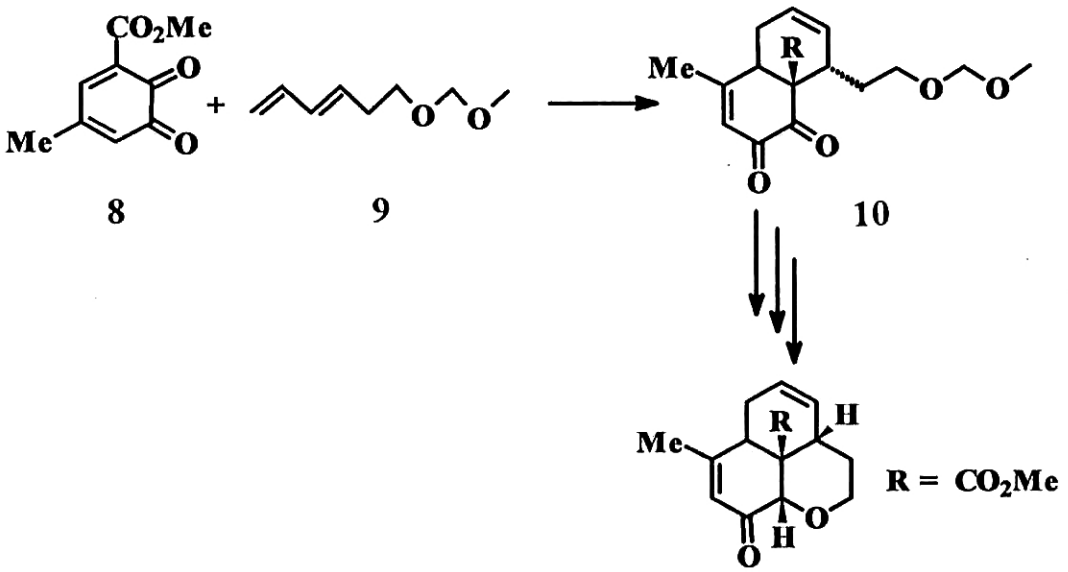
Cycloaddition to the carbonyl group of *o*-chloranil does not occur with all dienes. However penta-1,3-diene and 2,3-diphenylbuta-1,3-diene yield the spirodihydropyran **7**.



7

2,3-Dimethyl-1-phenylbuta-1,3-diene yields a mixture of benzodioxin and the thermally labile spirodihydropyran, which rearranges to the benzodioxin.

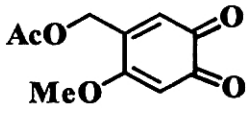
Weller and coworkers have investigated the cycloadditions of 3,5-disubstituted *o*-benzoquinone **8** and 4-chloro-3,5-disubstituted *o*-benzoquinones (methyl and carbomethoxy) with simple dienes like 2-acetoxy-1,3-pentadiene, 1,3-pentadiene, 5-carboethoxy-1,3-pentadiene etc. as a potential route to the quassinoid skeleton **11**.[4] Reaction of the quinone **8** with the protected 1,3-diene **9** is illustrative.



8 **9** **10**

11

Danishefsky has examined the Diels-Alder methodology involving *o*-quinone and acyclic dienes in a synthesis of Δ-1-octalone derivatives.[5] Thus the reaction of 4-methoxy-5-acetoxymethyl-1,2-benzoquinone **12** and 4-methoxy-5-methoxymethyl-1,2-benzoquinone **13** have been shown to occur smoothly with acyclic dienes. In these cases, cycloaddition occurs at the 5,6- rather than the 3,4- double bond. With 1-methoxybutadiene regiospecific formation of the 8-methoxy isomer **14** was observed. The adduct **14** has been converted in five steps to **15**.



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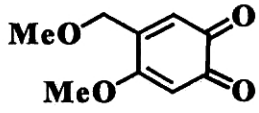
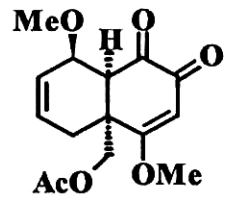
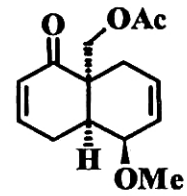


13



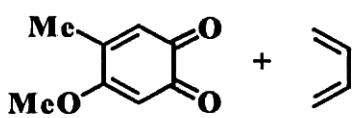
14



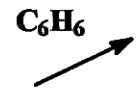
15

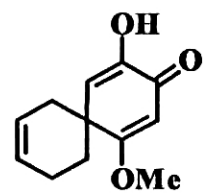
A remarkable solvent effect was observed in the cycloaddition of certain *o*-benzoquinones.[6] Conventional wisdom was that solvent effects are of relatively nominal importance in determining the course of Diels-Alder reactions.[7] This might be expected in the light of the concerted nature perceived for the [4+2] cycloaddition processes.

5-Methyl-4-methoxy-1,2-benzoquinone **16** reacts with 1,3-butadiene in benzene quite slowly. Upon heating at 105 °C for 5 hours, the 'abnormal' adduct **17** was isolated in 60% yield. This 'abnormal' process, involving enolisation of 5-methyl group followed by cycloaddition to the tautomeric quinonemethide is quite structure dependent. Reaction of **16** with butadiene in methanol at 100 °C for 20 hours gave **18** in 63% yield. Similar trend was observed in the cycloaddition of **16** with 1-methoxybutadiene.



16





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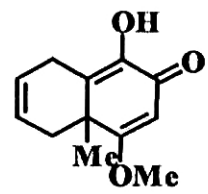
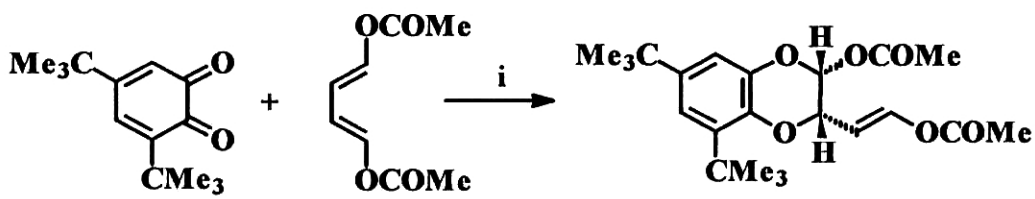


18

2.2 RESULTS AND DISCUSSION

In spite of the above investigations, much remains to be learned about the reactivity profile of *o*-quinones in cycloaddition and therefore we have undertaken some work in this area. Initially we focussed our attention on the cycloaddition of *o*-quinones with electron rich dienes. Reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone, 4-*tert*-butyl-*o*-benzoquinone, 3-methoxy-*o*-benzoquinone and 4-nitro-*o*-benzoquinone with various acyclic dienes have been studied and the results are discussed in this chapter.

3,5-Di-*tert*-butyl-*o*-benzoquinone on treatment with 1,4-diacetoxy-1,3-butadiene in toluene in a sealed tube (120 °C) afforded a product in 90% yield. This was characterized as the benzodioxin **19**. The reaction can be illustrated as follows.[8]

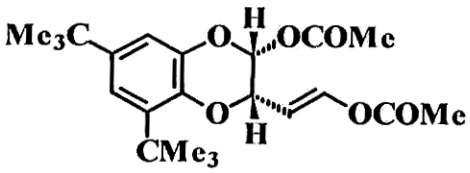


19

i, Toluene, sealed tube, 120 °C, 30h, 90%

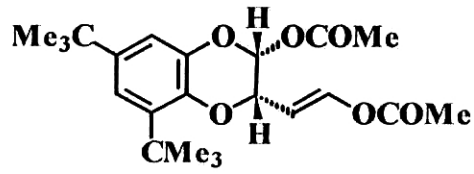
Infrared spectrum of **19** shows a strong absorption at 1770 cm^{-1} due to the presence of acetate group. In the ^1H NMR spectrum of **19** two tertiary butyl resonances appeared at δ 1.26 and 1.36 downfield from TMS. The two acetyl groups (-OCO$\underline{CH_3}$) appeared at δ 2.120 and 2.123. The doublet at δ 6.2 is coupled with the proton at δ 4.60 which is a double

doublet. The coupling constant (J = 3.3 Hz) for these two protons indicates that they are *cis* to each other. The large coupling constant (J = 12.5 Hz) for olefinic protons at δ 5.50 and 7.55 indicates a *trans* geometry for the alkene. The signals at δ 6.84 and 6.94 (J = 2.3 Hz) are due to the aromatic protons. In the ^{13}C NMR typical carbon signals have been observed for the carbons adjacent to ring oxygen at δ 89.32 and 70.50. The two ester carbonyls resonated at δ 167.5 and 169.61. The two acetate carbon ($\underline{C}H_3$-CO) signals appeared at δ 20.58 and 21.08. The two *tert*-butyl carbon signals resonated at δ 29.76 and 31.45 (Figure 1). The connectivity of the protons in **19** has been established by 2D COSY experiments (Figure 2).



19

Figure 1. ^{1}H and ^{13}C NMR spectra of **19**



19

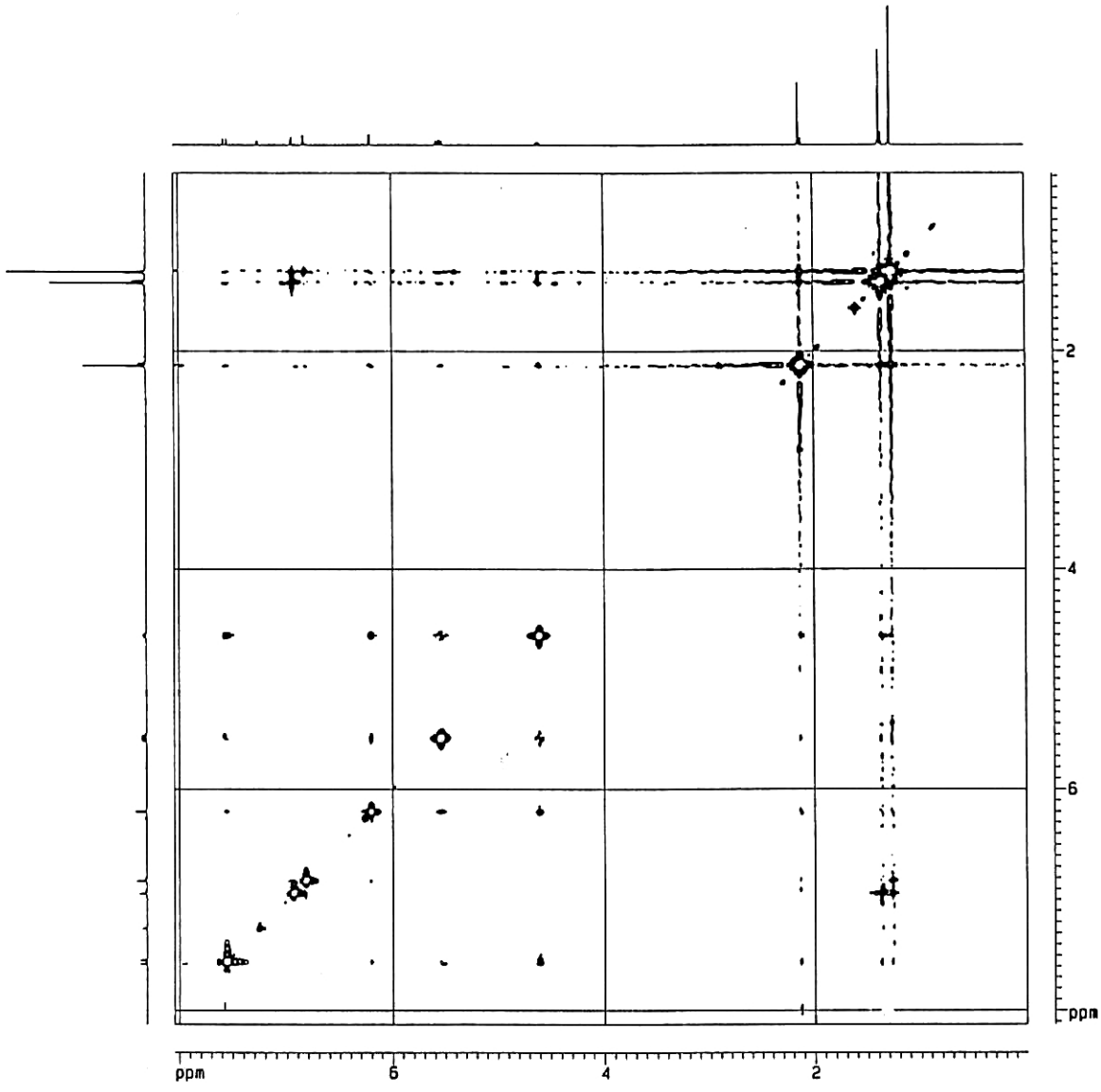
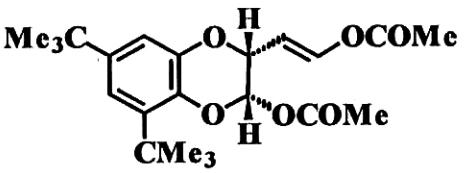


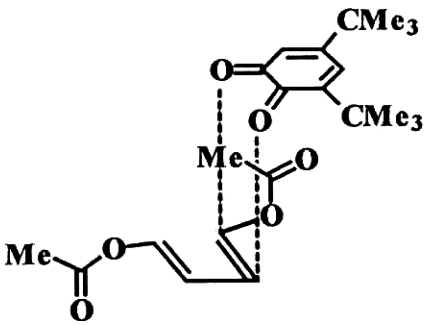
Figure 2. 2D COSY spectrum of **19**

From the 2D spectrum it has been found that the proton signal at δ 4.60 is coupled with signals at δ 7.55 and 6.20. Again the signal at δ 4.60 is coupled with the signal at δ 5.55.

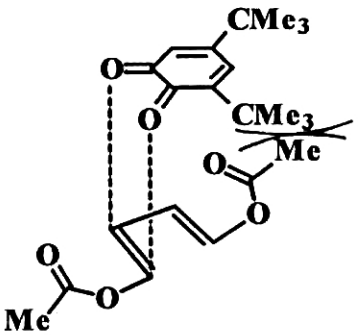
Although it is not possible to rule out the alternate structure **20** on the basis of spectral data, a transition state with no unfavourable steric interaction leading to **19** can be invoked. Examination of molecular models reveals that the transition state for **19** is less hindered than the transition state for **20**.



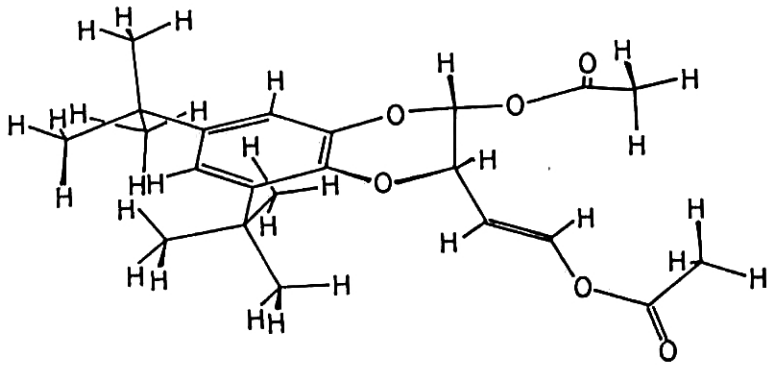
20



TS for **19**

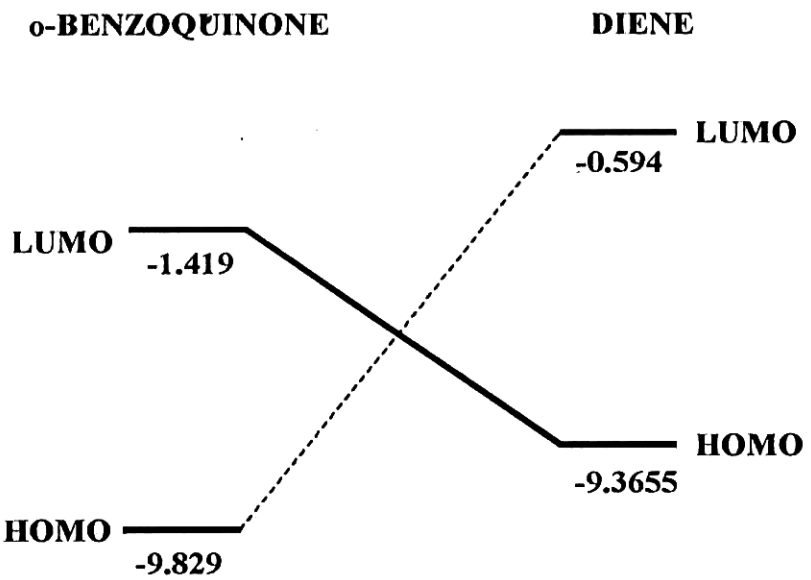


TS for **20**



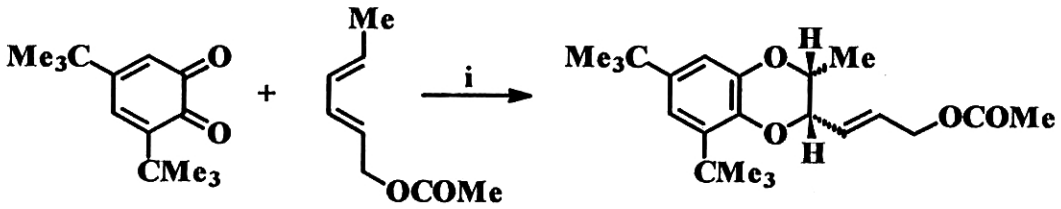
*Energy minimized structure of **19** (MMX method)*

The MNDO and AM1 calculations reveal that the energy gap between the *o*-quinone and the diene favours the inverse electron demand Diels-Alder reaction. The HOMO-LUMO energy gap for the quinone and the diene is higher than that of the LUMO-HOMO energy of the quinone and diene. The energy levels can be represented as follows.



HOMO-LUMO energy levels of 3,5-di-*tert*-butyl-*o*-benzoquinone and 1,4-diacetoxy-1,3-butadiene.

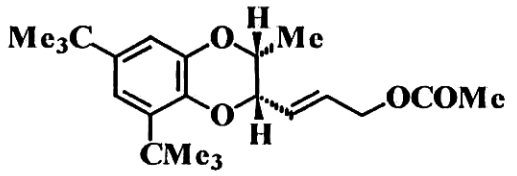
Similarly the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with 1-acetoxy-2,4-hexadiene in a sealed tube (toluene, 110 °C) gave the benzo-dioxin **21** in 72% yield.



21

i, Toluene, sealed tube, 110°C, 40 h, 72%

Compound **21** shows typical ^{1}H and ^{13}C NMR signals as in the previous case. The ^{1}H NMR spectrum of **21** exhibited a doublet at δ 1.30 (J= 6.34 Hz, 3H) assigned to the methyl protons. The proton adjacent to this methyl group appeared at δ 3.90 as a multiplet. The acetyl group ($\underline{CH_3}$-CO-O-) resonated at δ 2.103. The doublet centred around δ 4.65 (J = 4.65 Hz) has been assigned to the -CH_2- protons adjacent to the olefinic group. The multiplet at δ 4.15 (1H) has been assigned to the -OC$\underline{H}$- (in the dioxin ring) adjacent to the olefinic group. The olefinic protons are *trans* as indicated by the coupling constant (J = 12.09 Hz). The ^{13}C signals for the carbons adjacent to oxygen in the benzodioxin ring appeared at δ 72.69 and 77.45 in the ^{13}C NMR spectrum. The acetyl and methyl carbons appeared at δ 20.93 and 17.25 respectively. The -CH_2- carbon resonated at δ 63.99. The ester carbonyl appeared at δ 170.63 (Figure 3). The molecular ion peak at *m/z* 360 is also in agreement with the proposed structure. The connectivity of protons has been confirmed by 2D COSY experiments (Figure 4).



21

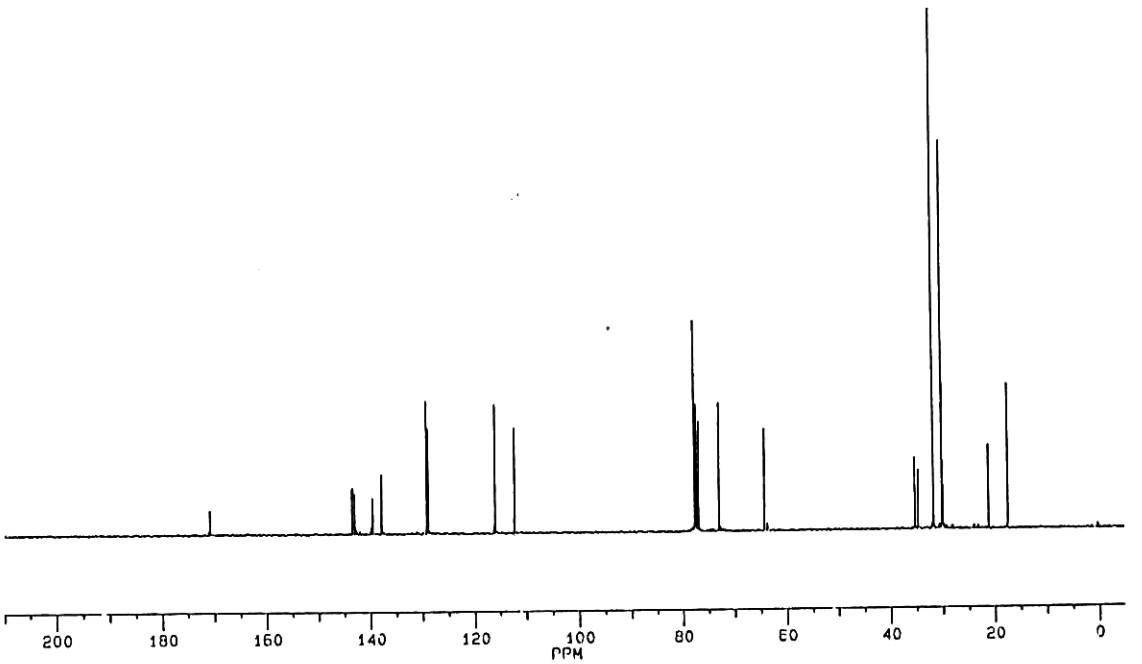
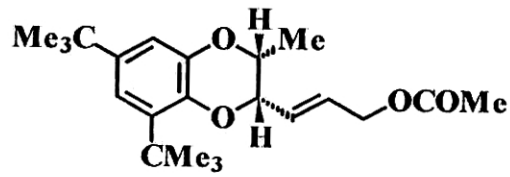


Figure 3. ^{1}H and ^{13}C NMR spectra of **21**



21

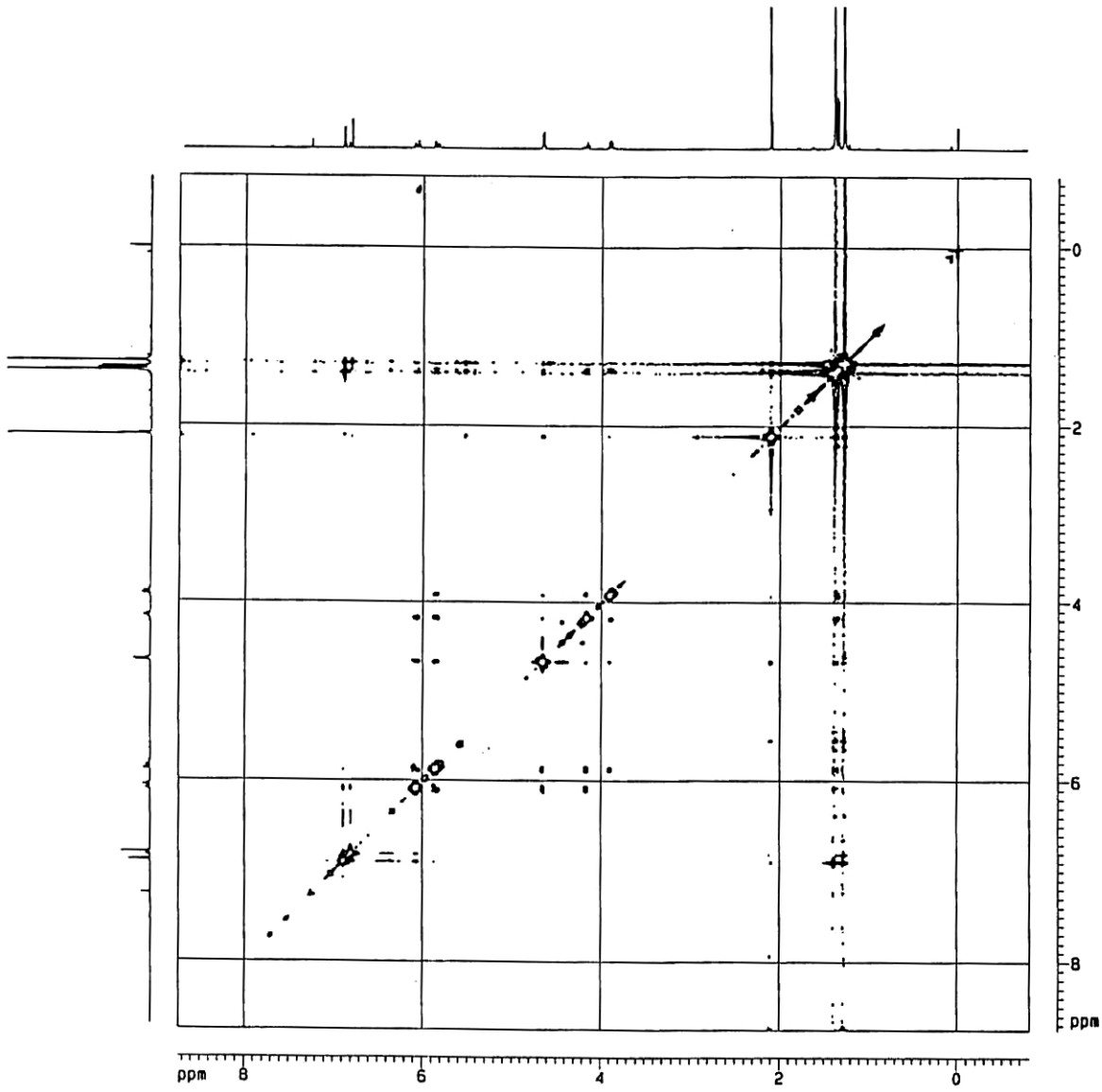
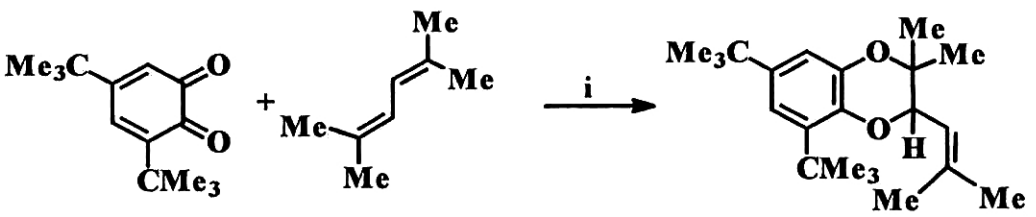


Figure 4. 2D COSY spectrum of **21**

In the COSY spectrum of **21**, the signal at δ 4.10 showed cross peaks at δ 5.80. The signal at δ 3.88 showed a cross peak at δ 4.15. The 5.83 ppm signal was coupled to the signal at 6.05 ppm, which has been assigned to the two olefinic protons. The signals at δ 6.05 are further coupled to the signal at δ 4.65.

The observed regiochemistry can be explained in terms of steric repulsion imposed by the *tert*-butyl group and acetoxy group in the transition state. A transition state like that of **19** would explain the regiochemistry of **21**.

Reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with 2,5-dimethyl-2,4-hexadiene gave the benzodioxin adduct **22** as a pale yellow viscous liquid in 84% yield. This was characterized by spectral analysis.

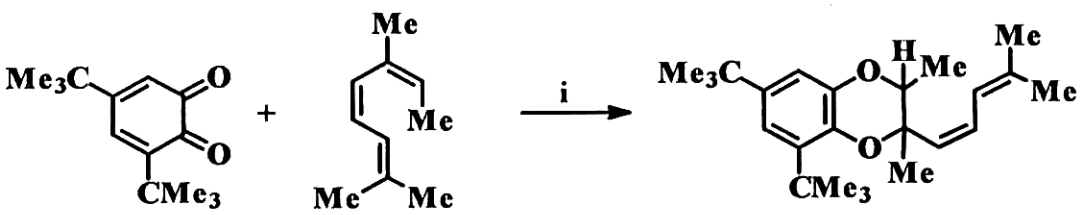


22

i, Neat, sealed tube, 100°C, 2 h, 84%

Compund **22** shows typical proton as well as carbon signals in the ^{1}H NMR and ^{13}C NMR spectra respectively. The ^{13}C signals for carbon atoms adjacent to oxygen in the dioxin ring appeared at δ 73.5 and 80.0. The -CH- proton resonates at δ 3.75 and gives a broad signal. The IR spectrum does not show any carbonyl absorption peaks. The best result for this reaction was obtained when the reagents were heated in a sealed tube without solvent.

A similar benzodioxin product **23** was isolated from the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with *trans,trans*-dimethyl-2,4,6-octatriene (*alloocimene*).



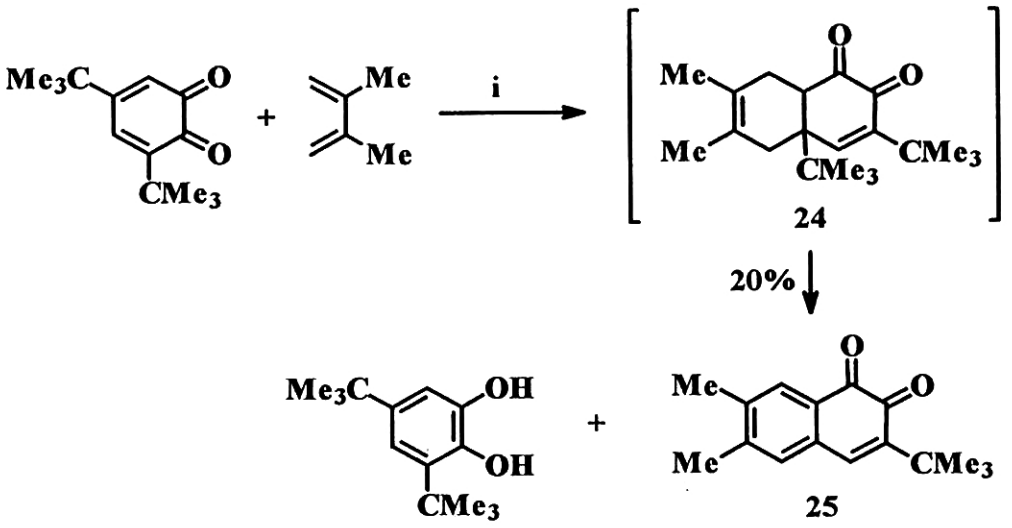
i, CH_2Cl_2, 10°C, 10days, 75%

23

The ^1H NMR spectrum of **23** showed a quartet at δ 4.0 (1H) assigned to the -OCH- proton in the benzodioxin ring. The addition took place at the 6,7-olefinic bond of alloocimene. The quartet at δ 4.0 is diagnostic for a product resulting from this mode of addition. The ^{13}C signals for carbons adjacent to oxygen in the benzodioxin ring appeared at δ 75.1 and 77.0. The IR spectrum does not show any carbonyl absorption. The molecular ion peak at *m/z* 356 is in agreement with the proposed structure.

Interestingly the reaction of 2,3-dimethyl-1,3-butadiene with 3,5-di-*tert*-butyl-*o*-benzoquinone afforded 4-*tert*-butyl-6,7-dimethyl-1,2-naphtho-quinone **25** (20%) when the reagents were heated in a sealed tube (90 °C) without any solvent. It has been proposed that the primary adduct **24** gets aromatized under the influence of the unchanged quinone present in the reaction mixture. Isolation of 3,5-di-*tert*-butylcatechol from the reaction mixture lends support to the suggested mechanism.

The overall reaction can be represented as follows.

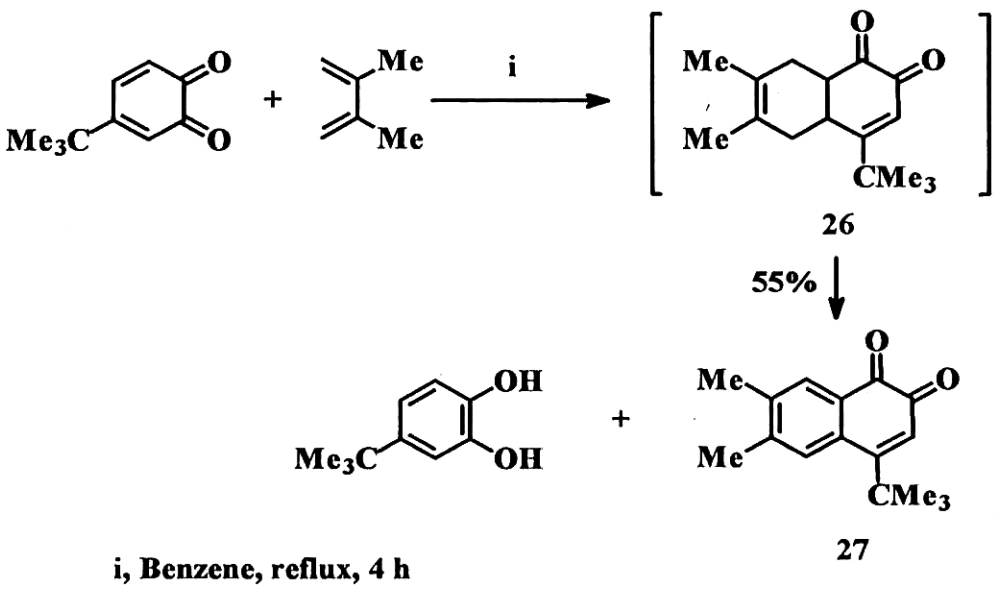


i, Neat, sealed tube, 90°C, 8 h

As usual, the product was characterized by analytical and spectroscopic methods. The *tert*-butyl group in **25** appeared as a singlet at δ 1.25 (9H) and the two methyl groups attached to the aromatic ring appeared as a singlet at δ 2.25 (6H) in ^{1}H NMR spectrum. The proton attached to C-4 of the quinone ring resonated at δ 7.65 as a singlet. The two aromatic protons appeared at δ 6.95 and 7.07. The IR spectrum shows strong carbonyl absorptions at 1670 and 1689 cm^{-1}, suggestive of the presence of quinone carbonyl groups. These carbonyl groups appeared at δ 206.0 and 208.0 in the ^{13}C NMR spectrum. The *tert*-butyl group and two methyl carbon signals appeared at δ 29.0, 20.0 and 19.5 respectively. The molecular ion peak at *m/z* 242 is in agreement with the proposed structure.

4-*tert*-Butyl-*o*-benzoquinone, prepared by the oxidation of 4-*tert*-butyl catechol with sodium periodate in H_2O/CH_2Cl_2 medium, undergoes cyclo-addition with 2,3-dimethyl-1,3-butadiene to give the naphthoquinone derivative **27**. Here also it is conjuctured that the primary adduct **26**

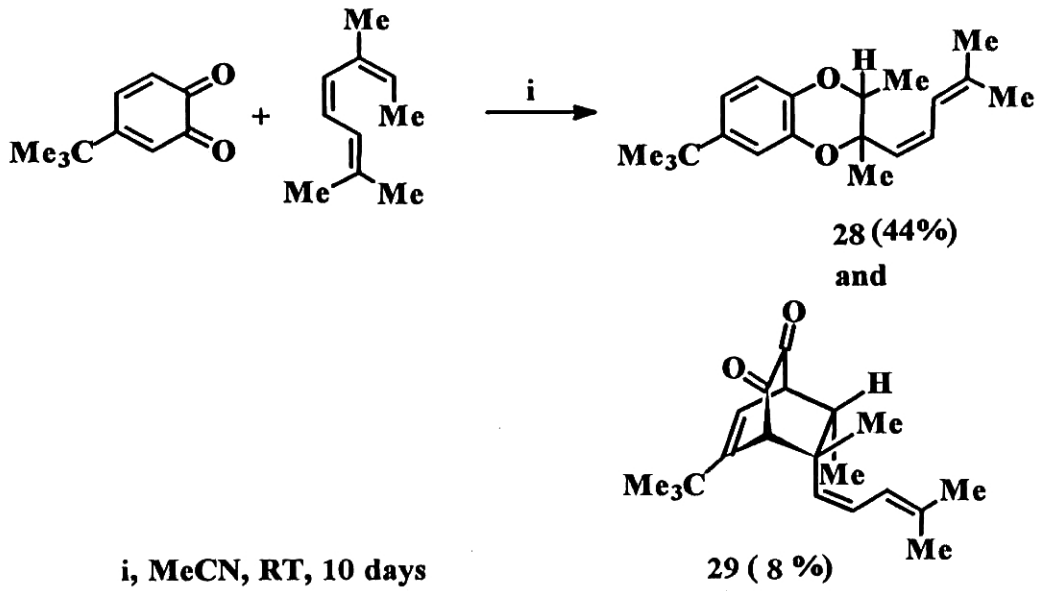
undergoes rapid dehydrogenation in the presence of excess of quinone. The final product was isolated in 55% yield.



i, Benzene, reflux, 4 h

IR spectrum of **27** shows the presence of quinone carbonyl at 1656 cm^{-1}. ^1H NMR spectrum of the product revealed the presence of three proton signals at δ 6.42, 7.7, and 7.95. The signal at δ 6.42 is due to C_3-H in the quinone ring. The two methyl resonances appeared at δ 2.35 and 2.4. The product **27** shows similar carbon resonances as in the case of **25**. The two peaks at δ 205.0 and 206.0 in the ^{13}C NMR spectrum have been assigned to the carbonyl carbons. As expected the mass spectrum exhibited a molecular ion peak at *m/z* 242.

The reaction of alloocimene and 4-*tert*-butyl-*o*-benzoquinone gave rise to the benzodioxin derivative **28** and the bicyclo[2.2.2]octene dione adduct **29** in 44% and 8% yields respectively.

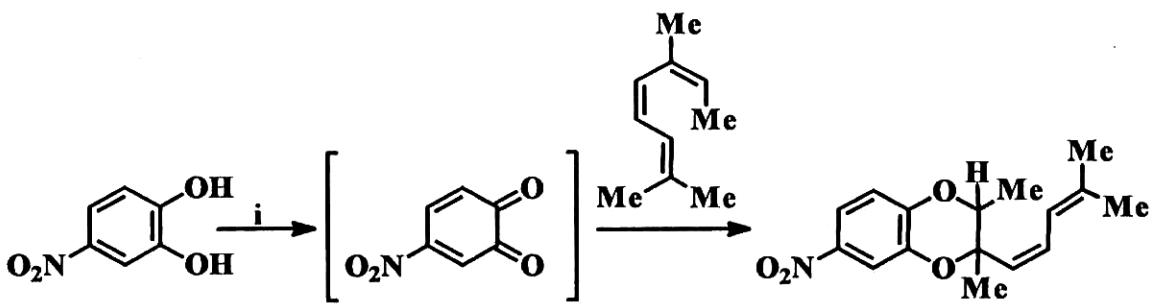


The product **28** does not show any carbonyl absorption in the IR spectrum. In the ^{1}H NMR spectrum of **28**, the *tert*-butyl group resonated at δ 1.25. The two methyl groups on the olefinic side chain appeared as a singlet at δ 1.30. The ^{1}H NMR spectrum also exhibited a broad singlet at δ 1.75 due to the two methyl groups on the dioxin ring. The single proton on the dioxin ring resonated as a quartet at δ 3.96 and it supports the suggested regiochemistry. The signals at δ 77.0 and 75.0 in the ^{13}C NMR spectrum have been assigned to the two carbon atoms on the dioxin ring. The olefinic and aromatic carbons appeared in the range δ 114-145. The high resolution mass spectrum with a molecular ion peak at *m/z* 300.2069 is in agrement with the proposed structure.

The adduct **29** is characterized as follows. A strong absorption at 1737 cm^{-1} in the IR spectrum indicates the presence of saturated carbonyl group. In the ^{1}H NMR spectrum of **29** the signals at δ 1.0 and 1.2 have been assigned to the bridgehead methyl protons. The two methyl groups on the side chain resonated at δ 1.65 as a singlet. The bridgehead protons displyed a multiplet at δ 3.0. The olefinic protons on the side chain appeared

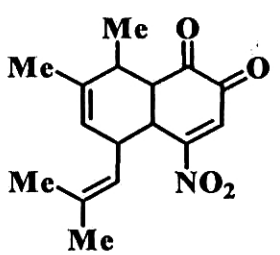
at δ 5.65 (m, 1H) and 6.5 (m, 2H). The C=O absorptions in the ^{13}C NMR appeared at δ 188.0 and 192.0. High resolution mass spectrum gave the molecular ion peak at *m/z* 300.2070.

Subsequent to the above investigations we turned our attention to the cycloaddition of an *o*-benzoquinone bearing strongly electron withdrawing group and 4-nitro-*o*-benzoquinone was chosen for these studies. In view of its instability, this quinone was generated *in situ* by the oxidation of 4-nitro-catechol with Ag_2O, and its cycloaddition was investigated with a number of dienes. With alloocimene the quinone undergoes cycloaddition by two different pathways as shown below.

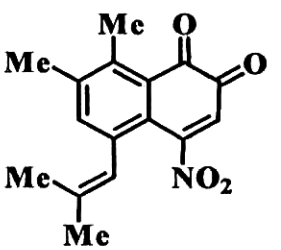


30 (8%)

and



31



32 (18%)

i, Ag_2O, Et_2O,0°C, 12 h

The products **30** and **32** were isolated in 8% and 18% yields respectively. The examination of the ^1H NMR spectrum of **30** showed that

the product is a benzodioxin adduct. The quartet appearing at δ 4.0 (1H, J = 7.2 Hz) is due to the proton adjacent to the -CH_3 group in the dioxin ring. This methyl group resonated at δ 1.31 (3H, J = 7.2 Hz) as a doublet. The methyl group adjacent to the other oxygen in the benzodioxin ring appeared as a singlet at δ 1.3 (3H). The two methyl groups attached to the olefinic bond resonated at δ 1.8 (6H) as superimposed singlets. The olefinic protons appeared at δ 5.7 (2H) and 6.5 (1H). The signals at δ 7.0 (1H) and 7.8 (2H) are assigned to the aromatic protons. From the spectrum, it was discerned that the addition took place across the 6,7- olefinic bond of alloocimene. ^{13}C NMR spectrum showed two carbon signals at δ 79.5 and 80.0 due to the carbons adjacent to oxygen atom in the benzodioxin ring. The four methyl carbons appeared at δ 27.0, 19.5, 18.5 and 16.5 respectively. IR spectrum of **30** does not show any carbonyl absorption. Mass spectrum showed the molecular ion peak at *m/z* 289.

The product **32** which is most probably derived by the aromatization of the primary adduct **31** has been characterized as follows. This red coloured solid showed typical quinone carbonyl absorption at 1661 cm^{-1} in the IR spectrum. The four methyl groups present in **32** resonated at δ 1.65, 1.95, 2.30 and 2.50 in the ^{1}H NMR spectrum. The aromatic and olefinic signals appeared at δ 6.2, 7.0 and 7.4. The carbon signals in the ^{13}C NMR spectrum at δ 17.43, 19.50, 20.90 and 25.86 have been assigned to the methyl groups. There are no sp3 carbon signals other than those of the methyl groups in the spectrum. ^{13}C NMR spectrum of **32** indicates the presence of two carbonyl absorptions at δ 182.11 and 183.32. DEPT experiment on **32** clearly indicated the absence of sp3 -CH- carbons.

Reactions of 3-methoxy-*o*-benzoquinone with various dienes like 1,4-diacetoxy-1,3-butadiene, 1-acetoxy-2,4-hexadiene, 1,4-diphenyl-1,3-butadiene, 2,5-dimethyl-2,4-hexadiene, 1,3-dimethyl-1,3-hexadiene, alloocimene etc. were tried under a variety of conditions. These reactions produced complex mixtures which could not be processed for the isolation of pure compounds. The reaction of 4-*tert*-butyl-*o*-benzoquinone with some of the above dienes also produced similar results.

In order to gain some insight into the results described in this chapter we have carried out some theoretical calculations. The methods used and the results of these calculations are given in the following sections.

2.3 THEORETICAL CALCULATIONS

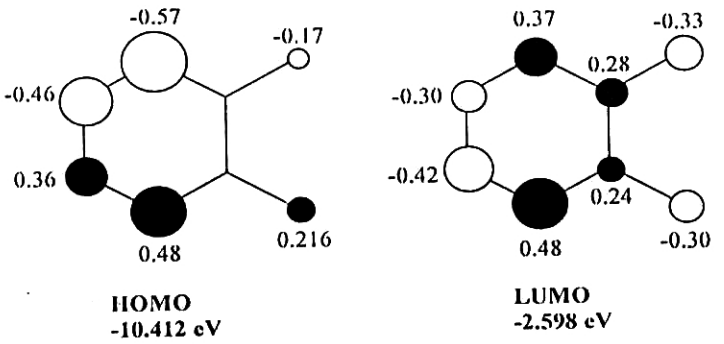
One of the most important descriptions of organic reactivity is on the basis of the electronic structures of the reactants and products. The spectacular success of Frontier Molecular Orbital (FMO)[9] theory and equivalent approaches based on orbital correlation diagram are widely recognized. In addition to the basic predictions whether a reaction is allowed or forbidden, several subtle features of reactivity can be understood on the basis of the above concepts. The energies, relative atomic orbital coefficients and nodal characteristics of FMO can be used to rationalize the relative rates as well as site, regio- and stereoselectivities of a variety of reactions. The study of pericyclic reactions has been particularly dominated by FMO arguments. Several other factors resulting from molecular electronic structure can be used to predict reactivity patterns. FMO based analysis of cycloadditions has been briefly presented in chapter 1. We have also been

interested in a more empirical understanding of this aspect of cycloaddition and therefore we resorted to a more mathematical approach.

Some of the popular methods used for molecular energy calculations are molecular mechanics[10], *ab initio* molecular orbital theory[11], semi-empirical molecular orbital methods[12] etc. We have used MNDO[13] and AM1[14] methods for the calculations and these belong to the semiempirical molecular orbital method. The major advantage of the semiempirical procedure is that equilibrium geometries, heat of formation, reasonable wave function and bonding descriptions all can be routinely calculated for even complex organic molecules. This method therefore represents a sensible computational choice for studying chemical reactivity problem.

2.4 DISCUSSION ON THEORETICAL STUDIES

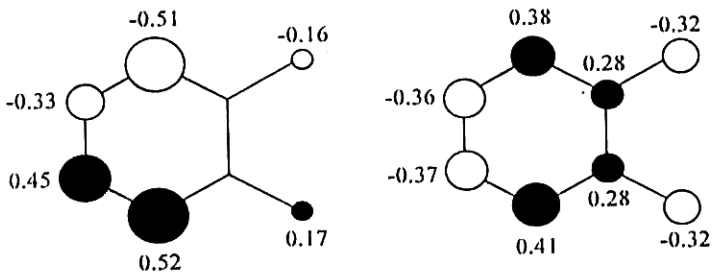
The MNDO and AM1 calculations were performed by MOPAC (version 5.01) program. The final heat of formation of the starting materials ie, *o*-quinones, acyclic dienes, carbo- and heterocyclic dienes, and fulvenes were determined by this method. The energies corresponding to the HOMO and LUMO of each molecule were obtained from the eigen vectors. The magnitude of these vectors in the XYZ directions determines the molecular orbital coefficients. These coefficients are very important in determining the molecular orbital picture and they control the regiochemistry of the Diels-Alder reaction. The key factors responsible for the cycloaddition are the energy of the interacting orbitals and the overlap between them. The molecular orbital coefficients of the *o*-quinones are given in the following chart 1.



HOMO
-10.412 eV

LUMO
-2.598 eV

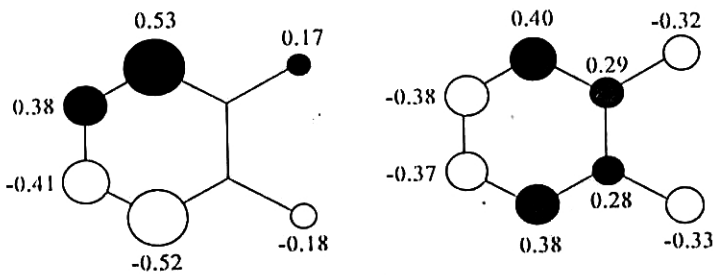
4-Nitro-*o*-benzoquinone



HOMO
-9.106 eV

LUMO
-2.006 eV

3-Methoxy-*o*-benzoquinone



HOMO
-9.8 eV

LUMO
-1.188 eV

3,5-Di-*tert*-butyl-*o*-benzoquinone

Chart 1. Molecular orbital coefficients of the *o*-quinones

The HOMO and LUMO energies of the reactants were determined by the above methods. These are given in Table 1.

Table 1. HOMO-LUMO energies of the reactants.

REACTANTS	$HOMO_{eV}$	$LUMO_{eV}$
1. 3,5-Di-*tert*-butyl-*o*-benzoquinone	-9.800	-1.188
2. 4-*tert*-Butyl-*o*-benzoquinone	-10.009	-1.435
3. 4-Nitro-*o*-benzoquinone	-10.412	-2.598
4. 3-Methoxy-*o*-benzoquinone	-9.106	-2.006
5. 1,4-Diacetoxy-1,3-butadiene	-9.365	-0.549
6. 1-Acetoxy-2,4-hexadiene	-9.332	0.107
7. 2,5-Dimethyl-2,4-hexadiene	-8.853	-0.056
8. Alloocimene	-9.290	0.425
9. 2,3-Dimethyl-1,3-butadiene	-9.800	0.986

From the above table, it has been found that all the reactions described in this chapter belong to inverse electron demand Diels-Alder category. The energy gap for $LUMO_{Quinone}$-$HOMO_{Diene}$ is smaller than the $HOMO_{Quinone}$-$LUMO_{Diene}$ energy levels.

2.5 EXPERIMENTAL DETAILS

All melting points are uncorrected and were determined on a Büchi-530 melting point apparatus. Melting points are reported only for crystalline compounds. The IR spectra were recorded on a Perkin-Elmer Model 882 infrared spectrophotometer. The UV spectra were recorded on a Shimadzu UV-2100 spectrometer. NMR spectra were recorded on Hitachi-60, JEOL EX-90, BRUKER-300 NMR spectrometer using chloroform-*d* as solvent. The chemical shifts are given in δ scale with tetramethylsilane as internal standard. The abbreviations s, d, dd, t, m and br s refer to singlet, doublet, doublet of doublet, triplet, multiplet and broad singlet respectively. The mass spectra were recorded on a Finnigan MAT Model 8430 and Fisons GC 8000-MD 800. Elemental analysis were carried out using a Perkin-Elmer Elemental Analyzer. HPLC was done on Shimadzu LC-10AS instrument and MPLC on Büchi 688 system. Solvents used for the experiments were purified by distillation before use. Column chromatography was done using 100-200 mesh silica gel and approprate mixture of petroleum ether (60-80°C) and ethyl acetate for elution.

3-Acetoxy-2-(1-acetoxyethenyl)-6,8-bis(1,1-dimethylethyl)-[1,4]benzo-dioxin (19).

A solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (0.20 g, 0.90 mmol) and 1,4-diacetoxybuta-1,3-diene (0.155 g, 0.90 mmol) in dry toluene (1 mL) was deoxygenated, sealed under nitrogen and heated at 120 °C for 30 h. The solvent was evaporated *in vacuo* and the product subjected to chromatography on silica gel column (5% ethyl acetate - light petroleum) to afford **19** (0.32 g, 90%) as colourless crystals. mp.113-115 °C.

IR, film : 2967, 2875, 1770, 1679, 1593, 1487, 1422, 1373, 1306, 1219, 1109, 1004 cm^{-1}.

UV, λ_{max} (MeOH) : 212 (18475), 280 (2200) nm.

^1H NMR : δ 7.55 (d, *J*=12.53 Hz, 1H), 6.94 (d, *J*=2.35 Hz, 1H, ArH), 6.84 (d, *J*=2.3 Hz, 1H, ArH) 6.20(d, *J*=3.3 Hz, 1H), 5.50 (dd, *J*=12.53 Hz, 1H), 4.6 (dd, *J*=3.3, 3.07 Hz, 1H), 2.123 (s, 3H), 2.12 (s, 3H), 1.36 (s, 9H), 1.26 (s,9H).

^{13}C NMR : δ 169.61, 167.5, 144.08, 140.5, 140.0, 138.1, 137.39, 117.03, 112.56, 107.94, 89.32, 70.5, 35.0, 34.46, 31.45, 29.76, 21.08, 20.58.

MS *m/z* : 391 (M^++1), 390 (M^+, 100%)

HRMS : $C_{22}H_{30}O_6$: 390.4591; Found: 390.4430.

3-Methyl-2-(1-acetoxyprop-2-enyl)-6,8-bis(1,1-dimethylethyl)[1,4]benzo-dioxin (21).

A solution of 3,5-di-*tert*-butyl-*o*-benzoquinone (0.20 g, 0.90 mmol) and 1-acetoxy-2,4-hexadiene (0.16 g, 1.14 mmol) in dry toluene (1mL) was deoxygenated, sealed under nitrogen and heated at 110 °C for 40 h. The solvent was removed *in vacuo* and the product subjected to chromatography on silica gel column (5% ethyl acetate-petroleum ether) to afford **21** as colourless crystals, mp. 65-67 °C.

IR, film : 2692, 2873, 1749, 1669, 1591, 1484, 1422, 1364, 1309, 1236, 1091, 1031, 972, 862 cm^{-1}.

^1H NMR : δ 6.85 (m, 2H), 6.05 (m, 1H), 5.83 (m, 1H), 4.65 (d, 2H), 4.15 (m, 1H), 3.88 (m, 1H), 2.10 (s, 3H), 1.35 (s, 9H), 1.30 (d, 3H), 1.25 (s, 9H).

^{13}C NMR : δ 170.63, 143.28, 142.74, 139.29, 137.60, 128.90, 128.76, 115.69, 111.94, 77.45, 72.69, 63.99, 35.07, 34.37, 31.49, 29.79, 20.92, 17.25

HRMS : $C_{22}H_{32}O_4$: 360.2300 found : 360.2287

3,3-Dimethyl-2-(1-methylpropenyl)-6,8-bis(1,1-dimethylethyl)[1,4]benzodioxin (22).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.20 g, 0.90 mmol) and 2,5-dimethyl-2,4-hexadiene (1 mL, 7.0 mmol) were taken in a tube and sealed under nitrogen atmosphere. The tube was then heated at 100 °C for 2h. The excess diene was removed *in vacuo* and the product subjected to chromatography on silica gel column (2% ethyl acetate-petroleum ether) to afford **22** (0.252 g, 84%) as pale yellow oil.

IR, film : 2896, 1589, 1489, 1235, 1029, 976, 850 cm^{-1}.

^{1}H NMR : δ 6.60 (m, 2H), 5.75 (m, 1H), 3.75 (br, 1H), 1.45 (br s, 6H), 1.40 (s, 9H), 1.30 (br s, 6H), 1.20 (s, 9H).

^{13}C NMR : δ 145.0, 143.5, 142.0, 140.5, 137.5, 134.5, 117.5, 115.0, 80.0, 73.5, 35.0, 34.0, 32.1, 32.0, 31.9, 29.75, 29.7, 29.5.

MS *m/z* : 330 (M^+), 220, 187, 99, 56.

2,3-Dihydro-2,3-dimethyl-2(4-methyl-1,3-pentadienyl)-6,8-bis(1,1-dimethylethyl)[1,4]benzodioxin (23).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.20 g 0.907 mmol) and allooocimene (0.6 g, 4.3 mmol) were dissolved in CH_2Cl_2 (10 mL) and kept at 10 °C for 10 days. The solvent was evaporated and the residue on column chromatography on silica gel afforded **23** (0.24 g, 75%) as pale yellow viscous oil.

IR, film : 2962, 1591, 1468, 1420, 1037 cm^{-1}.

^{1}H NMR : δ 6.90 (br s, 2H), 6.5-5.9 (m, 3H), 4.0 (q, 1H), 1.80 (s, 6H), 1.34 (d, 3H), 1.30 (s, 3H), 1.27 (s, 9H), 1.10 (s, 9H).

^{13}C NMR : δ 142.5, 142.0, 139.5, 139.0, 130.5, 128.0, 126.0, 118.5, 114.0, 77.0, 75.1, 34.5, 34.0, 27.0, 20.5, 20.2, 19.5, 18.5, 18.0

MS *m/z* : 356 (M^+), 198, 69, 54.

3-(1,1-Dimethylethyl)-6,7-dimethyl-1,2-naphthoquinone (25).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.5 g, 2.26 mmol) and 2,3-dimethyl-1,3-butadiene (0.5 g, 6.0 mmol) were taken in a glass tube and sealed under vacuum. It was then heated at 90 °C for 8h. The excess diene was removed *in vacuo* and the residue on column chromatography gave **25** as red crystals (0.108 g, 20%), mp.145-147 °C.

IR, film : 2965, 2872, 1689, 1670, 1655, 1602, 1451, 1391, 1292 cm^{-1}.

^{1}H NMR : δ 7.65 (s, 1H), 7.07 (s, 1H), 6.95 (s, 1H), 2.25 (s, 6H), 1.25 (s, 9H).

^{13}C NMR : δ 208.0, 206.0, 147.0, 146.0, 139.5, 139.0, 133.5, 131.0, 130.5, 115.5, 35.0, 29.0, 20.0, 19.5.

HRMS : $C_{16}H_{18}O_2$: 242.3034 ; Found : 242.3003.

4-(1,1-Dimethylethyl)-6,7-dimethyl-1,2-naphthoquinone (27).

4-*tert*-Butyl-*o*-benzoquinone (0.2 g, 1.21 mmol.) and 2,3-dimethyl-1,3-butadiene (0.5 g, 6.08 mmol) were dissolved in benzene (10 mL) and refluxed for 4 h. under nitrogen. The solvent was evaporated under reduced pressure and the residue on silica gel column chromatography (ethyl acetate-petroleum ether) afforded **27** (0.165 g, 55%) as a red solid.

IR, film : 2970, 1656, 1593, 1540, 1393, 1287, 1187 cm^{-1}.

^{1}H NMR : δ 7.95 (s, 1H), 7.7 (s, 1H), 6.42 (s, 1H), 2.4 (s, 3H), 2.35 (s, 3H), 1.5 (s, 9H).

^{13}C NMR : δ 206.0, 205.0, 146.5, 146.0, 140.0, 139.5, 134.0, 131.0, 130.0, 116.0, 35.0, 29.1, 20.0, 19.5.

Analysis calcd for $C_{16}H_{18}O_2$: C, 81.77; H, 9.15 ; Found : C, 81.60, H, 9.09.

Diels-Alder Adducts 28 and 29.

4-*tert*-Butyl-*o*-benzoquinone (0.207 g, 1.24 mmol) and alloocimene (0.5 mL, 2.9 mmol) were dissolved in acetonitrile (10 mL) and stirred at room temperature for 10 days. The solvent was removed and the residue on chromatography afforded **28** (0.164 g, 44%) and **29** (0.022 g, 8%) as viscous oils.

2,3-Dihydro-2,3-dimethyl-2-(4-methyl-1,3-pentadienyl)-7-(1,1-dimethyl-ethyl)[1,4]benzodioxin (28).

IR, film : 2969, 2877, 1591, 1507, 1381, 1282, 1075 cm^{-1}.

^{1}H NMR : δ 6.8 (m, 3H), 5.9 (m, 1H), 5.7 (m, 1H), 5.45 (m, 1H), 3.96 (q, 1H), 1.75 (br s, 6H), 1.3 (br s, 6H), 1.25 (s, 9H).

^{13}C NMR : δ 145.1, 142.2, 140.2, 137.1, 130.0, 128.0, 124.2, 117.1, 116.1, 114.2, 77.0, 75.0, 34.1, 31.0, 26.0, 23.0, 18.0, 15.2

HRMS : $C_{20}H_{28}O_2$: 300.2089 ; found : 300.2069

5-(1,1-Dimethylethyl)-7,8-dimethyl-8-(4-methyl-1,3-pentadienyl)bicyclo-[2.2.2]oct-5-ene-2,3-dione (29).

IR, film : 2966, 2878, 1737, 1676, 1505, 1462, 1373, 1271, 1213, 1089, 967 cm^{-1}.

^{1}H NMR : δ 6.5 (m, 2H), 6.0 (m, 1H), 5.65 (m, 1H), 3.0 (m, 3H), 1.65 (br s, 6H), 1.25 (s, 9H), 1.2 (s, 3H), 1.0 (d, 3H).

^{13}C NMR : δ 192.1, 188.0, 139.2, 133.5, 128.0, 125.0, 124.5, 121.3, 62.0, 54.0, 43.0, 42.1, 35.0, 31.5, 28.0, 27.5, 25.7, 18.5.

HRMS : $C_{20}H_{28}O_2$: 300.2089 ; found : 300.2070

Diels-Alder Adducts 30 and 32 :

4-Nitrocatechol (0.199 g, 1.28 mmol) was dissolved in dry ether (10 mL) and silver oxide (1.50 g, 6.4 mmol) was added and stirred at 0° C. To this solution alloocimene (0.836 g, 6.20 mmol) was added and stirred at 0° C for 12h. The inorganic residue was removed by passing through a short column of celite and washed with ether. The solvent was removed *in vacuo* and the residue on silica gel column chromatography afforded **30** (0.050 g, 8%, viscous oil) and **32** (0.065 g, 18%, red crystals, mp. 96-98 °C).

2,3-Dihydro-2,3-dimethyl-2-(4-methyl-1,3-pentadienyl)-7-nitro[1,4]benzo dioxin (30).

IR, film : 2976, 2874, 1591, 1526, 1497 cm^{-1}.

^1H NMR : δ 7.8 (m, 2H), 7.0 (m, 1H), 6.5 (m, 1H), 5.7 (m, 2H), 4.0 (q, 1H), 1.8 (s, 6H), 1.31 (d, 3H), 1.3 (s, 3H).

^{13}C NMR : δ 149.5, 143.0, 142.0, 139.5, 130.0, 129.5, 125.0, 119.0, 118.0, 114.0, 80.0, 79.5, 27.0, 19.5, 18.5, 16.5.

MS *m/z* : 290 (M^+ +1), 289 (M+), 194.

4-Nitro-5-(2-methylpropenyl)7,8-dimethyl-1,2-naphthoquinone (32).

IR, film : 2931, 1693, 1661, 1614, 1541, 1449 cm^{-1}.

^1H NMR : δ 7.4 (d, 1H), 7.0 (s, 1H), 6.2 (m,1H), 2.5 (s, 3H), 2.3 (s, 3H), 1.95 (s, 3H), 1.65 (s, 3H).

^{13}C NMR : δ 183.32, 182.11, 144.8, 143.2, 141.4, 139.6, 137.6, 131.5, 130.7, 125.5, 121.2, 25.86, 20.9, 19.5, 17.43.

MS *m/z* : 286 (M^+ +1), 260, 245, 217, 200, 190, 133.

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CHAPTER 3

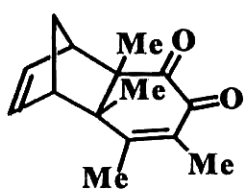
CYCLOADDITION REACTIONS OF *o*-QUINONES WITH CARBOCYCLIC AND HETEROCYCLIC DIENES

This chapter is divided into two sections. The first section deals with the cycloaddition of *o*-quinones with carbocyclic dienes. The second section describes the reactions of *o*-quinones with heterocyclic dienes.

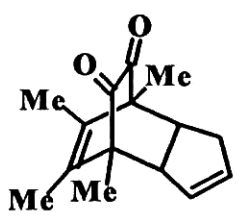
3.1 CYCLOADDITION REACTIONS OF *o*-QUINONES WITH CARBOCYCLIC DIENES

3.1.1 INTRODUCTION

In the first report on the Diels-Alder reaction of an *o*-benzoquinone, Smith and Hac[1] described the reaction of cyclopentadiene with tetramethyl-*o*-benzoquinone leading to a product for which structure **1** was assigned. However this adduct was shown by Horner and Spietschka[2] to have the oxalylindene structure **2** resulting from the quinone functioning as the diene and cyclopentadiene as the dienophile.



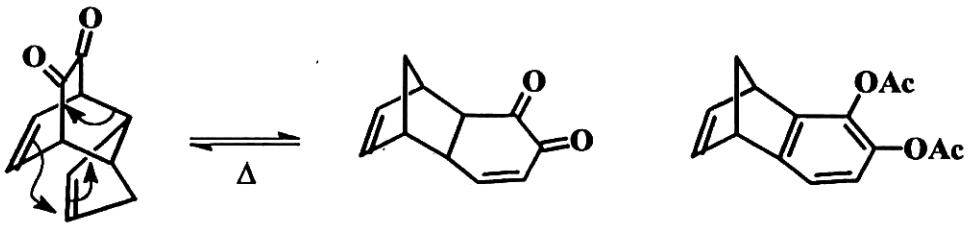
1



2

The relationship between the two adducts **1** and **2** was clearly demonstrated by Ansell and coworkers[3], who pointed out that these are both

"hexa-1,5-dienes" and that the two are potentially interconvertible by a Cope rearrangement as shown in scheme 1.

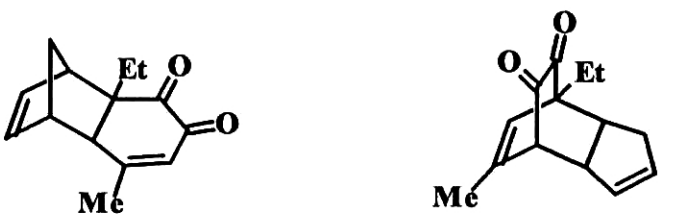


3 4 5

Scheme 1.

The methanonaphthoquinone **4** was easily transformed into **5** by aromatization followed by acylation.

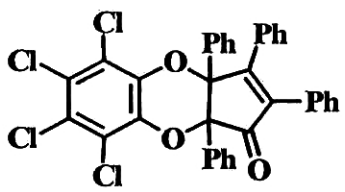
The reaction of cyclopentadiene with a number of *o*-benzoquinones carrying chloro-, methyl- and phenyl substituents were investigated and in almost all cases, the oxalyl indene type adducts were isolated. The equilibrium for this Cope rearrangement lies entirely on the side of the oxalyl indene, presumably due to steric factors favouring the bicyclo[2.2.2]octene system **3** rather than the bicyclo[2.2.1]heptene system, **4**. The reaction between 3-ethyl-5-methyl-*o*-benzoquinone and cyclopentadiene[3] gave a mixture of methanonaphthoquinone **6** and oxalylindene **7**.



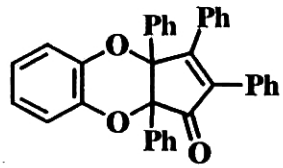
6 7

Almost all the reactions were carried out at ambient temperature, at which rearrangement was too slow to give the observed product ratios and therefore the authors surmised that the product composition is a consequence of kinetic and not thermodynamic control. It was postulated that the methanonaphthoquinone is the kinetically controlled product whereas the oxalylindene is the product of thermodynamic control.

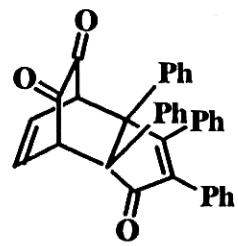
In 1969, Horspool and coworkers[4] reported the cycloaddition of *o*-chloranil with tetracyclone leading to the benzodioxin adduct **8** in good yield. With *o*-benzoquinone, a mixture of the benzodioxin and the bicyclo-[2.2.2] adducts (**9** and **10**) were obtained.



8



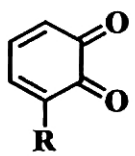
9



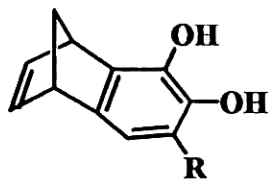
10

As already mentioned, *o*-benzoquinone reacts predominantly as a dienophile towards cyclopentadiene, and the variation of mode of addition and reactivity brought about by substitutions must be regarded as a modification of the basic dienophilic reactivity. Diels-Alder reaction between a number of *o*-benzoquinones carrying electron withdrawing groups (-CHO, -COEt, -COPh etc.)[5] at 4-position and cyclopentadiene have been reported in 1982. At room temperature, these reactions gave the thermally stable oxalyl indene adducts. Diels-Alder reaction between a number of *o*-benzo-quinones (**11**) carrying an electron withdrawing group at position 3 and cyclopentadiene have been reported[6] and in contrast to the above results,

the quinones behave as dienophiles in these cases. The addition takes place at the unsubstituted position of the quinone. Under the reaction conditions the products undergo aromatization to afford **12**



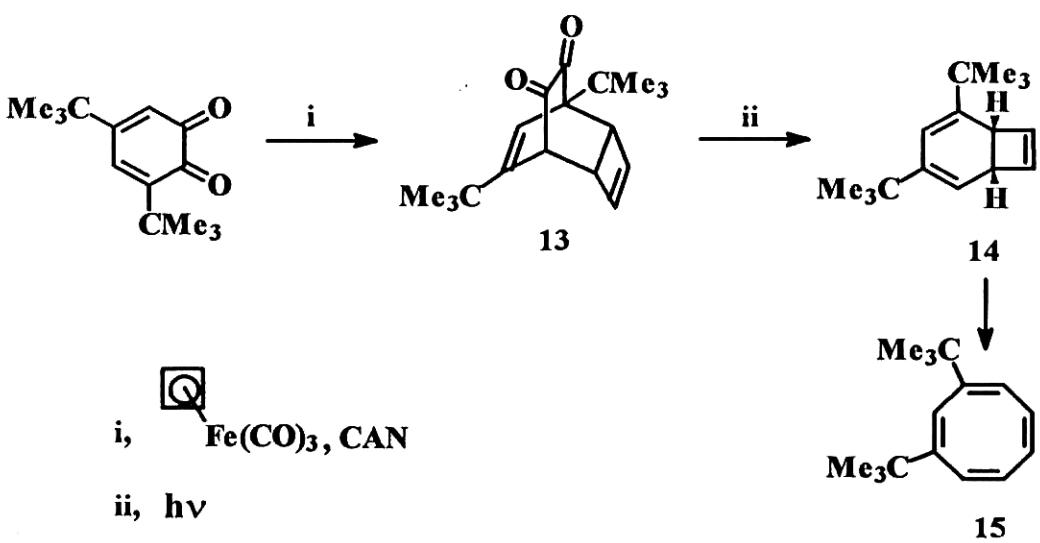
11



12

R = -CHO, -COMe, -CN etc

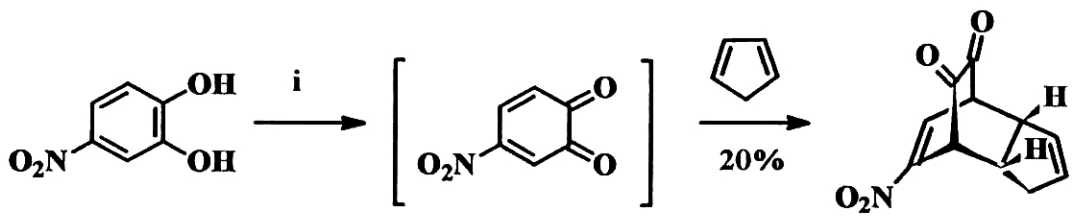
Paquette has used the cycloaddition reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with cyclobutadiene[7] to construct the cyclooctatetraene **15** . The cyclobutadiene generated *in situ* from the iron tricarbonyl complex by CAN oxidation has been trapped with the quinone as a [4+2] adduct **13**. The latter under photolytic conditions, eliminates two molecules of carbon monoxide and the resulting triene **14** undergoes electrocyclic ring opening to afford the cyclooctatetraene.



3.1.2 RESULTS AND DISCUSSION

The literature reports on the cycloaddition of *o*-quinones with cyclic dienes are of limited scope. We have therefore undertaken further investigations in this area using readily available cyclic dienes. The *o*-benzoquinones selected are 4-nitro-*o*-benzoquinone, 3,5-di-*tert*-butyl-*o*-benzoquinone and 4-*tert*-butyl-*o*-benzoquinone.

4-Nitro-*o*-benzoquinone was particularly interesting since there are no reports on its cycloaddition. As expected this quinone is extremely reactive and it cannot be isolated. However we have succeeded in trapping this 'hot' molecule by appropriate dienes. 4-Nitro-*o*-benzoquinone generated *in situ* by the silver oxide oxidation of 4-nitrocatechol on reaction with cyclopentadiene furnished the adduct **16** in 20% yield.



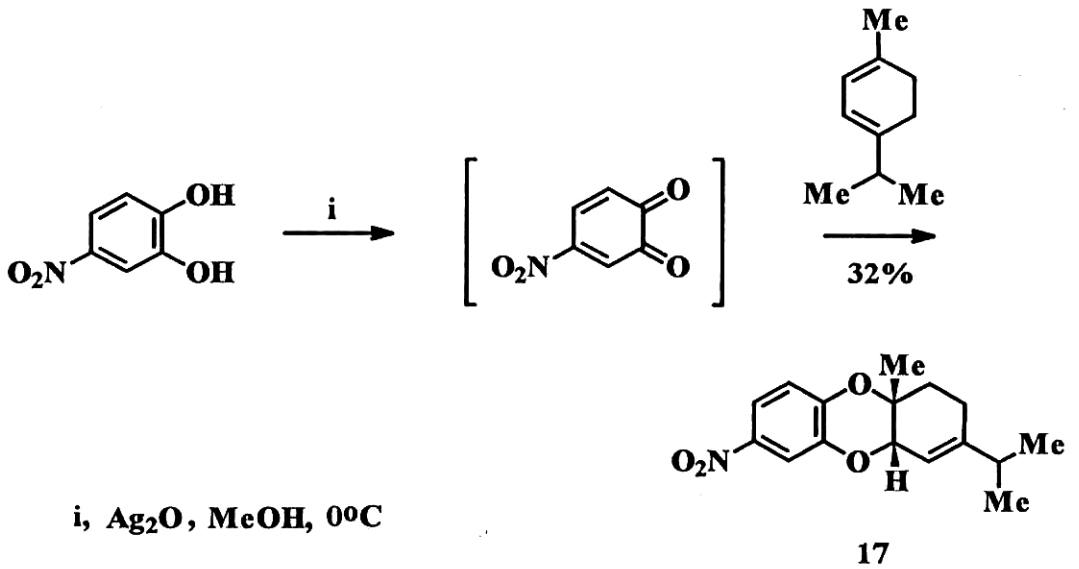
16

i, Ag_2O, MeOH, 0°C

The structure of the adduct **16** was ascertained from its spectral data. The IR spectrum of the adduct showed a strong absorption at 1730 cm^{-1}, indicating the presence of α-diketone. The *endo* stereochemistry has been assigned by considering the appropriate proton signals and on theoretical grounds. In the ^1H NMR spectrum, the bridgehead protons appeared at δ 3.4 as a multiplet. The three olefinic signals appeared at δ 6.5-5.6 as a multiplet. Examination of the ^{13}C NMR spectrum of **16** revealed the

presence of two carbonyl groups (δ 196.0 and 195.0). The signals at δ 56.2, 51.0, 45.0, and 42.5 have been assigned to the bridgehead and ring junction carbons respectively. The sp^3 carbon adjacent to the olefinic group of cyclopentene moiety resonated at δ 35.5. The mass spectrum which shows the presence of a molecular ion peak at *m/z* 219 is also in agreement with the assigned structure.

The reaction of 4-nitro-*o*-benzoquinone with α-terpinene took an entirely different course to afford the benzodioxin derivative **17** (32%) as the only isolable product.



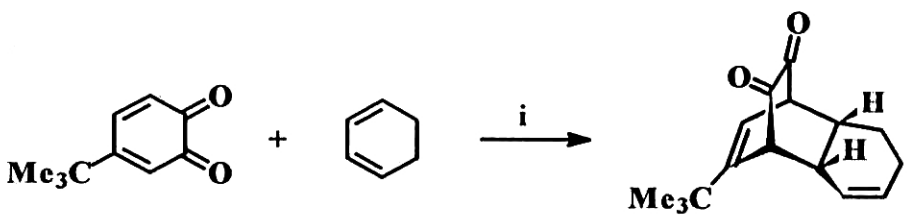
i, Ag_2O, MeOH, 0°C

17

The infrared spectrum of **17** did not show any carbonyl absorption. The isopropyl methyl protons resonated at δ 1.0 (d, 6H) and the ring junction methyl group appeared at δ 1.7 as a singlet. The four protons on the cyclo-hexene ring resonated as a broad multiplet centred at δ 2.10 (4H). The proton adjacent to oxygen atom of the dioxin ring appeared at δ 4.85(1H) as a broad singlet. The aromatic proton signals were observed at δ 7.7(2H) and 6.9(1H). Examination of the ^{13}C NMR spectrum of **17** revealed the presence of

benzodioxin ring and the signals due to the oxygen bearing sp^3 carbons appeared at δ 70.5 and 76.0. The three methyl signals were visible at δ 15.5, 17.5, and 22.5. The two sp^3 carbons on the cyclohexene ring appeared at δ 24.0 and 26.0, whereas the signal due to -CH- carbon was seen at δ 26.0. The mass spectrum showed the presence of a $(M^+ +1)$ ion peak at *m/z* 290. The regiochemistry has been assigned on the basis of spectral data and the assumption that the addition occurs at the less hindered olefinic bond of α-terpinene.

4-*tert*-Butyl-*o*-benzoquinone on reaction with 1,3-cyclohexadiene afforded the bicyclo[2.2.2] adduct **18** in 10% yield.



18

i, MeCN, Na_2SO_4, Reflux, 1 h, 10%

IR spectrum of **18** showed a strong absorption at 1738 cm^{-1} indicating the presence of α-diketone. The olefinic signals appeared at δ 5.8 (m, 2H) and 5.5 (m, 1H). The bridgehead protons resonated at δ 3.35 (m, 1H) and 3.10 (m, 1H). The four protons on the cyclohexene ring appeared at δ 1.30 as a multiplet and the *tert* butyl group as a singlet at δ 1.00. The ^{13}C NMR spectrum was also in accordance with the assigned structure. The two carbonyl signals appeared at δ 190.0 and 190.5 in the ^{13}C NMR spectrum. The low yield of this reaction can be attributed to the oxidation of

cyclohexadiene to benzene by the quinone which in turn undergoes reduction to catechol.

Reactions of 3,5-di-*tert*-butyl-*o*-benzoquinone with 1,3-cyclohexadiene, 1-methoxycyclohexadiene and α-terpinene gave no isolable products. Similar results were obtained with 3-methoxy and 4-*tert*-butyl-*o*-benzoquinones with α-terpinene and 1-methoxycyclohexadiene.

The HOMO-LUMO energy levels of the reactants were determined by MNDO method and are given in the following Table 1.

Table 1. HOMO-LUMO energies of the reactants.

REACTANTS	$HOMO_{eV}$	$LUMO_{eV}$
1. 3,5-Di-*tert*-butyl-*o*-benzoquinone	-9.800	-1.188
2. 4-*tert*-Butyl-*o*-benzoquinone	-10.009	-1.435
3. 4-Nitro-*o*-benzoquinone	-10.412	-2.598
4. Cyclopentadiene	-9.040	0.304
5. Cyclohexadiene	-8.949	0.228
6. α-Terpinene	-8.836	0.043

From the above table it can be discerned that all the reactions described in this chapter are controlled by inverse electron demand.

3.1.3 EXPERIMENTAL DETAILS

6-Nitro-1,3a,4a,7,7a-hexahydro-4,7-ethanoindene-8,9-dione 16:

4-Nitrocatechol (0.2 g, 1.29 mmol) was dissolved in dry ether (10 mL) and freshly prepared silver oxide (1.5 g, 6.4 mmol) was added and stirred at 0 °C. To this mixture freshly distilled cyclopentadiene (1 mL, 15 mmol) was added and stirred for 5 h at 0 °C. The mixture was warmed to room temperature and stirred for another 15 hours. The inorganic material was removed by passing through a short column of celite and washed with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue on column chromatography yielded **16** (0.054 g, 20%) as yellow solid.

IR, KBr : 2980, 1730, 1699, 1574, 1449, 1317, 1250 cm^{-1}.

^1H NMR : δ 6.5-6.1 (m, 2H), 5.6 (m, 1H), 3.4 (m, 2H), 3.0 (m, 1H), 2.3 (m, 1H), 1.8 (m, 2H).

^{13}C NMR : δ 196.0, 195.0, 138.5, 135.3, 133.0, 130.0, 56.2, 51.0, 45.0, 42.5, 35.5.

MS *m/z* : 219 (M^+), 191, 175, 129.

HRMS : $C_{11}H_9O_4N$: 219.1917 ; Found : 219.1801

2-(2-Methylethyl)-4a-methyl-7-nitro-cyclohex-1-ene-[1,4]benzodioxin (17):

4-Nitrocatechol (0.195 g, 1.26 mmol) was dissolved in dry methanol (8 mL) and freshly prepared silver oxide (1.5 g, 6.4 mmol) was added at 0 °C. To the above mixture α-terpinene (1.1 g, 8.0 mmol) was added and stirred for 62 h at room temperature under nitrogen atmosphere. The inorganic material was removed by passing through a short column of celite and washed with methanol. The solvent was removed *in vacuo* and the residue on column chromatography afforded **17** (0.117 g, 32%) as pale yellow crystalline solid, mp. 82-84 °C.

IR, KBr : 2972, 1597, 1525, 1498, 1350, 1270 cm^{-1}.

^1H NMR : δ 7.7 (m, 2H), 6.9 (d, 1H), 5.25 (s, 1H), 4.85 (br s, 1H), 2.1 (br, 4H), 1.7 (s, 3H), 1.4 (m, 1H), 1.0 (d, 6H).

^{13}C NMR : δ 146.1, 142.2, 140.5, 131.0, 122.1, 120.1, 117.5, 116.5, 76.0, 70.5, 26.5, 26.0, 24.1, 22.5, 17.5, 15.5.

MS *m/z* : 290 ($M^+ + 1$), 289 (M+), 274, 245, 166, 149, 107, 79, 77, 55.

HRMS : $C_{16}H_{19}O_4N$: 289.3214 ; Found : 289.3015.

(1α,4α,4aα,8aα)-2-(1,1-Dimethylethyl)-1,4,4a,5,6,8a-hexahydro-1,4-ethanonaphthalene-9,10-dione (18):

4-*tert*-Butyl-*o*-benzoquinone (0.183 g, 1.11 mmol.) was dissolved in dry acetonitrile (10 mL) and sodium sulfate (5 g) was added to it. 1,3-Cyclohexadiene (0.5 mL, excess) was added to the above solution and refluxed for one hour under argon atmosphere. The solvent and excess diene were removed under vacuum and the residue on column chromatography afforded **18** (0.027 g, 10%) as pale yellow oil.

IR, CCl_4 : 2968, 2873, 1738, 1600, 1492, 1471, 1366 cm^{-1}.

^1H NMR : δ 5.8 (m, 2H), 5.5 (m, 1H), 3.35 (m, 1H), 3.1 (m, 1H), 2.7 (m, 1H), 2.0 (m, 1H), 1.3 (m, 4H), 1.0 (3, 9H).

^{13}C NMR : δ 190.5, 190.0, 135.0, 134.5, 119.8, 117.5, 54.5, 50.0, 49.5, 34.5, 27.0, 26.5, 26.0.

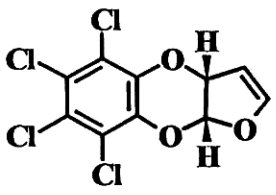
MS *m/z* : 245 (M^++1), 197, 156, 94, 73.

HRMS : $C_{16}H_{20}O_2$: 244.1460 ; found : 244.1283

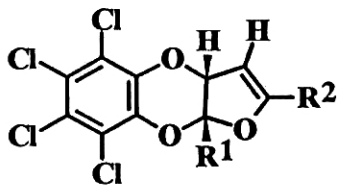
3.2 CYCLOADDITION REACTIONS OF *o*-QUINONES WITH HETEROCYCLIC DIENES

3.2.1 INTRODUCTION

Tetrachloro-*o*-benzoquinone and tetrabromo-*o*-benzoquinone are readily available and their cycloadditions with furans and isobenzofuran have been reported in detail.[8] *o*-Chloranil gave a single product on treatment with furan in boiling benzene. Based on the spectral data, the dihydrobenzodioxin structure **19** has been assigned to the product. Similar dihydrobenzodioxin adducts **20** and **21** were obtained by reaction between *o*-bromanil and 2-methylfuran and 2,5-diphenylfuran respectively.



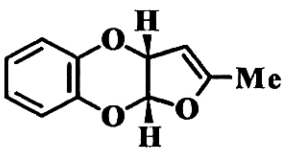
19



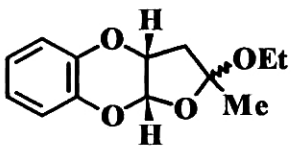
20 : R^1 = H, R^2 = Me
21 : R^1 = R^2 = Ph

The reactions of unsubstituted *o*-benzoquinones with furans are very sluggish and the dihydrobenzodioxin adducts are obtained in negligibly low

yields (0.5-1%). The reaction of *o*-benzoquinone with 2-methylfuran was remarkably solvent dependent. Reaction in dichloromethane gave the normal dihydrofurobenzodioxin **22**. However in chloroform (which contains ethanol as stabilizer), a new product **23** was isolated.



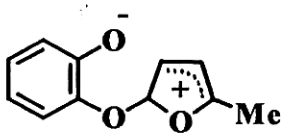
22



23

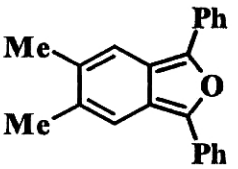
The incorporation of ethanol into the product is presumably part of the overall reaction sequence pointing perhaps to a two step mechanism and not a concerted cycloaddition. Alcohol alone does not add to the double bond under the same conditions and requires strong acid catalysis; the process is analogous to the addition of alcohols to dihydropyrans.

The formation of dihydrobenzodioxin adduct can be envisaged as due to electrophilic attack of the quinone on the furan to produce the more highly stabilized carbocation **24**.

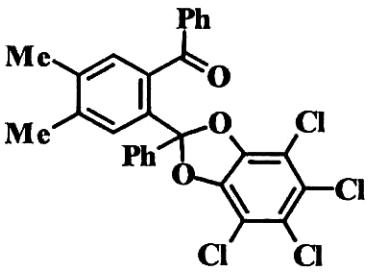


24

This can account for the addition of the quinones to the unsubstituted olefinic bond, although this might also be expected on steric grounds. Further evidence for a two step addition was obtained from the reaction of *o*-chloranil and 1,2-benzoquinone with substituted isobenzofuran **25**. *o*-Chloranil and **25** in chloroform gave a single compound **26** in 88% yield.

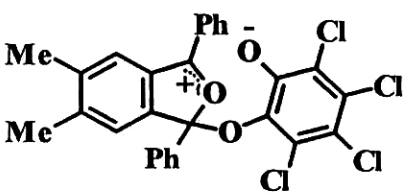


25

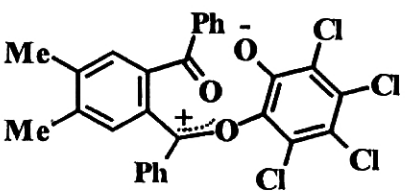


26

Adducts of this type cannot arise from a concerted process. By analogy with previous observations, electrophilic attack producing a carbocation system (**27** and **28**) followed by cyclization to give the acetal **26** is envisaged.



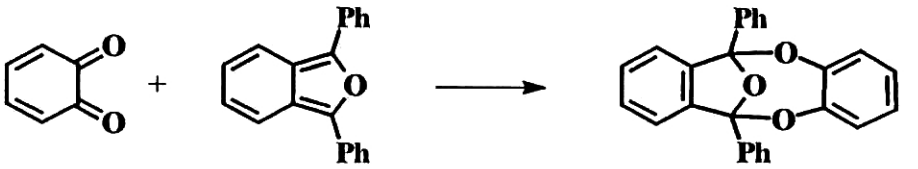
27



28

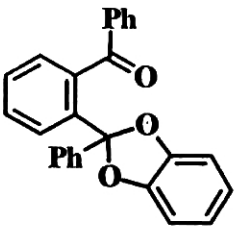
The reaction of *o*-chloranil with 2,3-diphenylfuran, 2,3,5-triphenyl furan, 2-methyl-4,5-diphenylfuran and 3-methyl-4,5-diphenylfuran afforded the benzodioxin adducts in good yilelds.[9]

Friedrichsen has reported[10] the reaction of 1,2-benzoquinone and isobenzofuran leading to the products **29** and **30**.



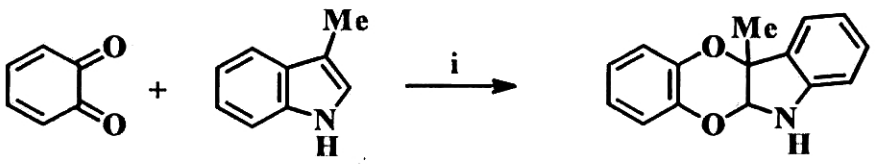
29

+



30

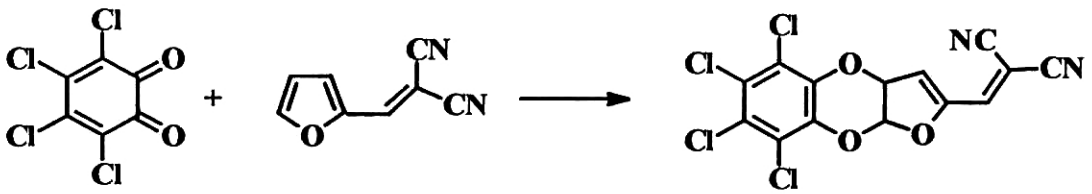
The α-dicarbonyl structure of 1,2-benzoquinone provides a useful variant of the diene system and it too has been the subject of several Diels-Alder studies. Komatsu and coworkers[11] have reported the cycloaddition reaction of 1,2-benzoquinones with 3-substituted indoles. The dioxin type adduct **31** was isolated in very low yield.



31

i, $CHCl_3$, trace HOAc, 1 h

o-Chloranil on reaction with furfurylidenemalononitrile afforded a mono adduct **32** whereas the di-adduct was obtained with furfurylidene cyanoacetic ester.[12-14]

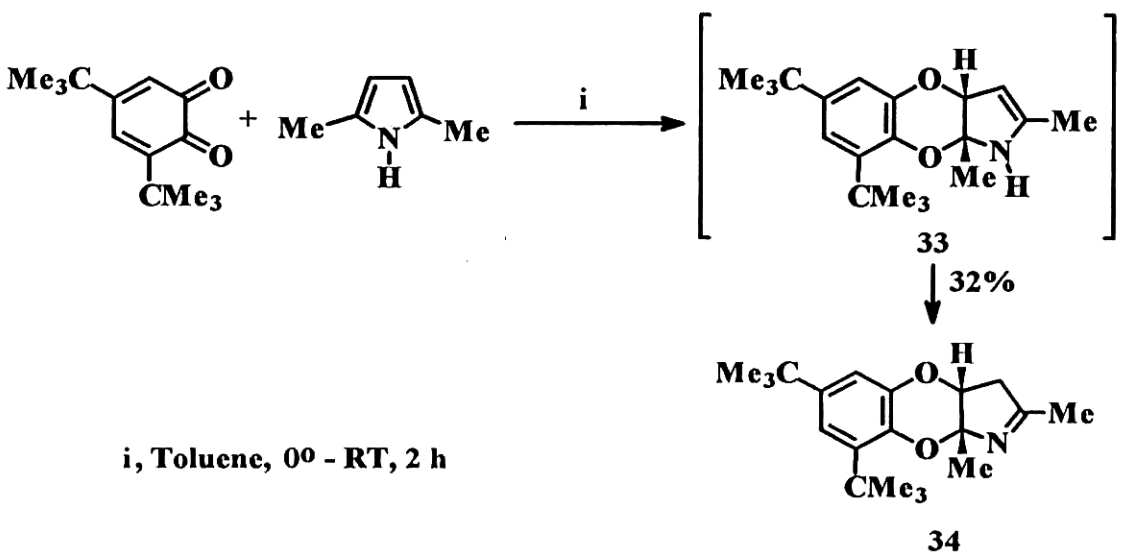


32

3.2.2 RESULTS AND DISCUSSION

It was evident from the literature survey that there has been no work on the reaction of *o*-quinones with pyrroles and thiophenes and therefore we have undertaken some studies and our results are presented here.

Reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with 2,5-dimethylpyrrole at room temperature furnished the pyrroleno[1,4]benzodioxin adduct **34** in 32% yield. Presumably the primary product formed, an enamine **33**, isomerized to the imine under the reaction conditions.



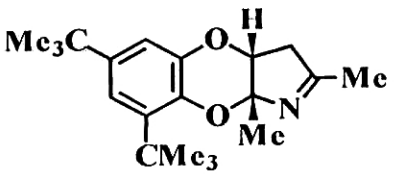
i, Toluene, 0° - RT, 2 h

34

The structure of **34** was determined by analytical and spectral data. The IR spectrum of **34** does not show any carbonyl and -NH absorption.

The ^1H NMR spectrum of **34** showed two singlets at δ 1.22 (9H) and 1.26 (9H), assigned to the two *tert*- butyl groups. The two methyl groups on the pyrroline ring resonated at δ 1.45 and 2.25. The $-CH_2-$ protons appeared at δ 2.83 as a doublet whereas the -CH- proton adjacent to the $-CH_2-$ group in the benzodioxin ring appeared at δ 4.28 as a triplet. The aromatic protons appeared as a singlet at δ 6.82 (2H). Examination of the ^{13}C NMR spectrum showed the presence of two highly deshielded sp^3 carbon signals, and these are assigned to the carbon atoms of the dioxin ring. The carbon atom situated between oxygen and nitrogen appeared at δ 102.80. The other carbon atom on the dioxin ring resonated at δ 78.52. The $-CH_2-$ carbon atom resonated at δ 45.52. The signal at δ 174.05 has been assigned to the imine carbon atom. The mass spectrum (*m/z* : 316, M^+ +1) is in accordance with the assigned structure.

Since there is a possibility for charge transfer complex formation between the quinone and the pyrrole prior to the cycloaddition we studied the UV profile of this reaction. In a series of UV spectra of the reaction mixture no charge transfer band was observed for the above reaction. In all possibility therefore, the reaction involves a direct addition followed by isomerization.



34

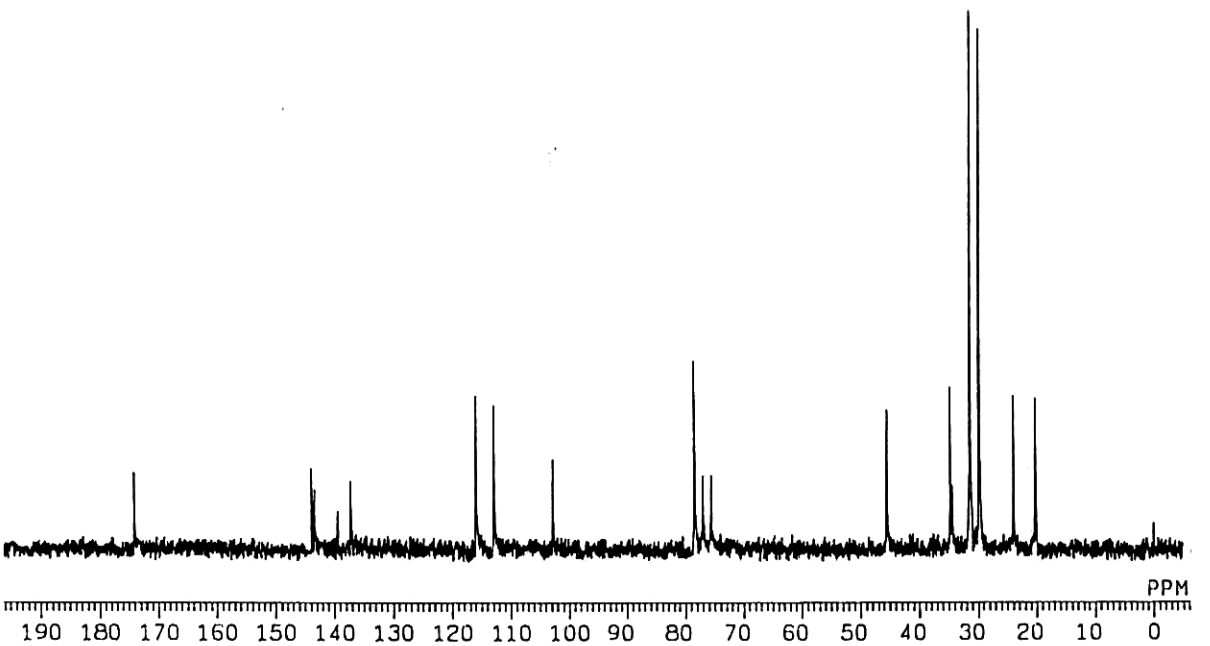
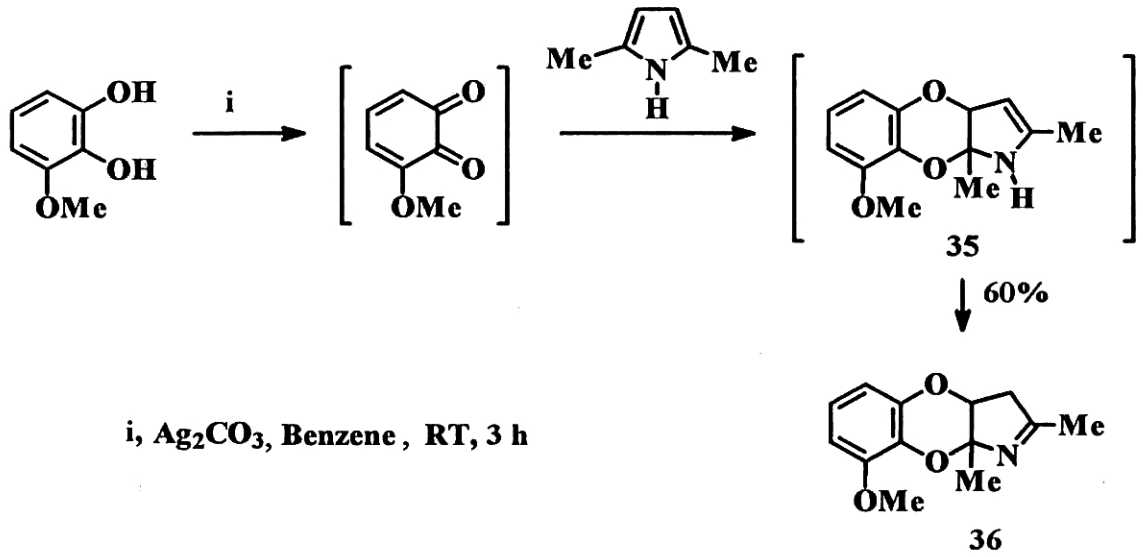


Figure 1. ^{1}H and ^{13}C NMR spectra of **34**

Similarly reaction of 3-methoxy-*o*-benzoquinone, generated *in situ* by the silver carbonate oxidation of 3-methoxycatechol, with 2,5-dimethylpyrrole afforded the benzodioxin adduct **36** in 60% yield.

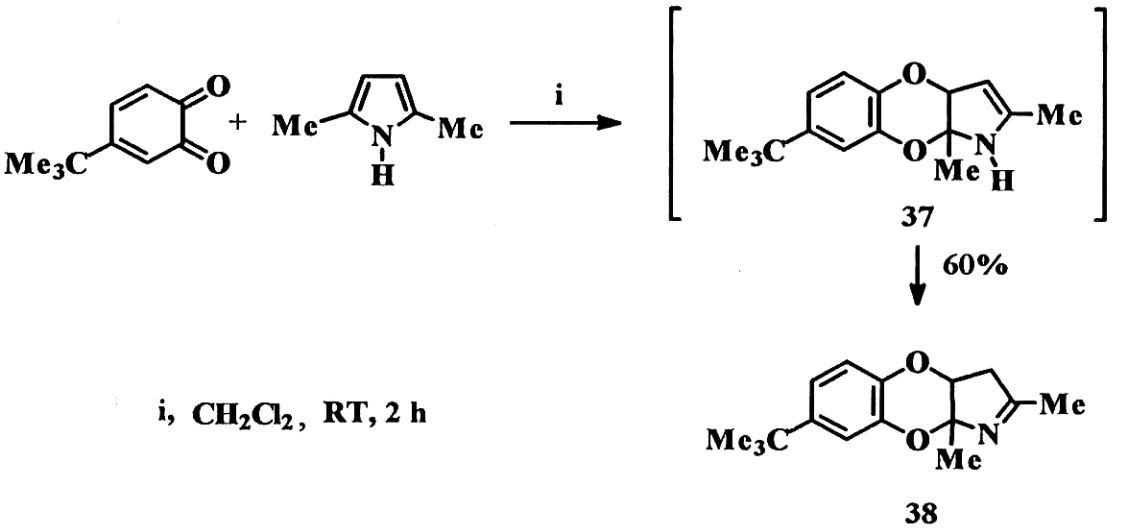


i, Ag_2CO_3, Benzene, RT, 3 h

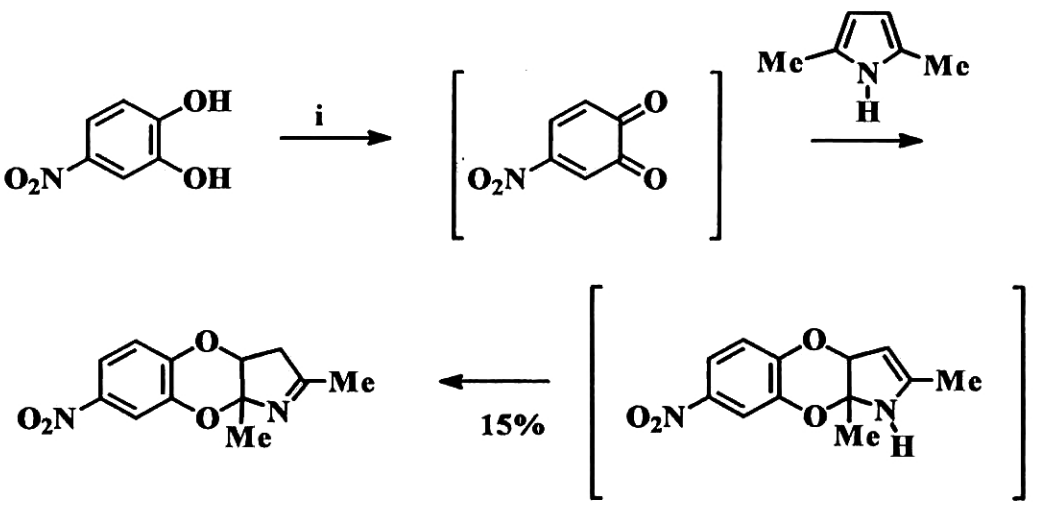
HPLC and GC-MS analysis of **36** show that it contains two isomers in the ratio 2:1. The retention time for the two isomers are very close so that the isolation of these two isomers is not possible. IR spectrum of **36** does not show any carbonyl and -NH absorption. ^1H NMR shows the presence of two methyl signals at δ 1.57 and 2.01 downfield from TMS. The $-CH_2-$ protons appeared at δ 2.85 as a multiplet (due to the presence of isomers). But the -CH- group vicinal to the $-CH_2-$ group displayed a triplet at δ 4.46 (J = 3.0 Hz) and the aromatic signals were visible at δ 6.60-6.80 (m, 3H). From the ^{13}C NMR spectrum it is further evident that an isomerization has occurred under the reaction conditions. The methyl carbons resonated at δ 20.31 and 23.83. The signal at δ 45.64 has been assigned to the $-CH_2-$ carbon atom. The -OMe signal appeared at δ 56.17. The carbon signal at δ 101.10 has been assigned to the -O-C-N- carbon atom and the second carbon on the ring resonated at δ 78.37. The imine carbon atom resonated

far down field from TMS at δ 174.94. The mass spectrum with M^+ ion peak at *m/z* 233 is also in accordance with the assigned structure.

4-*tert*-Butyl- and 4-nitro-*o*-benzoquinones also gave the same type of benzodioxin adducts, **38** and **40** respectively with 2,5-dimethylpyrrole as shown below.



i, CH_2Cl_2, RT, 2 h



40

39

i, Ether, 0°C, 10 h

The benzodioxin adducts **38** and **40** yielded spectroscopic data similar to those of **34**. The adducts **38** and **40** did not show any carbonyl and -NH absorptions. The ^{1}H and ^{13}C NMR spectra are in accordance with the assigned structure. ^{1}H NMR spectrum of **38** displayed a triplet at δ 4.15 (2H) and this signal has been assigned to the proton adjacent to the oxygen in the dioxin ring. The $-CH_2-$ group appeared at δ 2.60 as a doublet. The signal for the *tert*-butyl group and the two methyl groups appeared as singlets respectively at δ 1.20, 1.35 and 1.90. The aromatic signals appeared at δ 6.60 as a multiplet. In the ^{13}C spectrum, the carbon signals appeared in accordance with the assigned structure.

In a similar way the adduct **40** has also been characterized by its spectral data. The signal at δ 4.4 (t, 1H) has been assigned to the ring junction proton adjacent to the oxygen atom. The $-CH_2-$ protons resonate at δ 2.8 as a doublet. The two methyl groups resonate at δ 2.0 and 1.5 down field from TMS. The aromatic protons appeared as two multiplets in the ratio 2:1 at δ 7.5 and 6.6.

Reactions of *o*-quinones like 3,5-di-*tert*-butyl-, 4-*tert*-butyl-, 3-methoxy- and 4-nitro-*o*-benzoquinones with other heterocyclic dienes like furan, furfural, furfuryl alcohol, furfuryl acetate, pyrrole, N-methylpyrrole, 2-methylthiophene, 3-methylthiophene etc. were tried under different experimental conditions but these led to intractable carbonaceous materials.

The HOMO-LUMO energy levels of the starting materials were determined by MNDO method. (For the HOMO-LUMO energies of *o*-quinones, see Table 1 of this chapter). For dimethylpyrrole, the HOMO-LUMO energy is -8.357 and 0.9458 eV respectively. From the HOMO-LUMO energy differences, it is evident that the above reactions proceed by inverse electron demand.

3.2.3 EXPERIMENTAL DETAILS

(3a-*cis*)-6,8-bis(1,1-Dimethylethyl)-3a,9a-dihydro-2,9a-dimethyl-3H[1,4] benzodioxino[2,3-*b*]pyrrole (34).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.22 g, 1.01 mmol.) and 2,5-dimethylpyrrole (0.20 g, 2.1 mmol.) were dissolved in dry toluene (10 mL) and stirred under nitrogen for 2 hours. The solvent was removed *in vacuo* and the residue on column chromatography furnished **34** (0.11 g, 32%) as a pale yellow crystalline solid, mp. 136-138 °C.

IR, KBr : 2967, 1645, 1590, 1486, 1421, 1266 cm^{-1}.

^1H NMR : δ 6.82 (s, 2H), 4.28 (t, 1H), 2.83 (d, 2H), 2.25 (s, 3H), 1.45 (s, 3H), 1.26 (s, 9H), 1.22 (s, 9H).

^{13}C NMR : δ 174.05, 143.92, 143.41, 139.50, 137.26, 115.90, 112.92, 102.80, 78.52, 45.52, 34.72, 34.36, 31.41, 29.83, 23.98, 20.25

MS *m/z* : 316 (M^++1), 315 (M^+), 300, 207, 165, 149, 96, 94, 57.

Analysis calcd for $C_{20}H_{29}O_2N$: C, 76.14 ; H, 9.27 ; N, 4.40.

found : C, 76.10 ; H, 9.19 ; N, 4.38

(3a-*cis*)-8-Methoxy-3a,9a-dihydro-2,9a-dimethyl-3H[1,4]benzodioxino-[2,3-*b*]pyrrole (36).

3-Methoxycatechol (0.53 g, 3.78 mmol) was dissolved in benzene (10 mL) and silver carbonate (1.2 g) was added to it and stirred. To the above solution, 2,5-dimethylpyrrole (0.5 mL, excess) was added and stirred for 5 h at room temperature. The inorganic material was removed by passing through a short column of celite and the filtrate was concentrated *in vacuo*. The residue obtained on column chromatography furnished the adduct **36** (0.53 g, 60%) as pale yellow viscous oil.

IR, CH_2Cl_2 : 2940, 1608, 1501, 1479, 1295, 1098 cm^{-1}.

^{1}H NMR : δ 6.8 (m, 1H), 6.6 (m, 2H), 4.46 (t, *J*= 3Hz, 1H) 3.83 (s, 3H), 2.85 (m, 2H), 2.0 (s, 3H), 1.57 (s, 3H).

^{13}C NMR : δ 174.94, 120.64, 120.52, 110.41, 109.13, 105.19, 104.62, 101.10, 78.37, 56.17, 45.64, 23.83, 20.31.

MS *m/z* : 233 (M^+), 140, 95, 94, 69, 54.

(3a-*cis*)-7-(1,1-Dimethyethyl)-3a,9a-dihydro-2,9a-dimethyl-3H[1,4]benzo-dioxino[2,3-*b*]pyrrole (38).

A sample of 4-*tert*-butyl-o-benzoquinone (0.2 g, 1.2 mmol.) and 2,5-dimethylpyrrole (0.5 mL, excess) were dissolved in dichloromethane (5mL) and stirred under nitrogen at 0 °C. It was then warmed to room temperature and stirred for 2 h. The solvent was removed and the residue on column chromatography furnished **38** (0.187, 60%) as pale yellow viscous oil.

IR, CH_2Cl_2 : 2980, 1640, 1595, 1420 cm^{-1}.

^{1}H NMR : δ 6.60 (m, 3H), 4.15 (t, 1H), 2.60 (d, 2H), 1.9 (s, 3H), 1.35 (s, 3H), 1.20 (s, 9H).

^{13}C NMR : δ 174.0, 144.0, 143.5, 138.0, 117.0, 113.5, 109.5, 101.0, 79.0, 46.0, 34.5, 30.0, 24.0, 21.0

MS *m/z* : 260 (M^+ +1), 220, 178, 164, 140, 72.

(3a-*cis*)-7-Nitro-3a,9a-dihydro-2,9a-dimethyl-3H[1,4]benzodioxino[2,3-*b*]-pyrrole (40).

To an ice cooled solution of 4-nitrocatechol (0.155 g, 1.0 mmol) in dry ether (10 mL), silver oxide (1.0 g) was added and stirred for 5 minutes. To this solution, 2,5-dimethylpyrrole (0.2 mL, excess) was added dropwise by a syringe and stirred for 10 h. The inorganic material was removed by filtration and the filtrate was concentrated *in vacuo*. The residue on column chromatography furnished **40** (0.037 g, 15%) as yellow viscous oil.

3.3 REFERENCES

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CHAPTER 4

CYCLOADDITION REACTIONS OF *o*-QUINONES WITH FULVENES

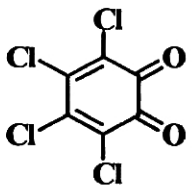
4.1 INTRODUCTION

Fulvenes are an important class of organic compounds. The first compound of this type, dimethylfulvene was prepared by Diels and Alder[1] in 1929 and they studied its cycloaddition with maleic anhydride. Later in 1935 the synthesis of tetra- and pentamethylenefulvene and their Diels-Alder reaction with maleic anhydride were reported by Kohler.[2] Subsequently the orientation in the transition state for the reaction between pentamethylene-fulvene and maleic anhydride was investigated by Woodward.[3] Since then, a

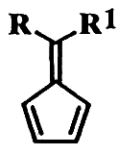
number of cycloaddition reactions involving fulvenes have been reported by various groups.[4-7]

The cycloadditions of *o*-quinones and fulvenes present a very interesting situation. In such cases, either the quinone or the fulvene can function as the diene or the dienophile. Additionally such systems offer the prospect of higher order cycloadditions. There has been some work on the cycloaddition of *o*-quinones to fulvenes, but this has been mostly concerned with the cycloaddition of tetrachloro- and tetrabromo-*o*-benzoquinones.

Tetrachloro-*o*-benzoquinone **1** reacts with 6,6-diphenyl- and 6,6-bis (*p*-methoxy) phenylfulvene (**2** and **3**) forming [4+2] cycloadducts[8] of the dihydrobenzodioxin type, **4** and **5** respectively.

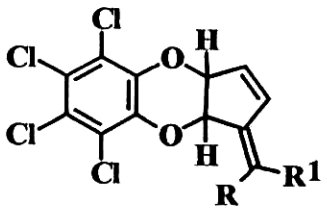


1



2 : R = R1 = Ph

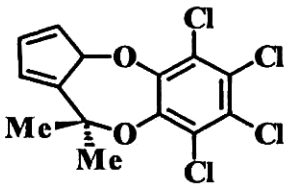
3 : R = R1 = MeO-Ph



4 : R = R1 = Ph

5 : R = R1 = MeO-Ph

The reaction of 6,6-dimethylfulvene with *o*-chloranil afforded a mixture of the [6+4] adduct **6** along with the dimeric product **7**. The latter is discerned to be formed *via* the [4+2] cycloaddition to the primary adduct **6**. Similar results were observed in the cycloaddition of *o*-chloranil with pentamethylenefulvene.



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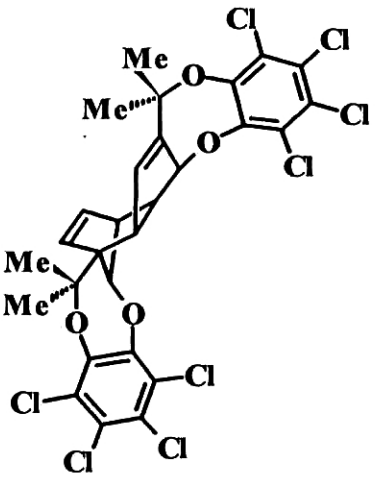

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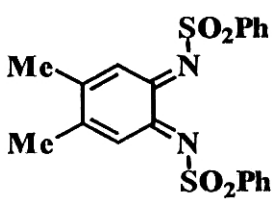
In contrast, it has been reported that in the Diels-Alder reaction of 3-methyl-*o*-benzoquinone with symmetrical fulvenes, the latter serve as 2π components leading to bicyclo[2.2.2] adducts.[9] Interestingly in all these cases the *o*-quinone functions as a diene leading to inverse electron demand Diels-Alder reactions. It may be emphasized that work in this area has essentially been limited to the cycloaddition of symmetrical fulvenes such as 6,6-dimethyl- and 6,6-diphenylfulvenes with tetrachloro-*o*-benzoquinone.

In related work it was observed[10] that the *o*-benzoquinonediimine **8** underwent both [4+2] and [6+4] cycloaddition reaction with 6,6-diphenyl-fulvene leading to **9** and **10** respectively.



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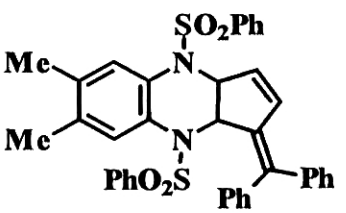

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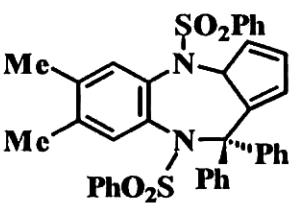

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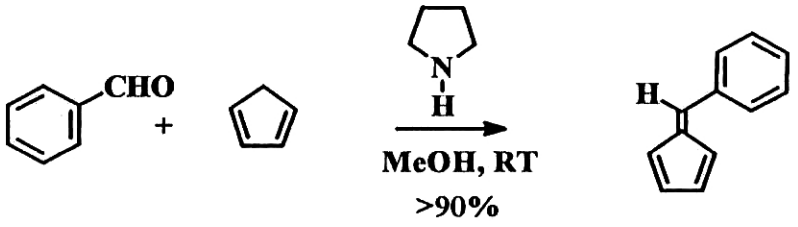
4.2 RESULTS AND DISCUSSION

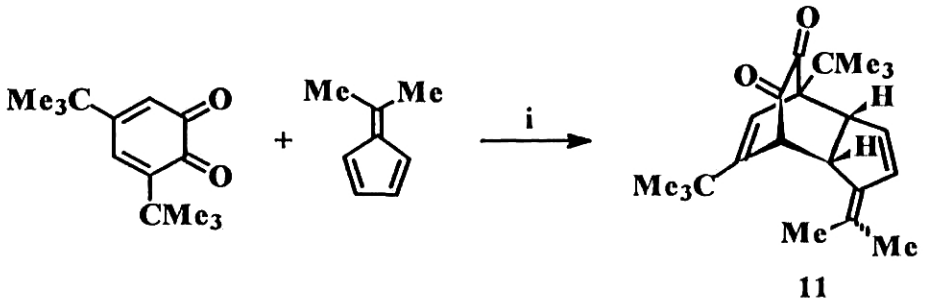
As evident from the literature survey presented in the introductory section there have been only isolated reports on the cycloadditions of *o*-quinones to fulvenes. Therefore we have carried out a systematic investigation aimed at gaining a deeper understanding of such reactions.

All the fulvenes mentioned in this chapter have been prepared by the literature procedure.[11,12] Condensation of cyclopentadiene with the appropriate aldehyde or ketone in presence of pyrrolidine furnished the fulvenes in good yields and these have been characterized by spectroscopic methods.

Example:



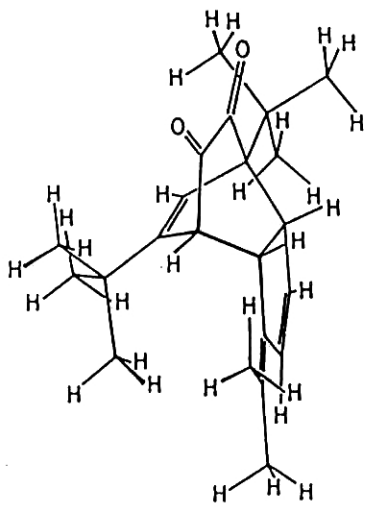
6,6-Dimethylfulvene, one of the simplest members of the fulvene family, undergoes cycloaddition with 3,5-di-*tert*-butyl-*o*-benzoquinone to furnish the bicyclo[2.2.2]octene dione adduct **11** in 80% yield. The reaction can be illustrated as follows.



11

i, Benzene, reflux, 8 h, 80%

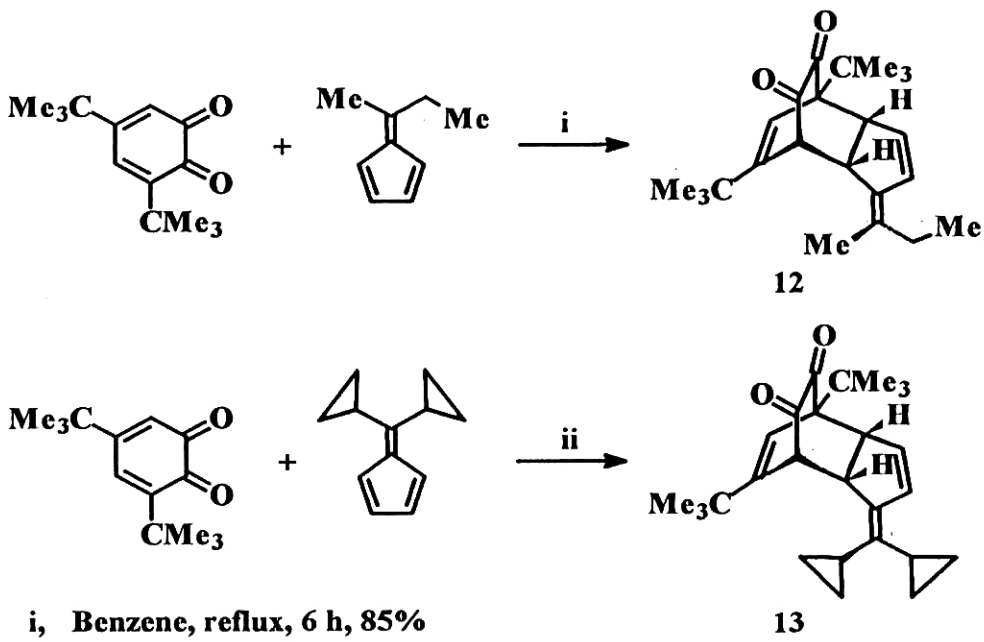
The IR spectrum of **11** showed a strong absorption at 1738 cm^{-1} indicating the presence of an α-diketone. The ^{1}H and ^{13}C NMR spectra are in accordance with the assigned structure. Examination of the ^{1}H NMR spectrum of **11** showed the presence of three proton signals other than those of methyl groups. These signals appeared at δ 3.25 (d, 1H) and 3.64 (m, 2H). The *cis* stereochemistry is discerned from the coupling constants (J = 9.5, 1.7 Hz) of the ring junction protons. This is in agreement with the calculated J values (J = 9.6, 1.7 Hz; MMX method). The three olefinic signals appeared at δ 5.73, 5.86 and 6.40. The two *tert*-butyl groups and two methyl groups resonated at δ 0.97, 1.20 and 1.71, 1.78 respectively. In the ^{13}C NMR spectrum the superimposed signal at δ 27.87 has been assigned to the two *tert*-butyl groups. The signals for the two methyl groups appeared at δ 20.86 and 21.07. The two quaternary carbon atoms on the *tert*-butyl group resonated at δ 33.88 and 35.10 respectively. The bridgehead sp3 carbon signals were observed at δ 61.10 and 51.53. The other two carbon signals in the sp3 carbon region have been assigned to the ring junction carbons. The six carbon signals at δ 120.74, 123.96, 132.58, 135.55, 138.95 and 150.00 have been assigned to the sp2 carbon atoms. The two signals at δ 192.34 and 190.20 indicated the presence of two carbonyl groups. The mass spectrum is also in accordance with the assigned structure.



Energy minimized conformation of 11 (MMX method)

The structure of an analogous adduct has been confirmed by single crystal X-ray crystallography. This is discussed later in this chapter (product **25**, page 99).

Similar adducts **12** and **13** were isolated from the reactions of 3,5-di-*tert*-butyl-*o*-benzoquinone respectively with 6-ethyl-6-methyl- and 6,6-dicyclopropylfulvene. The reactions can be illustrated as follows.



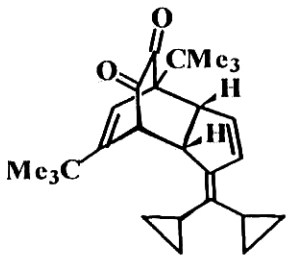
i, Benzene, reflux, 6 h, 85%

ii, Benzene, sealed tube, 100 °C, 10 h, 62%

The *endo* stereochemistry has been assigned to the adducts **12** and **13** from their ^{1}H NMR spectral data. IR spectrum of **12** showed the presence of a strong absorption at 1733 cm^{-1}. In the ^{1}H NMR spectrum the signal integrating for 9H at δ 1.1 has been assigned to one of the *tert*-butyl groups. The other *tert*-butyl group resonated at δ 1.35 (s, 9H). The methyl group appeared at δ 1.85 whereas the -CH_3- of ethyl group appeared at δ 1.25 as a triplet. The -CH_2- adjacent to -CH_3- resonated at δ 2.2 as a quartet. The bridgehead and ring junction protons appeared at δ 3.4 (d, 1H) and 3.7 (m,

2H) respectively. In the ^{13}C NMR spectrum, the two carbonyl carbons appeared at δ 190.0 and 192.3. The bridgehead and ring junction carbons appeared at δ 41.5, 50.0, 51.0 and 61.0.

In the adduct **13**, the cyclopropyl proton signals appeared at δ 0.25, 0.40, 0.7-0.85 and 1.45 down field from TMS. The corresponding carbon signals appeared at δ 5.0, 5.5, 6.0, 7.0, 12.0 and 16.0. The rest of the ^{1}H and ^{13}C signals are similar to that of adduct **11** (The ^{1}H and ^{13}C NMR spectra are given on page 86). The mass spectra of **12** and **13** are also in accordance with the proposed structures.



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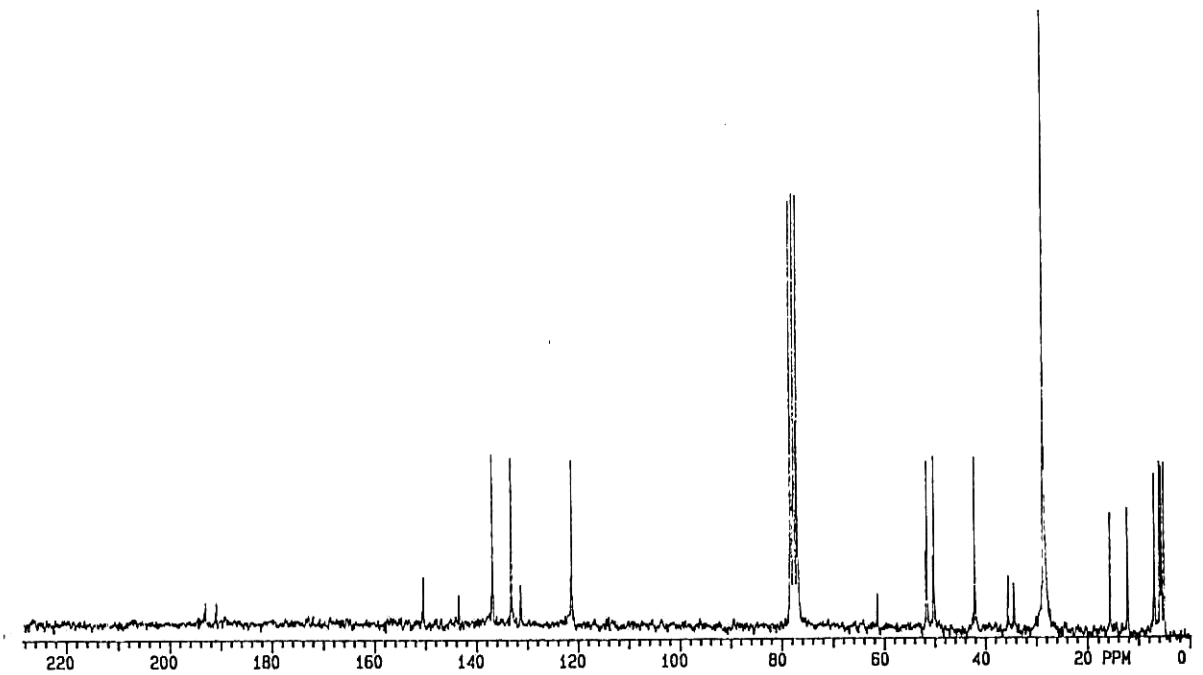
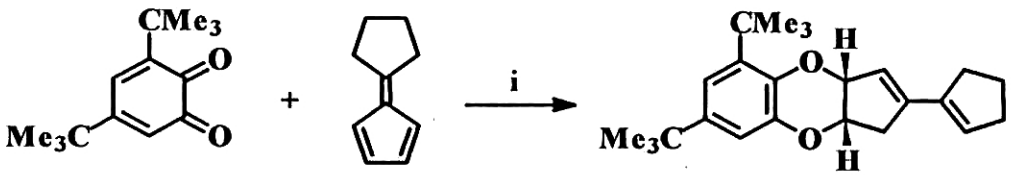


^{1}H and ^{13}C NMR spectra of **13**

After having studied the cycloaddition reactions of the fulvenes derived from acyclic ketones, we turned our attention to the fulvenes from cyclic ketones. First we studied the cycloaddition reaction of 6,6-tetramethylene-fulvene with 3,5-di-*tert*-butyl-*o*-benzoquinone. This reaction took a surprisingly different course leading to **14** presumably resulting from the rearranged fulvene and the quinone now serving as a 1,4-dioxabutadiene.

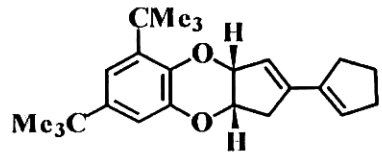


14

i, Benzene, reflux, 8 h, 85%

The product **14** has been characterized by extensive spectroscopic analysis. IR spectrum of **14** does not show any characteristic carbonyl absorption. The peak at 1421 cm^{-1} in the IR spectrum is due to the -C-O- vibration in the dioxin ring. The ^1H NMR spectrum of **14** exhibited two singlets at δ 1.26 (9H) and 1.38 (9H) which have been assigned to the two *tert*-butyl groups. Examination of the ^1H NMR spectrum of **14** indicated the presence of two sp3 proton signals far down field from TMS. These signals appeared at δ 4.70 (q, 1H, J = 4.9 Hz) and 5.00 (d, 1H, J = 4.7 Hz) and have been assigned to the ring junction protons adjacent to the two oxygen atoms in the benzodioxin ring. The proton spectrum of **14** exhibited one doublet at δ 2.84 (J = 4.7Hz, 2H) and has been assigned to the proton at C11 (for numbering, see the crystal structure, p. 92). The hydrogens at position 15 and 17 appeared at δ 2.5 (4H) as a multiplet. The multiplet at δ 1.9 (2H) has been assigned to the proton at position 16. The aromatic protons showed two doublets at δ 6.79 and 6.86. The signals at δ 5.67 and 5.81 have been

assigned to the two olefinic protons. Examination of the ^{13}C NMR spectrum of **14** revealed the presence of 20 carbon signals. Out of these, four have been assigned to the two *tert*-butyl groups. These appeared at δ 29.92, 31.55, 34.40 and 34.90. The signal at δ 23.30 has been assigned to the carbon atom at position 16. The carbon atoms at position 15 and 17 appeared at δ 32.39 and 33.25. The C11 carbon resonated at δ 38.45. The two carbon atoms on the benzodioxin ring appeared at δ 75.16 and 79.57. The downfield signal (δ 79.57) has been assigned to the carbon at position 2. The four carbon signals at δ 112.25, 115.80, 137.93, and 139.56 have been assigned to the olefinic carbons whereas the aromatic carbons appeared at δ 123.30, 131.18, 140.72, 142.04, 143.25 and 144.22. The assignments of carbon signals have been confirmed by QUART, DEPT and APT measurements. DEPT study on **14** showed the presence of four -CH_2- carbons and these appeared at δ 23.29, 32.39, 33.25 and 38.44 (Figure 1 and 2)



14

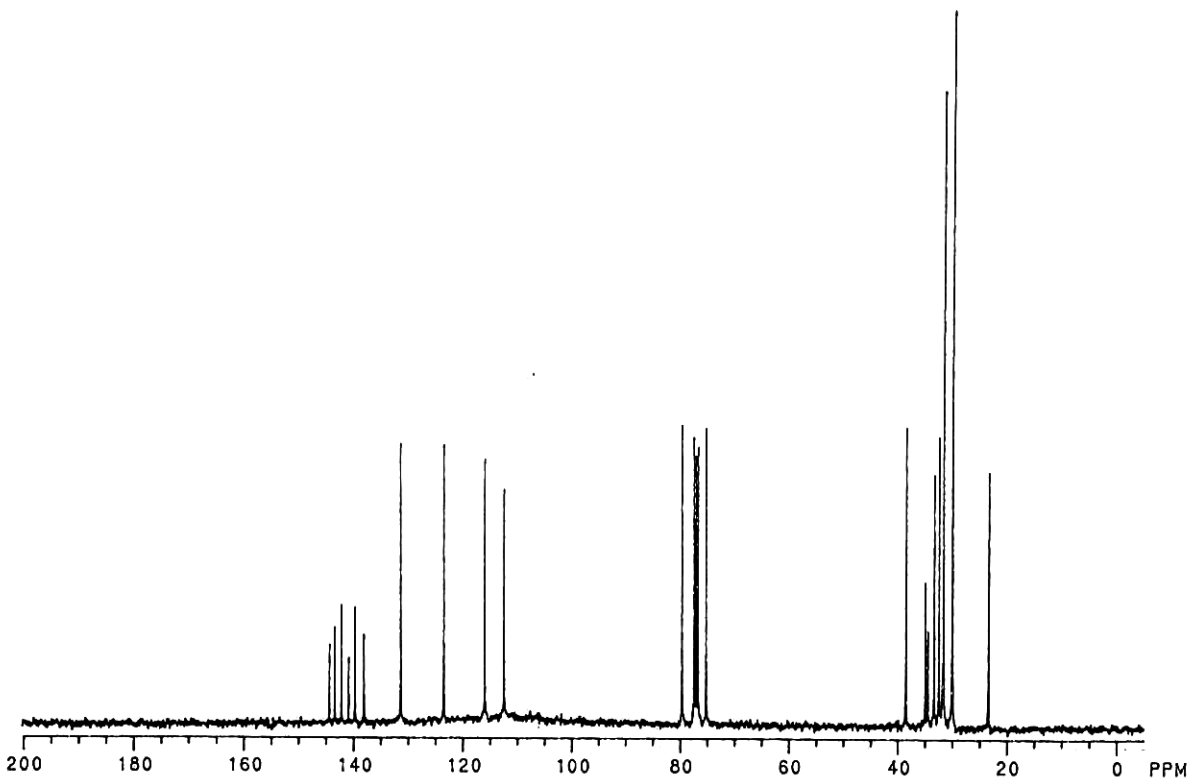
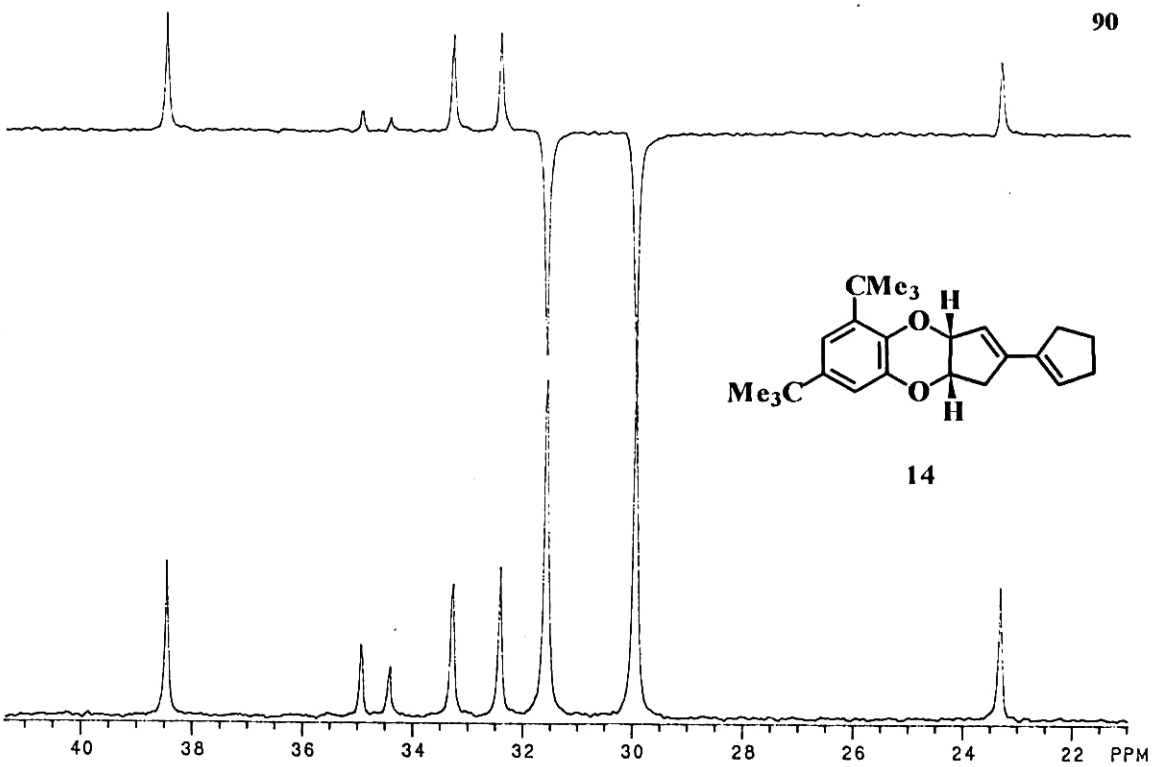


Figure 1. ^{1}H and ^{13}C NMR spectra of **14**



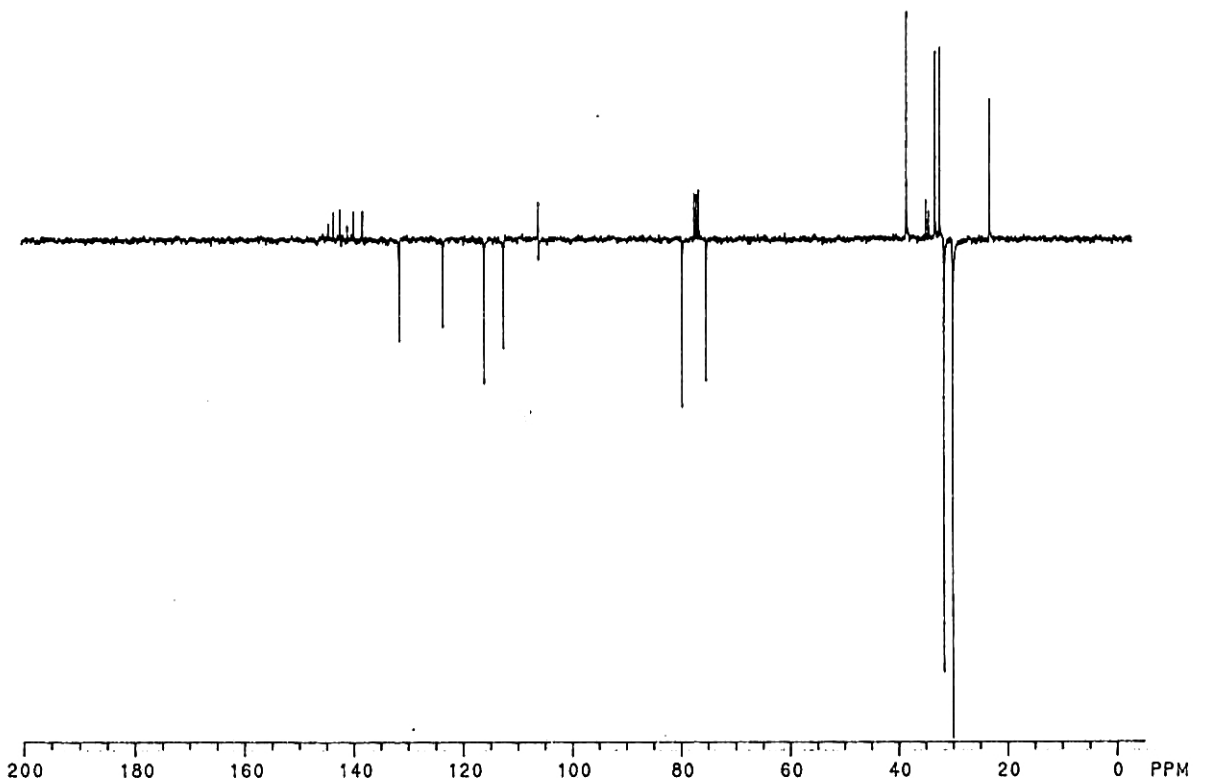
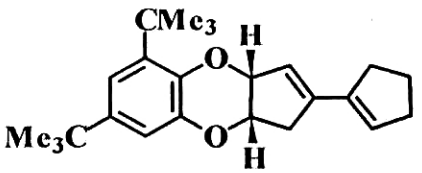


Figure 2. ^{1}H - ^{13}C connectivity experiments on **14**

The proton connectivity has been established by 2D COSY experiments (Figure 3).



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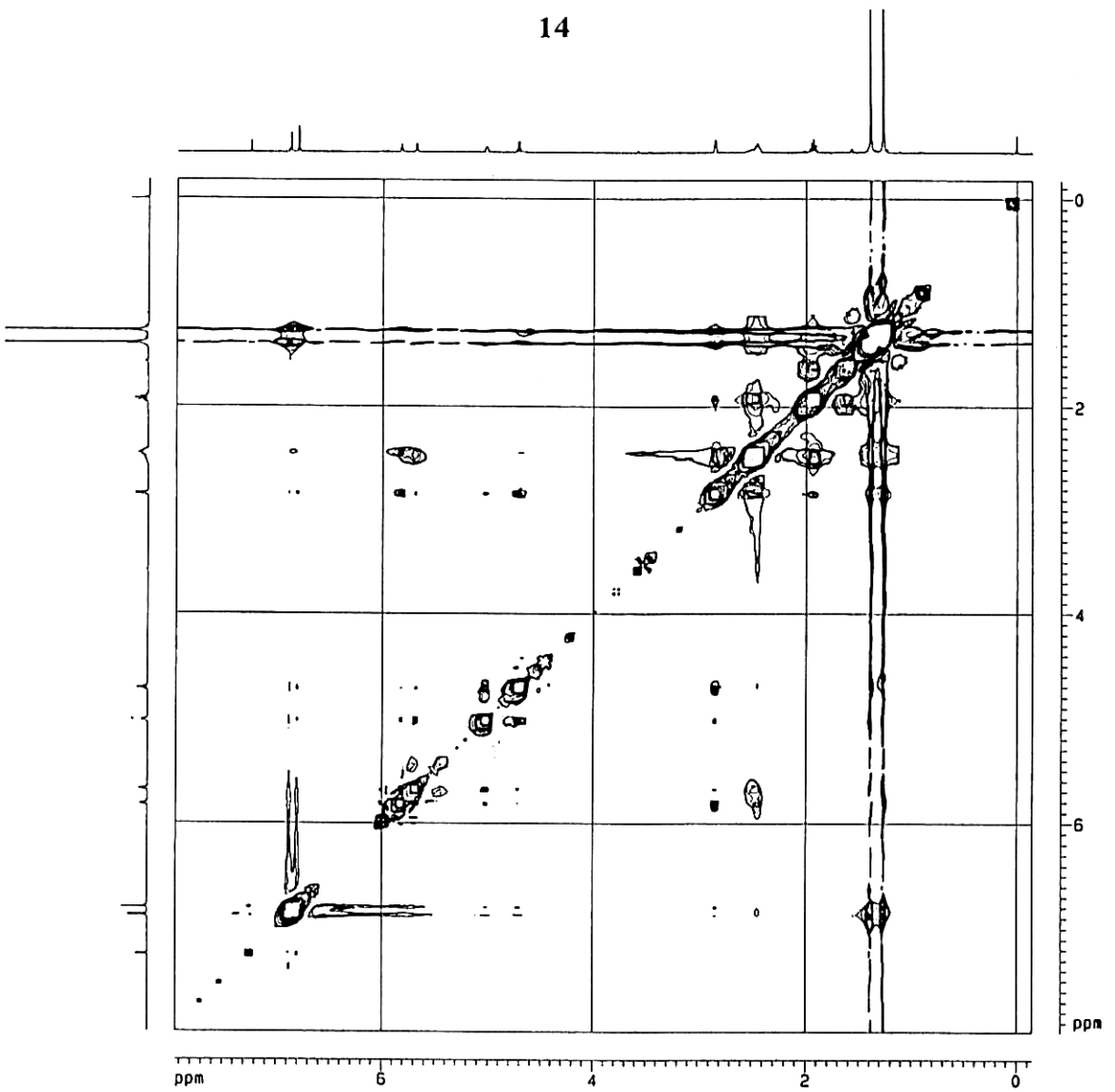
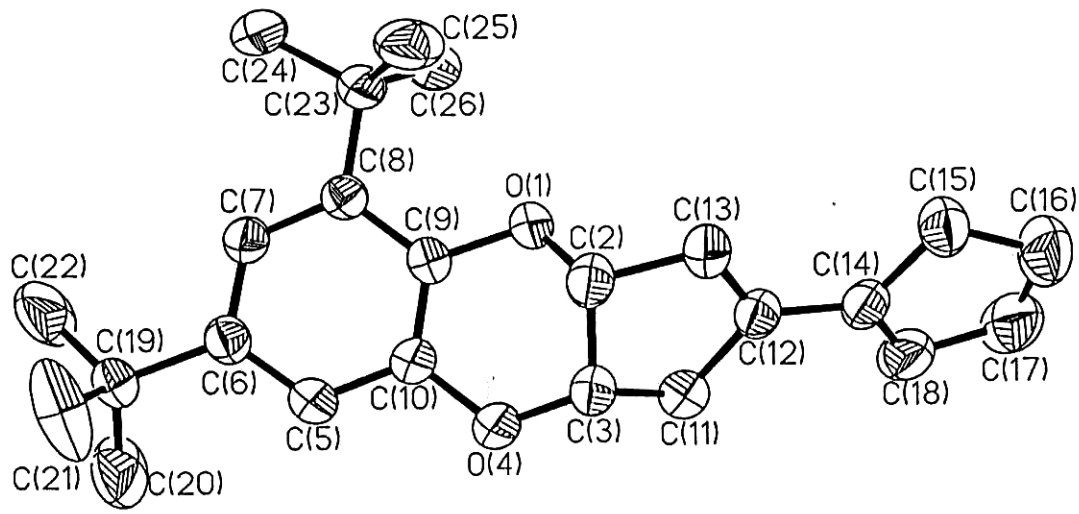


Figure 3. 2D COSY spectrum of **14**

From the 2D spectrum of **14** it has been found that the signals at δ 1.95 is coupled with signals at δ 2.50. Further, the signal at δ 2.50 is coupled with the olefinic signal at δ 5.67. Again the signal at δ 4.70 is coupled with the signal at δ 2.84. These clearly indicate the connectivity between various protons in **14**. Final confirmation of the structure assigned for **14** was obtained by single crystal X-ray crystallography (Figure 4).[#] The C(12)-C(13) and C(14)-C(18) distances were found to be 1.331 and 1.325 A° respectively. The molecular structure, the atom numbering scheme and important bond distances and angles are shown in Figure 4.



X-Ray crystal structure of **14**

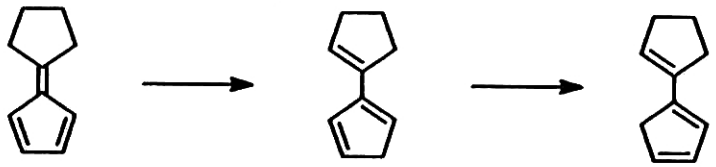
Figure 4

Pertinent bond distances (A°) and angles (deg.) are as follows:

O(1)-C(2) 1.453, C(2)-C(3) 1.52, C(2)-C(13) 1.492, C(12)-C(13) 1.331, C(12)-C(14) 1.459, C(14)-C(18) 1.325, C(16)-C(17) 1.502, O(1)-C(2)-C(3) 109.2, C(13)-C(12)-C(11) 110.3, C(13)-C(12)-C(14) 125.9, C(14)-C(18)-C(17) 112.2.

[#]X-Ray analysis was done by Dr. Nigam P. Rath of Missouri University, USA.

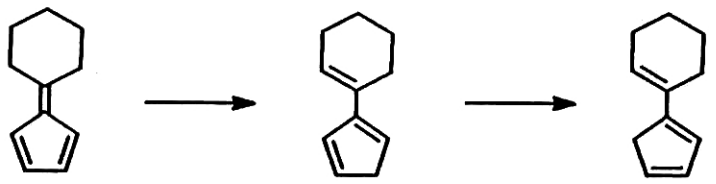
While the mechanistic pathway leading to **14** remains obscure, it may be suggested that the 6,6-tetramethylenefulvene **15** suffers slow isomerization to the cyclopent-1-enyl cyclopentadiene **17** which then undergoes cyclo-addition to the quinone to afford **14**. Our attempts to obtain direct evidence for the isomerization of fulvene have been unsuccessful. This may be attributed to the fact that the equilibrium heavily favours the more stable fulvene **15**. However a stepwise addition mechanism also cannot be ruled out. The isomerization of **15** can be represented as follows.



15 **16** **17**

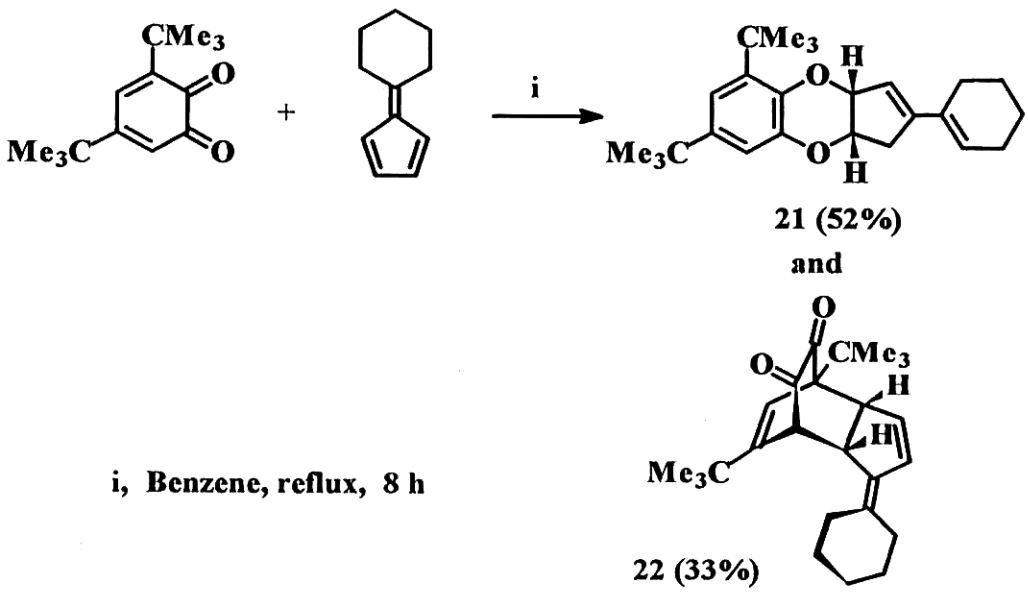
Although it is not clear why the quinone serves as a heterodiene towards **17**, it may be pointed out that a similar reactivity pattern was observed with an acyclic triene, *trans*, *trans*-2,6-dimethyl-2,4,6-octatriene.[13]

With 6,6-pentamethylenefulvene **18** a mixture of the adducts **21** and **22** were obtained. The two products result from the cyclohex-1-enyl cyclopenta-diene **20** and the fulvene **18** respectively.



18 **19** **20**

The reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with the fulvene can be illustrated as follows.

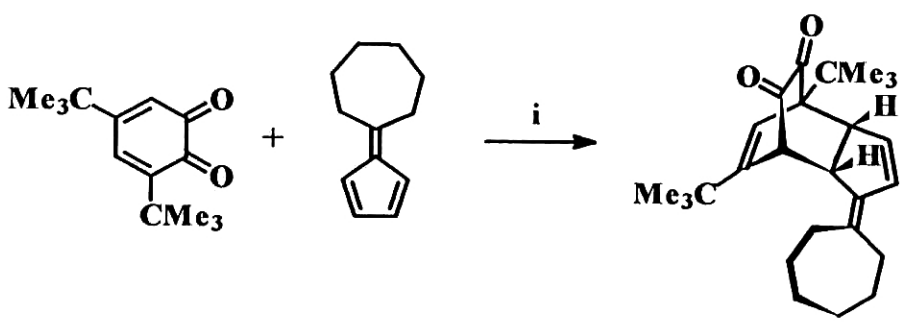


The products **21** and **22** were characterized by elaborate spectral analysis. Adduct **21** showed ^{1}H and ^{13}C NMR signals similar to those of **14**. IR spectrum does not show any carbonyl absorption. The two *tert*-butyl groups appeared at δ 1.10 and 1.25 as singlets. The four protons adjacent to the olefinic bond of cyclohexene ring resonated as a multiplet centred at δ 2.0 whereas the other four protons appeared at δ 1.40 (m). The $-CH_2-$ group of cyclopentene moiety exhibited a broad doublet at δ 2.55. The protons adjacent to oxygen atom of the dioxin ring appeared at δ 4.35 and 4.70 as multiplets. The corresponding carbon signals appeared at δ 75.0 and 79.5 respectively in the ^{13}C NMR spectrum. The sp3 carbon atoms on the cyclohexene ring resonated at δ 22.0, 22.5, 25.5 and 26.0 whereas the sp3 carbon on the cyclopentene ring resonated at δ 37.5. The other carbon signals are similar to those of adduct **14**. The high resolution mass spectrum

showing peak at 366.2560 is also in accordance with the proposed structure.

The adduct **22** showed a strong absorption at 1747 cm^{-1} in the IR spectrum indicating the presence of α-diketone. The ^{1}H and ^{13}C NMR spectra are in accordance with the proposed structure. The two *tert*-butyl groups appeared at δ 1.01 and 1.22 whereas the cyclohexyl group appeared at δ 1.55 (m, 6H) and 2.24 (m, 4H). The bridgehead and ring junction protons resonated at δ 3.31 (1H), 3.57 (1H) and 3.67 (1H). The signals at δ 3.31 and 3.67 appeared as two doublets with a *J* value of 9.9 Hz. This value is diagnostic for a *cis* ring junction. The three olefinic protons resonated at δ 5.74, 5.85 and 6.47. Examination of the ^{13}C NMR spectrum of **22** revealed the presence of bridgehead as well as ring junction carbon atoms resonating at δ 61.0, 52.0, 49.8 and 41.0. The carbonyl carbons showed two peaks at δ 190.0 and 192.0. High resolution mass spectrum with molecular ion peak at 366.2544 is also in accordance with the proposed structure.

With 6,6-hexamethylenefulvene, only the bicyclo[2.2.2] adduct **23** was formed. Evidently no isomerization of 6,6-hexamethylenefulvene occurred under the conditions of cycloaddition.

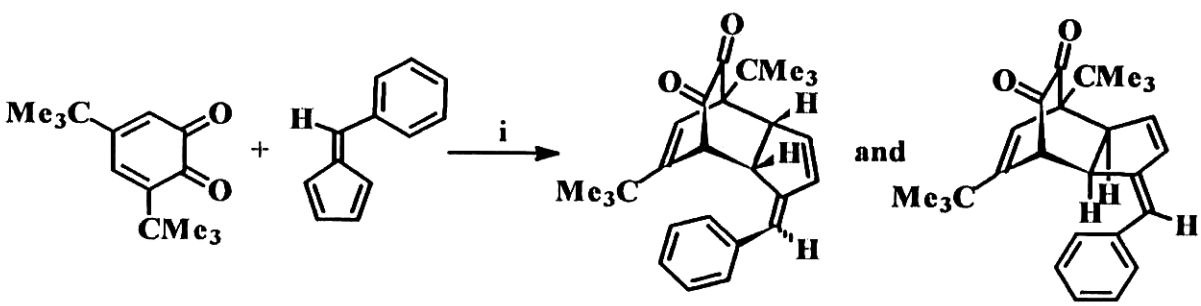


i, Toluene, reflux, 2.5 h, 84% **23**

IR spectrum of **23** showed a strong absorption at 1744 cm^{-1}, indicating the presence of α-diketone. The proton signals at δ 1.45 (m, 8H) and 2.25 (m, 4H) are due to the cycloheptyl group. The carbon signals due to the cycloheptyl ring appeared at δ 27.0, 29.0, 30.5, 32.3 and 32.5. The rest of the signals are similar to those of adduct **11**. HRMS of **23** showed molecular ion peak at 380.5360 in accordance with the assigned structure.

Subsequent to the investigations on the cycloadditions of *o*-quinones with 6,6-dialkyl- and 6,6-cycloalkylfulvenes we turned our attention to the cycloadditions involving 6-aryl substituted fulvenes. The initial experiments were conducted with 6-phenylfulvene. This fulvene was synthesized from benzaldehyde by condensation with cyclopentadiene in presence of pyrrolidine.

Phenylfulvene undergoes cycloaddition with 3,5-di-*tert*-butyl-*o*-benzo-quinone to afford the products **24** and **24a** in 82 and 8% yields respectively. The major product was identified as the *endo* adduct **24**. The *exo* adduct has identical R_f value and therefore we were not able to detect the same by TLC. Initially we were dealing with small amount of reactants (1 mmol) and could isolate only the major isomer. During the purification process the *exo* isomer gets washed out and we were not able to detect it. But later, in experiments done on larger scale it was possible to isolate the crystalline *exo* isomer by Pasteur style physical separation. The reaction between 6-phenylfulvene and 3,5-di-*tert*-butyl-*o*-benzoquinone can be illustrated as follows.

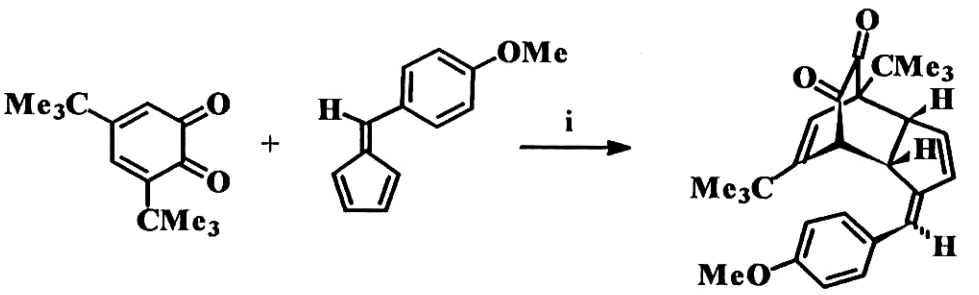


i, Toluene, sealed tube, 120°C, 24 h **24 (82%)** **24a (8%)**

IR spectrum of **24** showed a strong absorption at 1731 cm^{-1} which indicated the presence of α-diketone. The ^1H NMR spectrum of **24** showed two singlets corresponding to nine protons each at δ 0.8 and 1.2 assignable to the two *tert*-butyl groups. The one bridgehead and two ring junction protons appeared as a multiplet at δ 3.7 (3H). The ^1H NMR spectrum also exhibited a singlet at δ 7.1 due to the aromatic protons and a multiplet at δ 6.2-5.6 due to the olefinic protons (4H). The ^{13}C NMR spectrum of **24** showed two signals at δ 190.0 and 192.0 which have been assigned to the two carbonyl groups. The ring junction and bridgehead carbons resonated at δ 41.0, 49.0, 51.0 and 61.0. The mass spectrum of **24** showed molecular ion peak at *m/z* 374 and this also is in accordance with the assigned structure.

The structure of the *exo* adduct (**24a**) has been confirmed by spectral analysis. The IR spectrum of **24a** showed a strong absorption at 1737 cm^{-1} indicating the presence of α-diketone. In the ^1H NMR spectrum, the two *tert*-butyl groups resonated at δ 0.85 and 1.20. The ring junction protons appeared at δ 3.8 as a multiplet corresponding to 3 protons. The olefinic protons appeared at δ 5.78 (1H), 6.1 (1H) and 6.35 (2H) as multiplets. The phenyl ring protons resonated at δ 7.3. The ^{13}C NMR spectrum of **24a** is similar to that of the *endo* adduct. The *tert*-butyl groups resonated at δ 27.5, 28.0, 34.5 and 35.0. The bridgehead and ring junction carbons appeared at δ 41.5, 48.5, 51.0 and 52.0. The olefinic and aromatic carbons resonated in the region δ 121.0-150.5. The signals at δ 192.0 and 193.0 have been assigned to the carbonyl groups.

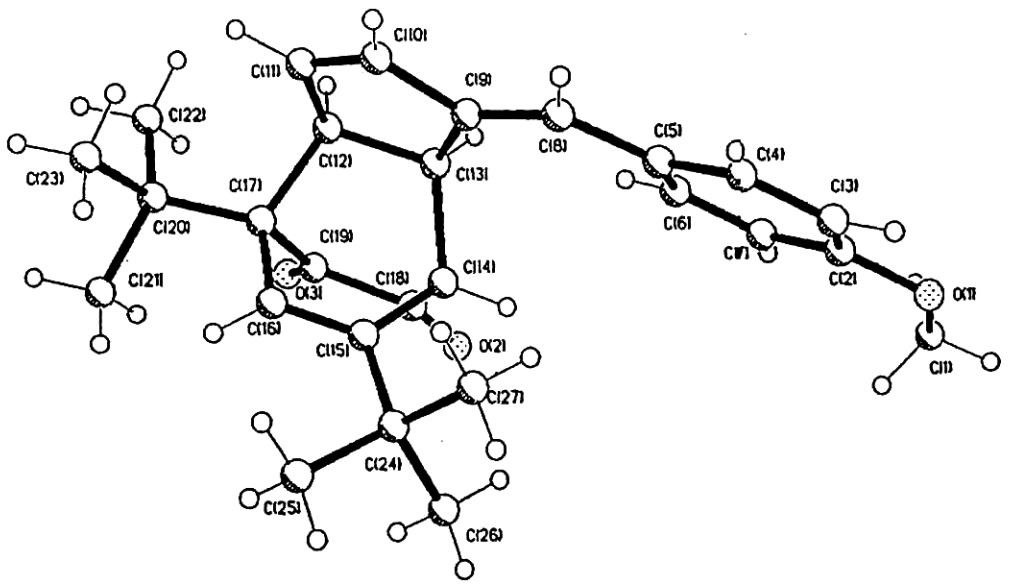
4-Methoxy phenylfulvene also gave the bicyclo[2.2.2]octene dione adduct **25** in 56% yield with 3,5-di-*tert*-butyl-*o*-benzoquinone.



i, Toluene, sealed tube, 110°C, 5 h, 56% **25**

IR spectrum of **25** with a strong absorption at 1732 cm^{-1} indicated the presence of α-diketone. Examination of the ^1H NMR spectrum of **25** showed a multiplet of three protons at δ 3.6 and this has been assigned to the bridgehead and the ring junction protons. The $-OCH_3$ group on the phenyl ring appeared at δ 3.70. The rest of the proton signals ie, aromatic and olefinic protons appeared at δ 7.0-6.75 (m, 4H) and 6.15-5.6 (m, 4H) respectively. In the ^{13}C NMR spectrum, the bridgehead and ring junction carbons appeared at δ 55.0, 51.0, 48.5 and 41.0. The $-OCH_3$ carbon resonated at δ 61.0. The signals at δ 190.0 and 192.5 have been assigned to the two carbonyl groups. The mass spectrum with a molecular ion peak at *m/z* 404 is also in accordance with the assigned structure. Trace amounts of the *exo* isomer was also detected in this reaction. The structure of the *endo* adduct has been confirmed by single crystal X-ray crystallography (Figure 5).[#]

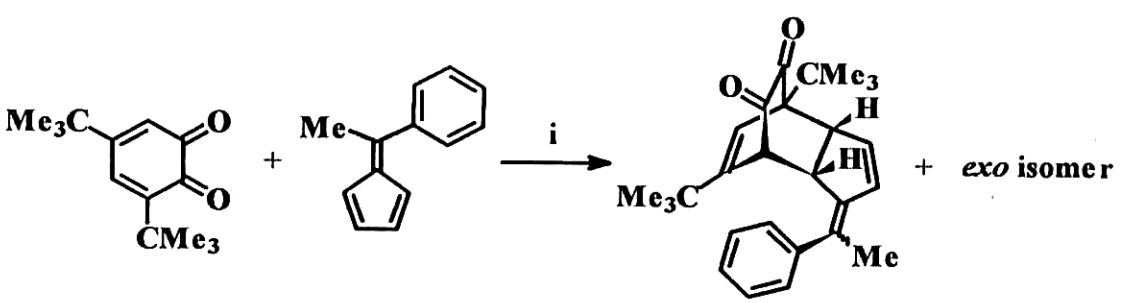
[#]X-Ray analysis was done by Professor Paul G. Williard of Brown University, USA



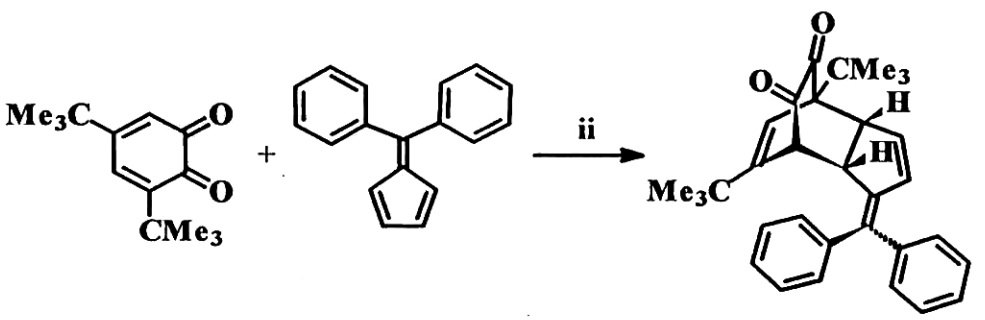
X-Ray crystal structure of **25**

Figure 5

Similar bicyclo[2.2.2]adducts (**26** and **27**) were isolated from the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with 6-methyl-6-phenyl- and 6,6-diphenylfulvenes. Trace amounts of *exo* isomer was detected in the former case.



i, Toluene, sealed tube, 110 °C, 13 h, 85% **26**

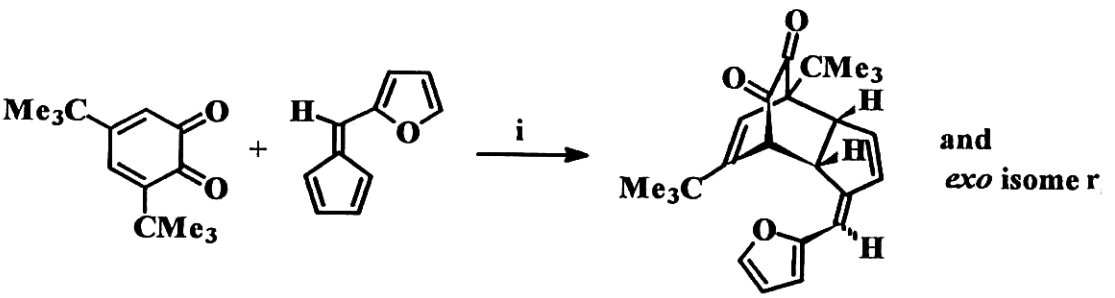


ii, Toluene, sealed tube, 110 °C, 12 h, 90% **27**

IR spectrum of **26** showed a strong absorption at 1735 cm^{-1} indicating the presence of α-diketone. The two *tert*-butyl and methyl groups appeared at δ 1.0 (9H), 1.1 (9H) and 2.0 (3H) as singlets. The bridgehead and ring junction protons resonated at δ 3.4 (2H) and 3.6 (1H) as multiplets. Corresponding bridgehead and ring junction carbons resonated at δ 61.0, 51.0, 45.8 and 42.0 in the ^{13}C NMR spectrum. The carbonyl carbons appeared at 190.0 and 192.0. The mass spectrum showed a molecular ion peak at *m/z* 388.

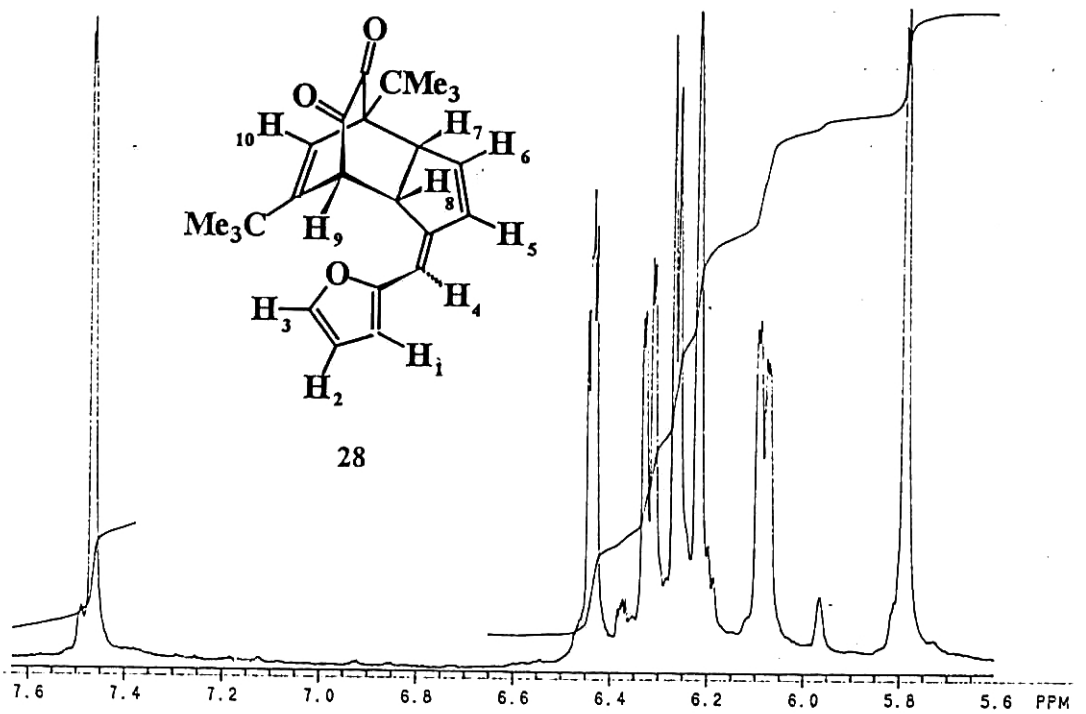
Similarly the adduct **27** showed an absorption at 1734 cm^{-1} suggesting the presence of α-diketone. One of the *tert*-butyl groups resonated at δ 0.70 as a singlet whereas the second one resonated at δ 1.25. The bridgehead and ring junction protons appeared as two broad singlets in the ratio 1: 2 at δ 3.2 and 3.5. The three olefinic protons resonated at δ 5.80, 6.15 and 6.50. The two phenyl rings gave a multiplet corresponding to ten protons at δ 7.3. The bridgehead and ring junction carbons appeared at δ 59.84, 53.01, 48.30 and 48.06 in the ^{13}C NMR spectrum. The carbonyl absorptions moved slightly upfield in comparison to those of similar adducts (eg. **24**, **25** and **26**) and were visible at δ 189.5 and 189.92. The mass spectrum with a molecular ion peak at *m/z* 450 is also in agreement with the assigned structure.

The fulvene derived from 2-furfural also furnished the bicyclo-[2.2.2]octene dione adduct **28** with 3,5-di-*tert*-butyl-*o*-benzoquinone. In this case also a trace amount of the *exo* isomer was detected (HPLC).



i, Benzene, sealed tube, 100 °C, 2 h, 91% **28**

A strong band at 1731 cm^{-1} in the IR spectrum of **28** indicated the presence of α-diketone. In order to assign the regio- and stereochemistry of the adduct **28**, we have studied this molecule spectroscopically. The proton numbering scheme is given below.



Partial ^1H NMR spectrum of **28** showing olefinic proton couplings

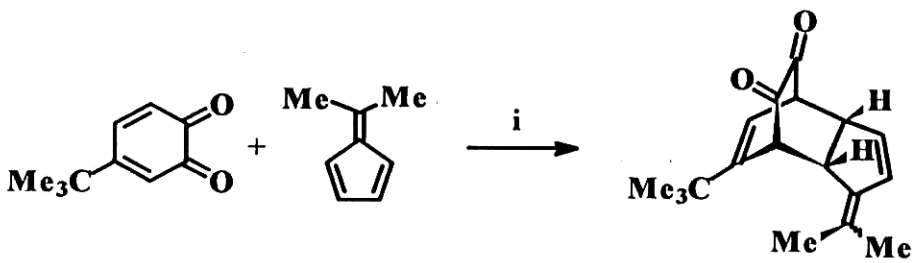
The details of the proton decoupling study are given here. The protons at the ring junction $H_{7\&8}$ appeared as a multiplet at δ 3.77. The bridgehead proton H_9 resonated as a singlet at δ 3.95. The doublet at δ 5.78 (J = 1.7 Hz) has been assigned to H_{10}. The olefinic signals at δ 6.21 (s, H_4), 6.32 (dd, J = 1.57, 1.6 Hz, H_5) and 6.08 (dd, J = 2.0, 1.8 Hz, H_6) have been assigned to the protons H_4, H_5 and H_6 respectively. The three protons on the furan ring showed the signals at δ 6.25 (d, J = 3.4 Hz, H_1), 6.43 (dd, J = 1.6, 1.8 Hz, H_2) and 7.46 (d, J=1.2 Hz, H_3). When the proton signal at δ 3.77 is irradiated, the signals due to $H_{4,5,\&6}$ were affected. The double doublets at δ 6.32 and 6.08 were transformed to simple doublets. Again when the decoupler is at $H_{7\&8}$ (δ 3.70), the singlet at δ 3.95 split into a doublet. When the H_9 signal at δ 3.99 is irradiated, the splitting pattern of H_8 changed and the doublet at δ 5.78 (H_{10}) became a singlet. This clearly indicates the allylic coupling. When H_2 is decoupled at δ 6.4, the doublets at δ 7.46 (H_3) and 6.25 (H_1) became two singlets. When the decoupler is at δ 7.4 (H_3) the double doublet corresponding to H_2 at δ 6.35 became a doublet and now it has the J value of 3.3 Hz, equivalent to that of H_1. Thus all the proton signals have been assigned unambiguously on the basis of the decoupling experiments.

Examination of the ^{13}C NMR spectrum of **28** showed the presence of 19 carbon signals. The two *tert*-butyl groups showed a signal at δ 28.0 and the quaternary carbon atoms resonated at δ 34.0 and 35.0. The bridgehead and ring junction carbons appeared at δ 61.0, 51.0, 50.0 and 41.0. The sp3 carbon signals on the furan ring adjacent to the heteroatom were visible at δ 150.0 and 152.5. The signals at δ 190.0 and 193.0 have been assigned to the two bridgehead carbonyl carbons. The mass spectrum of **28** showing a

molecular ion peak at *m/z* 364 is also in accordance with the assigned structure.

The reactions of 4-*tert*-butyl-*o*-benzoquinone with fulvenes follow the same trend and these are discussed below.

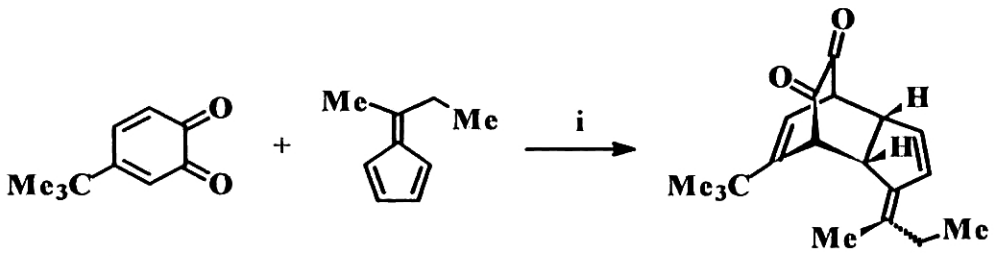
With 6,6-dimethylfulvene, 4-*tert*-butyl-*o*-benzoquinone afforded the bicyclo[2.2.2]octene dione adduct **29** in 80% yield.



i, Benzene, RT, 8 h, 80% **29**

IR spectrum of **29** showed a strong absorption at 1734 cm^{-1} indicating the presence of α-diketone. The *tert*-butyl group appeared as a singlet at δ 1.21. The two methyl groups resonated at δ 1.77 and 1.80. The bridgehead and ring junction protons appeared at δ 3.6 (2H) and 3.7 (2H). The olefinic protons showed three multiplets at δ 5.8, 5.9 and 6.44. The bridgehead and ring junction carbons appeared at δ 59.0, 52.0, 50.0 and 42.0 in the ^{13}C NMR spectrum. The carbonyl carbons resonated at δ 192.0 and 193.0. The mass spectrum of **29** showed a molecular ion peak at *m/z* 270 in accordance with the assigned structure.

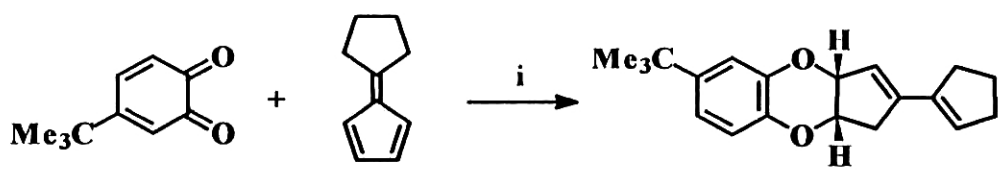
Reaction of 4-*tert*-butyl-*o*-benzoquinone with 6-ethyl-6-methylfulvene also furnished the analogous product **30** in 78% yield and it was easily characterized by its IR, ^{1}H & ^{13}C NMR and mass spectral data.



i, Benzene, RT, 8 h, 78% **30**

Subsequent to the investigations on the cycloadditions of 4-*tert*-butyl-*o*-benzoquinone with 6,6-dialkylfulvenes, we turned our attention to the cycloaddition involving 6,6-cycloalkylfulvenes. The results are similar to those obtained with 3,5-di-*tert*-butyl-*o*-benzoquinone and these are discussed below.

With tetramethylenefulvene, the adduct **31** was isolated in 84 % yield.# The reaction can be represented as follows.

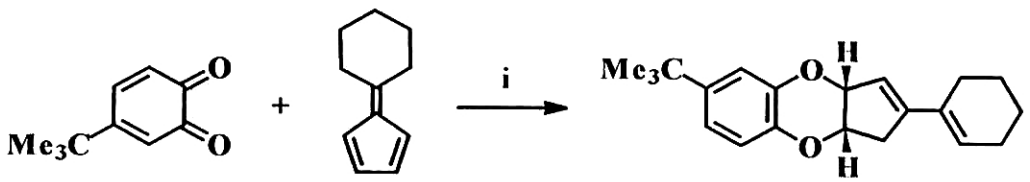


i, Benzene, RT, 4 h, 84% **31**

As surmised previously, the product **31** probably arises from the isomerized form of tetramethylenefulvene. The structure of **31** has been assigned by spectroscopic analysis (See experimental for the data).

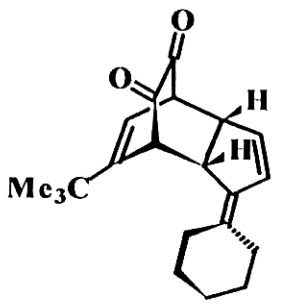
The structure for **31** was assigned tentatively, an isomeric formula cannot be ruled out on the basis of available data.

With 6,6-pentamethylenefulvene, a mixture of the adducts **32** and **33** were obtained.



32 (10%)

and



33 (74%)

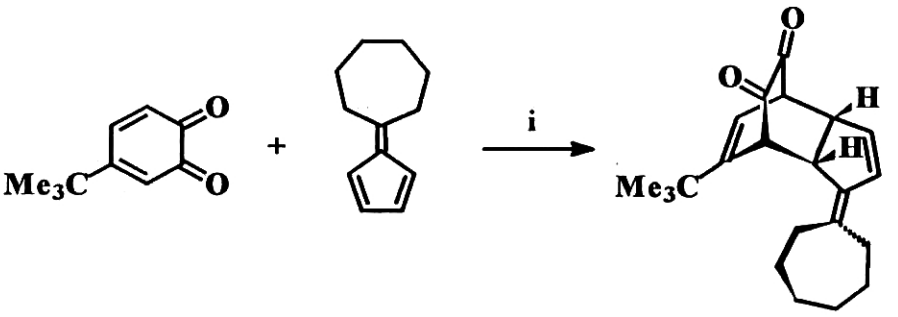
i, Benzene, RT, 4 h

The products **32** and **33** resulted from the cycloaddition of cyclohex -1-enyl cyclopentadiene **20** and the fulvene **18**. IR spectrum of **32** does not show any carbonyl absorption. The protons on the dioxin ring appeared at δ 5.0 and 4.65 as broad singlet and quartet respectively. The -CH_2-protons on the cyclopentene ring appeared at δ 2.75. The -CH_2 protons on the cyclohexene ring resonated at δ 2.15 and 1.6 as multiplets. The sp3 carbon atoms on the dioxin ring resonated at δ 78.5 and 74.0 in the ^{13}C NMR spectrum. The molecular ion peak at *m/z* 310 is also in accordance with the assigned stucture.

Adduct **33** showed a strong absorption at 1736 cm^{-1} in the IR spectrum indicating the presence of α-diketone. The cyclohexyl protons resonated at δ 2.25 (4H) and 1.55 (6H) as broad singlets. The bridgehead and ring junction protons appeared at δ 3.7 (1H), 3.55 (2H) and 3.35 (1H) in the ^{13}C NMR

spectrum. The corresponding carbon signals appeared at δ 53.5, 51.5, 46.0 and 39.5. The molecular ion peak at *m/z* 310 is also in accordance with the assigned structure.

With 6,6-hexamethylenefulvene, only the bicyclo[2.2.2]adduct **34** was formed. Evidently no isomerization of 6,6-hexamethylenefulvene occurred under the reaction conditions.

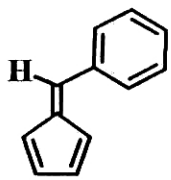
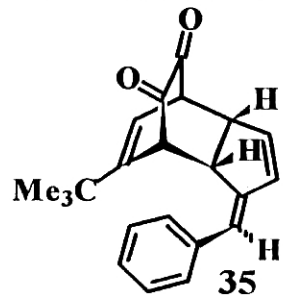
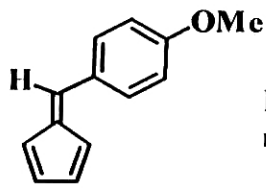
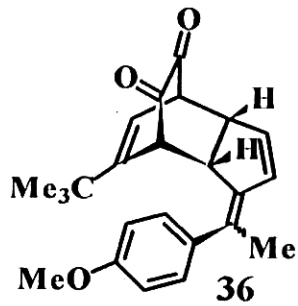
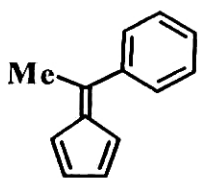
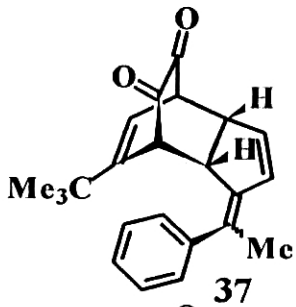
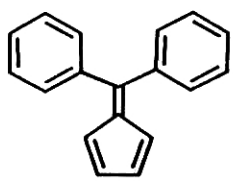
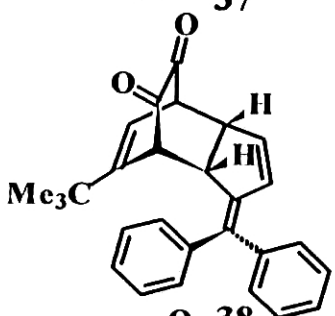
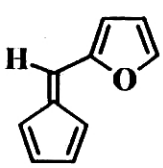
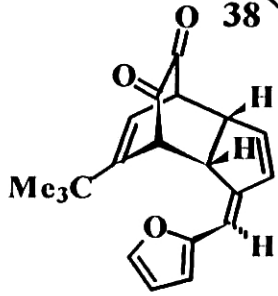


i, Benzene, reflux, 8 h, 75% **34**

IR spectrum of **34** showed a strong absorption at 1734 cm^{-1} indicating the presence of α-diketone. The protons on the cycloheptane ring appeared at δ 1.6 (8H) and 2.2 (4H) as multiplets. The ring junction protons appeared at δ 3.5 (2H) and 3.3 (2H) as multiplets and the corresponding carbon signals appeared at δ 60.0, 51.5, 50.0 and 40.5 ppm in the ^{13}C NMR spectrum. The carbonyl carbons appeared at δ 192.0 and 193.0. The mass spectrum with peak at *m/z* 324 is also in accordance with the assigned structure.

Similar bicyclo[2.2.2] adducts were obtained from the reactions of 4-*tert*-butyl-*o*-benzoquinone with 6-phenyl-, 6-(4-methoxy)phenyl-, 6-methyl-6-phenyl-, 6,6-diphenyl and 6-furylfulvenes. The results are summarized in Table 1.

Table 1. Cycloaddition reactions of 4-*tert*-butyl-*o*-benzoquinone with fulvenes

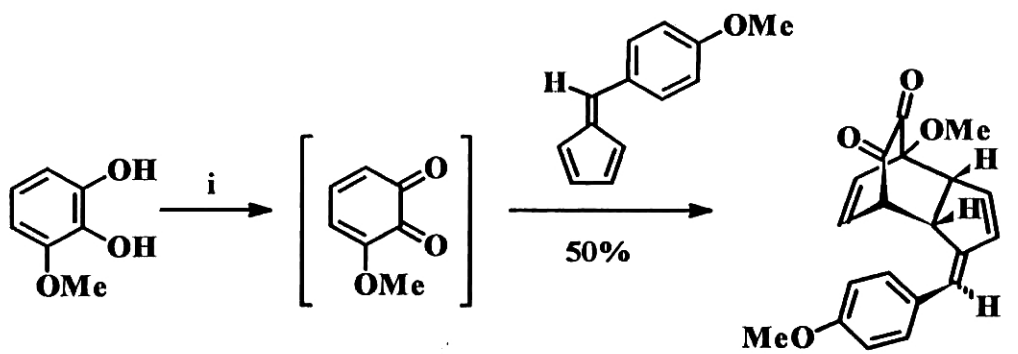
Entry	Fulvene	Conditions	Product[1]	Yield (%)[2]
1		Toluene, 90 °C, 4 h	 **35**	87
2		Benzene, reflux, 8 h	 **36**	64
3		Toluene, reflux, 6 h	 **37**	68
4		Toluene, reflux, 12 h	 **38**	90
5		Benzene, reflux, 12 h	 **39**	92

[1] Only *endo* isomer was detected [2] Isolated yield

The adducts **35**, **36**, **37**, **38** and **39** were charaterized by spectroscopic metohds. All the above compounds showed IR absorption in the range 1730-1735 cm^{-1} and they showed typical proton and carbon signals in the ^{1}H and ^{13}C NMR spectra. The mass spectra are also in accordance with the assigned structures.

In continuation of the above investigations, we have studied the reactions of 3-methoxy-*o*-benzoquinone with various fulvenes and the results are discussed below.

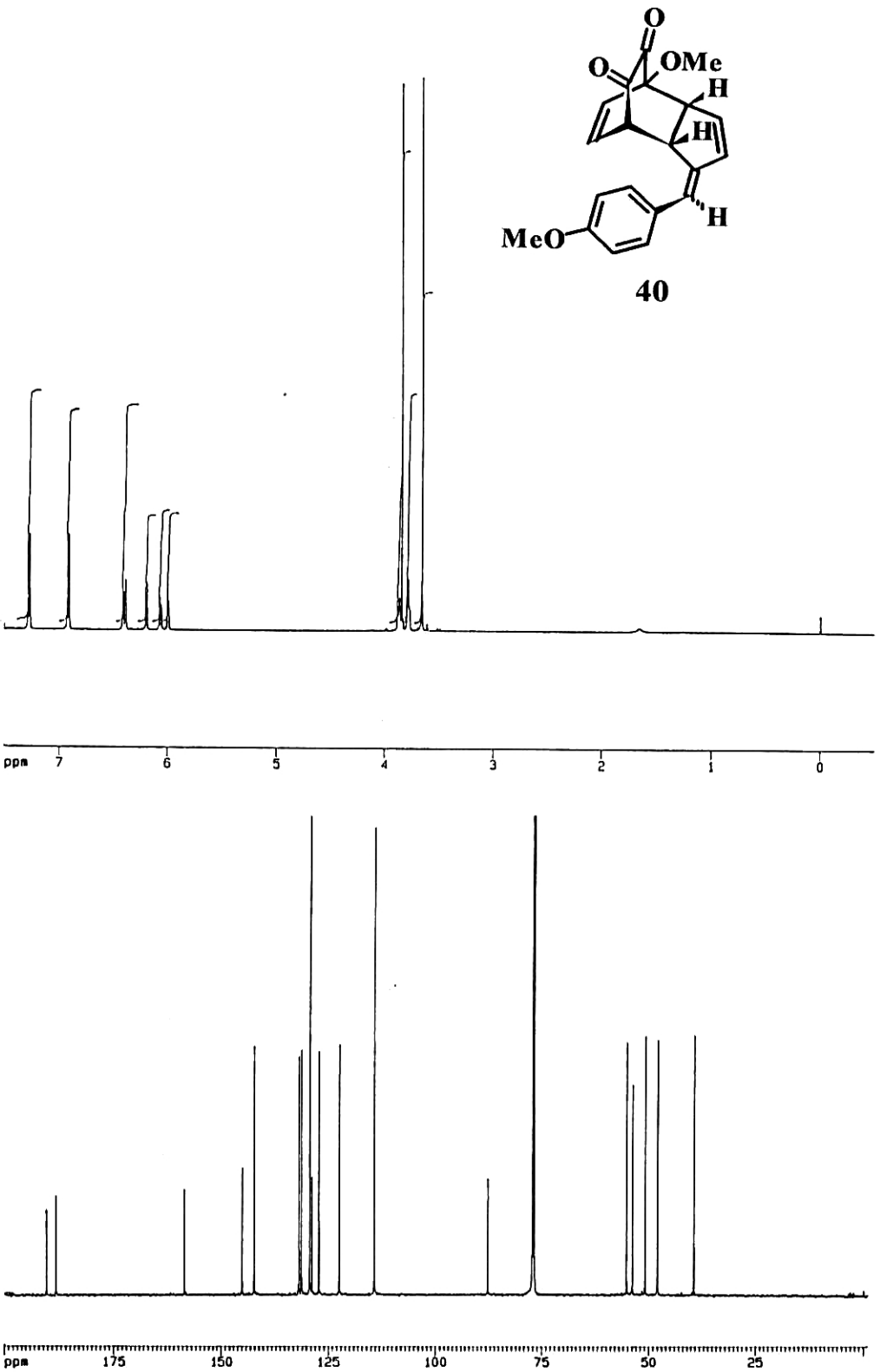
First we studied the reaction of 3-methoxy-*o*-benzoquinone with 6-(4-methoxy) phenylfulvene, and the bicyclo[2.2.2]adduct **40** was isolated in 50% yield. The quinone was prepared *in situ* by the oxidation of 3-methoxy-catechol in benzene with silver carbonate.



i, Ag_2CO_3, Benzene, reflux, 30 min. **40**

The IR spectrum of **40** showed a strong absorption at 1742 cm^{-1} indicating the presence of α-diketone. The regio- and stereochemistry of the adduct **40** were derived from extensive NMR analysis. ^{1}H NMR spectrum of **40** showed the presence of 18 protons. The two methoxy groups appeared at δ 3.65 and 3.83. The bridgehead and ring junction protons resonated at δ 3.86 (1H) and 3.77 (2H) as multiplets. The olefinic protons showed five signals at

δ 5.99 (dd, 1H), 6.06 (dd, 1H), 6.18 (dd, 1H), 6.39 (d, 1H) and 6.41 (dd, 1H). The aromatic ring protons gave two doublets at δ 6.92 (2H) and 7.27 (2H). The proton connectivity of the molecule **40** was established by 2D COSY experiments. Carbon-13 spectrum of **40** showed the presence of 20 carbon atoms. The ^{13}C- 90° DEPT showed that 12 -CH- moieties are present. Examination of the ^{13}C- 135° DEPT showed no $-CH_2-$ groups present, and the two $-CH_3$ groups whose carbons resonated at δ 55.3 and 54.0 are clearly the $-OCH_3$ groups. The signals at δ 188.1 and 190.3 in the ^{13}C NMR spectrum have been assigned to the carbonyl groups. The compound **40** showed four quaternary carbons, at δ 87.6, 128.8, 145.0 and 158.7. The $-OCH_3$ group at δ 3.65 is connected to the carbon at δ 87.6. The $-OCH_3$ group on the aromatic ring is connected to the carbon at δ 158.7. The relevent spectra are given in the following pages.

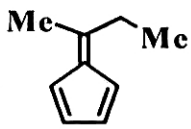
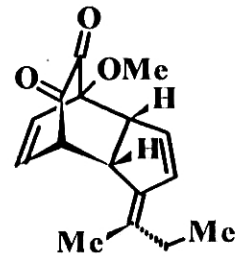
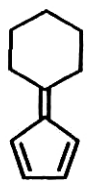
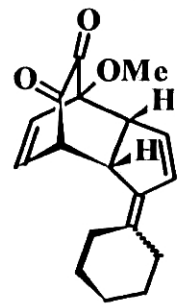
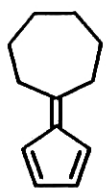
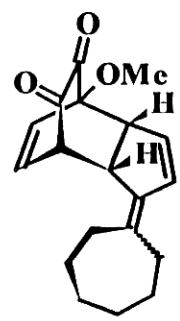


40

^{1}H and ^{13}C NMR spectra of **40**

Reactions of 3-methoxy-*o*-benzoquinone with 6-ethyl-6-methyl-, 6,6-pentamethylene-, and 6,6-hexamethylenefulvenes also furnished the bicyclo-[2.2.2]octene dione adducts. The results are given in the following Table 2.

Table 2. Cycloaddition reactions of 3-methoxy-*o*-benzoquinone with alkyl and cycloalkyl fulvenes

Entry	Fulvene	Conditions	Product	Yield (%)[1]
1		Benzene, RT, 5 h	 **41**	61
2		Benzene, reflux, 30 min.	 **42**	68
3		Benzene, reflux, 30 min.	 **43**	75

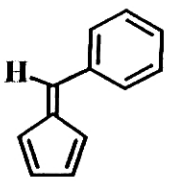
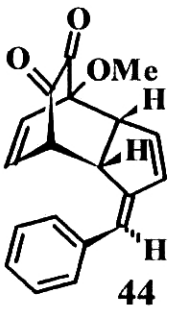
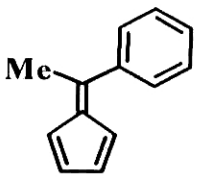
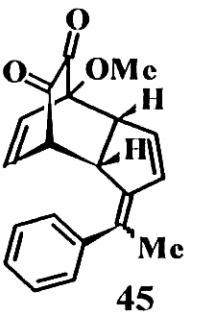
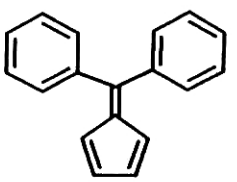
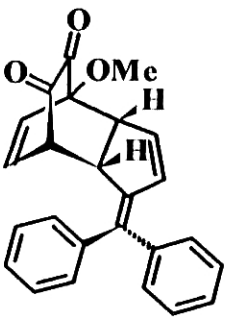
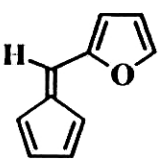
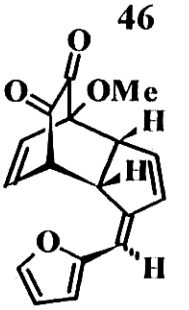
[1] Isolated yield

The IR spectra of the adducts **41**, **42**, and **43** showed strong absorption in the range 1743-1746 cm^{-1}, suggesting the presence of α-diketone. In the ^1H NMR spectrum of **41**, the bridgehead and the ring junction protons appeared at δ 3.70 (m, 1H) and 3.40 (m, 2H). The methoxy group resonated at δ 3.75 as a singlet. The methyl group appeared at δ 1.95 as a singlet whereas the ethyl group resonated at δ 1.20 (t, 3H) and 2.20 (q, 2H). The olefinic protons showed the signals at δ 6.55 (1H), 6.18 (2H) and 5.85 (1H). In the ^{13}C NMR spectrum of **41**, the $-OCH_3$ carbon resonated at δ 54.0. The bridgehead and ring junction carbons appeared at δ 88.0, 49.5, 41.5 and 40.0. The signals at δ 190.0 and 188.0 have been assigned to the carbonyl groups.

The proton NMR of **42** showed two multiplets at δ 2.2 (4H) and 1.6 (6H) indicating that the product arose from the unisomerized fulvene. The $-OCH_3$ protons resonated at δ 3.65. The bridgehead and ring junction protons appeared at δ 3.45 as a multiplet. ^{13}C NMR spectrum also exhibited the carbon signals corresponding to the proposed structure. The structure of the adduct **43** was also established by similar NMR analysis.

Reactions of 6-phenyl-, 6-methyl-6-phenyl-, 6,6-diphenyl- and 6-furyl-fulvenes furnished similar bicyclo[2.2.2]adducts with 3-methoxy-*o*-benzo-quinone. The results are given in Table 3.

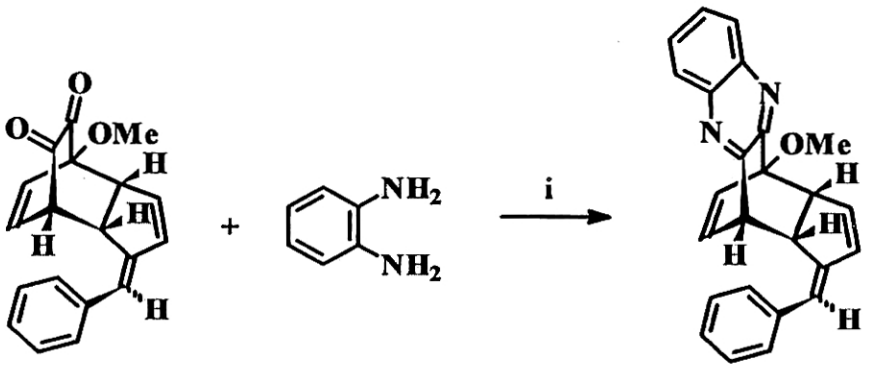
Table 3. Cycloaddition reactions of 3-methoxy-*o*-benzoquinone with aryl substituted fulvenes

Entry	Fulvene	Conditions	Product [1]	Yield (%) [2]
1		Benzene, reflux, 30 min.	 **44**	56
2		Benzene, reflux, 30 min.	 **45**	57
3		Benzene, reflux, 30 min.	 **46**	70
4		Benzene, reflux, 30 min.	 **47**	63

[1] Trace amount of *exo* isomer was also detected [2] Isolated yield

The adducts **44**, **45**, **46** and **47** afforded similar spectroscopic data. All compounds showed carbonyl absorption at 1739-1745 cm^{-1} in the IR spectra.

The ^1H NMR spectrum of **44** showed a multiplet centred at δ 3.45 integrating for 6 protons. The olefinic protons appeared at δ 5.9 as a broad multiplet. Since we had some difficulty in assigning the ring junction and bridgehead protons, we made the quinoxaline derivative of **44** by reaction with 1,2-diaminobenzene.



i, MeOH, RT, 12 h, 50% **44a**

An examination of the ^1H NMR spectrum of **44a** allowed the following assignments. The bridgehead and ring junction protons resonated at δ 3.4, 3.7 and 4.5 and the $-OCH_3$ group appeared at δ 4.0. The protons on the quinoxaline ring resonated far down field from TMS and gave a multiplet at δ 7.9-8.4.

The adducts **45**, **46** and **47** yielded similar spectroscopic data. In **47**, the $-OCH_3$ group appeared at δ 3.6. The bridgehead and ring junction protons resonated at δ 3.9 (m, 1H) and 3.7 (br s, 2H). The olefinic proton on the furan ring adjacent to the oxygen atom resonated at δ 7.4 as a doublet. Examination of the ^{13}C NMR spectrum of **47** showed the presence of five

sp3 carbons. Of these, the one at δ 54.0 has been assigned to the -OCH_3 group. The rest of the signals, at δ 88.0, 50.5, 50.0 and 40.5, have been assigned to the bridgehead and the ring junction carbons. The signals at δ 190.5 and 188.0 have been assigned to the carbonyl carbons. The mass spectrum showed a molecular ion peak at *m/z* 282 in accordance with the assigned structure.

Reactions of 3-methoxy-*o*-benzoquinone with 6,6-dimethyl- and 6,6-tetramethylenefulvene afforded intractable mixtures.

Inorder to explain the observed reactivity, we have carried out some MNDO and AM1 calculations using MOPAC program. The energies of the starting materials were optimized by this method. The HOMO and LUMO energies were derived from this program and are given below (Table 4).

Table 4. HOMO - LUMO energies of the quinones and fulvenes.

	REACTANT	$HOMO_{eV}$	$LUMO_{eV}$
1.	3,5-Di-*tert*-butyl-*o*-benzoquinone	-9.800	-1.188
2.	4-*tert*-Butyl-*o*-benzoquinone	-10.009	-1.435
3.	3-Methoxy-*o*-benzoquinone	-9.106	-2.006
4.	6,6-Dimethylfulvene	-8.413	-0.999
5.	6,6-Tetramethylenefulvene	-8.894	-0.557
6.	6,6-Pentamethylenefulvene	-8.886	-0.565
7.	6,6-Hexamethylenefulvene	-8.886	-0.577
8.	6,6-Dicyclopropylfulvene	-8.842	-0.540
9.	6-Phenylfulvene	-8.891	-0.487
10.	6-Furylfulvene	-8.851	-0.893

From the above table it is clear that all the reactions described in this chapter can be classified as inverse electron demand Diels-Alder reactions. The $LUMO_{quinone}$-$HOMO_{fulvene}$ interaction is favourable in every case.

4.3 EXPERIMENTAL DETAILS

(See p.47 for general information about experiments)

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(dimethyl)methylene]-4,7-ethanoindene-8,9-dione (11).

3,5-Di-*tert*-butyl-*o*-benzoquinone (2.0 g, 9.0 mmol) and 6,6-dimethyl-fulvene (1.0 g, 9.4 mmol) were dissolved in dry benzene (20 mL) and refluxed for 8 h. The solvent was removed *in vacuo* and the residue was subjected to chromatography on a silica gel column (petroleum ether/ethyl acetate) to afford **11** (2.37 g, 80%) as yellow crystals, m p. 145-147 °C.

IR , KBr : 2966, 2913, 1738, 1591, 1466, 1367, 1239 cm^{-1}.

^1H NMR : δ 6.42 (dd, 1H), 5.86 (d, 1H), 5.73 (d, 1H), 3.64 (t, 2H), 3.25 (d, 2H), 1.78 (s, 3H), 1.71 (s, 3H), 1.20 (s, 9H), 0.977 (s, 9H).

^{13}C NMR : δ 192.34, 190.20, 150.00, 138.95, 135.55, 132.58, 123.96, 120.74, 61.10, 51.53, 50.02, 41.43, 35.10, 33.88, 27.87, 21.07, 20.86.

HRMS : $C_{22}H_{30}O_2$: 326.459 ; Found : 326.4360

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(methylethyl) methylene]-4,7-ethanoindene-8,9-dione (12).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0. 1g, 0.45 mmol) and 6-methyl-6-ethylfulvene (0.4 g, 3.3 mmol,) were dissolved in dry benzene (10 mL) and refluxed under nitrogen for 6 h. The solvent was removed *in vacuo* and the residue was subjected to chromatography on silica gel (pet.ether/EtOAc) to afford **12** (0.131 g, 85%) as viscous yellow oil.

IR, film : 2968, 2878, 1733, 1624, 1468, 1369, 1236, 1165, 1107, cm^{-1}.

^1H NMR : δ 6.6 (m, 1H), 6.0 (m, 2H), 3.7 (m, 2H), 3.4 (d, 2H), 2.2 (q, 2H), 1.85 (s, 3H), 1.35 (s, 9H), 1.25 (t, 3H), 1.1 (s, 9H).

^{13}C NMR : δ 192.3, 190.0, 150.0, 138.5, 135.0, 132.5, 130.0, 120.5, 61.0, 51.0, 50.0, 41.5, 35.0, 34.0, 28.0, 27.5, 27.0, 18.5, 12.5.

MS *m/z* : 340 (M^+), 314, 197, 152, 113.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethyethyl)-3a,4,7,7a-tetrahydro-1-[(dicyclopropyl)methylene]-4,7-ethanoindene-8,9-dione (13).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.125 g, 0.56 mmol) and 6,6-dicyclo propylfulvene (0.09 g, 0.56 mmol) were dissolved in dry benzene (1 mL) in a glass tube and it was sealed under nitrogen and heated at 100 °C for 10 h. The solvent was removed *in vacuo* and the product subjected to chromatography on silica gel using petroleum ether/ ethyl acetate mixture as eluent to yield the cycloadduct **13** (0.133 g, 62%) as yellow solid.

IR, KBr : 2968, 2880, 1745, 1733, 1563, 1467, 1368, 1274, 1125, cm^{-1}.

^{1}H NMR : δ 6.75 (d, 1H), 5.9 (d, 1H), 5.75 (s, 1H), 3.8 (d, 1H), 3.62 (d, 2H), 3.45 (d, 1H), 1.45 (m, 2H), 1.25 (s, 9H), 0.96 (s, 9H) 0.85-0.7 (m, 6H), 0.4 (m, 1H), 0.25 (m, 1H).

^{13}C NMR : δ 193.0, 191.0, 151.0, 143.8, 137.0, 133.0, 131.0, 121.0, 61.5, 51.8, 50.0, 42.0, 35.8, 34.2, 28.0, 16.0, 12.0, 7.0, 6.0, 5.5, 5.0.

MS *m/z* : 378 (M^+), 297, 184, 132, 120.

(3a-*cis*)-2-(1-Cyclopenten-1-yl)-5,7-bis(1,1-dimethyethyl)-3a,9a-dihydro-1H-cyclopenta[*b*][1,4]benzodioxin (14).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.503 g, 2.28 mmol.) and 6,6-tetramethylenefulvene (0.5 g, 3.78 mmol) were dissolved in dry benzene (10 mL) and refluxed for 8 h. The solvent was removed *in vacuo* and the product was subjected to chromatography on silica gel to afford **14** (0.68 g, 85%) as colourless crystals. mp. 114-116°C.

IR, KBr : 2960, 2930, 2872, 1587, 1484, 1421, 1362, 1313, 1289 cm^{-1}.

^{1}H NMR : δ 6.86 (d, 1H), 6.79 (d, 1H), 5.81 (s, 1H), 5.67 (s, 1H), 5.008 (d, *J* =4.7 Hz, 1H), 4.703 (q, *J*=4.9 Hz, 1H), 2.84 (d, *J*=4.7 Hz, 2H), 2.5 (m, 4H), 1.95 (m, 2H), 1.388 (s, 9H), 1.266(s, 9H).

^{13}C NMR : δ 144.22, 143.25, 142.04, 140.72, 139.56, 137.93, 131.18, 123.30, 115.80, 112.25, 79.57, 75.16, 38.45, 34.90, 34,40, 33.25, 32.39, 31.55, 29.92, 23.30.

MS *m/z* : 353 (M^+ +1), 325, 300, 280, 224, 222, 207, 198, 163, 116, 53.

Diels-Alder adducts 21 and 22. 3,5-Di-*tert*-butyl-*o*-benzoquinone (0.20 g, 0.91 mmol) and 6,6-pentamethylenefulvene (0.50 g, 3.42 mmol) were dissolved in benzene (5 mL) and it was refluxed under nitrogen for 8 h. The solvent was removed *in vacuo*, and the residue on column chromatography afforded the products **21** (0.174 g, 52%) and **22** (0.109 g, 33%) as viscous oils.

(3a-*cis*)-2-(1-Cyclohexen-1-yl)-5,7-bis(1,1-dimethylethyl)-3a,9a-dihydro-1H-cyclopenta[*b*][1,4]benzodioxin (21).

IR, KBr : 2960, 2870, 1590, 1485, 1422, 1363, 1305, 1236, 1088 cm^{-1}.

^{1}H NMR : δ 6.45 (d, 1H), 6.4 (d, 1H), 5.6-5.4 (m, 2H), 4.7 (m, 1H), 4.35 (q, 1H), 2.55 (m, 2H), 2.0 (m, 4H), 1.4 (m, 4H), 1.25 (s, 9H), 1.1 (s, 9H).

^{13}C NMR : δ 146.5, 144.3, 143.0, 141.0, 138.0, 133.5, 128.5, 120.5, 116.0, 112.5, 79.5, 75.0, 37.5, 35.0, 34.0, 31.5, 30.0, 26.0, 25.5, 22.5, 22.0.

HRMS : $C_{25}H_{34}O_2$: 366.2559 ; found : 366.2560.

[3a-(3aα,4α,7α,7aα]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(cyclohexyl)methylene]-4,7-ethanoindene-8,9-dione (22).

IR, film : 2963, 2880, 1747, 1625, 1484, 1400, 1266, 1168, 787 cm^{-1}.

^1H NMR : δ 6.47 (dd, 1H), 5.85 (d, 1H), 5.75 (s, 1H), 3.67 (d, 1H), 3.57 (s, 1H), 3.31 (d, 1H), 2.24 (m, 4H), 1.55 (m, 6H), 1.221 (s, 9H), 1.01 (s, 9H).

^{13}C NMR : δ 192.0, 190.0, 150.0, 136.0, 135.0, 132.5, 132.0, 120.5, 61.0, 52.0, 49.8, 41.0, 35.0, 34.0, 31.5, 28.0, 27.5, 27.0, 26.5.

HRMS : $C_{25}H_{34}O_2$: 366.2558 ; found : 366.2544.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(Dimethyethyl)-3a,4,7,7a-tetrahydro-1-[(cycloheptyl)methylene]-4,7-ethanoindene-8,9-dione (23).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.40 g, 1.18 mmol.) and 6,6-hexamethylenefulvene (0.33 g, 2.11 mmol.) were dissolved in dry toluene (5 mL) and refluxed for 2.5 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **23** (0.577 g, 84%) as yellow solid.

IR, KBr : 2928, 2877, 1744, 1732, 1621, 1467, 1368, 1236, 1018 cm^{-1}.

^1H NMR : δ 6.4 (dd, 1H), 5.8 (br d, 1H), 5.7 (s, 1H), 3.55 (m, 2H), 3.2 (br d, 1H), 2.25 (m, 4H), 1.45 (m, 8H), 1.15 (s, 9H), 0.9 (s, 9H).

^{13}C NMR : δ 192.5, 190.2, 150.5, 138.5, 135.8, 134.0, 132.5, 121.0, 61.0, 51.5, 50.2, 41.5, 35.0, 34.0, 32.5, 32.3, 30.5, 29.0, 27.9, 27.0.

HRMS : $C_{26}H_{36}O_2$: 380.5460 ; found : 380.5369.

Diels-Alder Adducts 24 and 24a. 3,5-Di-*tert*-butyl-*o*-benzoquinone (0.5 g, 2.26 mmol) and 6-phenylfulvene (0.57 g, 3.71 mmol) were dissolved in toluene (1 mL) and taken in a tube. The tube was then sealed under nitrogen and heated at 120 °C for 24 h. The solvent was removed *in vacuo*

and the cycloadducts **24** (0.692 g, 82%) and **24a** (0.068 g, 8%) were isolated by crystallization from benzene.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethyethyl)-3a,4,7,7a-tetrahydro-1-[(phenyl)methylene]-4,7-ethanoindene-8,9-dione (24) (*Endo* adduct).

mp. : 178-179 °C

IR, KBr : 2968, 2910, 2878, 1731, 1632, 1470, 1397, 1367, 1230, 1166, 1121, 1025, 954, 874 cm^{-1}.

^1H NMR : δ 7.1 (s, 5H), 6.2-5.6 (m, 4H), 3.7 (m, 3H), 1.2 (s, 9H), 0.8 (s, 9H).

^{13}C NMR : δ 192.0, 190.0, 150.0, 146.0, 141.0, 136.0, 135.0, 129.0, 128.0, 127.0, 123.0, 121.0, 61.0, 51.0, 49.0, 41.0, 35.0, 34.0, 28.0

MS *m/z* : 374 (M^+), 348, 301, 220, 183.

***Exo* adduct 24a.** mp. : 184-186 °C

IR, KBr : 2967, 1737, 1630, 1470 cm^{-1}.

1H NMR : δ 7.3 (m, 5H), 6.35 (m, 2H), 6.1 (m, 1H), 5.78 (m, 1H), 3.85-3.7 (m, 3H), 1.2 (s, 9H), 0.85 (s, 9H).

13C NMR : δ 193.0, 192.0, 150.5, 147.0, 141.0, 137.0, 135.0, 129.0, 128.0, 127.0, 122.5, 121.0, 52.0, 51.0, 48.5, 41.5, 35.0, 34.5, 28.0, 27.5.

MS *m/z* : 374 (M^+), 348, 147, 96.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(4-methoxyphenyl)methylene] 4,7-ethano-1H-indene-8,9-dione (25). 3,5-Di-*tert*-butyl-*o*-benzoquinone (0.23 g, 1.07 mmol) and 6-(4-methoxy) phenylfulvene (0.5 g, excess) were taken in a glass tube and toluene (1 mL) was added. The tube was then sealed under nitrogen and heated at 110 °C for 5 h. The solvent was removed *in vacuo* and the residue on chromato-

graphy afforded **25** (0.225 g, 56%) as yellow crystalline solid. mp. 178-180 °C

IR, KBr : 2969, 1732, 1674, 1610, 1517, 1449, 1373, 1301, 1252, 1178, 1032, 960, 876 cm^{-1}.

^1H NMR : δ 7.0-6.75 (m, 4H), 6.15-5.60 (m, 4H), 3.7-3.65 (m, 6H), 1.2 (s, 9H), 0.85 (s, 9H).

^{13}C NMR : δ 192.5, 190.0, 158.5, 150.0, 144.5, 141.0, 134.0, 129.0, 122.0, 121.0, 114.4, 61.0, 55.0, 51.0, 48.5, 41.0, 35.0, 34.0, 28.0, 27.5

MS *m/z* : 404 (M^+), 349, 321, 241, 195.

[3a-(3aα,4α,7α,7aα)]4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(methyl phenyl)methylene]-4,7-ethanoindene-8,9-dione (26).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.2 g, 0.90 mmol) and 6-methyl-6-phenylfulvene (0.221 g, 1.30 mmol) were dissolved in toluene (1 mL) and taken in a glass tube. The tube was then sealed under nitrogen and heated at 110 °C for 13 h. The solvent was removed *in vacuo* and the product was subjected to chromatography on silica gel using petroleum ether ethyl acetate mixture as eluent to afford **26** (0.30 g, 85%) as yellow crystals. mp. 184-185 °C

IR, KBr : 2970, 1735, 1602, 1423, 1369, 1238, 1069 cm^{-1}

^1H NMR : δ 6.95 (m, 5H), 6.0 (m, 1H), 5.5 (m, 2H), 3.6 (m, 2H), 3.4 (m, 2H), 2.0 (s, 3H), 1.1 (s, 9H), 1.0 (s, 9H).

^{13}C NMR : δ 192.0, 190.0, 154.0, 150.0, 141.5, 137.0, 135.5, 135.0, 128.5, 128.0, 127.5, 126.5, 121.0, 61.0, 51.0, 48.5, 42.0, 35.0, 34.0, 28.0, 27.0, 21.0

MS *m/z* : 388 (M^+), 361, 302, 298, 204.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(diphenyl)methylene]4,7-ethanoindene-8,9-dione (27).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.14 g, 0.63 mmol) and 6,6-diphenyl fulvene (0.175 g, 0.712 mmol) were dissolved in toluene (1 mL) and taken in a glass tube. It was then sealed and heated at 110 °C for 12 h. The solvent was removed *in vacuo* and the product was subjected to chromatography to afford **27** (0.257 g, 90%) as yellow crystals. mp. 202-204 °C

IR, KBr : 2974, 1734, 1604, 1516, 1450, 1302, 1254 cm^{-1}.

^1H NMR : δ 7.3 (m, 10H), 6.5 (dd, 1H), 6.15 (d, 1H), 5.8 (d, 1H), 3.55 (br s, 2H), 3.2 (br s, 1H), 1.25 (s, 9H), 0.7 (s, 9H).

^{13}C NMR : δ 189.92, 189.5, 153.94, 142.6, 141.86, 141.53, 138.07, 136.93, 129.71, 129.48, 128.61, 127.98, 127.24, 127.12, 123.12, 59.84, 53.01, 48.3, 48.06, 35.1, 33.82, 27.25, 27.08

MS *m/z* : 450 (M^+), 412, 385, 201.

[3a-(3aα,4α,7α,7aα)]-4,6-bis(1,1-Dimethylethyl)-3a,4,7,7a-tetrahydro-1-[(furyl)methylene]-4,7-ethanoindene-8,9-dione (28).

3,5-Di-*tert*-butyl-*o*-benzoquinone (0.50 g, 2.27 mmol) and 6-furyl-fulvene (0.5 g, 3.4 mmol) were dissolved in benzene (1 mL) and taken in a glass tube . The tube was then sealed under nitrogen and heated at 100 °C for 2 h. The solvent was removed *in vacuo* and the product subjected to chromatography to yield **28** (0.925 g, 91%) as yellow crystals.

mp. 168-170 °C

IR, KBr, : 2960, 2880, 1731, 1617, 1481, 1398, 1368, 1232, 1167, 912, 733 cm^{-1}.

^1H NMR : δ 7.25 (d, 1H), 6.3-5.6 (m, 6H), 3.8 (br s, 1H), 3.65 (br s, 2H), 1.2 (S, 9H), 0.9 (s, 9H).

^{13}C NMR : δ 193.0, 190.0, 152.5, 150.0, 145.0, 143.0, 140.0, 136.0, 121.0, 112.0, 110.0, 109.5, 61.0, 51.0, 50.5, 41.0, 35.0, 34.0, 28.0

MS *m/z* : 364 (M^+), 331, 298, 205, 169.

[3a-(3aα,4α,7α,7aα)]-6-(1,1-Dimethylethyl)-1-[(dimethyl)methylene]-4,7-ethanoindene8,9-dione (29).

4-*tert*-Butyl-*o*-benzoquinone (0.44 g, 2.72 mmol) and 6,6-dimethyl-fulvene (0.58 g, 4.7 mmol) were dissolved in benzene (10 mL) and stirred at room temperature for 8 h. The solvent was removed *in vacuo* and the residue on chromatography (pet. ether/ EtOAc-eluent) afforded **29** (0.588 g, 80%) as yellow semi solid.

IR, film : 2870, 1734, 1625, 1370, 1284, 1165 cm^{-1}.

^{1}H NMR : δ 6.44 (m, 1H), 5.9 (m, 1H), 5.8 (m, 1H), 3.7 (m, 2H), 3.6 (m, 2H), 1.8 (s, 3H), 1.77 (s, 3H), 1.21 (s, 9H).

^{13}C NMR : δ 193.0, 192.0, 151.0, 140.0, 135.0, 132.5, 124.0, 121.0, 59.0, 52.0, 50.5, 42.0, 35.1, 27.6, 21.3, 20.8

MS *m/z* : 270 (M^+), 216, 194, 82, 63.

Diels-Alder Adduct 30: 4-*tert*-Butyl-*o*-benzoquinone (0.2 g, 1.21 mmol) and 6-methyl-6-ethylfulvene (0.3 g, 2.4 mmol) were dissolved in benzene (10 mL) and stirred at room temperature for 8 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **30** (0.27 g, 78%) as yellow semi solid.

IR, film : 2869, 1735, 1384, 1285, 1160 cm^{-1}.

^{1}H NMR : δ 6.6 (m, 1H), 6.2 (m, 2H), 3.75 (m, 2H), 3.5 (m, 2H), 1.85 (s, 3H), 1.35 (q, 2H), 1.25 (s,9H), 1.2 (t, 3H).

^{13}C NMR : δ 192.0, 191.5, 150.5, 140.0, 135.5, 133.0, 132.5, 125.0, 59.0, 51.0, 50.0, 41.5, 35.0, 28.0, 27.0, 18.5, 12.5

MS *m/z* : 284 (M^+), 212, 182, 78, 64.

Diels-Alder Adduct 31: 4-*tert*-Butyl-*o*-benzoquinone (0.342 g, 2.08 mmol) and 6,6-tetramethylenefulvene (0.5 g, 3.78 mmol) were dissolved in benzene (10 mL) and stirred at room temperature for 4 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **31** (0.518 g, 84%) as pale yellow semi solid.

IR, film : 2930, 2869, 1584, 1480, 1423, 1314 cm^{-1}.

^{1}H NMR : δ 6.8 (m, 3H), 5.85 (m, 1H), 5.75 (m, 1H), 4.95 (m, 1H), 4.65 (q, 1H), 2.75 (br d,2H), 2.15 (m,4H), 1.6 (m, 4H), 1.25 (s, 9H).

^{13}C NMR : δ 146.5, 142.5, 133.0, 132.0, 128.5, 128.0, 120.5, 118.0,116.5, 114.0, 78.5, 74.0, 36.5, 34.0, 31.5, 26.0, 25.5, 22.5, 22.0.

MS *m/z* : 297 (M^+ +1), 296 (M^+), 231, 176, 86, 75.

Diels-Alder Adducts 32 and 33: 4-*tert*-Butyl-*o*-benzoquinone (0.8 g, 4.87 mmol) and 6,6-pentamethylenefulvene (0.9 g, 6.15 mmol) were dissolved in benzene (10 mL) and stirred at room temperature for 4 h. The solvent was removed *in vacuo* and the residue on chromatography afforded **32** (0.138 g, 10 %) and **33** (1.11 g, 74%) as viscous oils.

32:

IR, film : 2869, 1591, 1485, 1420, 1350 cm^{-1}.

^{1}H NMR : δ 6.8 (m, 3H), 5.8 (br d, 2H), 5.0 (br s, 1H), 4.65 (q, 1H), 2.75 (br d, 2H), 2.15 (m, 4H), 1.6 (m, 4H), 1.25 (s, 9H).

^{13}C NMR : δ 146.5, 142.5, 133.0, 132.0, 128.5, 128.0, 120.5, 118.0, 116.5, 114.0, 78.5, 74.0, 36.5, 34.0, 31.5, 26.0, 25.5, 22.5, 22.0

MS *m/z* : 311 (M^+ +1), 310 (M^+), 283, 189, 154, 130.

33:

IR, film : 2830, 1746, 1485, 1400 cm^{-1}.

^1H NMR : δ 6.45 (dd, 1H), 5.85 (dd, 1H), 5.6 (dd, 1H), 3.7 (t, 1H), 3.55 (m, 2H), 3.35 (br d, 1H), 2.25 (br s, 4H), 1.55 (br s, 6H), 1.0 (s,9H).

^{13}C NMR : δ 190.5, 190.3, 151.5, 136.0, 134.0, 133.0, 132.0, 118.0, 53.5, 51.5, 46.0, 39.5, 35.0, 32.0, 31.0, 28.0, 26.0

MS *m/z* : 310 (M^+), 280, 172, 140, 96, 56.

Diels-Alder Adduct 34: 4-*tert*-Butyl-*o*-benzoquinone (0.3 g, 1.82 mmol) and 6,6-hexamethylenefulvene (0.35 g, 2.18 mmol) were dissolved in benzene (15 mL) and refluxed under nitrogen for 8 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **34** (0.44 g, 75%) as yellow solid.

IR, film : 2925, 1743, 1623, 1236 cm^{-1}.

^1H NMR : δ 6.43 (dd, 1H), 5.8 (m, 2H), 3.5 (m, 2H), 3.3 (m, 2H), 2.2 (m, 4H), 1.6 (m, 8H), 1.2 (s, 9H).

^{13}C NMR : δ 193.0, 192.0, 149.5, 138.0, 134.5, 134.0, 132.5, 120.0, 60.0, 51.5, 50.0, 40.5, 35.0, 32.5, 34.4, 32.0, 30.0, 29.0, 27.5, 27.0

MS *m/z* : 324 (M^+), 286, 231, 197, 146, 86.

Diels-Alder Adduct 35: 4-*tert*-Butyl-*o*-benzoquinone (0.5 g, 3.04 mmol) and 6-phenylfulvene (0.617 g, 4.0 mmol) were dissolved in toluene (10 mL) and heated at 90 °C for 4 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **35** (0.84 g, 87%) as a yellow crystals. mp. 180-182 °C

IR, film : 2884, 1732, 1630, 1745, 1368 cm^{-1}.

^{1}H NMR : δ 7.1 (s, 5H), 6.25 (m, 2H), 5.6 (m, 2H), 3.6 (m, 4H), 1.0 (s, 9H).

^{13}C NMR : δ 190.5, 190.0, 151.5, 147.0, 140.0, 136.5, 135.0, 128.5, 127.5, 126.5, 122.5, 118.0, 53.0, 47.0, 40.0, 35.0, 28.0

Analysis calcd for $C_{22}H_{22}O_2$: C, 41.39; H, 4.37. Found : C, 41.37; H, 4.30.

Diels-Alder Adduct 36: 4-*tert*-Butyl-*o*-benzoquinone (0.3 g, 1.82 mmol) and 6-(*p*-methoxy) Phenylfulvene (0.4 g, 2.17 mmol) were dissolved in benzene (10 mL) and refluxed for 8 h. The solvent was removed *in vacuo* and the residue on column chromatography afforded **36** (0.407 g, 64%) as yellow solid.

IR, film : 2969, 1730, 1610, 1517, 1254 cm^{-1}.

^{1}H NMR : δ 6.9 (m, 2H), 6.8 (m, 2H), 6.15 (m, 2H), 5.75 (m, 1H), 5.6 (m, 1H), 3.7 (s, 3H), 3.6 (m, 2H), 3.58 (m, 2H), 1.20(s, 9H).

^{13}C NMR : δ 192.0, 190.0, 158.5, 150.5, 145.0, 141.5, 134.5, 129.5, 123.0, 122.0, 115.0, 61.0, 55.5, 51.5, 49.0, 41.5, 35.0, 28.0

MS *m/z* : 348 (M^+), 301, 287, 148, 78.

Diels-Alder Adduct 37: 4-*tert*-Butyl-*o*-benzoquinone (0.2 g, 1.21 mmol) and 6-phenyl-6-methylfulvene (0.28 g, 1.66 mmol) were dissolved in toluene (10 mL) and refluxed for 6 h under nitrogen. The solvent was removed *in vacuo* and the residue on chromatography afforded **37** (0.275 g, 68 %) as yellow solid.

IR, KBr : 2969, 1734, 1603, 1425, 1367, 1068 cm^{-1}.

^{1}H NMR : δ 6.9 (s, 5H), 5.4 (m, 3H), 3.6 (m, 2H), 3.4 (m, 2H), 2.0 (s, 3H), 1.2 (s, 9H).

^{13}C NMR : δ 191.5, 190.0, 154.5, 151.0, 140.5, 138.0, 135.5, 135.0, 128.5, 128.0, 127.5, 126.0, 121.5, 61.0, 51.0, 49.0, 43.0, 35.0, 28.0, 22.0

MS *m/z* : 332 (M^+), 306, 229, 147, 91.

Diels-Alder Adduct 38: 4-*tert*-Butyl-*o*-benzoquinone (0.3 g, 1.82 mmol) and 6,6-diphenylfulvene (0.5 g, 2.17 mmol) were dissolved in toluene (10 mL) and refluxed for 12 h. The solvent was removed *in vacuo* and the residue was subjected to column chromatography to afford **38** (0.648 g, 90%) as yellow solid. mp. 216-218 °C

IR, KBr : 2974, 1735, 1605, 1516, 1450, 1255 cm^{-1}.

^{1}H NMR : δ 7.1 (m, 10 H), 6.4 (m, 1H), 6.2 (m, 2H), 5.85 (d, 1H), 3.5 (m,2H), 3.3 (m, 2H), 1.25 (s, 9H).

^{13}C NMR : δ 190.0, 189.0, 153.0, 143.0, 142.0, 141.5, 138.6,135.0, 130.0, 129.48, 128.71, 127.9, 127.24, 127.0, 123.0, 59.5, 53.0, 48.5, 48.0, 35.1, 27.2

MS *m/z* : 394 (M^+), 361, 294, 263, 174, 83.

Diels-Alder Adduct 39: 4-*tert*-Butyl-*o*-benzoquinone (0.3 g, 1.82 mmol) and 6-furylfulvene (0.35 g, 2.42 mmol) were dissolved in benzene (10 mL) and refluxed under nitrogen for 12 h. The solvent was removed *in vacuo* and the residue on column chromatography yielded **39** (0.518 g, 92%) as yellow semi solid.

IR, film : 2878, 1733, 1618, 1480, 1378 cm^{-1}.

^{1}H NMR : δ 7.5 (d, 1H), 6.3-5.7 (m, 6H), 3.9 (br s, 1H), 3.8 (m, 1H), 3.7 (m, 2H), 1.25 (s, 9H).

^{13}C NMR : δ 193.5, 191.5, 152.5, 151.0, 145.5, 143.0, 140.0, 136.5, 121.5, 112.0, 110.5, 109.5, 61.0, 51.5, 50.0, 41.0, 35.0, 28.0

MS *m/z* : 308 (M^+), 271, 204, 188, 96.

[3a-(3aα,4α,7α,7aα)]-4-methoxy-1-[(4-methoxyphenyl)methylene]-4,7-ethanoindene-8,9-dione (40).

3-Methoxycatechol (0.588 g, 4.2 mmol) was dissolved in benzene (10 mL) and silver carbonate (2.0 g) was added and stirred under nitrogen. To the above solution 6-(4-methoxy) phenylfulvene (0.72 g, 4.0 mmol) was added and refluxed for 30 minutes. The inorganic material was removed by passing through a short column of celite and washed with benzene. The solvent was removed *in vacuo* and the residue on chromatography afforded **40** (0.53 g, 50%) as yellow crystals. mp. 170-172 °C

IR, film : 2940, 2842, 1742, 1609, 1510, 1462, 1352, 1300, 1252, 1177, 1032, 882, 777 cm^{-1}.

^1H NMR : δ 7.3-6.6 (m, 4H), 6.4-5.8 (m, 5H), 4.0-3.6 (m, 3H), 3.8 (s, 3H), 3.6 (s, 3H).

^{13}C NMR : δ 190.0, 188.0, 159.0, 145.0, 142.0, 132.0, 131.0, 129.0, 128.5, 127.0, 123.0, 114.0, 87.5, 55.5, 54.0, 51.0, 48.0, 40.0

MS *m/z* : 322 (M^+), 291, 263, 248, 191, 97, 65.

Diels-Alder Adduct 41: 3-Methoxycatechol (0.499 g, 3.56 mmol) was dissolved in benzene (10 mL) and silver carbonate (1.5 g) was added and stirred under nitrogen. To the above solution 6-ethyl-6-methylfulvene (0.47 g, 3.96 mmol) was added and the stirring continued for 5 h at room temperature. The inorganic material was removed by passing through a short column of celite and washed with benzene. The solvent was removed *in vacuo* and the residue on column chromatography afforded **41** (0.561 g, 61%) as yellow semi solid.

IR, film : 2939, 1743, 1516, 1462, 1354, 1260, 1180, 887, 763 cm^{-1}.

^{1}H NMR : δ 6.55 (dd, 1H), 6.18 (br d, 2H), 5.85 (br d, 1H), 3.75 (s, 3H), 3.7 (m, 1H), 3.4 (m, 2H), 2.2 (q, 2H), 1.95 (s, 3H), 1.2 (t, 3H).

^{13}C NMR : δ 190.0, 188.0, 138.5, 137.0, 136.5, 131.5, 130.0, 127.0, 88.0, 54.0, 49.5, 41.5, 40.0, 28.0, 18.5, 13.0

MS *m/z* : 258 (M^+), 210, 194, 137, 86.

Diels-Alder Adduct 42: 3-Methoxycatechol (0.409 g, 2.9 mmol) was dissolved in benzene (10 mL) and silver carbonate (1.5 g) was added and stirred under nitrogen. To this solution 6,6-pentamethylenefulvene (0.42 g, 2.9 mmol) was added and refluxed for 30 minutes. Worked up as in the previous case and the residue on column chromatography afforded **42** (0.57 g, 68%) as yellow crystalline solid. mp. 119-121 °C.

IR, film : 2931, 2855, 1746, 1702, 1668, 1550, 1451, 1358, 1230, 1079, 1032, 788 cm^{-1}.

^{1}H NMR : δ 6.5-5.6 (m, 4H), 3.65 (s, 3H), 3.45 (m, 3H), 2.2 (m, 4H), 1.6 (m, 6H).

^{13}C NMR : δ 190.0, 188.0, 136.0, 135.5, 134.0, 132.0, 130.0, 127.0, 87.5, 54.0, 52.0, 49.0, 39.0, 32.0, 31.0, 28.0, 26.0

MS *m/z* : 284 (M^+), 212, 180, 76.

Diels-Alder Adduct 43: 3-Methoxycatechol (0.502 g, 3.58 mmol) and silver carbonate (1.5 g) were taken in benzene (10mL) and 6,6-hexamethylene-fulvene (0.7 g, 4.37 mmol) was added. It was refluxed for 30 minutes and worked up as earlier. The residue on column chromatography afforded **43** (0.788 g, 75%) as yellow solid.

IR, KBr : 2927, 2877, 1743, 1621, 1467, 1368, 1090 cm^{-1}.

^{1}H NMR : δ 6.5 (dd, 1H), 6.1 (m, 2H), 5.7 (dd, 1H), 3.85 (m, 1H), 3.65 (s, 6H), 3.4 (m, 2H), 2.4 (m, 4H), 1.6 (m, 8H).

^{13}C NMR : δ 190.0, 188.0, 138.5, 136.5, 135.0, 131.5, 130.0, 126.5, 88.0, 53.5, 51.0, 49.0, 39.5, 32.0, 30.0, 28.0, 27.7, 27.3

MS *m/z* : 299 (M^+ +1), 298 (M^+), 270, 255, 199, 171, 160, 104, 78, 40.

Diels-Alder Adduct 44: 3-Methoxycatechol (0.45 g, 3.25 mmol) and silver carbonate (1.5 g) were taken in benzene (10 mL) and 6-phenylfulvene (1.0 g, 6.5 mmol) was added. It was refluxed for 30 minutes and worked up as usual. The residue on column chromatography afforded **44** (0.529 g, 56%) as yellow crystals. mp. 146-148 °C

IR, KBr : 2944, 2842, 1744, 1627, 1450, 1359, 1077 cm^{-1}.

^{1}H NMR : δ 7.0 (m, 5H), 5.9 (m, 5H), 3.45 (s, 3H), 3.34 (m, 3H).

^{13}C NMR : δ 190.5, 189.0, 146.0, 45.0, 142.5, 132.5, 131.0, 129.5, 128.5, 127.5, 123.0, 114.0, 87.3, 54.0, 51.5, 48.0, 40.5

HRMS : $C_{19}H_{16}O_3$: 292.1098 ; found : 292.1099

Quinoxaline Derivative of the adduct 44 (44a) : The bicyclic adduct **44** (0.10 g, 0.34 mmol) and 1,2-diaminobenzene (0.1 g, excess) were dissolved in methanol (10 mL) and stirred for 12 h at room temperature. The solvent was removed *in vacuo* and the residue on column chromatography afforded **44a** (0.59 g, 50%) as pale yellow viscous oil.

IR, film : 2938, 2886, 2247, 1655, 1497, 1317 cm^{-1}.

^{1}H NMR : δ 8.4 (m, 2H), 7.9 (m, 2H), 7.5 (m, 5H), 6.7-6.2 (m, 5H), 4.5 (m, 1H), 4.0 (s, 3H), 3.7 (m, 1H), 3.4 (m, 1H).

^{13}C NMR : δ 156.0, 148.0, 147.0, 142.0, 140.0, 139.0, 137.0, 136.0, 135.0, 133.0, 130.5, 130.0, 129.5, 129.0, 128.5, 128.0, 127.5, 127.0, 122.0, 120.0, 84.0, 55.0, 54.0, 47.5, 45.0.

MS *m/z* : 349 (M^+), 302, 281, 238, 176, 86.

Diels-Alder Adduct 45: 3-Methoxycatechol (0.5 g, 3.6 mmol) and silver carbonate (1.5 g) were taken in benzene (10 mL) and 6-phenyl-6-methylfulvene (0.7 g, 4.16 mmol) was added. It was refluxed for 30 minutes and worked up as earlier. The residue on column chromatography afforded **45** (0.632 g, 56%) as yellow semi solid.

IR, film : 2940, 2839, 1745, 1628, 1465, 1360 cm^{-1}.

^1H NMR : δ 6.85 (m, 5H), 5.6 (m, 4H), 3.45 (s, 3H), 3.3 (m, 3H), 2.0 (s, 3H).

^{13}C NMR : δ 192.5, 191.0, 146.0, 145.0, 142.0, 133.5, 131.0, 129.5, 128.5, 128.0, 127.0, 123.5, 115.0, 87.0, 55.0, 51.0, 49.0, 42.0, 22.0

MS *m/z* : 306 (M^+), 276, 257, 194, 84, 73.

Diels-Alder Adduct 46: 3-Methoxycatechol (0.4 g, 2.89 mmol) and silver carbonate (1.5 g) were taken in benzene (10 mL) and 6,6-diphenylfulvene (0.7 g, 3.039 mmol) was added. It was refluxed for 30 minutes and worked up as earlier. The residue on column chromatography afforded **46** (0.746 g, 70%) as yellow crystals. mp. 175-177 °C

IR, KBr : 2940, 2841, 1739, 1605, 1468, 1375 cm^{-1}.

^1H NMR : δ 7.25 (m, 10 H), 6.5 (m, 2H), 6.15(m, 2H), 3.4 (s, 3H), 3.25 (m, 2H).

^{13}C NMR : δ 192.0, 190.5, 150.0, 143.0, 141.5, 140.0, 138.5, 135.0, 130.0, 129.8, 128.5, 127.5, 127.0, 125.0, 123.0, 87.0, 58.0, 53.0, 42.0

MS *m/z* : 368 (M^+), 324, 289, 258, 87,57.

Diels-Alder Adduct 47: 3-Methoxycatechol (0.508 g, 3.6 mmol) and silver carbonate (1.5 g) were taken in benzene (10 mL) and 6-furylfulvene

(0.527 g, 3.6 mmol) was added. It was refluxed for 30 minutes and worked up as earlier. The residue on column chromatography afforded **47** (0.652 g, 63%) as yellow crystals. mp. 138-140 °C.

IR, KBr : 2940, 1745, 1520, 1470, 1360, 1250, 885 cm^{-1}.

^1H NMR : δ 7.4 (d, 1H), 6.4-5.9 (m, 7H), 3.9 (m, 1H), 3.7 (br s, 2H), 3.6 (s, 3H).

^{13}C NMR : δ 190.5, 188.0, 152.0, 145.0, 143.0, 141.0, 133.5, 131.0, 127.0, 112.0, 10.0, 88.0, 54.0, 50.5, 50.0, 40.5

MS *m/z* : 282 (M^+), 241, 159, 142, 73, 56.

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SUMMARY

The thesis entitled **NOVEL [4π+2π]CYCLOADDITION REACTIONS OF *o*-QUINONES** embodies the results of extensive investigations undertaken to gain new insight into the reactivity of *o*-benzoquinones in cycloaddition reactions.

A general introduction to the chemistry of *o*-benzoquinones with emphasis on cycloadditions along with a qualitative study of the Diels-Alder reaction is presented in Chapter 1. A definition of the present research problem has also been incorporated.

The second chapter deals with the cycloaddition reactions of *o*-quinones with acyclic dienes. We found that reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with most of the dienes afforded benzodioxin derivatives (eg. **19**, **21**, **22** and **23**) in good yields. Interestingly such hetero Diels-Alder reactions involving *o*-benzoquinones and acyclic dienes are unprecedented. Cycloaddition of 3,5-di-*tert*-butyl-*o*-benzoquinone with 2,3-dimethylbutadiene afforded the substituted naphthoquinone **25** presumably by the aromatization of **24** concomitant with the loss of a *tert*-butyl group. Similarly **27** was isolated from the reaction of 4-*tert*-butyl-*o*-benzoquinone and 2,3-dimethylbutadiene. From the reaction of 4-*tert*-butyl-*o*-benzoquinone and alloocimene both the benzodioxin **28** and the bicyclo[2.2.2]adduct **29** were isolated. Subsequently we have studied the reactions of 4-nitro-*o*-benzoquinone with various dienes. With alloocimene, the dioxin **30** and naphthoquinone **32** were isolated.

In order to explain the reactivity of *o*-benzoquinones in cycloaddition reactions, we have carried out some MNDO and AM1 calculations using MOPAC program. A general introduction to the theoretical studies is

included in chapter 2. The HOMO-LUMO energies of all the reactants were calculated by this program and it was found that all the reactions can be explained in terms of inverse electron demand Diels-Alder reaction. The energy gap for $LUMO_{quinone}$ - $HOMO_{diene}$ is smaller than the $HOMO_{quinone}$ - $LUMO_{diene}$ energy level.

Chapter 3 deals with the cycloaddition reactions of *o*-quinones with carbocyclic and heterocyclic dienes. It is interesting to note that the reaction of 4-nitro-*o*-benzoquinone with cyclopentadiene afforded the bicyclo[2.2.2]-octene dione **16** whereas α-terpinene gave the benzodioxin adduct **17** under similar conditions. The reaction of 4-*tert*-butyl-*o*-benzoquinone with 1,3-cyclohexadiene afforded the bicyclo adduct **18**. Subsequently the cyclo-addition reactions of heterocycles such as pyrroles and thiophenes with *o*-quinones were investigated. Reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with 2,5-dimethylpyrrole afforded the adduct **34**. Presumably the primary adduct **33** formed, isomerizes to the imine **34** under the reaction conditions. Similar products were isolated from the reactions of 3-methoxy-, 4-*tert*-butyl, and 4-nitro-*o*-benzoquinones with 2,5-dimethylpyrrole (products **36**, **38** and **40**). Here also the reactions can be explained in terms of inverse electron demand Diels-Alder reaction.

The last chapter (chapter 4) deals with the cycloadditions of *o*-quinones with various fulvenes. Reaction of 3,5-di-*tert*-butyl-*o*-benzo-quinone with 6,6-dimethyl-, 6-ethyl-6-methyl- and 6,6-dicyclopropyl-fulvenes afforded the bicyclo adducts **11**, **12** and **13** in high yields. But in the case of 6,6-tetramethylenefulvene, the product **14** was isolated in 85% yield. The structure of **14** was confirmed by X-ray crystallography. It is proposed that **14** arises from the cycloaddition of the quinone to the cyclopentylidene cyclopentadiene **17**, resulting from the isomerization of the fulvene.

In the reaction of 6,6-pentamethylenefulvene with 3,5-di-*tert*-butyl-*o*-benzoquinone, the benzodioxin **21** and the bicyclo[2.2.2]adduct **22** were formed. Reactions of other fulvenes like 6,6-hexamethylene-, 6-phenyl-, 6,6-diphenyl-, 6-furylfulvene etc. led to the bicyclo[2.2.2] adducts in good yields. The structure of the representative adduct **25** has been confirmed by X-ray crystallography. In some cases, the *exo* isomer was also detected. The cycloadditions of 4-*tert*-butyl-*o*-benzoquinone with fulvenes follow the same trend. Finally we have studied the reactions of 3-methoxy-*o*-benzoquinone with various fulvenes and the bicyclic adducts were isolated in good yields.

In conclusion, we have uncovered some novel and fascinating chemistry in the cycloaddition of *o*-benzoquinones to a variety of dienes. In the process, facile syntheses of a variety of interesting heterocycles and bicyclo compounds have been achieved. In particular, the bicyclo[2.2.2] octene diones and the benzodioxin derivatives appear attractive from the point of view of further chemical transformations. It is also anticipated that the reactions we have developed may be useful in the synthesis of certain *o*-quinone derived natural products.

List of Publications

1. Hetero Diels-Alder Reactions of 3,5-Di-*tert*-Butyl-*o*-Benzoquinone with Acyclic Dienes: Novel Synthesis of 1,4-Benzodioxines
   V. Nair and S. Kumar, *J. Chem. Soc., Chem. Commun.*, **1994**, 1341.
2. [4π+2π]Cycloadditions of *o*-Quinones to Fulvenes: A Facile Synthesis of Bicyclo[2.2.2]Octen-7,8-Diones.
   V. Nair, S. Kumar and P. G. Williard, *Tetrahedron Lett.*, **1995**, 0000.
3. [4π+2π]Cycloadditions of *o*-Quinones and Symmetrical 6,6-Dialkyl and Cycloalkylfulvenes.
   V. Nair, S. Kumar, N. P. Rath and G. O. Morton,
   Chemistry Lett., **1995**, 0000.