PART I
A STUDY OF SOME DIALKOXYCARBONIUM IONS
PART II
SYNTHESES FROM 2, 3, 4, 4, 5, 6 - HEXAMETHYL - 2, 5 - CYCLOHEXADIENONE

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MONICA VERMA
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This is to certify that the

thesis entitled

Part I. A Study of some Dialkoxycarbonium Ions.

Part II. Syntheses from 2,3,4,4,5,6-Hexamethyl-2,5-cyclohexadienone.

presented by

Monica Verma

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of the requirements for

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Harold Hart
Major professor

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ABSTRACT

PART I

A STUDY OF SOME DIALKOXYCARBONIUM IONS

PART II

SYNTHESES FROM 2,3,4,4,5,6-HEXAMETHYL-2,5-CYCLOHEXADIENONE

By

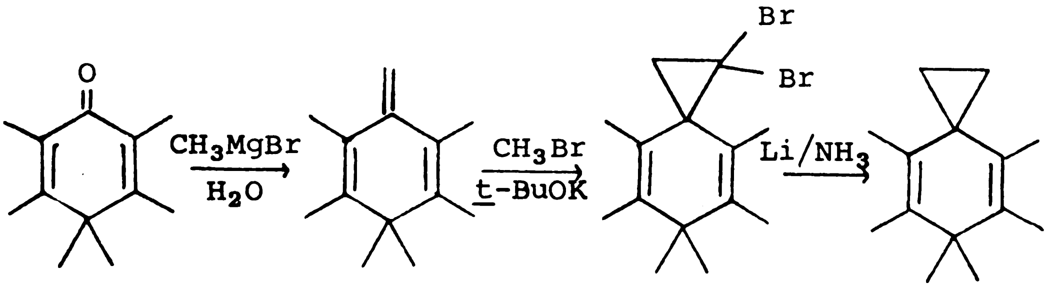
Monica Verma

The purpose of this investigation was to determine the chemical shifts for the aromatic protons of 2-phenyl-1,3-dioxolenium cation, and to correlate them with the charge densities at the corresponding positions on the phenyl ring. For this purpose we prepared 2-(phenyl-3,5-d_2)-1,3-dioxolenium cation and 2-(phenyl-4-d)-1,3-dioxolenium cation and the chemical shifts of the *ortho*, *meta*, and *para* protons were uniquely assigned. The π-electron densities were calculated by the "ω-technique" which is a variation of the Hückel molecular orbital method. The calculated charge densities were plotted *versus* the proton chemical shifts and a qualitative correlation between charge densities and proton chemical shifts was observed.

In addition to this nmr-charge density study, five new dioxolenium salts were synthesized and characterized. They are the monocationic 2-mesitoyl-1,3-dioxolenium tetrafluoroborate and the four dicationic salts:

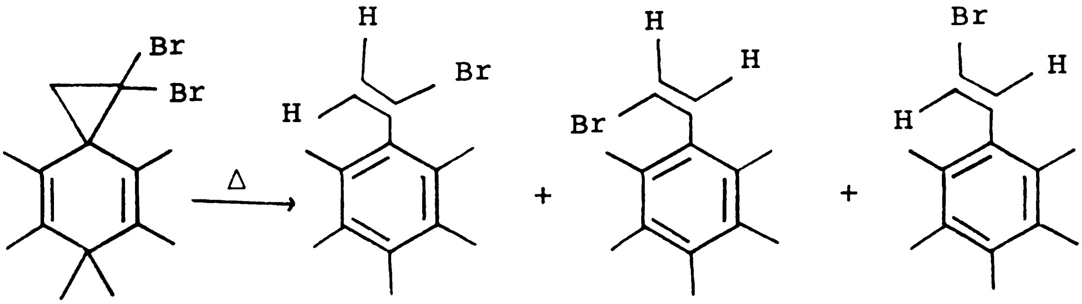
2,2'-(*o*-phenylene)bis-1,3-dioxolenium tetrafluoroborate, 2,2'-(*trans*-1,4-cyclohexane)bis-1,3-dioxolenium tetrafluoroborate, 2,2'-(1,8-naphthalene)bis-1,3-dioxolenium tetrafluoroborate and 2,2'-(1,4-naphthalene)bis-1,3-dioxolenium tetrafluoroborate. The nmr spectra of these new cations were compared with those of known dioxolenium cations.

For the second part of this work several new small ring and bicyclic compounds were synthesized from 2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (**35**) and their chemistry was investigated. The first was the spiro hydrocarbon 4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (**37**). Dienone **35** had already been converted to 1-methylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene (**39**) in good yield.[1] Addition of dibromocarbene to **39** gave 2,2-dibromo-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (**71**) which, by reduction with lithium and liquid ammonia, gave **37**. 2,2-Dichloro-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (**91**) was also prepared by the addition of dichlorocarbene to **39**. Compound **37** was found to rearrange to hexamethylbenzene in solution, both thermally and with acid.



35 **39** **71** **37**

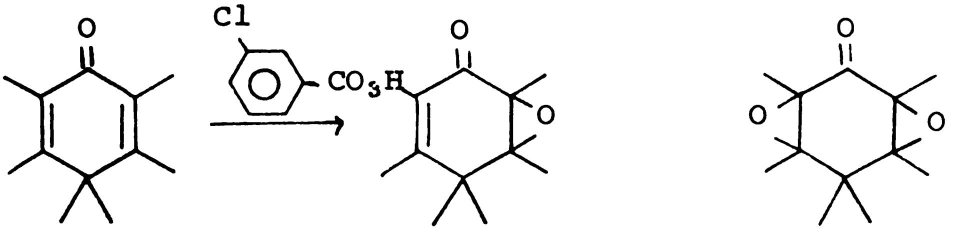
The chemistry of the precursor **71** was also investigated. It was found to polymerize on photolysis. Treatment of **71** with methyllithium did not yield an allene. When **71** was heated in solution, it gave three isomeric products, α-bromo-pentamethylstyrene (**80**), *cis*-β-bromo-pentamethylstyrene (**81**) and *trans*-β-bromo-pentamethylstyrene (**82**).



71 **80** **81** **82**

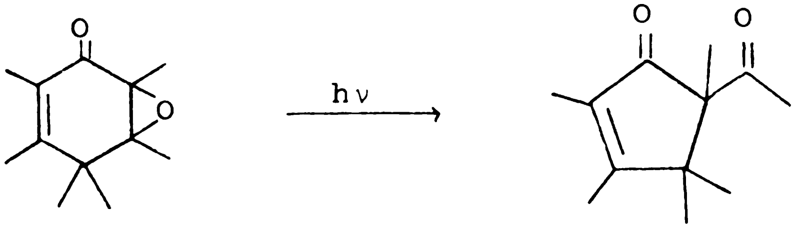
In deuterated solvents, very little deuterium was incorporated into the products. A plausible free radical mechanism is proposed for this reaction. The rate of rearrangement of **71** was accelerated in the presence of a radical source (benzoyl peroxide) and was found to be proportional to the concentration of benzoyl peroxide.

Dienone **35** was oxidized with *m*-chloroperbenzoic acid and two new compounds, 2,3-epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (**94**) and 2,3;5,6-diepoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (**95**) were obtained.



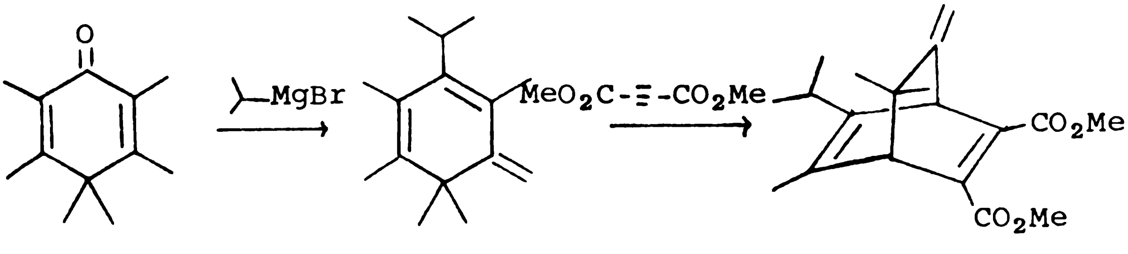
35 **94** **95**

Their photochemistry was investigated and 94 was found to rearrange to 6-acetyl-2,3,4,4,5-pentamethyl-2-cyclopentenone (102) on photolysis whereas 95 remained unchanged.



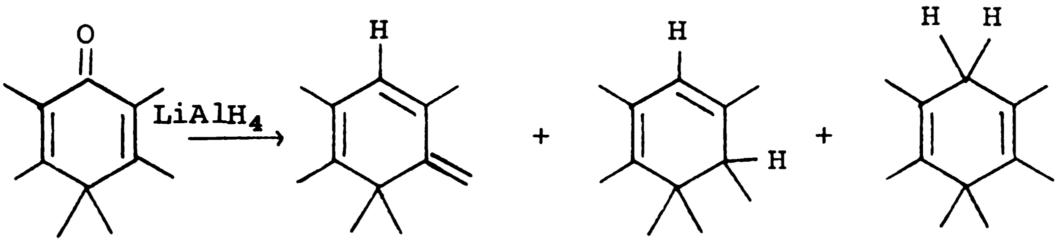
94 102

We also prepared 1-methylene-3-isopropyl-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (107) from dienone 35 and isopropylmagnesium bromide. Triene 107 formed an adduct (64) with dimethyl acetylenedicarboxylate.



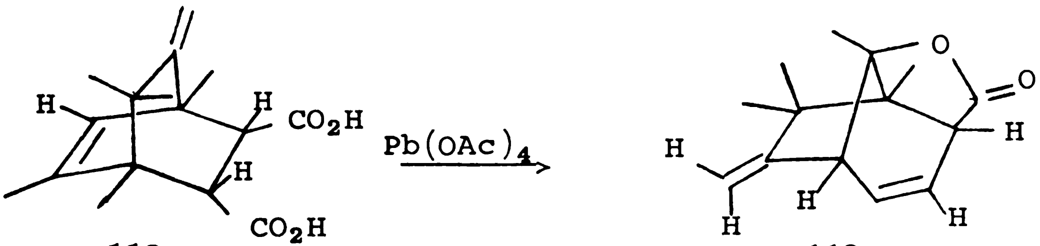
35 107 64

When dienone 35 was reduced with lithium aluminum hydride three products were detected: 1-methylene-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (108), 1,3,4,5,5,6-hexamethyl-1,3-cyclohexadiene (109) and 1,2,3,3,4,5-hexamethyl-1,4-cyclohexadiene (110).



35 108 109 110

Triene 108 formed an adduct (111) with maleic anhydride which on hydrolysis gave the diacid 112.



112 113

Diacid 112 was found to rearrange to a γ-lactone thought to be 113, by oxidation with lead tetraacetate.

REFERENCES

1. J. D. DeVrieze, Ph.D. Thesis, Michigan State University, E. Lansing, Michigan 1968.

PART I

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PART II

SYNTHESES FROM 2,3,4,4,5,6-HEXAMETHYL-2,5-CYCLOHEXADIENONE

By

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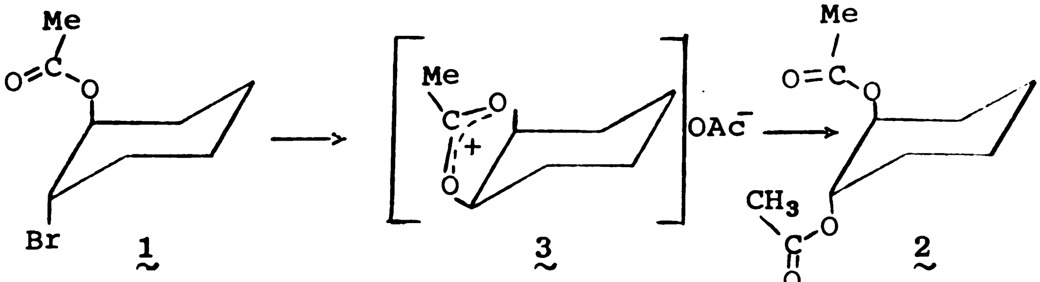
PART I

A STUDY OF SOME DIALKOXYCARBONIUM IONS

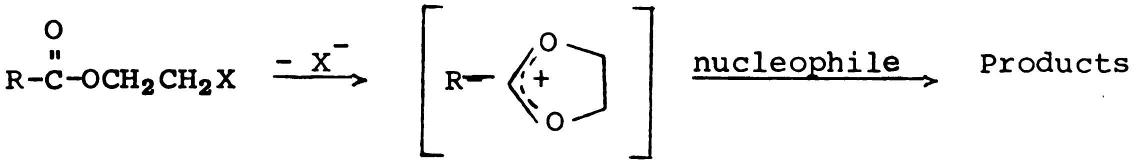
INTRODUCTION

As early as 1939 Tipson[1], observed that in general halogenoacetal sugars, on treatment with silver acetate in glacial acetic acid, dry toluene or a similar solvent, yield a sugar acetate having *trans* acetate groups at C_1 and C_2 regardless of whether the original sugar itself had *cis* or *trans* hydroxyl groups at C_2 and C_3. Isbell[2] later observed that this result could only be obtained if the C_2 acetate group was *trans* to the halogen, as it can participate in the displacement only when it is in the *trans* configuration. However, it was not until 1942 when Winstein[3] postulated dioxolenium cationic intermediates, that these results were explained with precision. Winstein observed that *trans*-2-acetoxy-cyclohexyl bromide (1), on treatment with silver acetate, gave exclusively a *trans*-diacetate (2). He explained these results by postulating a 2-substituted-1,3-dioxolenium cation (3) as an intermediate for this reaction.



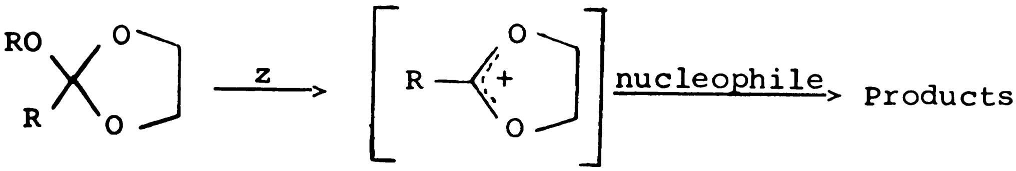
By now 1,3-dioxolenium cations have been well characterized. They occur as intermediates in a variety of reactions and have also been synthesized and isolated. The preparation of these ions can be grouped into three general reactions.

1. <u>Displacement of a β-substituent by Participation of a Carboxy Group</u>.



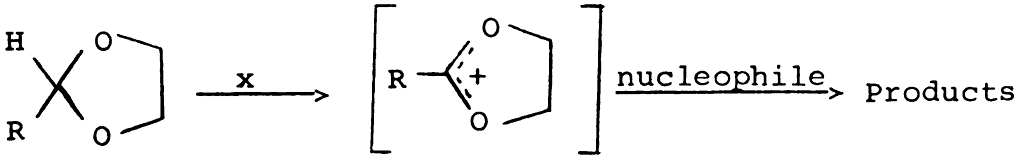
When X is a halogen the reaction is brought about by silver salts, organometallic reagents or a Lewis acid. When X is an ether, alcohol or ester function, the reaction is usually acid catalyzed, with a protic or Lewis acid. If X is a labile group such as a tosylate or a brosylate, solvolysis yields the 1,3-dioxolenium cationic intermediate. Reactions of this type have been reviewed by Pacsu[4] and Lemieux.[5] The preparation of the dioxolenium cations for this work also falls under this category.

2. <u>Acid-catalyzed Hydrolysis of Cyclic Ortho Esters</u>.



The reaction is brought about when Z is a protic or a Lewis acid.[6-10]

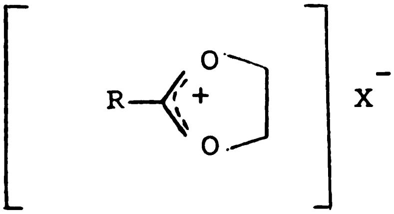
3. Oxidation of a Cyclic Acetal.



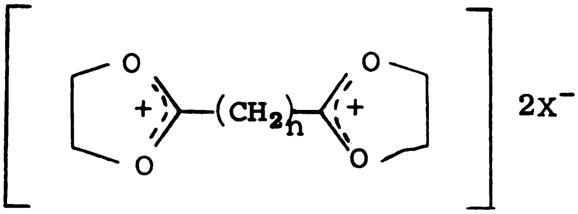
In this case X is Cl_2, Br_2, $BrCCl_3$ or NBS.[7,11-15]

The preparation and isolation of 1,3-dioxolenium cations by the reaction of 2-haloethyl esters with silver tetrafluoroborate was devised by Meerwein and coworkers.[8] Subsequent work showed that Lewis acids such as boron trifluoride and antimony pentachloride can also be used.[9,11] Four distinct families, outlined below, of these cyclic dialkoxycarbonium ions (1,3-dioxolenium cations) have been made by Hart and Tomalia[16,17] by Meerwein's method.

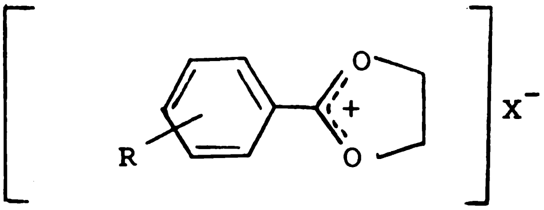
1. 2-Alkyl-1,3-dioxolenium cations:



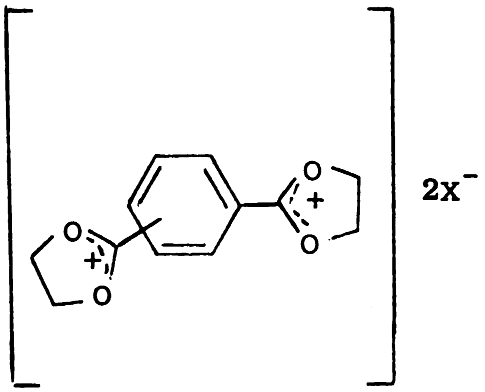
2. 2,2'-Alkylene-bis-1,3-dioxolenium dications:



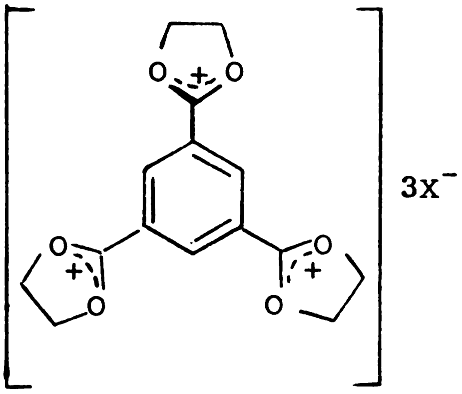
3. 2-Aryl-1,3-dioxolenium cations:



4. 2,2' and 2,2',2"-Aryl-1,3-dioxolenium dications and trications:

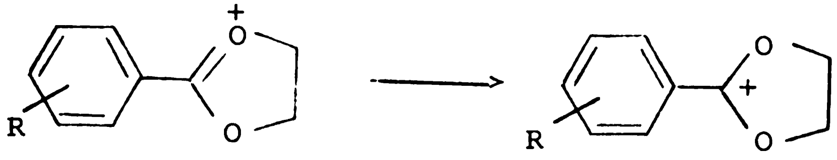


and



Recently Beringer and coworkers[18] used the same procedure as Hart and Tomalia to make 2-(2',6'-dimethoxyphenyl)-1,3-dioxolenium tetrafluoroborate. They have also studied the reactions of this cation with various nucleophiles.

Tomalia and Hart[17] examined the nmr spectra of the 2-aryl-1,3-dioxolenium cations and found a quantitative correlation between the proton-nmr chemical shifts, of <u>meta</u> and *para* substituted 2-phenyl-1,3-dioxolenium cations and Hammett σ values. The chemical shifts of the dioxolenium ring protons of these ions were plotted against Hammett σ and σ^+ values. A better linear correlation was obtained with σ than with σ^+ values, which suggests that the major contributor to the resonance hybrid is **4** rather than **5**.



4 **5**

As δ, the chemical shift, is directly related to the Hammett σ values, it should also be proportional to log k/k_0, where k and k_0 are rate constants for the ring opening reaction of substituted and unsubstituted 2-aryl-1,3-dioxolenium cations. This represents a quantitative correlation, by magnetic resonance, of charge densities in this carbonium ion system.

In this work we have determined the chemical shifts for the aromatic protons of 2-phenyl-1,3-dioxolenium tetrafluoroborate by preparing deuterium labeled tetrafluoroborates. Both 2-(phenyl-3,5-d_2)-1,3-dioxolenium tetrafluoroborate and 2-(phenyl-4-d)-1,3-dioxolenium tetrafluoroborate were prepared for this purpose. We have calculated the charge densities at various positions on the phenyl ring of 2-phenyl-1,3-dioxolenium ion and have correlated these with the chemical shifts. We have also determined the chemical shifts for the benzoylium (or phenyloxocarbonium) ion by using _para_ and _meta_ deuterated benzoic acid.

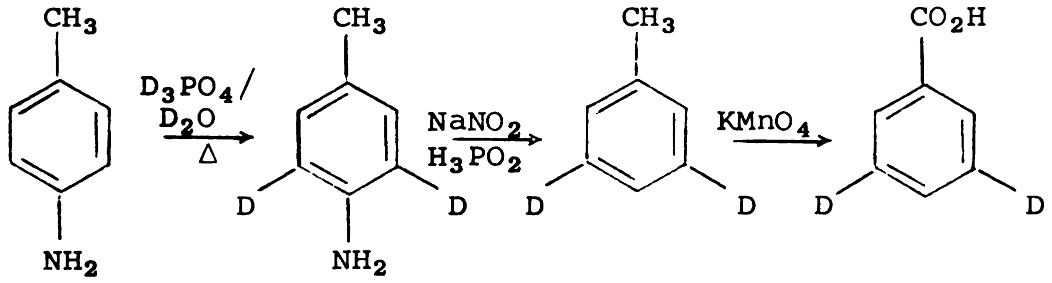
In addition to this nmr-charge density study, five new dioxolenium salts were synthesized and characterized. They are the monocationic 2-mesitoyl-1,3-dioxolenium tetrafluoroborate and the four dicationic salts 2,2'-(_o_-phenylene)bis-1,3-dioxolenium tetrafluoroborate, 2,2'-(1,8-naphthalene)-bis-1,3-dioxolenium tetrafluoroborate, 2,2'-(1,4-naphthalene)-bis-1,3-dioxolenium tetrafluoroborate and 2,2'-(_trans_-1,4-cyclohexane)bis-1,3-dioxolenium tetrafluoroborate. The reasons for synthesizing each of these particular dioxolenium compounds will be presented in the Results and Discussion Section.

RESULTS AND DISCUSSION

A. The NMR Spectrum of and Charge Distribution in the 2-Phenyl-1,3-dioxolenium Cation.

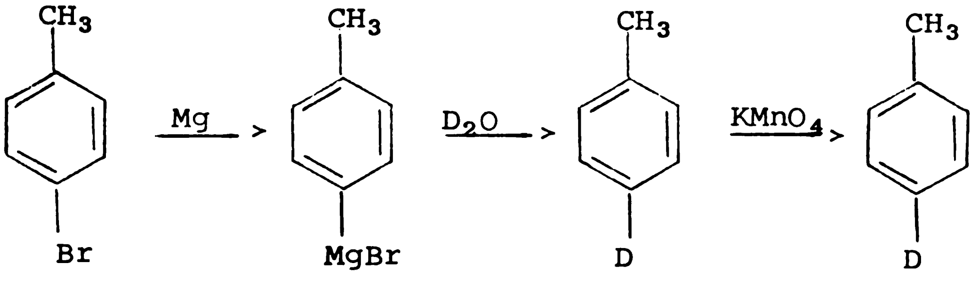
We wanted to determine the proton chemical shifts for the aromatic protons of the 2-phenyl-1,3-dioxolenium cation, and correlate them with the charge densities at the corresponding positions on the phenyl ring. For this purpose we decided to prepare 2-(phenyl-3,5-d_2)-1,3-dioxolenium cation and 2-(phenyl-4-d)-1,3-dioxolenium cation, so that the chemical shifts of the *ortho*, *meta* and *para* protons could be uniquely assigned.

The first step in the synthesis of these ions was the preparation of benzoic-3,5-d_2 acid and benzoic-4-d acid. The protons *ortho* to the amino group of *p*-toluidine (**6**) were easily replaced by deuterium when **6** was heated with a 50:50 mixture of phosphoric-d_3 acid and deuterium oxide, yielding *p*-toluidine-2,6-d_2 (**7**). Compound **7** was reduced to toluene-3,5-d_2 (**8**) with sodium nitrite and hypophosphorous acid. Benzoic-3,5-d_2 acid (**9**) was obtained by the oxidation of **8** with potassium permanganate. The nmr spectrum of **9** consisted of two singlets at τ 2.54 (1H) and 1.96 (2H). The areas allow these shifts to be assigned to the para and ortho protons respectively.



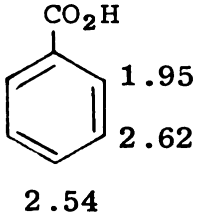
6 7 8 9

To prepare benzoic-4-d acid (13) we started with p-bromotoluene (10) which was converted to the corresponding Grignard reagent (11). This was decomposed by deuterium oxide to yield toluene-4-d (12) which on oxidation with potassium permanganate gave 13. Compound 13 was characterized by its nmr spectrum which consisted of two doublets at τ 2.62 (2H, *J* = 8.25 Hz) and at 1.94 (2H, *J* = 8.25 Hz), which can be assigned to the meta and ortho protons respectively.

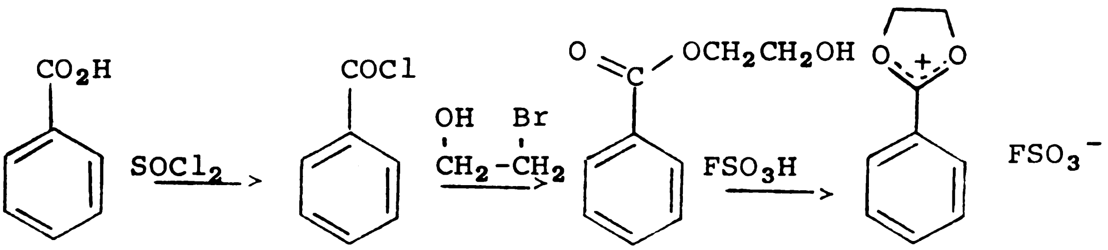


10 11 12 13

The assignments of chemical shifts for benzoic acid are therefore as shown:

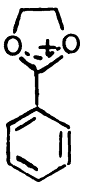
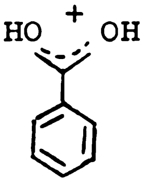
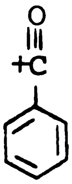


The deuterated benzoic acids were converted to the acid chlorides by reaction with thionyl chloride. The corresponding 2-hydroxyethyl esters were prepared by refluxing a solution of the acid chlorides, in methylene chloride, with ethylene glycol until the evolution of hydrogen chloride had ceased. The 2-hydroxyethyl esters of benzoic acid, on addition of fluorosulfonic acid, form the 2-phenyl-1,3-dioxolenium cation instantly.



The exact chemical shifts for the <u>ortho</u> and <u>para</u> protons on the phenyl ring were obtained from the nmr spectrum of 2-(phenyl-3,5-d_2)-1,3-dioxolenium cation and the chemical shifts for the <u>meta</u> and <u>ortho</u> protons were obtained from the nmr spectrum of 2-(phenyl-4-d)-1,3-dixolenium cation. The chemical shifts are given in Table I. They were found to be almost identical to those of protonated benzoic acid, as reported by Farnum.[19]

Table I. Proton nmr chemical shifts of some phenyl carbonium ions.

Compound	Chemical Shifts, τ values		
	ortho	meta	para
 [a]	1.72	2.24	1.97
 [b]	1.72	2.24	1.94
 [c]	1.44	2.01	1.13

[a] Observed.

[b] D. G. Farnum, J. Am. Chem. Soc., 89, 2970 (1967).

[c] Formed in fuming sulfuric acid containing 20-25% SO_3.

It has been reported by Traficante[20] that benzoic acid, when dissolved in 95-100% sulfuric acid forms protonated benzoic acid but when it is dissolved in sulfuric acid containing 10-35% sulfur trioxide it forms the corresponding acylium ion. The chemical shifts for the aromatic protons of this acylium ion have not yet been reported. Since we had benzoic-3,5-d_2 acid ($\utilde{9}$) and benzoic-4-d acid ($\utilde{13}$) on hand, we decided to determine the exact chemical shifts of the *ortho*, *meta* and *para* protons of this acylium ion. The labeled benzoic acids were dissolved in sulfuric acid containing 20-25% sulfur trioxide to form 5% solutions. The nmr spectra were recorded. The chemical shifts obtained are given in Table I.

It was not surprising to find that the chemical shifts for the aromatic protons of the 2-phenyl-1,3-dioxolenium cation were nearly identical to those of protonated benzoic acid. Both of these cations are dioxycarbonium ions. The difference between the two is that the protons on the oxygen in protonated benzoic acid are replaced by an ethylene bridge in the dioxolenium cation. This change apparently has little effect on the aromatic protons.

It was our goal to calculate the charge densities at the various positions in the phenyl ring using molecular orbital methods, and to correlate these calculated parameters with the observed proton nmr chemical shifts. Tomalia and Hart[17] have already demonstrated a quantitative relationship between the proton nmr chemical shifts of the aliphatic protons and the corresponding Hammett σ values for *meta* and *para* substituted 2-phenyl-1,3-dioxolenium cations. Since Jaffe[21] has shown the Hammett σ values are proportional to the electron charge densities, there should be a correlation between the proton nmr chemical shifts for the aromatic protons of 2-phenyl-1,3-dioxolenium cation and the π electron densities at the carbon atoms to which they are attached. Such correlation has been demonstrated before.[22,23,24]

The π electron densities were calculated by a variation of the Hückel molecular orbital method known as the "ω-technique." The calculations were carried out with a 3600 Control Data Corporation computer using a program written by Professor R. S. Schwendeman of the Department of Chemistry, Michigan State University. The coulomb integral, which is a function of the nuclear charge of the atom, was taken as a constant value, α_0, for the carbon atom. The resonance integral is related to the degree of overlap and is constant for a given overlap between two carbon "p" orbitals at a given distance. The resonance integral was taken as a constant, β_0, for the carbon atom. A change in the atomic number of an atom affects both the coulomb and resonance integrals. The relationship for the new values of these integrals can be expressed in terms of α_0 and β_0 as

$$\alpha = \alpha_0 + h\beta_0 \tag{1}$$

$$\beta = k\beta_0 \tag{2}$$

where h and k are constants that depend upon the hetero-atom which replaces carbon. It was necessary to select appropriate values of h and k for the oxygen atoms and the bonds to oxygen in the 1,3-dioxolenium ions. There is some question about what are the most suitable values to use.

Streitwieser's[25] recommended value for h is 2.5, for positively charged oxygen. This value is suggested for use with the HMO method only. The use of the ω-technique requires this value to be adjusted for the best fit. The value of h used for this work is 3.7. The value of k was taken as 0.9. This value is intermediate between the value recommended for a carbon-oxygen single bond (0.8) and that for a carbon-oxygen double bond (1.0).[25] This choice is based on the suggestion of Sandorfy[26] that the value of k is a simple function of bond length.

The "ω-technique" was used here because it allows the coulomb integral to be adjusted for changes in charge on each atom. Wheland and Mann[27] proposed that the value of α should be linearly related to the charge and may be formulated as:

$$\alpha = \alpha_0 + (1 - q_r)\omega\beta_0 \qquad (3)$$

where "ω" is a dimensionless parameter whose value may be so chosen as to give best agreement with experiment. The value $\omega = 1.4$ seems to be well accepted and was used here. The total electron density at an atom is taken as q_r and is defined as:

$$q_r = \sum_j n_j c_{jr}^2 \qquad (4)$$

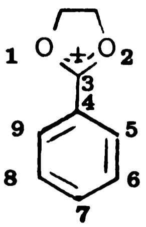
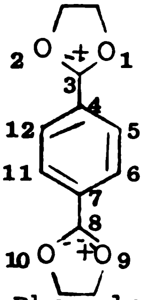
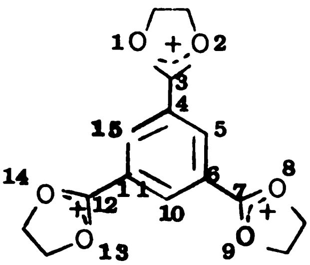
c_{jr} is the coefficient of atom r in the jth MO, which is occupied by n_j electrons. The sum is taken over all the molecular orbitals. In an all-carbon system each atom contributes a nuclear charge of +1 to the π system; hence the net charge ζr is

$$\zeta r = 1 - q_r \qquad (5)$$

In the ω-technique the calculated π-electron densities are substituted in equation (3) and the molecular orbital calculations repeated. This process is iterative, and is continued until the values for the molecular energy levels and charges on the atoms converge to constant values. The program does this automatically, it being only necessary to specify the number of iterations. The details for punching the data cards have been described by Young.[28] The results are recorded in Table II.

Fraenkel et. al.[22] demonstrated a linear relationship between the proton chemical shifts of cyclopentadienyl anion, benzene and tropylium cation and the net charge on the carbon atom. Benzene was chosen as the reference base, both for the proton chemical shifts, δ, and for the net charge density ζ. Thus since the π-electron density on the carbon atom in benzene is unity, $\zeta = 0$. We adopt the further convention that δ is positive for proton resonances appearing at higher field than the benzene resonance and negative for resonances at lower field. Since benzene was the reference, the chemical shifts of cyclopentadienyl anion and the tropylium cation had to be corrected for ring current effects. A correction of -0.11 ppm and +0.6 ppm was calculated for cyclopentadienyl anion and the tropylium cation respectively, using Pople's model.[22]

Table II. Calculated charge densities and proton chemical shifts of some ions.

Compound		Charge Density	Proton Chemical Shift (δ)
Cyclopentadienyl Anion		-0.2000	-2.22
Benzene		0	0
Tropylium Cation		+0.1428	1.60
2-Phenyl-1,3-dioxolenium Cation			
	1,2	-0.8516	
	3	0.3912	
	4	0.0180	
	5,9	0.0797	0.91
	6,8	0.0282	0.39
	7	0.0780	0.69
2,2'-*p*-Phenylenebis-1,3-dioxolenium Cation			
	1,2,9,10	-0.8392	
	3, 8	0.4238	
	4, 7	0.0643	
	5,6,11,12	0.0952	1.35
2,2',2"-Phenylenetris-1,3-dioxolenium Cation			
	1,2,8,9,13,14	-0.8415	
	3,7,12	0.4200	
	4,6,11	0.0515	
	5,10,15	0.2115	2.21

Benzene is taken as the reference (δ = 0) for these chemical shifts.

The chemical shifts of the cyclopentadienyl anion and the tropylium cation should also be corrected for the effect of the charge on the carbon atom to which the hydrogen atom is bonded. This charge effect changes the electron density on the hydrogen atom. Musher[29] has corrected the chemical shifts for this charge effect, by calculating the change in nuclear magnetic shielding ($\Delta\sigma$) using equation 6.

$$\Delta\sigma = -2.9 \times 10^{-12} E_z - 7.38 \times 10^{-19} E^2 \qquad (6)$$

Where E is the electric field and E_z is the field along the bond axis. When the corrected chemical shifts were plotted versus the net charge, a straight line with a slope of 11.2 ppm/electron was obtained. From this linear correlation we obtain:

$$\delta = \zeta k \qquad (7)$$

When the calculated charge densities for the 2-phenyl-1,3-dioxolenium cation were plotted versus the proton chemical shifts (see Figure 1) they fitted the plot for cyclopentadienyl anion, benzene and tropylium cation only moderately well. The deviation can be explained by the fact that besides the altered electron density other factors can also contribute to the proton resonance shift. These additional contributions may be due to:

a. the magnetic anisotropy of substituents or hetero atoms in the aromatic ring;

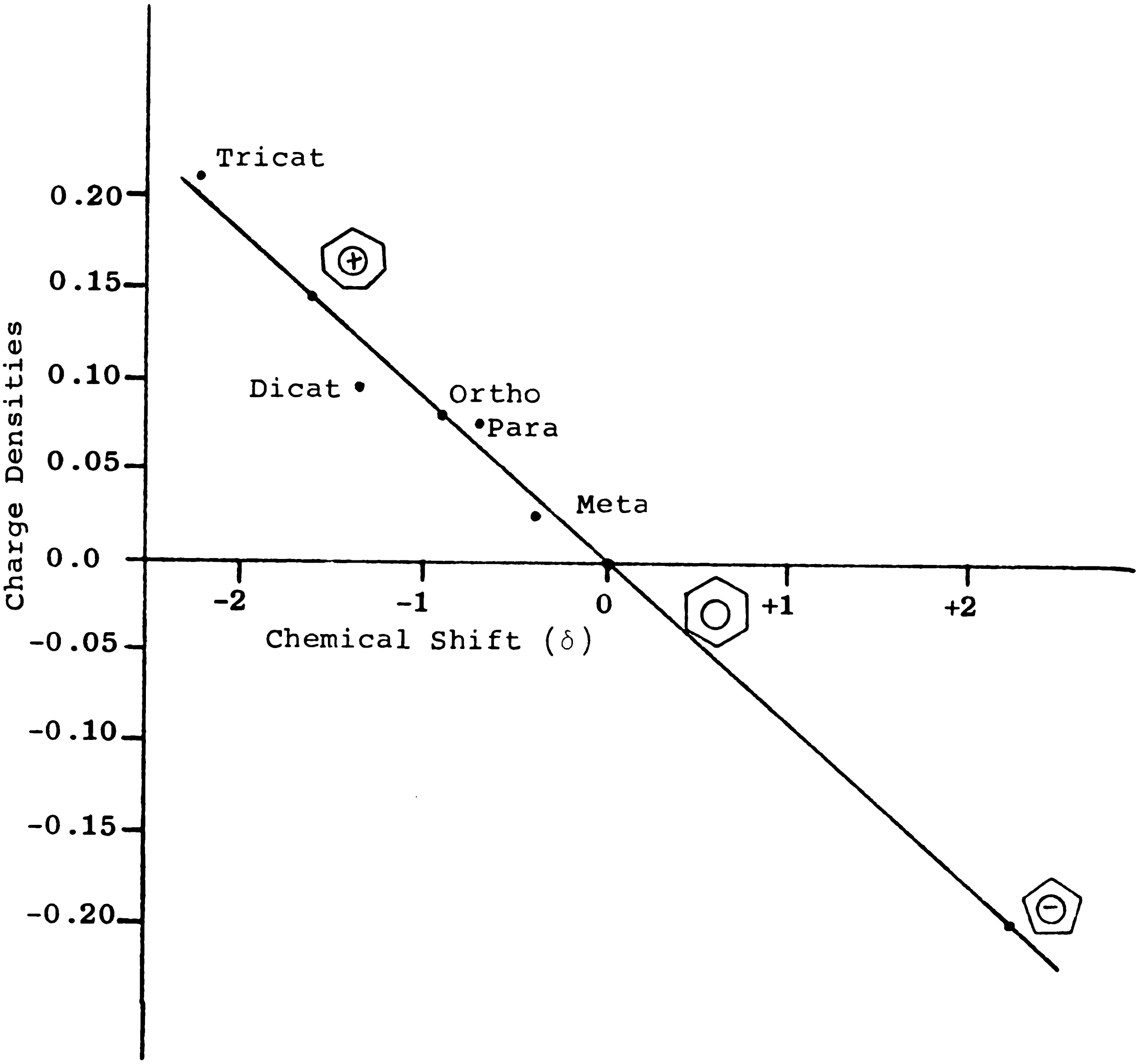


Figure 1. Calculated charge densities *versus* chemical shifts.

b. ring current effects of neighboring rings in the polycyclic aromatic compounds;

c. ion association effects of aromatic ions, and

d. solvent effects.

The magnitude of the proton resonance shift arising from the magnetic anisotropy of the substituent groups in individual molecules cannot be estimated with sufficient accuracy at present to permit a satisfactory correction with measured shifts. Since this contribution has a $1/R^3$ dependence, it will effect primarily those protons in the molecule that are close to the anisotropic center. Thus the anisotropic effect of the dioxolenium ring would mainly effect the <u>ortho</u> aromatic protons.

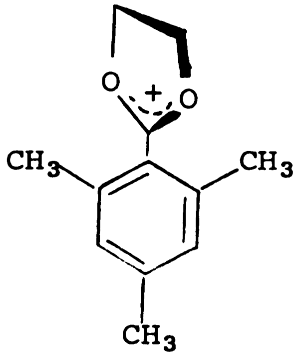
The ring current effects[22] can be dealt with more readily. Since benzene has been chosen as the reference, no correction is required for benzenoid systems.

With aromatic positive and negative ions, an association with counterions in solution may be anticipated. The counterion causes a shift in proton resonance of the aromatic ion. Introduction of bulky groups which would hinder association with counterions would lower this effect. Solvent effects also contribute to the observed chemical shift.[30] By the use of a solvent with a high dielectric constant and dilute solutions counterion and solvent effects can be minimized. A 5% solution of 2-phenyl-1,3-dioxolenium cation in fluorosulfonic acid was used to avoid solvent effects.

The charge densities of the dication and trication were also calculated and plotted against the proton chemical shifts (Table II and Figure 1). A qualitative correlation between charge densities and proton chemical shifts was observed. However, until precise calculations can be done to determine the degree to which other factors contribute to the observed chemical shifts a quantitative correlation of charge density with the chemical shift will not be obtained.

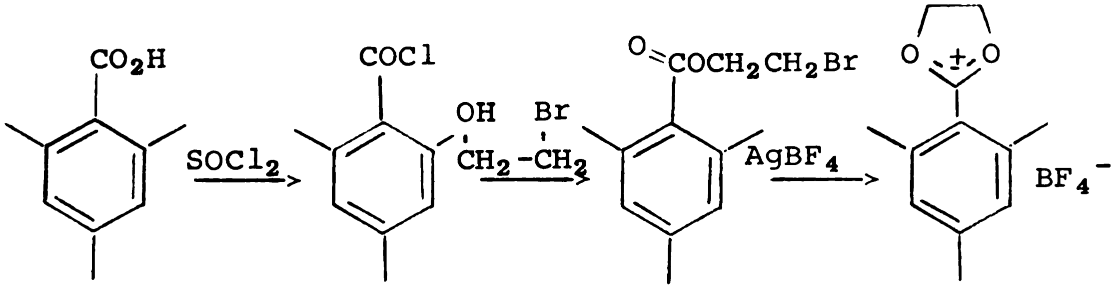
B. Preparation of Some New Dioxolenium Cations.

The preparation of some new aryl dioxolenium cations with ortho substituents was undertaken to study their effect on the geometry of the dioxolenium cations. Others were prepared to compare their nmr spectra with those of known dioxolenium cations. The first ion studied was the 2-mesitoyl-1,3-dioxolenium cation (**14**) (as the tetrafluoroborate), because we expected that the two ortho methyl groups might restrict the rotation of the dioxolenium ring and prevent it from becoming coplanar with the aromatic ring. The noncoplanarity of the two rings (structure **14**) might encourage the concentration of the charge in the dioxolenium ring and this would be reflected in a lower field shift for the proton resonance of the dioxolenium ring protons. In fact there was some doubt that the dioxolenium cation would form if coplanarity was not possible.



14

For the preparation of 14, mesitoic acid (15) was converted to mesitoyl chloride (16) by treatment with thionyl chloride. An attempt to make 2-hydroxyethyl mesitoate, a possible precursor of the desired cation, by refluxing 16 with ethylene glycol was unsuccessful; instead, the dimesitoate of ethylene glycol was obtained. However, 2-bromoethyl mesitoate 17 was readily prepared by refluxing a solution of 16, in carbontetrachloride, with 2-bromoethanol. Cation 14 was made from 17 according to Meerwein's procedure,[8] by the addition of anhydrous silver tetrafluoroborate to a vigorously stirred solution of 17 in methylene chloride. A yellow precipitate, which consisted of silver bromide and the salt of 14, formed immediately. The precipitate was suspended in acetonitrile; silver bromide, being insoluble, was removed by filtration. When anhydrous ether was added to the acetonitrile filtrate, the salt of cation 14 precipitated out of solution as a white solid.



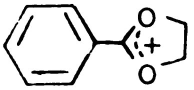
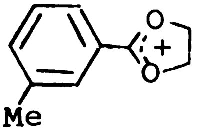
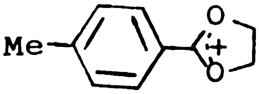
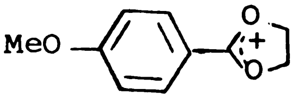
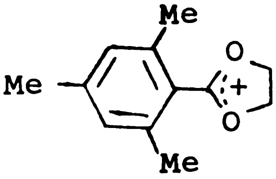
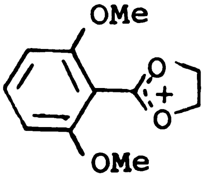
15 **16** **17** **14**

The other dioxolenium cations were made by the same procedure used for the preparation of **14**. In all the cases we started with the corresponding aromatic acids. Different solvents were used for the separation of the dioxolenium cations from silver bromide in each case. These are reported in the Experimental section.

The nmr spectrum of **14** (Figure 3) consisted of singlets at τ 7.70 (3H, *para* methyl group), 7.48 (6H, *ortho* methyl groups), 4.67 (4H, ring protons), and 2.94 (2H, aromatic protons). Comparison with related ions[17] (Table III) shows that the chemical shift of the dioxolenium ring protons of **14** is not affected in any unusual way by the two *ortho* methyl groups.

The chemical shift of dioxolenium ring protons is directly proportional to the net charge in the dioxolenium ring, which in turn depends on the nature and the position of the aryl substituent. If the substituent has a positive inductive effect and is substituted in the *para* position where a resonance contribution is also possible, it tends

Table III. Proton nmr chemical shifts for 2-aryl-1,3-dioxolenium cations .

Compound	Solvent	Chemical Shifts, τ Values		
		Ring Protons	Aromatic Protons	Other Protons
 (18)[a]	FSO_3H	4.58	2.45-1.53	
 (19)[a]	FSO_3H	4.60	2.57-1.76	CH_3- 7.53
 (20)[a]	FSO_3H	4.63	2.55 1.80(d)	CH_3- 7.45
 (21)[a]	FSO_3H	4.67	2.73 1.69(d)	CH_3O- 5.92(s)
 (14)	CF_3CO_2H	4.67	2.94(s)	p-CH_3- 7.70(s) o-CH_3- 7.48(s)
 (22)[b]	CF_3CO_2H	4.77	2.27(s)	CH_3O- 6.06(s)

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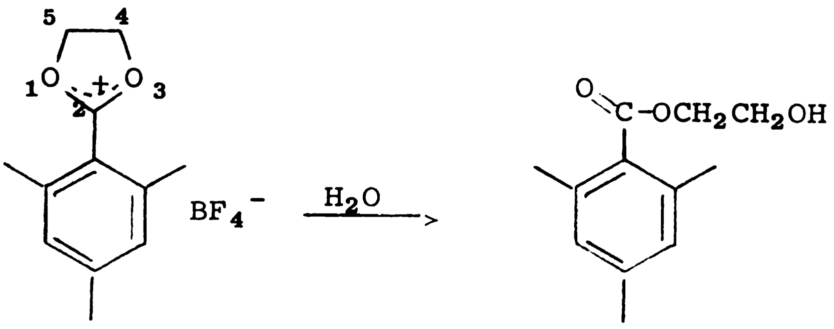
[a] D. A. Tomalia and H. Hart, Tetrahedron Letters, 29, 3383 (1966).

[b] F. M. Beringer and S. A. Gatton, J. Org. Chem., 32, 2630 (1967).

to reduce the charge in the dioxolenium ring. This would result in a higher field shift of the dioxolenium ring proton resonance. If the substituent is in the *meta* position on the phenyl ring, only the inductive effect is significant. This explains the higher field appearance for the ring proton resonance of 20 compared to 19 (Table III). A similar conclusion is reached for ion 21; methoxyl is a better electron donor than methyl, if the resonance effect is significant. It is noted, however, that the magnitude of these substituent effects is very small. Therefore delocalization of the charge into the aryl ring cannot be an overriding factor in the stabilization of these ions. For this reason, it is not surprising that one can prepare ions such as 14 and 22, with two *ortho* substituents. Due to the positive inductive effect of the methyl groups of 14, even the *meta* aromatic protons of this compound (τ 2.94) are more shielded than those of 2-phenyl-1,3-dioxolenium cation (18, τ 2.24).

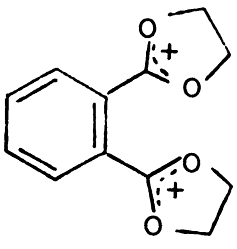
Cation 14 was hydrolyzed with ice cold water in order to find out if the nucleophile would attack 14 at C_2 or at either C_4 or C_5 to give the ring opened product, 2-hydroxyethyl mesitoate (23). Ester 23 was obtained on hydrolysis. It was characterized by its nmr spectrum (CCl_4) which consisted of a singlet at τ 7.82 (9H, methyl groups) and two triplets at 6.64 (2H, *J* = 4 Hz) and 5.81 (2H, *J* = 4 Hz) for the two nonequivalent methylene groups. The aromatic protons were observed at τ 3.33 (s, 2H). The ir spectrum (CCl_4) had bands at 1721 (C=O) and at 3580 cm^{-1} (OH). The chemical analysis was in good agreement for a molecular formula of $C_{12}H_{16}O_3$.



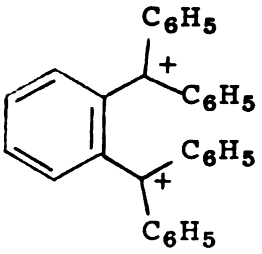
14

23

The preparation of 2,2'-(o-phenylene)bis-1,3-dioxolenium tetrafluoroborate (24) was undertaken because the corresponding para and meta dicarbonium ions are known[17] and we were interested in finding out if 24 could be made, because dication 24 has two positively charged moieties on neighboring carbon atoms which might have a destabilizing effect. Some difficulty was anticipated in the formation of 24 because a difference of 10^6 in the pK_{R^+} of formation of dication 25 as compared to the meta and para analogs has been reported.[31] The reasons given for this observation were that the steric

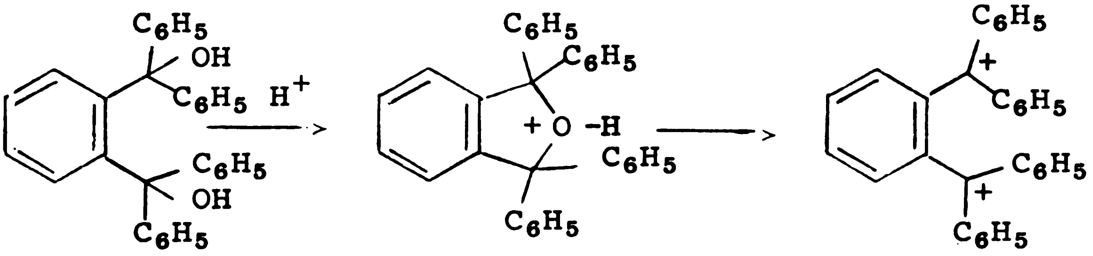


24



25

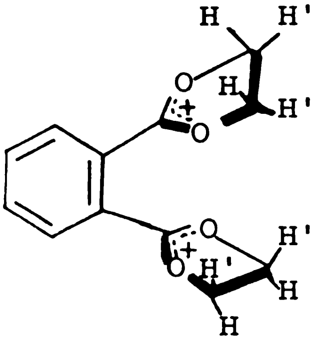
effects limit the geometries available to 25; also, the proximity of two positive charges in 25 may have a destabilizing effect. The formation of dication 25 occurs in two steps from tetraphenyl-*o*-xylene glycol (26). First the monocation 27 is formed. The major factor for the difficulty



26 27 25

in forming 25 is attributed to the larger energy difference between the monocation 27 and dication 25 as compared to the energy difference between the monocations and dications obtained from the tetraphenyl *para* and *meta* xylene glycols. This larger energy difference is due to oxygen participation, which is possible only in the *ortho* monocation.

There was also some question that the two *ortho* substituted dioxolenium rings of 24 may interact with one another and thus restrict the geometries available to 24. In case the geometry of 24 approaches structure 28 we would have two sets of equivalent protons (H and H') on the dioxolenium rings and one would not expect to observe a singlet in the nmr spectrum for the dioxolenium ring proton resonance.

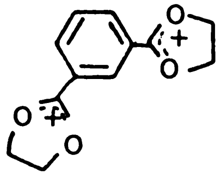
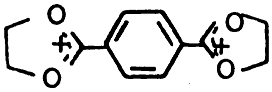
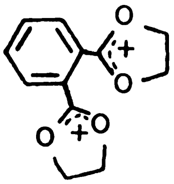
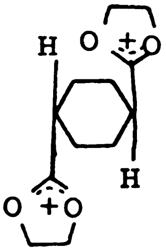
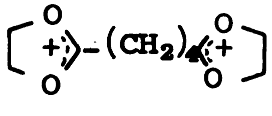


28

No difficulty was experienced during the preparation of 24. The dioxolenium ring proton resonance was observed as a sharp singlet at τ 4.33, indicating that no serious interactions of the dioxolenium rings was present.

As mentioned earlier, the proton resonance of the dioxolenium ring protons depends on the nature and the position of the aryl substituent. In the case of 24, 29, and 30 (Table IV) let us consider one of the dioxolenium rings to be part of the 2-aryl-1,3-dioxolenium cation structure and the other dioxolenium ring to be the substituent. The substituent in this case has a <u>negative</u> inductive and resonance effect, which increases the charge in the dioxolenium ring. For 29 only the inductive effect would be significant whereas in 30 both the inductive and resonance effects can operate. This is reflected by the lower field proton resonance of the dioxolenium ring of 30 compared to that of 29. For 24, the inductive effect would be stronger than in 30 as this effect is inversely proportional to the distance of the substituent from the reaction site. For

Table IV. Proton nmr chemical shifts of some dioxolenium dications.

Compound	Solvent	Chemical Shifts, τ Values	
		Ring Protons	Other Protons
 [a] (29)	FSO_3H	4.40	1.97-0.74(m)
 [a] (30)	FSO_3H	4.37	2.28 (s)
 (24)	FSO_3H	4.33	1.88-1.15(m)
 (31)	CF_3CO_2H	4.68	8.78-7.50(m)
 [b] (32)	FSO_3H	4.64	7.98(m) 6.90(m)

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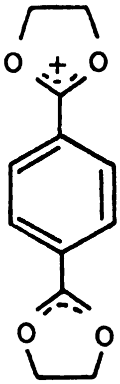
[a] D. A. Tomalia and H. Hart, Tetrahedron Letters, 29, 3389 (1966).

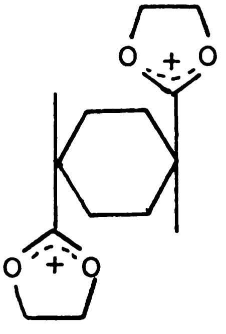
[b] D. A. Tomalia, Ph.D. Thesis, Michigan State University, East Lansing, Michigan, 1967.

this reason the dioxolenium ring proton resonance of 24 is observed lower field to that of 30. Resonance effects in 24 are probably not very important because of the difficulty in attaining planar conformations. This difficulty is insufficient, however, to result in two different chemical shifts for the aliphatic protons.

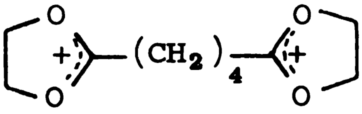
The purpose of making 2,2'-(trans-1,4-cyclohexane)bis-1,3-dioxolenium tetrafluoroborate (31) was to compare it with its unsaturated analog (30). As expected the ring protons of 30 were more deshielded than in 31 (Table IV), since the effect of the second positive charge, on the ring protons, can be transmitted more effectively by the π electrons of 30 than through the σ bonds of 31. However the ring proton resonance of 31 is comparable to that of 32. In both these cases the dioxolenium rings are separated by four methylene groups.



30



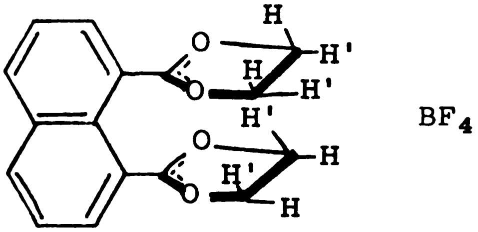
31



32

As before 31 was hydrolyzed and just enough material was obtained to record the ir spectrum which showed bands at 1715 (C=O) and 3500 cm^{-1} (OH). This experiment was conducted to show that the carbonium ion had indeed formed, and could be trapped by the hydroxyl anion.

The 2,2'-(1,8-naphthalene)bis-1,3-dioxolenium tetrafluoroborate (33) was made because it was expected that the steric interference of the two dioxolenium rings would be more serious than in 24, and in fact the rings might be locked in a position where they would be bisected by the naphthalene ring as shown below.

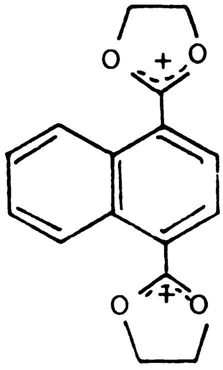


33

In this position we would have two sets of equivalent protons, H and H'. Thus one would expect a different pattern in the nmr spectrum of 33 than the usual singlet signal, for the proton resonance of the ring protons. However the ring proton resonance once again was a singlet in the nmr spectrum. Therefore the dioxolenium rings probably do not interfere with each other. Dication 33 was made by the same general procedure, from the bis-bromoethyl ester. Fluorosulfonic acid could not be used to extract this cation from the combined precipitate of silver bromide and 33, as it sulfonates the naphthalene ring. The nmr spectrum in fluorosulfonic acid consisted of two sets of multiplets in the aromatic region at τ 0.85 and 1.62. The chemical shift is lower than would be expected for the aromatic protons; also the dioxolenium ring protons appeared as three singlets at τ 4.42, 4.73 and 5.24 in a ratio of 1:1.36:2.33. It is suspected that the fluorosulfonic acid attacked the naphthalene ring because the nmr spectrum in acetonitrile consisted of a singlet at τ 4.56 (8H) and a multiplet at 2.52-1.68 (6H). All attempts to make 33 from bis-2-bromoethyl 1,8-dinaphthoate using 'magic' acid were unsuccessful.

Dication 33 was hydrolyzed by the usual procedure and just enough of the product was recovered to obtain the ir spectrum (CCl_4) which showed bands at 1710 (C=O) and 3505 cm^{-1} (OH).

In order to compare the nmr spectrum of 33 with another naphthalene dication, 2,2'-(1,4-naphthalene)bis-1,3-dioxolenium tetrafluoroborate (34) was prepared.



34

The dioxolenium ring proton resonance of 34 was observed at τ 4.55 which is very close to that of 33 (τ 4.56). It was expected that the ring protons of 34 would be more deshielded than those of 33 because the two dioxolenium rings are on the same aromatic ring in 34 and the effect of the second ring would be more effective at withdrawing charge in this position. However, proximity effects, which are more severe in **33**, may account for the lower than expected chemical shift of the dioxolenium ring protons.

EXPERIMENTAL

A. General

1. Microanalyses: Microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

2. Nuclear Magnetic Resonance Spectra: These spectra were recorded on a Varian Model A-60 instrument using tetramethylsilane as an internal standard. For carbonium ion solutions tetramethylammonium tetrafluoroborate was taken as the internal standard and its chemical shift was taken as τ 6.9.[32]

3. Infrared Spectra: Infrared spectra were obtained on a Unicam SP 200 spectrophotometer. The positions of all bands were measured from the nearest polystyrene calibration point (2851, 1603, 1495, 1029 cm^{-1}).

4. Solvents: Anhydrous methylene chloride and acetonitrile were prepared by distilling these solvents from phosphorus pentoxide; they were stored over molecular sieve type 5A.

5. Miscellaneous: The preparation of the tetrafluoroborates was carried out in a dry box equipped with two dishes of phosphorus pentoxide.

B. Preparation of 2-(Phenyl-3,5-d_2)-1,3-dioxolenium Tetrafluoroborate

1. *p*-Toluidine-2,6-d_2 (**7**): *p*-Toluidine (12 g, 0.124 mole) was added to a 50:50 mixture of deuterated phosphoric acid and deuterium oxide, which was prepared by combining 56.19 g (0.396 mole) of phosphorus pentoxide and 48 ml of deuterium oxide. The resulting mixture was placed in a pyrex tube which was degassed, sealed, and heated at 110^0 in an oil bath for 24 hr. The tube was then cooled to -78^0, and opened. The contents were transferred to a beaker and neutralized with sodium bicarbonate. The resulting mixture was extracted with 150 ml of ether. The ethereal extract was washed with water, dried (Na_2SO_4) and concentrated to give 11 g (91.5%) of *p*-toluidine. An nmr analysis indicated that 90% of the hydrogens in the 3 and 5 positions had been exchanged for deuterium. The procedure was repeated with the product but only 95% deuterium could be obtained in the 3 and 5 positions: nmr (CCl_4): τ 7.82 (s, 3H), 6.71 (s, 2H), 3.14 (s, 2H).

2. Toluene-3,5-d_2 (**8**): *p*-Toluidine-3,5-d_2 (10.7 g, 0.1 mole), 40 ml of concentrated hydrochloric acid and 25 ml of water were placed in a one liter flask. To the cooled (ice bath), magnetically stirred mixture was added slowly a solution of 7.25 g (0.102 mole) of sodium nitrite in 20 ml of water, so that the temperature was maintained between -5^0 to 0^0. As the reaction proceeded the mixture became more fluid and the nitrite was added more quickly; 0.5-0.75 hr

was required for diazotization. Hypophosphorous acid (50%, 156 ml, 1.5 mole) was added to the diazonium solution over fifteen min at 0°. Moderate stirring at a temperature between -5° to 0° was continued for an additional hour; the flask was then stoppered and placed in the refrigerator for 24 hr. The reaction product consisted of an orange oil floating on an aqueous phase. The oil was separated and the aqueous solution was washed with two portions of ether. The combined oil and ether extracts were washed with 20% aqueous sodium hydroxide, then with water, dried over potassium carbonate and distilled, to give 7.75 g (79%) of toluene-3,5-d_2 [Lit.[33] 70-75% yield]; nmr (CCl_4): τ 7.7 (s, 3H), 2.88 (s, 3H).

3. Benzoic-3,5-d_2 Acid (**9**): In a two-liter, three-necked flask fitted with a thermometer and a condenser was placed 10 g (0.109 mole) of **8** and 750 ml of water. The mixture was heated to 95° and 34.5 g (0.218 mole) of potassium permanganate was added at this temperature. The reaction mixture was maintained at 100°. After 8 hr, the reaction mixture had decolorized completely. The unoxidized toluene was removed by steam distillation. The brown residue that had formed was filtered and extracted twice with 100-ml portions of hot water. The filtrate and the water extracts were concentrated to 200 ml and acidified with conc hydrochloric acid. Benzoic acid precipitated from the solution giving 7.45 g (56%) [Lit[34] 90% yield]; nmr (CCl_4): τ 2.59 (s, 1H) and 2.04 (s, 2H).

4. <u>2-Hydroxyethyl Benzoate-3,5-d_2</u>: Benzoic-3,5-d_2 acid (9) (1.5 g, 0.0123 mole) was placed in a 50-ml round-bottomed flask and a few drops of thionyl chloride, just enough to 'wet' the benzoic acid, were added. The mixture was heated on a steam bath until no more hydrogen chloride or sulfur dioxide was evolved. An excess of ethylene glycol (3 g, 0.0485 mole) was added to the benzoyl chloride formed above and the mixture was refluxed for 5 hr until the evolution of hydrogen chloride had ceased. Excess ethylene glycol was distilled at 59° (~0.5 mm) and 2-hydroxyethyl benzoate-3,5-d_2 distilled at 103-105° (1.0 mm) to give 1.28 g (62%).

5. <u>2-(Phenyl-3,5-d_2)-1,3-dioxolenium Cation</u>: 2-Hydroxyethyl benzoate-3,5-d_2 (20 mg) was placed together with tetramethylammonium tetrafluoroborate (5 mg) in an nmr tube. Fluorosulfonic acid (0.4 ml) was added to form a 5% solution. The dioxolenium cation formed instantly; nmr (FSO_3H): τ 4.54 (s, 4H), 2.01 (s, 1H), 1.72 (d, 2H, J = 1.2 Hz, ortho protons).

C. Preparation of 2-(Phenyl-4-d)-1,3-dioxolenium Cation:

1. <u>Toluene-4-d (12)</u>: Magnesium turnings (7.2 g, 0.296 atom) were placed in a three-necked, one-liter flask fitted with a reflux condenser and dropping funnel. The equipment was dried by passing dry nitrogen through it for one hour. Anhydrous ether (50 ml) was added to the magnesium turnings. A solution of 45.6 g (0.264 mole) of *p*-bromotoluene in 150 ml of anhydrous ether was added slowly to the magnesium. The

mixture was refluxed for 2 hr over a steam bath. Deuterium oxide (5.2 ml, ~0.264 mole) was added slowly over 30 min. The reaction mixture was allowed to stand for another 30 min. Excess iodine was added to decompose any unreacted Grignard reagent. Toluene-4-d was distilled to give 11 g (44.8%): bp 110°; nmr (CCl_4): τ 7.7 (s, 3H), 2.88 (s, 4H).

2. Benzoic-4-d Acid (13): Toluene-4-d was oxidized by the same procedure as that described for toluene-3,5-d_2: yield 56%; nmr (CCl_4): τ 2.59 (d, 2H, *J* = 8.25 Hz), 1.94 (d, 2H, *J* = 8.25 Hz).

3. 2-Hydroxyethyl Benzoate-4-d: The procedure used here was the same as described for 2-hydroxyethyl benzoate-3,5-d_2: yield 62%.

4. 2-(Phenyl-4-d)-1,3-dioxolenium cation: 2-Hydroxyethyl benzoate-4-d (20 mg) was taken together with tetramethylammonium tetrafluoroborate (5 mg) in an nmr tube. To this was added 0.4 ml of fluorosulfonic acid to form a 5% solution. The dioxolenium cation formed instantly; nmr (FSO_3H): τ 4.54 (s, 4H), 2.25 (d, 2H, *J* = 8.3 Hz, meta protons), 1.72 (d, 2H, *J* = 8.3 Hz, ortho protons).

D. Preparation of 2-Mesitoyl-1,3-dioxolenium Tetrafluoroborate (14):

1. Mesitoyl Chloride (16): A mixture of 3.5 g (0.022 mole) of mesitoic acid (15) and 4.0 g (2.52 ml, 0.0336 mole) of thionyl chloride was placed in a 50-ml flask and refluxed

gently until the evolution of sulfur dioxide and hydrogen chloride ceased. Excess thionyl chloride was removed by distillation at atmospheric pressure, bp 79°. The acid chloride was distilled: bp 145-146° (60 mm). [Lit[35] bp 145-146° (60 mm)]. A quantitative yield was obtained.

2. Attempted Preparation of 2-Hydroxyethyl Mesitoate (23): Mesitoyl chloride (4.1 g, 0.022 mole) was dissolved in 25 ml of carbon tetrachloride. To this solution was added 1.36 g (0.022 mole) of ethylene glycol and the resulting solution was refluxed for 4 hr. The solution was concentrated and the residue obtained was crystallized from benzene. The product is thought to be the dimesitoate of ethylene glycol: mp 102-103°; ir (CCl_4): 1720 cm^{-1} (C=O); nmr (CCl_4): τ 7.79 (s, 18H, methyl groups), 5.48 (s, 4H, methylene protons), 3.28 (s, 4H, aromatic protons).

3. 2-Bromoethyl Mesitoate (17): To a solution of 10.25 g (0.055 mole) mesitoyl chloride in 50 ml of carbon tetrachloride was added 6.875 g (0.055 mole) of 2-bromoethanol. The resulting solution was refluxed for 4 hr, concentrated and distilled to give 13.7 g (50.5%) of 2-bromoethyl mesitoate: bp 106-108° (0.05 mm); ir (CCl_4): 1724 cm^{-1} (C=O); nmr (CCl_4): τ 7.75 (s, 9H), 6.51 (t, 2H, J = 6 Hz), 5.52 (t, 2H, J = 6 Hz), 3.26 (s, 2H). The nmr spectrum is shown in Figure 2.

Anal. Calcd for $C_{12}H_{15}O_2Br$: C, 53.11; H, 5.55; Br, 29.47.

Found: C, 53.19; H, 5.61; Br, 29.38.

4. 2-Mesitoyl-1,3-dioxolenium Tetrafluoroborate (14): A solution of 5.42 g (0.02 mole) of 2-bromoethyl mesitoate in 25 ml of mehtylene chloride was placed in a 125-ml erlenmeyer flask equipped with a magnetic stirrer. Powdered silver tetrafluoroborate (3.88 g, 0.02 mole) was added in one portion to the stirred ester solution, under anhydrous conditions. A yellow precipitate formed immediately. The reaction mixture was allowed to stir for an additional hour at room temperature. The precipitate, which consisted of silver bromide and the desired tetrafluoroborate, was extracted by anhydrous acetonitrile. The acetonitrile solution was filtered to remove insoluble impurities. The tetrafluoroborate was precipitated from the acetonitrile solution by addition of anhydrous ether. A yield of 2.04 g (38%) was obtained: nmr (CH_3CN): τ 7.70 (s, 3H), 7.48 (s, 6H), 4.67 (s, 4H), 2.94 (s, 2H). The nmr spectrum is shown in Figure 3.

Anal. Calcd for $C_{12}H_{15}O_2BF_4$: C, 51.84; H, 5.44.
Found: C, 51.78; H, 5.39.

5. 2-Hydroxyethyl Mesitoate (23): On adding 0.8223 g (0.00296 mole) of 2-mesitoyl-1,3-dioxolenium tetrafluoroborate (14) to 40 ml of ice cold water with stirring, a colorless oil formed which was extracted with ether and purified by vpc using a 5-ft column packed with 20% SE-30 on chromsorb W at 191^0 with a helium flow rate of 75 ml/min. The retention time was 9 min: ir (CCl_4): 1721 (C=O) and 3580 cm^{-1} (OH); nmr (CCl_4): τ 7.82 (s, 9H), 6.64 (t, 2H,

J = 4 Hz), 5.81 (t, 2H, *J* = 4 Hz), 3.33 (s, 2H).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.747.

Found: C, 68.98; H, 7.70.

E. Preparation of 2,2'-(*o*-Phenylene)bis-1,3-dioxolenium Tetrafluoroborate (24)

1. Phthaloyl Chloride: An intimate mixture of 8.4 g (0.05 mole) phthalic acid and 20.8 g (0.1 mole) of phosphorus pentachloride was heated at 100° for 4 hr. The phosphorus oxychloride which formed was distilled at atmospheric pressure (bp 105°). Phthaloyl chloride was distilled to give 10 g (50%): bp 91-93° (0.5 mm). [Lit[36] bp 270°].

2. 2-Bromoethyl Phthalate: To a solution of 4.06 g (0.02 mole) of phthaloyl chloride in 30 ml of methylene chloride was added 5 g (0.04 mole) of 2-bromoethanol. The resulting solution was refluxed for 5 to 6 hr until the evolution of hydrogen chloride had ceased. The solution was concentrated and distilled to give 4.375 g (56%) of 2-bromoethyl phthalate. The ester turns yellow on storage and should be used immediately: bp 191-193° (0.5 mm); nmr (CCl_4): τ 6.42 (t, 4H, *J* = 6.1 Hz), 5.44 (t, 4H, *J* = 6.1 Hz), 2.40 (s, 4H). The nmr spectrum is shown in Figure 4.

3. 2,2'-(*o*-Phenylene)bis-1,3-dioxolenium Tetrafluoroborate (24): A solution of 1.90 g (0.005 mole) of 2-bromoethyl phthalate in 10 ml of methylene chloride was placed

in a dry box. Powdered silver tetrafluoroborate (1.94 g, 0.01 mole) was added in one portion to the magnetically stirred ester solution. The mixture was stirred for 2 hr. The yellow precipitate which formed initially turned grayish as the reaction proceeded. The precipitate was filtered and washed with two 15-ml portions of methylene chloride. The dioxolenium cation was extracted with 10 ml of fluorosulfonic acid: nmr (FSO_3H): τ 4.33 (s, 8H), 1.88 - 1.15 (m, 4H). The nmr spectrum is shown in Figure 5.

F. Preparation of 2,2'-(*trans*-1,4-Cyclohexane)bis-1,3-dioxolenium Tetrafluoroborate (31):

1. *trans*-1,4-Cyclohexanedicarboxylic Acid Chloride: A mixture of 6 g (0.034 mole) of *trans*-1,4-cyclohexanedicarboxylic acid (Aldrich) and 24 ml of thionyl chloride was heated under reflux for 24 hr with the exclusion of moisture. Thionyl chloride was removed from the mixture under reduced pressure. The solution was distilled to give 5.8 g (78.4%) of the acid chloride: bp 84-86^{0} (0.1 mm); mp 67^{0}; [Lit[37] mp 67^{0}].

2. 2-Bromoethyl 1,4-Cyclohexanedicarboxylate: A solution of 5.8 g (0.078 mole) of 1,4-cyclohexanedicarboxylic acid chloride in 20 ml of methylene chloride was added slowly to a solution of 7.0 g (0.056 mole) of 2-bromoethanol in methylene chloride. The mixture was refluxed for 6 hr. The solution was concentrated to an oil which solidified on storage in a refrigerator. The solid was dissolved in Freon

114B2 from which 2.7 g (26%) of crystals of the dicarboxylate were obtained: mp 61-62°; ir (CCl_4): 1773 cm^{-1} (C=O); nmr (CCl_4): τ 8.78-7.75 (m, 10H), 6.54 (t, 4H, J = 6.5 Hz), 5.65 (t, 4H, J = 6.5 Hz). The nmr spectrum is shown in Figure 6.

Anal. Calcd for $C_{12}H_{18}Br_2O_4$: C, 37.34; H, 4.699; Br, 41.40.
Found: C, 37.32; H, 4.58; Br, 40.86.

3. 2,2'-(trans-1,4-Cyclohexane)bis-1,3-dioxolenium Tetrafluoroborate (31): The procedure used here was the same as that described for 9. 2-Bromoethyl-trans-1,4-cyclohexanedicarboxylate (1 g, 0.00259 mole) was used together with 1.008 g (0.00518 mole) of powdered silver tetrafluoroborate. The desired tetrafluoroborate was extracted with trifluoroacetic acid instead of fluorosulfonic acid: nmr (CF_3CO_2H): τ 8.78 - 7.50 (m, 10H), 4.68 (s, 8H). The nmr spectrum is shown in Figure 7.

4. 2-Hydroxyethyl trans-1,4-Cyclohexanedicarboxylate: The trifluoroacetic acid solution of 12 which was used to obtain the nmr spectrum, was added slowly to a well stirred solution of ice cold water (15 ml). The aqueous solution was neutralized ($NaHCO_3$) and extracted with ether. The ethereal extract was concentrated to yield 2-hydroxyethyl trans-1,4-cyclohexanedicarboxylate: ir ($CHCl_3$): 1715 (C=O) and 3500 cm^{-1} (OH).

G. Preparation of 2,2'-(1,8)Naphthalene)bis-1,3-dioxolenium Tetrafluoroborate (33)

1. 1,8-Naphthoyl Chloride: A mixture of 4 g (0.0185 mole) of 1,8-naphthalene dicarboxylic acid (K & K Laboratories), 6 g (0.0287 mole) of phosphorus pentachloride and 6 ml of phosphorus oxychloride was heated under reflux with the exclusion of moisture for 48 hr, formation of lumps being prevented by occasionally shaking the reaction flask during the first 24 hr. The unreacted acid was filtered and phosphorus oxychloride was distilled under reduced pressure at room temperature, from the filtrate. The acid chloride was extracted with 10 ml of dry carbon disulfide. On standing for a few hours the acid chloride crystallized from the carbon disulfide solution as pale yellow or colorless crystals. The mother liquor was drained and the crystals were washed with a few ml of solvent. Residual solvent was removed by evacuating the flask. A yield of 1.9 g (40.5%) was obtained: mp 83-85°. [Lit[38] mp 84-86°.]

2. 2-Bromoethyl 1,8-Dinaphthoate: A solution of 1 g (0.00395 mole) of 1,8-naphthoyl chloride in 10 ml of methylene chloride was refluxed with 0.99 g (0.0079 mole) of 2-bromoethanol until effervescence of hydrogen chloride had ceased. The methylene chloride was concentrated and the residue was crystallized from chloroform. A yield of 1.2 g (69%) of the diester was obtained: mp 105-106.5°; ir (CCl_4): 1716 cm^{-1} (C=O); nmr (CCl_4): τ 6.45 (t, 4H, *J* = 6.5 Hz), 5.45 (t, 4H, *J* = 6.5 Hz), 2.70-1.91 (m, 6H). The nmr spectrum is

shown in Figure 8.

Anal. Calcd for $C_{16}H_{14}Br_2O_4$: C, 44.64; H, 3.28; Br, 37.20.
Found: C, 44.52; H, 3.34; Br, 37.09.

3. 2,2'-(1,8-Naphthalene)bis-1,3-dioxolenium Tetrafluoroborate (33): A solution of 1 g (0.0023 mole) of 2-bromoethyl 1,8-dinaphthoate in 10 ml of methylene chloride was placed in a dry box in a 50-ml erlenmeyer flask equipped with a magnetic stirrer. To this solution was added 0.895 g (0.046 mole) of powdered silver tetrafluoroborate. The resulting solution was stirred for 4 hr. A yellow precipitate formed initially, but it took on a grayish color as the reaction proceeded. The precipitate was filtered and washed with two 50-ml portions of methylene chloride. The solid was suspended in 10 ml of acetonitrile and the insoluble material was filtered. Anhydrous ether was added to the acetonitrile solution and the resulting white precipitate was collected to yield 0.398 g (38.8%) of the tetrafluoroborate: nmr (CH_3CN) τ 4.56 (s, 8H), 2.52-1.68 (m, 6H). The nmr spectrum is shown in Figure 9.

4. 2-Hydroxyethyl 1,8-Dinaphthoate: An acetonitrile solution of the ion 33 was added slowly to a well stirred solution of ice cold water (25 ml). The aqueous solution was concentrated to yield 2-hydroxyethyl 1,8-dinaphthoate: ir ($CHCl_3$): 1710 (C=O) and 3505 cm^{-1} (OH).

5. Attempted Preparation of 33 Using 'Magic' Acid: A solution of 100 mg of 2-bromoethyl 1,8-dinaphthoate in a

minimum amound of methylene chloride was added to a well-stirred mixture of 0.8 ml of fluorosulfonic acid and 0.2 ml of antimony pentafluoride at -78°. The solution had to be warmed slightly to allow the tetrafluoroborate to be formed. The fluorosulfonic acid layer was pipetted into an nmr tube. The solution, which was initially light yellow, turned black as the nmr spectrum was being taken: nmr ($FSO_3H + SbF_5$): τ 4.7, 4.5, 4.36, 4.02, 3.71. More signals appeared as time elapsed.

H. Preparation of 2,2'-(1,4-Naphthalene)bis-1,3-dioxolenium Tetrafluoroborate (34)

1. 2-Bromoethyl 1,4-Dinaphthoate: A mixture of 2 g (0.0098 mole) of 1,4-naphthalenedicarboxylic acid (K & K Laboratories), 4 g of phosphorus pentachloride and 4 ml of phosphorus oxychloride was heated under reflux, with the exclusion of moisture, for 6 hr. Phosphorus oxychloride was distilled under reduced pressure at room temperature. The residual impure acid chloride was dissolved in 25 ml of chloroform to which 1.45 g (0.0196 mole) of 2-bromoethanol was added. The resulting solution was refluxed for 8 hr. A dark yellow oil was obtained which was not distilled, as it decomposed on heating, but was used directly in the following experiment.

2. 2,2'-(1,4-Naphthalene)bis-1,3-dioxolenium Tetrafluoroborate (34): A solution of 1 g (~ 0.0023 mole) of impure 2-bromoethyl 1,8-dinaphthoate in 10 ml of methylene

chloride was placed in a 50-ml erlenmeyer flask equipped with a magnetic stirrer, in a dry box. To this solution was added 0.895 (0.0046 mole) of powdered silver tetrafluoroborate. The resulting solution was stirred for 4 hr. The initially formed yellow precipitate took on a grayish color as the reaction proceeded. The precipitate was filtered and washed with two 5-ml portions of methylene chloride. The precipitate was suspended in 10 ml of acetonitrile and the insoluble material was filtered. Anhydrous ether was added to the acetonitrile solution and the resulting white precipitate was collected to yield 0.2768 g (27.2%) of the tetrafluoroborate: nmr (CH_3CN): τ 4.55, (s, 8H), 2.91-2.00 (m, 6H). The nmr spectrum is shown in Figure 10.

NMR SPECTRA

For the nmr spectra of carbonium ions tetramethylammonium tetrafluoroborate was taken as the internal standard and its chemical shift was taken as 6.9.[32]

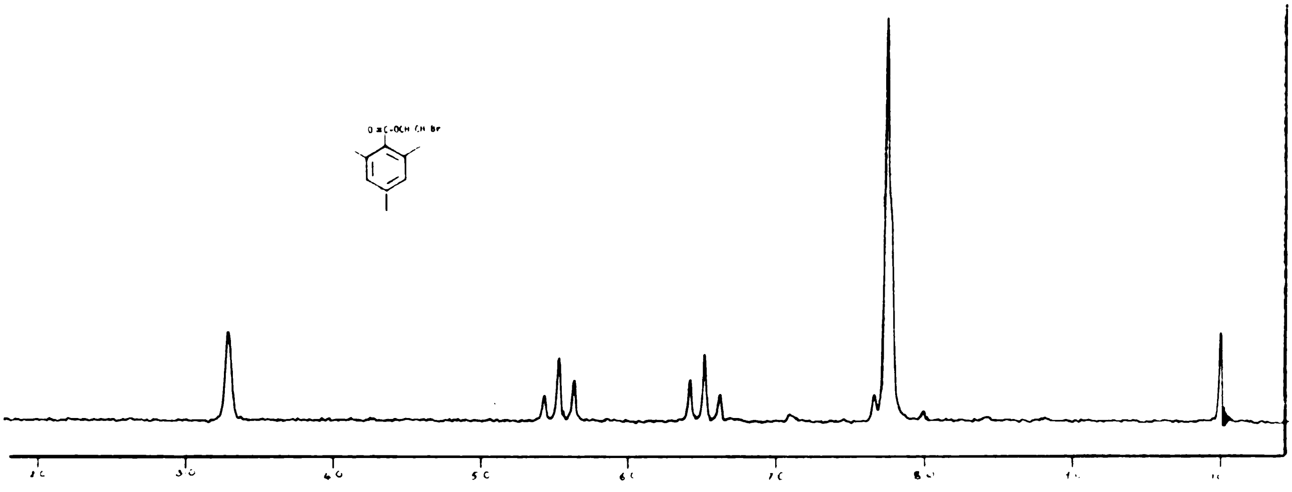


Figure 2. Nmr spectrum (CCl_4) of 2-bromoethyl mesitoate (17).

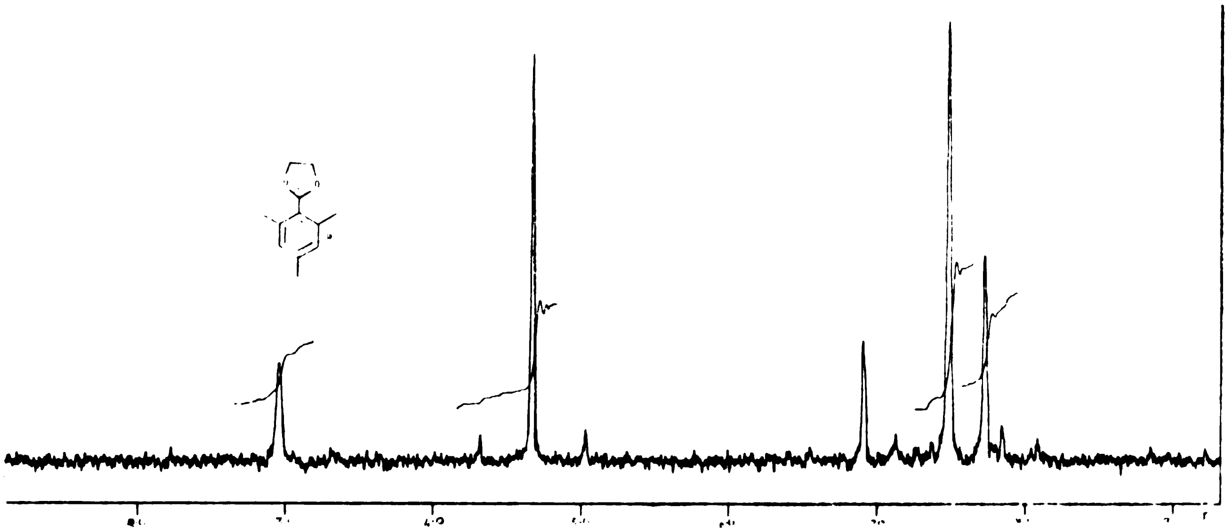


Figure 3. Nmr spectrum (CH_3CN) of 2-mesitoyl-1,3-dioxolenium tetrafluoroborat[illegible] 1).

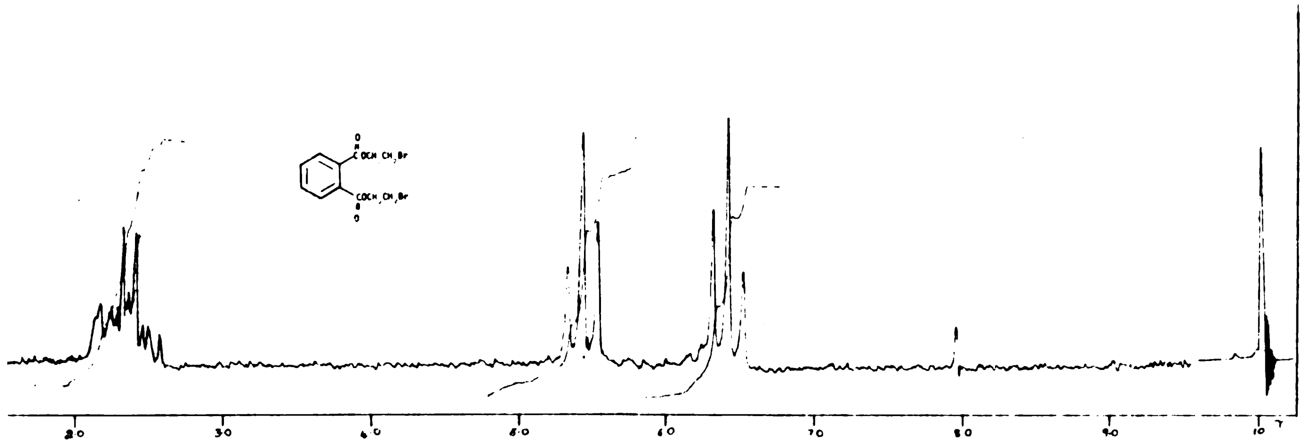


Figure 4. Nmr spectrum (CCl_4) of 2-bromoethyl phthalate.

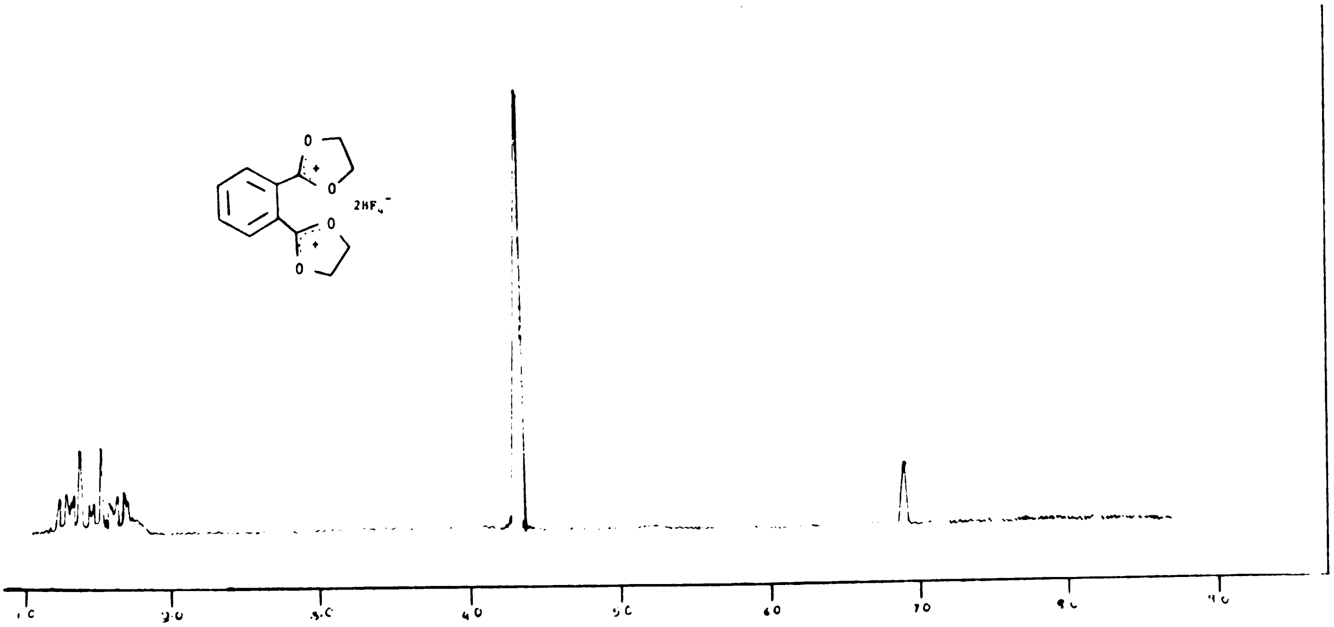


Figure 5. Nmr spectrum (FSO_3H) of 2,2'-(*o*-phenylene)bis-1,3-dioxolenium tetrafluoroborate (**24**)

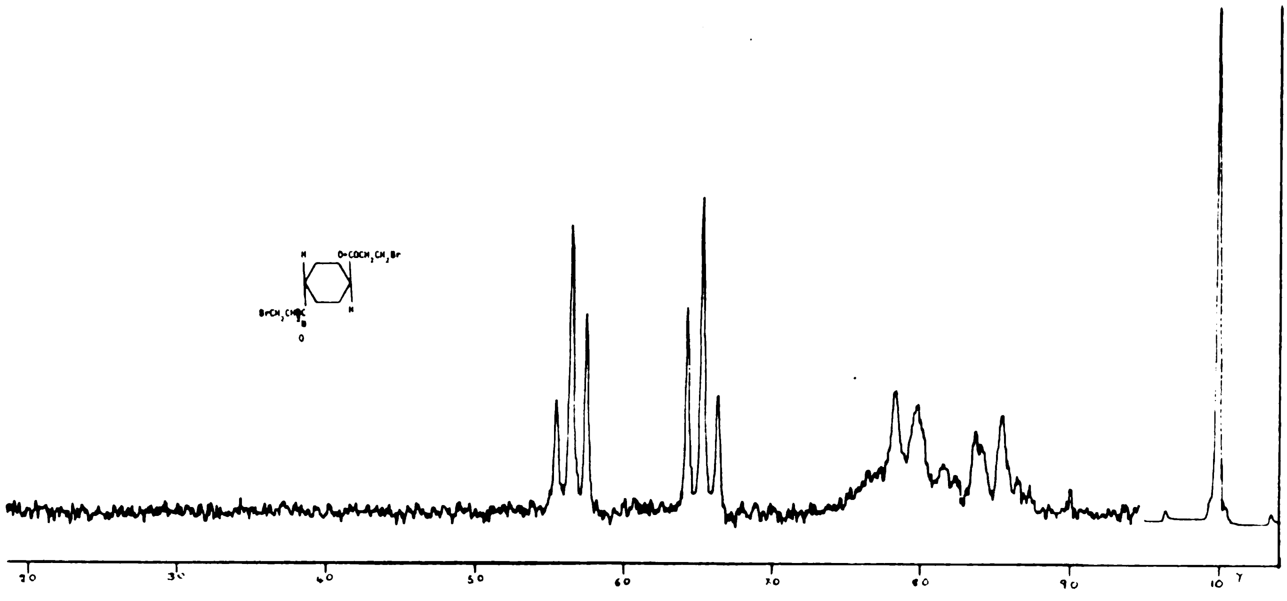


Figure 6. Nmr spectrum (CCl_4) of 2-bromoethyl 1,4-cyclohexanedicarboxylate.

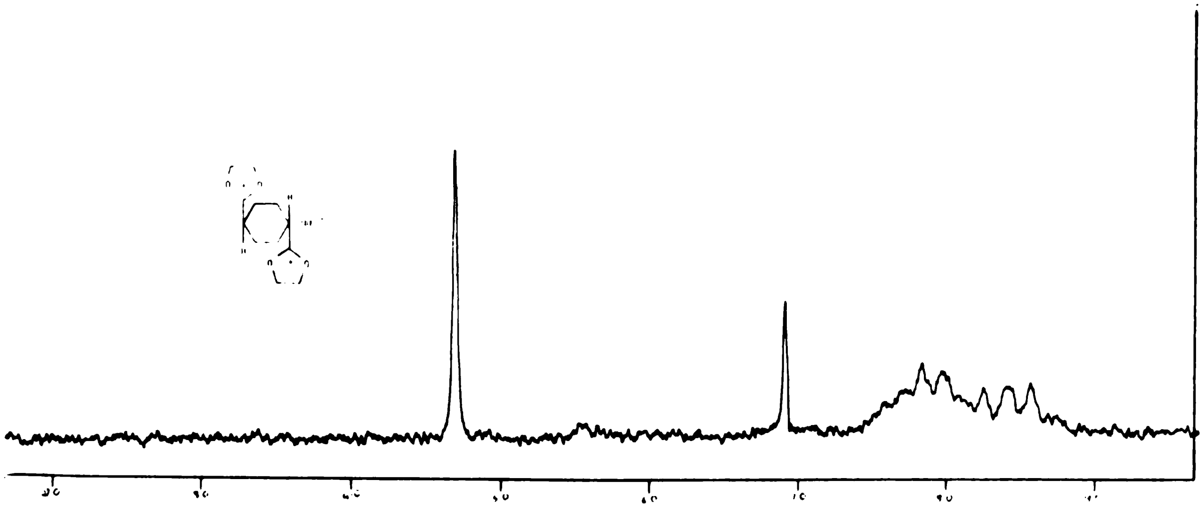


Figure 7. Nmr spectrum (CF_3CO_2H) of 2,2'-(trans-1,4-cyclohexane)bis-1,3-dioxolenium tetrafluoroborate (31).

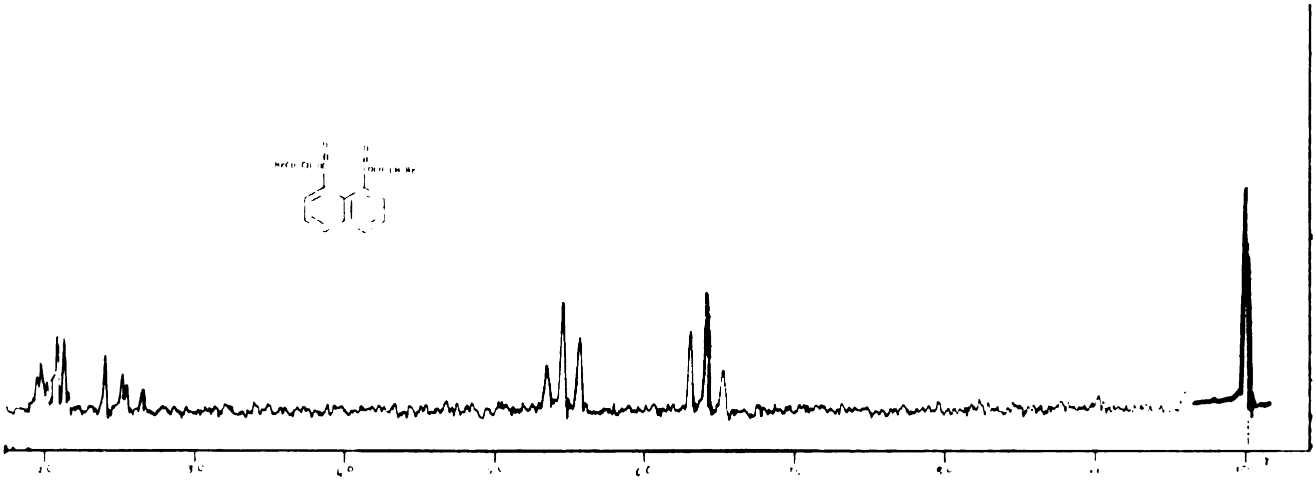


Figure 8. Nmr spectrum (CCl_4) of 2-bromoethyl 1,8-dinaphthoate.

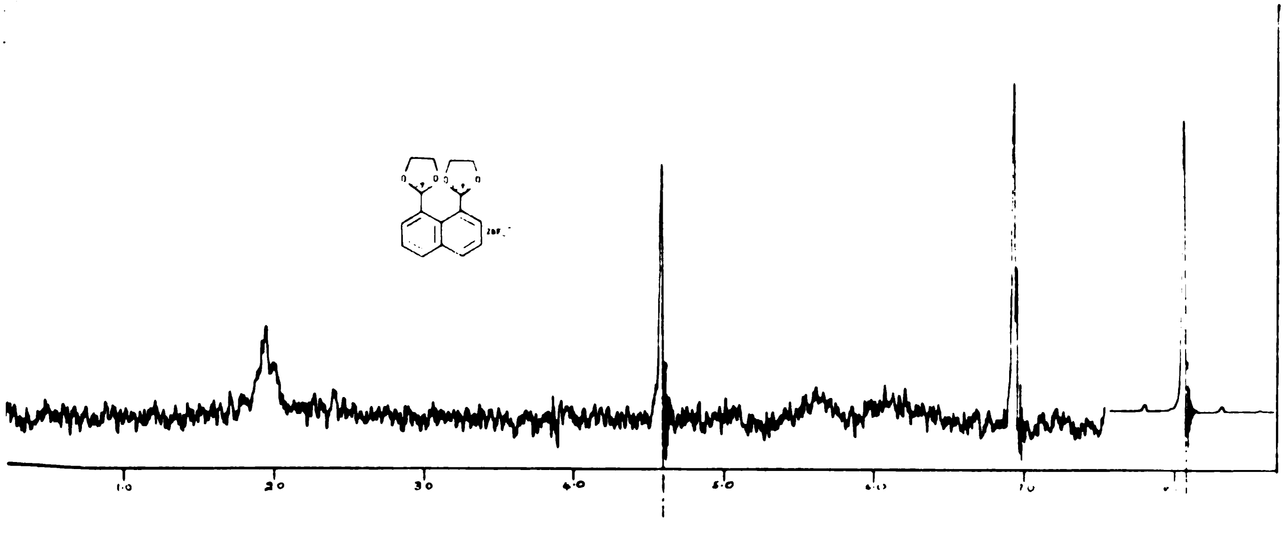


Figure 9. Nmr spectrum (CH_3CN) of 2,2'-(1,8-naphthalene)bis-1,3-dioxolenium tetrafluoroborate (33).

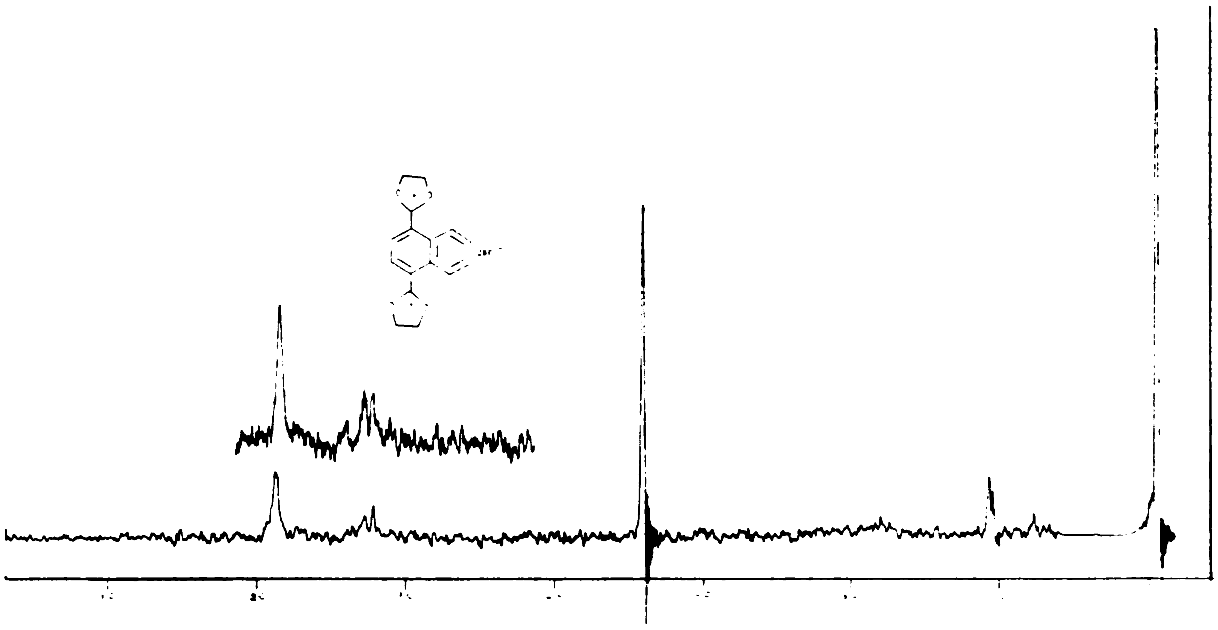


Figure 10. Nmr spectrum (CH_3CN) of 2,2'-(1,4-naphthalene)bis-1,3-dioxolenium tetrafluoroborate (34).

SUMMARY

1. 2-(Phenyl-3,5-d_2)-1,3-dioxolenium cation and 2-(phenyl-4-d)-1,3-dioxolenium cation were prepared.

2. The nmr chemical shifts of the aromatic protons of 2-phenyl-1,3-dioxolenium cation were determined and the π electron densities at the carbon atoms to which they are attached were calculated. A qualitative correlation between charge densities and the proton chemical shifts was observed.

3. Five new dioxolenium salts were synthesized and their nmr spectra were compared with those of known dioxolenium cations. They are the monocationic 2-mesitoyl-1,3-dioxolenium tetrafluoroborate (**14**) and the four dicationic salts 2,2'-(*o*-phenylene)bis-1,3-dioxolenium tetrafluoroborate (**24**), 2,2'-(*trans*-1,4-cyclohexane)bis-1,3-dioxolenium tetrafluoroborate (**31**), 2,2'-(1,8-naphthalene)bis-1,3-dioxolenium tetrafluoroborate (**33**) and 2,2'-(1,4-naphthalene)bis-1,3-dioxolenium tetrafluoroborate (**34**).

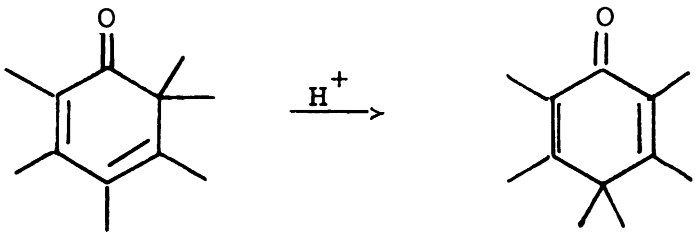
PART II

SYNTHESES FROM

2,3,4,4,5,6-HEXAMETHYL-2,5-CYCLOHEXADIENONE

INTRODUCTION

2,3,4,4,5,6-Hexamethyl-2,5-cyclohexadienone (35) has been prepared in high yields by the acid-catalyzed isomerization of 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone (36) in our laboratory.[39]



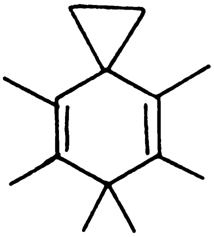
36 35

Dienone 35 is a white crystalline solid, very stable and easy to handle and because it was readily available to us, it was used as the starting material for the synthesis of some new compounds. The work done with dienone 35 can be divided into three parts.

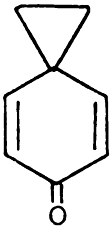
A. Preparation of 4,5,6,6,7,8-hexamethylspiro[2·5]octa-4,7-diene

One purpose of making 4,5,6,6,7,8-hexamethylspiro[2.5]-octa-4,7-diene (37) was that a hydrocarbon with the spiro-[2.5]octa-4,7-diene structure had not yet been isolated out of solution. In fact the only closely related known compound to this system is spiro[2.5]octa-4,7-dien-6-one (38).[40]

other derivatives of this ketone are also known.

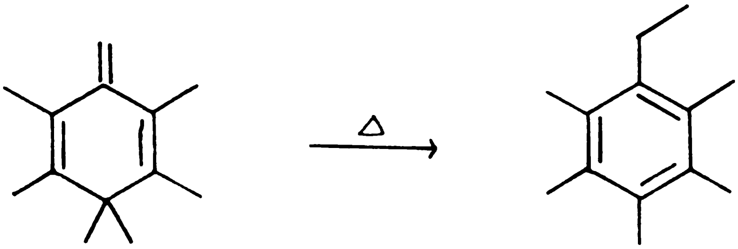


37



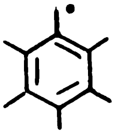
38

The main purpose for making 37 was to investigate the thermal reaction of this compound. It was expected to exhibit some thermal reactions because a closely related compound, 1-methylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene (39) undergoes a thermal rearrangement to ethylpentamethylbenzene (40).[41]



39 40

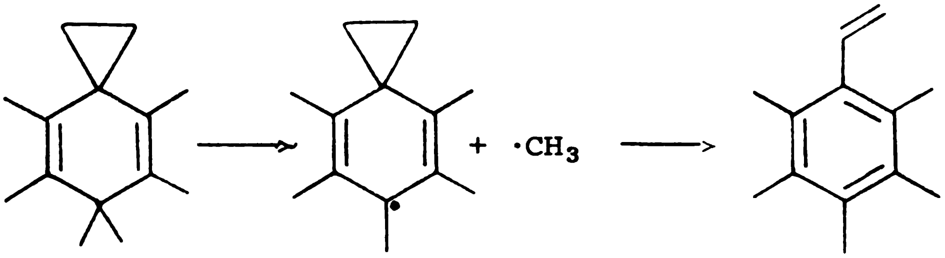
The thermal conversion of 39 to 40 was found to proceed by a radical chain mechanism, and is initiated either by the cleavage of 39 to pentamethylbenzyl radicals and methyl radicals (equation 8) or by a radical initiator (R) to produce methyl radicals (equation 9).

39 ⟶  + $\cdot CH_3$ (8)

41′

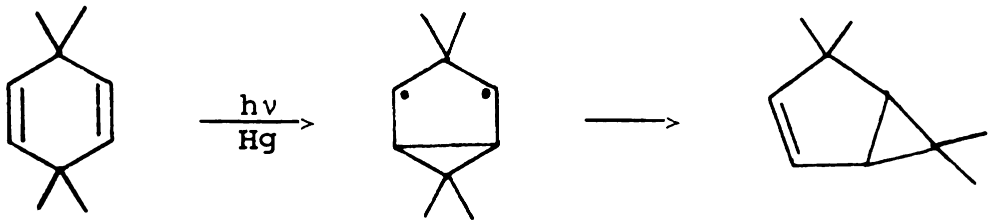
$$\mathbf{39} + \mathbf{R} \longrightarrow (\mathbf{41}' + \mathrm{R})\cdot + \cdot\mathrm{CH_3} \quad (9)$$

Similarly **37** might cleave on pyrolysis to give methyl radicals and radical **41** which may rearrange further to give other products such as pentamethyl styrene (**42**).



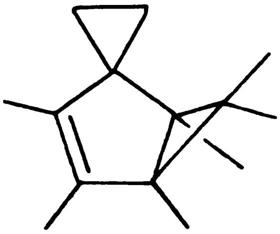
37 **41** **42**

We also hoped to investigate the photochemistry of **37**. Several examples of the photochemical isomerization of 1,4-cyclohexadienes to bicyclo[3.1.0]hex-2-enes have been reported.[42] For example 3,3,6,6-tetramethyl-1,4-cyclohexadiene (**43**) on photolysis in the vapor phase with mercury sensitization gave mainly 4,4,6,6-tetramethylbicyclo[3.1.0]-hexene (**45**).[43] A di-π-methane mechanism has been proposed

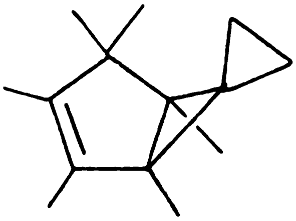


43 **44** **45**

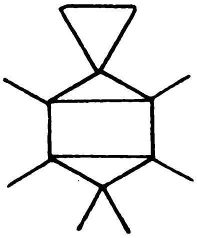
for this reaction. Accordingly **37** was expected to isomerize to structure **46** or **46'** on photolysis. Based on the photochemical results of other nonconjugated dienes such as norbornadiene[44] and 1,5-cyclooctadiene[45] compounds 47 and 48 may also be postulated as possible photoproducts.



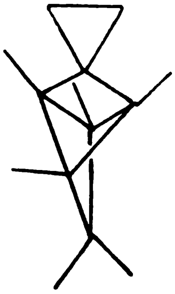
46



46'



47

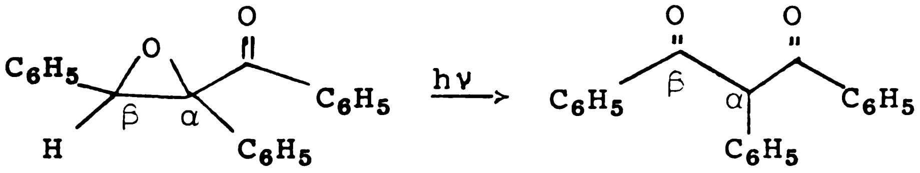


48

Compound 37 was successfully synthesized. Its preparation and chemistry as well as that of the precursors obtained during the preparation of 37 will be presented in the Results and Discussion section.

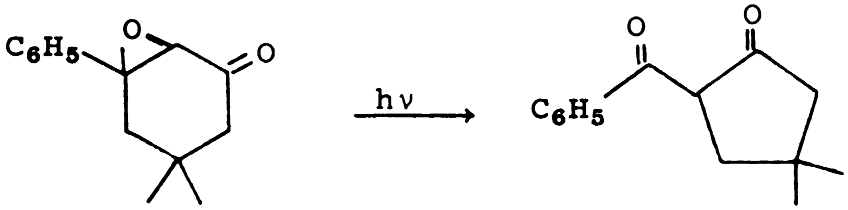
B. Preparation and Photolysis of 2,3-Epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone and 2,3;5,6-Diepoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone

The preparation of 2,3-epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone and 2,3;5,6-diepoxy-2,3,4,4,5,6-hexamethyl-2,4-cyclohexadienone was undertaken because they seemed to be interesting subjects for a photochemical investigation. The photochemical behavior of α,β-epoxyketones has been studied by various investigators. Even as early as 1918 Bodforss[46] had observed the photochemical rearrangement of the α,β-epoxyketone chalcone oxide (49) to dibenzoylphenylmethane (50) on irradiation with ultraviolet light.



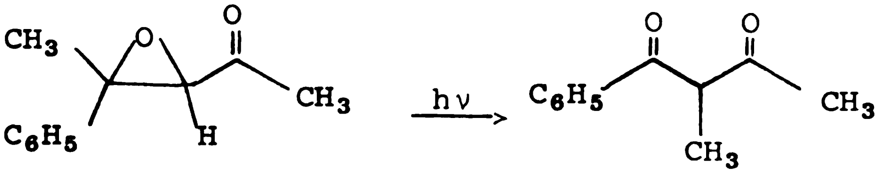
49 50

The reaction was thought to proceed in two steps; C_α-O bond fission of the oxirane ring followed by 1,2-shift of the β-hydrogen to the α-position. Recently Reusch and coworkers[47] and Jeger and coworkers[48] found that β-alkyl groups also shift in a similar manner. Both Reusch[47] (equation 10) and Zimmerman[49] (equation 11) have shown independently that a β-methylene or methyl group migrates preferably over a β-phenyl group.



(10)

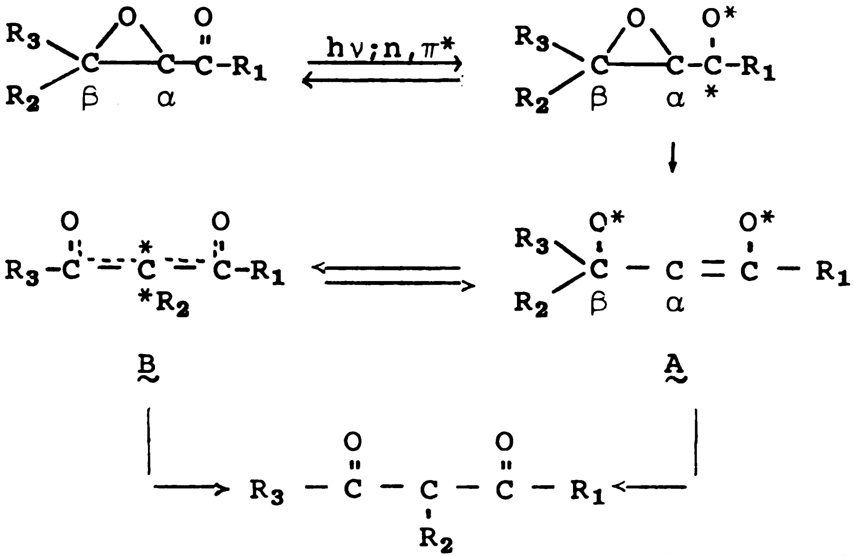
51 52



(11)

53 54

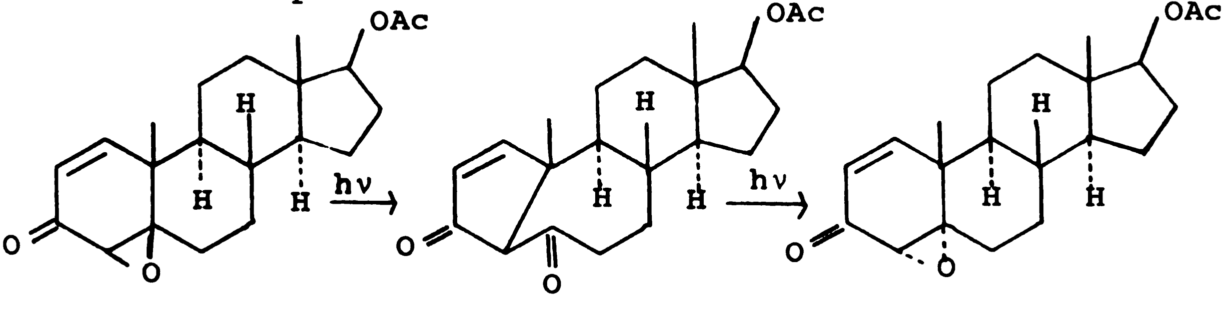
They also proposed that the photorearrangement of α,β-epoxyketones takes place by an n,π* excitation of the carbonyl group which causes the cleavage of the C_α-O bond of the oxirane ring to an intermediate **A**, followed by rearrangement of the β-substituent as shown below.



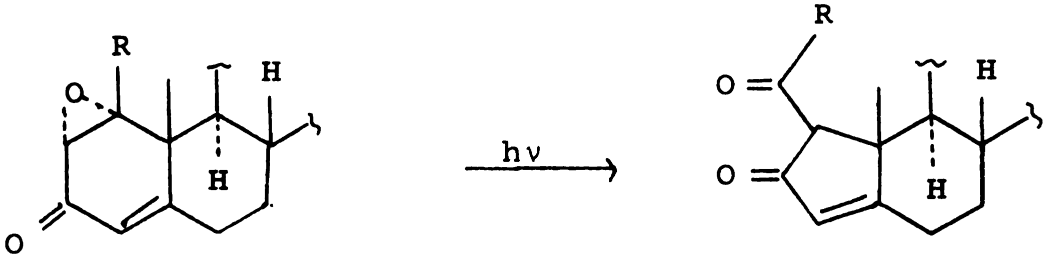
* = · or ±

From this mechanism it appears that the migratory aptitude of the β-substituent depends on the stability of the corresponding radical intermediate. The migratory aptitude of several β-substituents has been studied by Markos and Reusch[50] and they found: benzhydryl and benzyl > hydrogen > methylene > methyl >> phenyl.

Jeger and coworkers[48,51] have also studied the photochemistry of several steriodal epoxyketones, among which there are examples of Δ^2-unsaturated epoxyketones, three of which are presented below.



55 **56** **57**

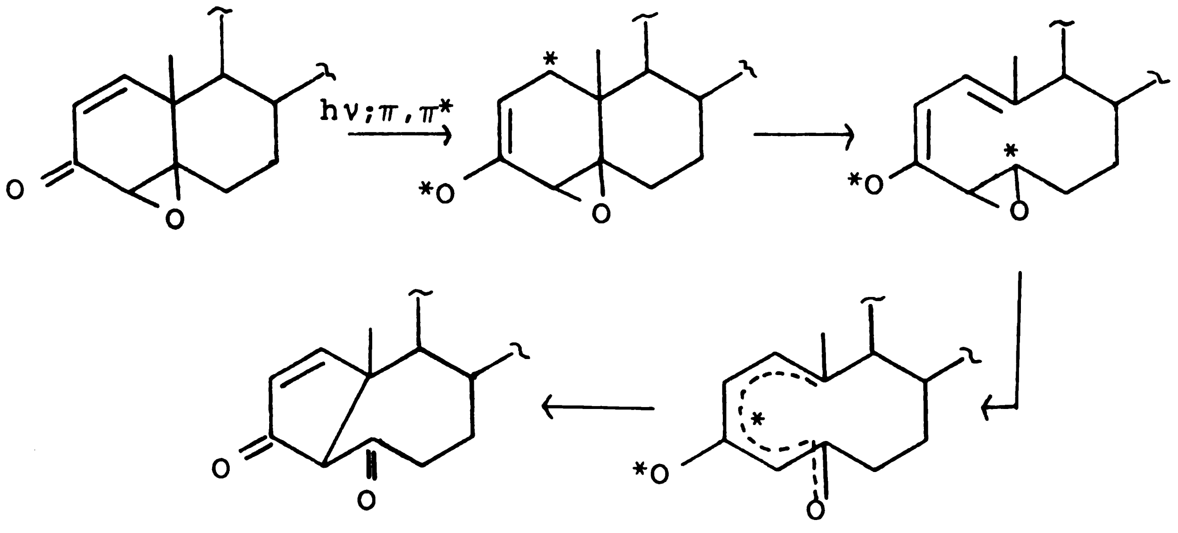


R = H R = H

R = CH_3 R = CH_3

58 59

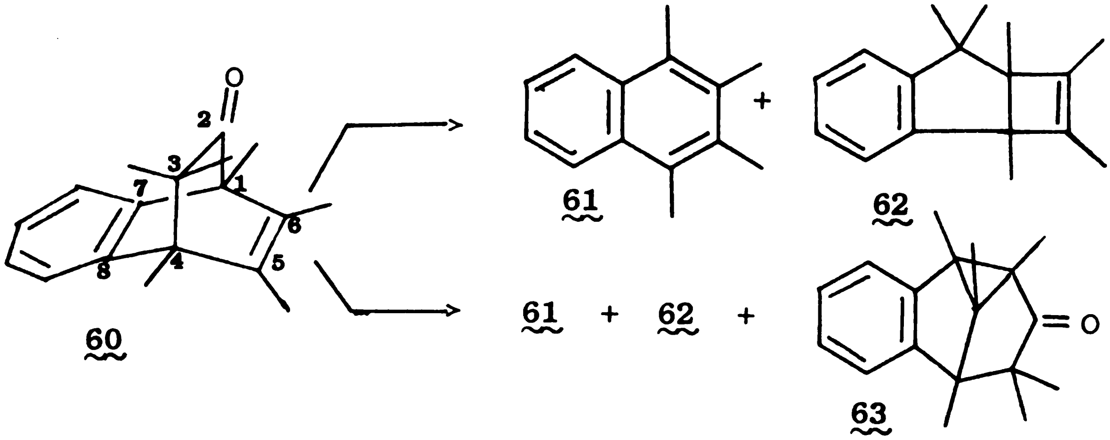
Jeger et. al. found that saturated epoxyketones rearranged on irradiation with light of wavelengths greater than 3100 Å, therefore probably rearrange by an n,π* excitation of the carbonyl group whereas Δ^2-unsaturated epoxyketones were found to be stable to n,π* excitation and rearranged only by exposure to 2537 Å light. The photoreaction in this case was brought about by a π,π* excitation of the carbonyl group. The following mechanism was proposed by the authors for the photoreaction of Δ^2-unsaturated epoxyketones.



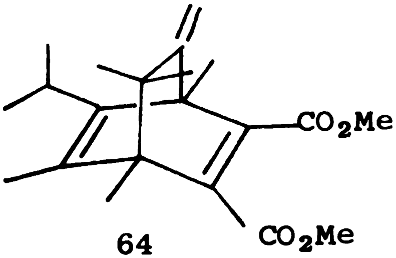
For our work we prepared 2,3-epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone which is an α,β-unsaturated epoxyketone and 2,3;5,6-diepoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone from dienone **35**. The preparation and the photochemical results will be presented in the Results and Discussion section.

C. Attempted Preparation of 2-Methylene-1,3,3,4,5-pentamethylbicyclo[2.2.2]octa-5,7-diene.

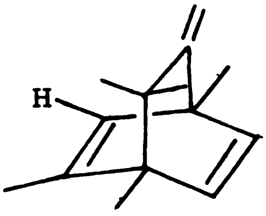
Lastly an attempt was made to synthesize 2-methylene-1,3,3,4,5-pentamethylbicyclo[2.2.2]octa-5,7-diene from dienone **35** because this compound has three double bonds so oriented that any two of them can participate in a di-π-methane rearrangement on photoexcitation. The chemistry of related ketones, the bicyclo[2.2.2]octadienones, has been studied by Murray.[52] Benzobicyclo[2.2.2]octadienone (**60**) on irradiation in ether gave 1,2,3,4-tetramethylnaphthalene (**61**) by the photoelimination of dimethyl ketene and benzobicyclo[3.2.0]heptene (**62**) by the photoelimination of carbon monoxide. However, acetone-sensitized irradiation of **60** gave ketone **63** in addition to **61** and **62**. Ketone **63** was shown to be formed by a 1,2-acyl migration from C_1 to C_6.



On the basis of these results 2-methylene-1,3,3,4,5-pentamethylbicyclo[2.2.2]octa-5,7-diene (65) was expected to eliminate dimethylallene or form a semibulvalene product corresponding to ketone 63, on photoexcitation. We had successfully synthesized compound 64 which contains the 2-methylene[2.2.2]octadiene structure, but this molecule has various substituents and a complicated nmr spectrum. Since the photoproducts are identified by their nmr spectra we decided to make a simpler molecule which would have a less complicated nmr spectrum. The preparation of bicyclooctadiene 65 was undertaken because a possible route for its preparation from dienone 35 could be formulated.

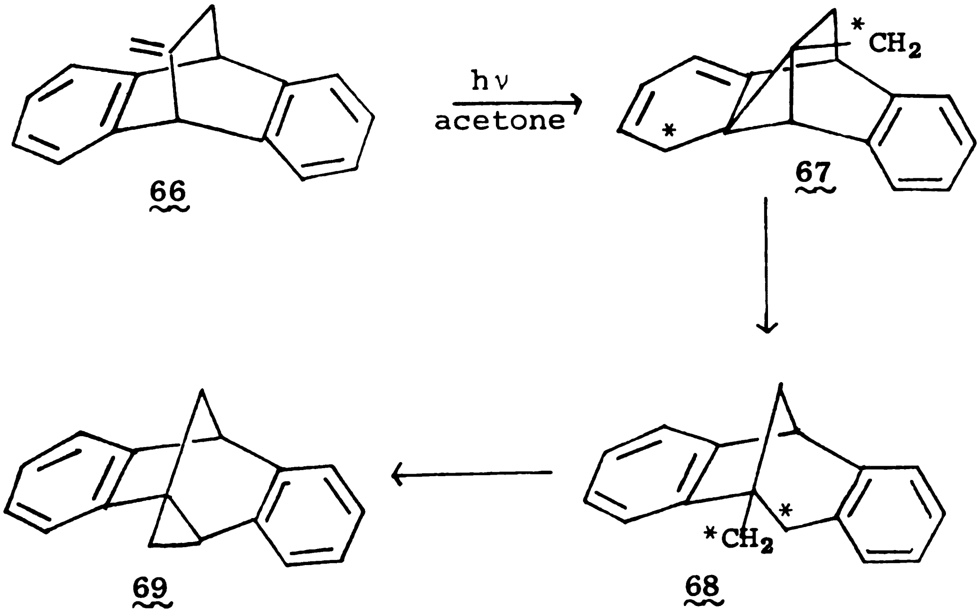


64



65

While this work was being written, Cristol and Mayo[53] published their work on the photoisomerization of 2-methylenedibenzobicyclo[2.2.2]octadiene (66) to dibenzotricyclo-[4.2.1.$0^{1,3}$]nonadiene (69). This reaction is also thought to take place *via* a di-π-methane rearrangement. This is the first example of a photochemical rearrangement of a 2-methylenebicyclo[2.2.2]octadiene system.

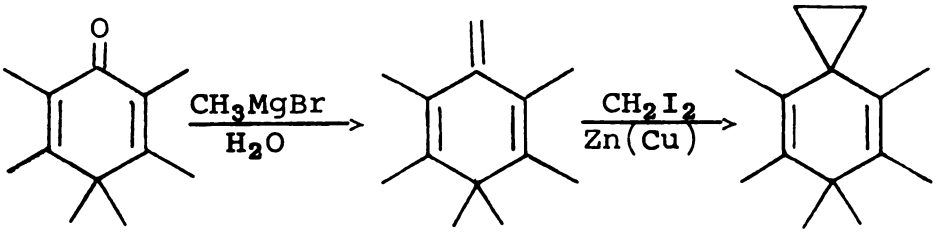


Attempts to make 65 were unsuccessful but an interesting rearrangement was observed in the process. Details for the preparation of 64 and the attempts to make 65 will be discussed in the next section.

RESULTS AND DISCUSSION

A. Preparation of 4,5,6,6,7,8-Hexamethylspiro[2.5]octa-4,7-diene

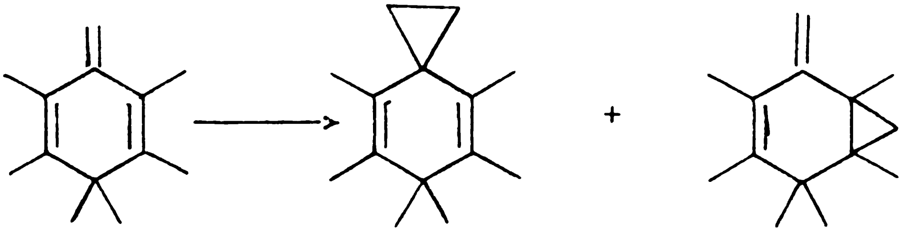
The synthesis of 4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (37) was undertaken because we were interested in investigating its thermal and photochemical behavior. Since 1-methylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene (39) had already been obtained in good yields from dienone 35[41], we hoped to obtain 37 from 39 in a one-step synthesis by the Simmons-Smith reaction. Methylene iodide together with the zinc-copper couple made by LeGoff's[54] procedure was used for the reaction. When methylene bromide was used instead of methylene iodide the reaction did not always take place.



35 39 37

The reaction mixture was analyzed by vpc using a 5 ft SE-30 column at 150°. The vpc trace showed three peaks with retention times of 3, 5 and 14 min for methylene iodide, starting material 39 and 37 respectively. From the areas of the peaks a 61.5% conversion of triene 39 to give 37 in a yield of 95% was calculated. The nmr spectrum (CCl_4) of 37 consisted of singlets at τ 9.28 (4H), 8.90 (6H), 8.74 (6H) and 8.40 (6H) which are in accord with structure 37. In addition to these signals a singlet at τ 7.78 was also observed which is probably caused by the presence of hexamethylbenzene as an impurity. Hexamethylbenzene seems to be forming in small amounts during the course of the reaction either from 37 or 39. This method was not found suitable for the preparation of 37 in large amounts, since it was difficult to separate hexamethylbenzene from 37 by vpc.

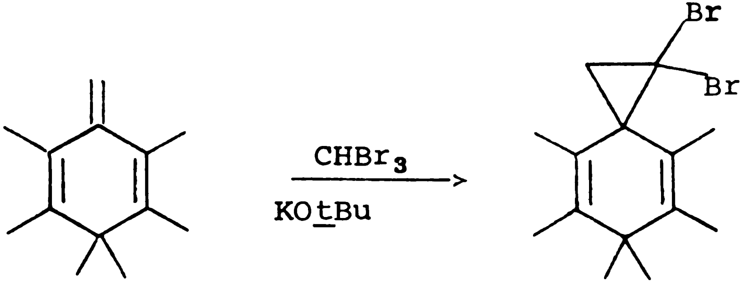
Compound 39 has both an exocyclic and endocyclic double bonds. Hence by subjecting 39 to a Simmons-Smith reaction two possible products (37 and 70) may be obtained.



39 37 70

However, only 37 was obtained. Attack at the highly substituted endocyclic bond is probably sterically hindered

A better route was sought for the preparation of 37. A dibromocarbene adduct of 39 was prepared which was expected to give the hydrocarbon 37 by reduction with a suitable reagent. Dibromocarbene was generated by reacting bromoform with potassium *t*-butoxide in the presence of 39 and 2,2-dibromo-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (71) was obtained in 52.7% yield.

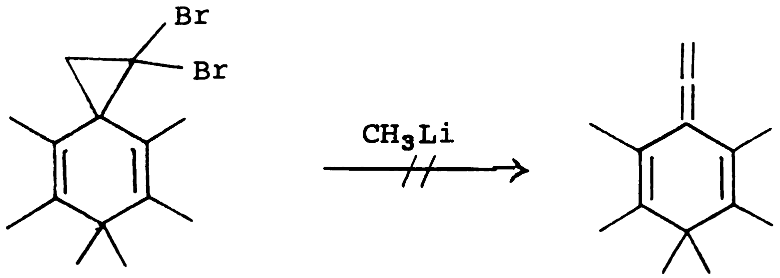


39 71

The uv spectrum (hexane) of 71 had maxima at 225 nm (ϵ 1470) and 244 nm (ϵ 955). The nmr spectrum (CCl$_4$, Figure 25) consisted of singlets at τ 8.86 (3H), 8.78 (3H), 8.38 (6H), 8.20 (6H) and 7.81 (2H). The mass spectrum showed a parent peak at mass 346 (Br = 79) and the chemical analysis was also in accord with structure 71. The mass spectrum will be discussed later, in greater detail in this section.

In order to investigate the photochemical behavior of 71, a 2% solution of 71 in pentane was irradiated first through a vycor filter and then through a corex filter, using a 450-watt Hanovia lamp. In both cases 71 underwent polymerization and a black residue deposited on the walls of the test tube containing the pentane solution.

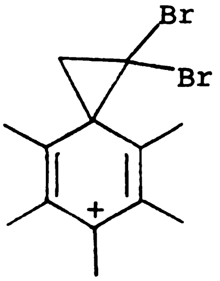
1,1-Dibromocyclopropanes form allenes in reasonable yields with magnesium or highly dispersed sodium,[55] and good yields of allenes are obtained with butyllithium and methyllithium.[56,57] An attempt was made to prepare allene 72 from compound 71 by treatment with methyllithium.



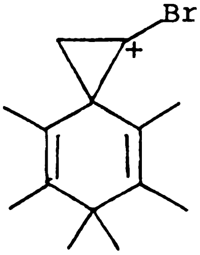
71 **72**

When **71** was treated with methyllithium at -78^0 the reaction did not occur because the nmr spectrum of the recovered material showed that starting material was unchanged. The reaction was repeated at 0^0 and a very complicated nmr spectrum was obtained for the reaction product. The absence of peaks in the vinylic region indicated that allene **72** had not formed. The vpc analysis of the product mixture showed that the volatile components consisted mostly of starting material and another compound which was not present in sufficient amount to be collected.

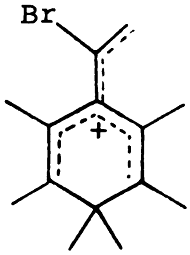
Compound **71** gave a very interesting mass spectrum. When the mass spectrum was first obtained the parent peak at mass 346 was not present. The temperature of the ionization chamber was as usual at 250^0. Two sets of peaks in an almost 1:1 ratio were observed at mass 267 and 269 and at 252 and 254. However, when the ionization chamber was cooled to 100^0 and the mass spectrum retaken peaks at 346, 348 and 350 mass units were observed in a 1:2:1 ratio. This pattern is typical of a molecule containing two bromine atoms since the relative abundance of the heavier isotope of bromine (atomic wt 81) is 98%. Peaks at mass 331, 333, and 335 in the same ratio are attributed to ion 73 which can be formed by the loss of a methyl group (15 mass units). Once again peaks at mass 267 and 269 and also at 252, 254 were observed in an almost 1:1 ratio. This type of pattern suggests fragments containing one atom of bromine. These are thus attributed to fragments 74 or 74' and 75 respectively.



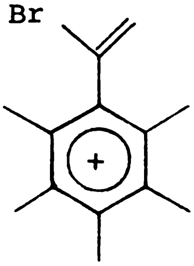
73



74

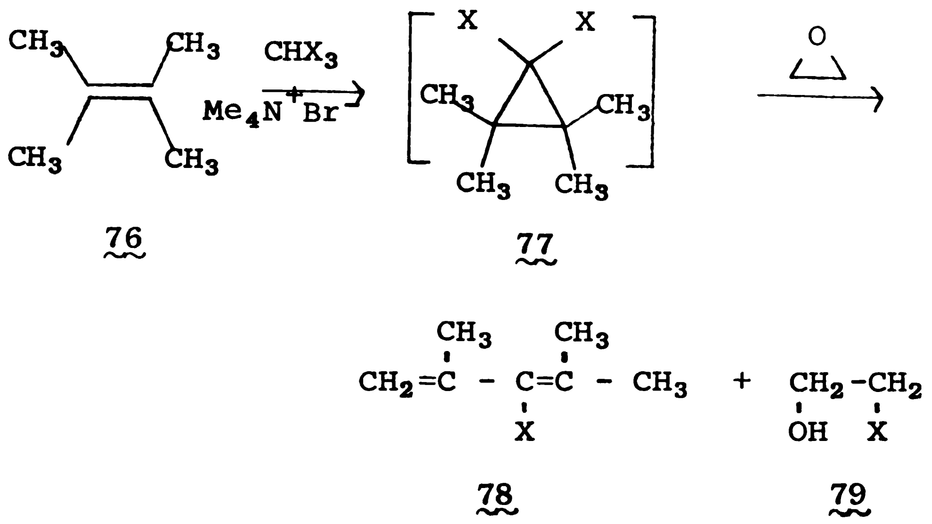


74'



75

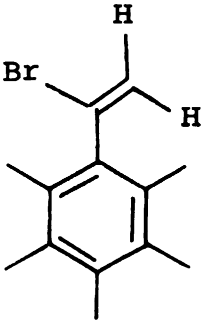
The absence of the parent peak in the mass spectrum at higher temperatures indicated that compound 71 was probably undergoing thermal rearrangements in the ionization chamber. In fact Weyerstahl and coworkers[58] have observed that 1,1-dihalocyclopropanes undergo thermal rearrangements. They found that by treating tetraalkylated ethylenes with trihalomethane, ethylene oxide and tetramethylammonium bromide at 150-170° the gem-dihalocyclopropane was not obtained but instead resulted in ring opening and hydrogen halide elimination giving a 2-halo-1,3-alkadiene as illustrated below.



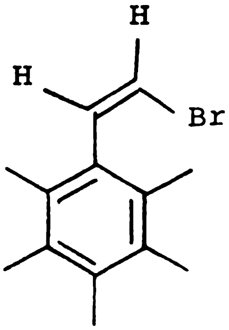
76 77 78 79

Trialkylethylenes gave 1,1-dihalocyclopropanes, 2-halo-1,3-alkadienes, or their mixtures, depending on the reaction temperature. Dialkylated 1,1-dihalocyclopropanes were stable in the presence of ethylene oxide even at elevated temperatures, but could be converted to 2-halodienes by pyrolysis or with quinoline catalyst.

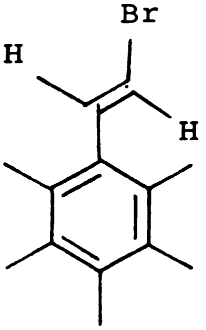
In order to study the thermal reaction of 71 it was pyrolyzed in solution in decalin, nitrobenzene or toluene. Three major thermal products were detected, in a total yield of 90-95% by vpc. The chemical analysis and the mass spectrum of these products showed that they were isomeric and had the molecular formula $C_{13}H_{17}Br$. On the basis of their nmr spectra these products have been assigned structures 80, 81 and 82.



80

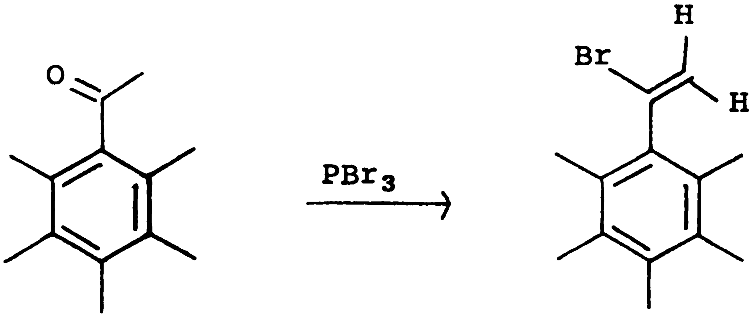


81



82

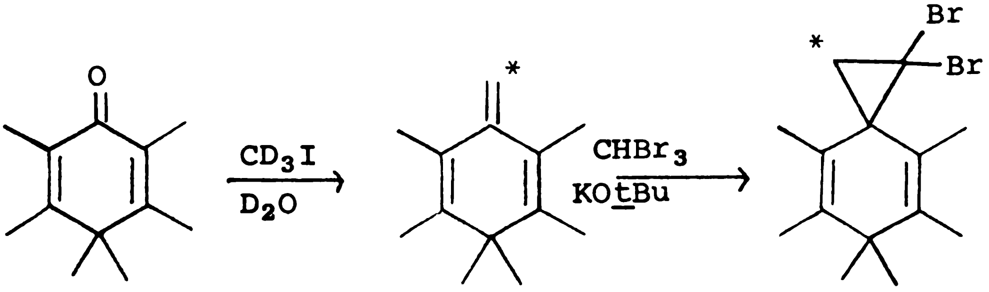
The spectrum of compound 80 showed singlets at τ 7.84 (9H) and 7.74 (6H) which are assigned to the aromatic methyl groups. The vinylic protons were observed at τ 4.42 (d, 1H, *J* = 1.25 Hz) and 4.10 (d, 1H, *J* = 1.25 Hz). The coupling constant of the vinylic protons suggests the presence of two nonequivalent hydrogens located at one end of a double bond, and justifies the assignment of structure 80. To further confirm this assignment compound 80 was synthesized independently by treating pentamethylacetophenone (83) with phosphorus tribromide. Compound 80 was obtained in a 59.5% yield. The nmr spectrum was identical with the one reported above.



83 80

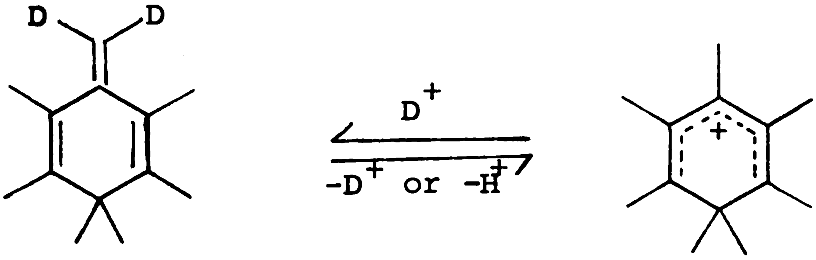
The nmr spectrum of compound 81 showed singlets at τ 7.95 (9H) and 7.90 (6H) and doublets at τ 3.62 (1H, *J* = 7.5 Hz) and 2.99 (1H, *J* = 7.5 Hz). The coupling constant of the vinylic protons suggests a *cis* configuration for the protons and therefore justifies structure 81. The nmr spectrum of 82 showed a singlet at τ 7.89 (15 H) and doublets at τ 4.15 (1H, *J* = 14 Hz) and 3.11 (1H, *J* = 14 Hz). The *trans* configuration is justified by the coupling constant of the vinylic protons.

It is clear that a hydrogen migration is involved in the formation of 81 and 82. In order to investigate the mechanism of this thermal reaction an attempt was made to prepare 2,2-dibromo-3,3-dideutero-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (85). For this reason 1-dideuteromethylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene (84) had to be prepared first, from methyl-d$_3$ iodide and dienone 35.



35 84 85

But we found, as was previously reported by DeVrieze,[41] that some label is lost during workup and only 72.5% deuterium label was obtained in the methylene group. Exchange is thought to occur *via* the heptamethylbenzenonium cation (84-H$^+$).



84 84-H^+

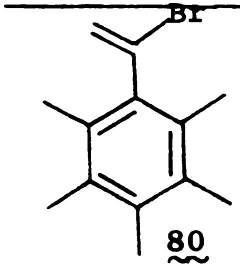
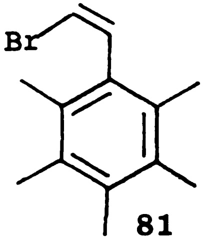
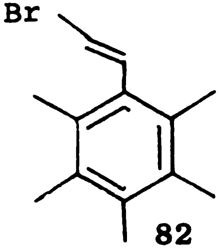
When we tried to exchange the methylene protons by treating a solution of unlabeled triene 84 in carbon tetrachloride with deuterium oxide containing a few drops of sulfuric-d_2 acid. The mass spectrum of the recovered material showed that not only the methylene protons but also the protons of the methyl groups at C_3 and C_5 were exchanged to some extent.

For our work we required 100% deuterium label in the methylene group because we wanted to calculate the deuterium content of the products from their mass spectra and the presence of hydrogen atoms in the methylene group would complicate the calculations. To overcome this difficulty unlabeled 71 was pyrolyzed in deuterated solvents. The results are summarized in Table V, and a sample calculation for the mole per cent of the singly labeled species is given below.

P = mass 346, P+1 = mass 347, P+2 = mass 348, P+3 = mass 349. Peak intensities in reference compound obtained in nondeuterated solvents

Mass:	P	P+1	P+2	P+3	
Intensity:	1.0	0.244	0.977	0.232	(A)

Table V. Results of pyrolysis of 2,2-dibromo-4,5,6,6,7,8-hexamethylspiro[2.5]-octa-4,7-diene (71) in deuterated solvents, at 150°

Solvent	Concentration of 71 in the solvent	% of Deuterium Incorporation in Products		
		 80	 81	 82
Toluene-d_8	50%	--	0 %	2.02%
Benzene-d_6	50%	0 %	0 %	0.434%
Toluene-d_8	5%	12.02%	8.0 %	11.3 %
Nitrobenzene-d_5	5%	5.32%	9.92%	3.76%

Peak heights (scale divisions) in labeled species

Mass:	P	P+1	P+2	P+3
Intensity:	20	6	19.5	4.5

(B)

The entire peak at mass P, 20 div, must be due to the unlabeled species. To compute the contribution of the unlabeled species to P, P+1, P+2 and P+3, the peak height at mass P is multiplied with the abundance of P, P+1, P+2 and P+3 in standard.

20x1 = 20 20x0.244 = 4.88 20 x 0.977 = 19.5 (C)
20x0.232 = 4.65

Subtract (C) from (B)

20	6	19.5	4.5
20	4.88	19.5	4.65
0	1.12	0.0	-.15

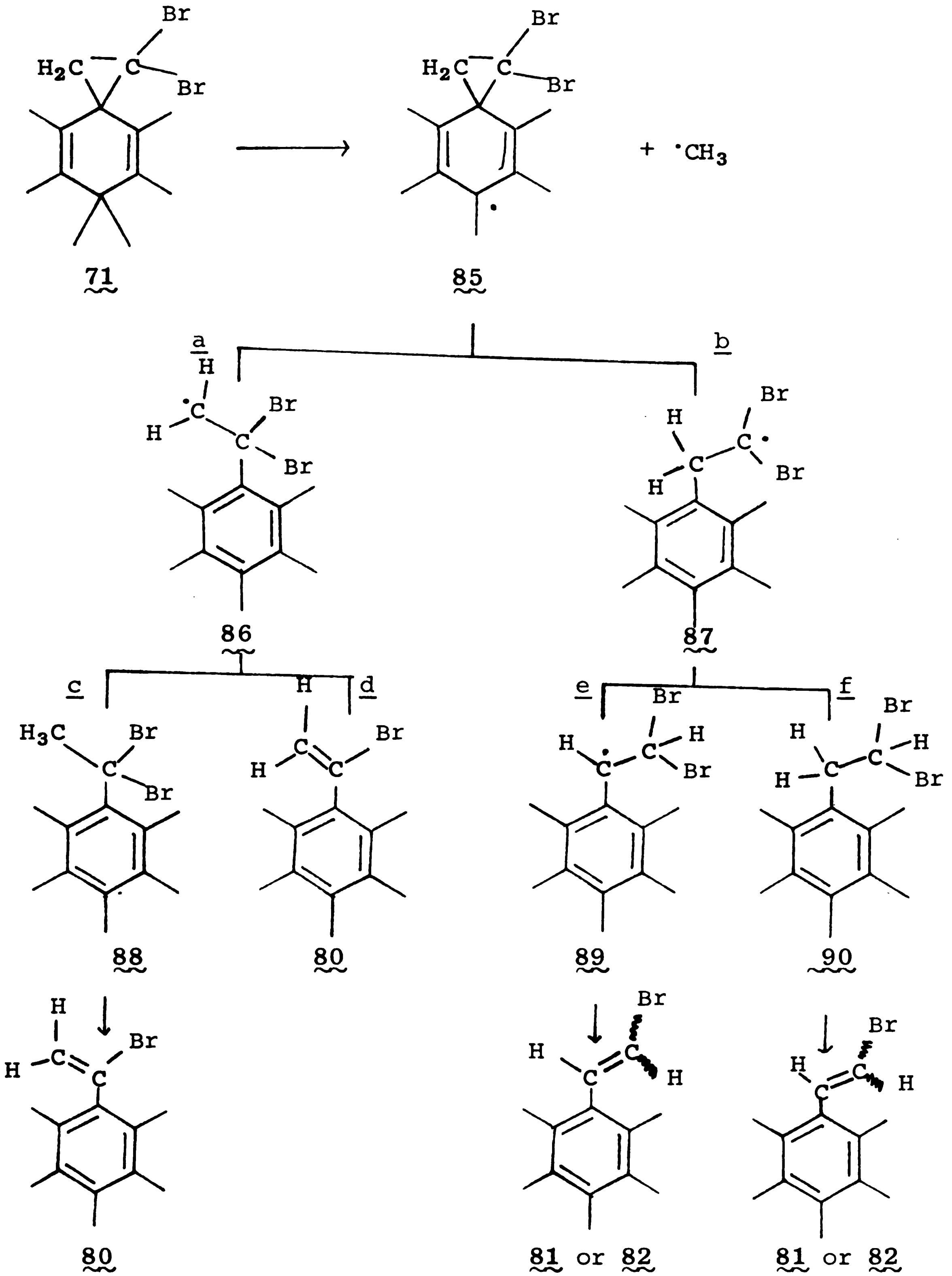
(D)

The peak height due to the singly labeled species is thus 1.12. The sum of corrected intensities is 20 + 1.12 = 21.12. The distribution in mole per cent is

1.12/21.12 x 100 = 5.32 mole percent of singly labeled species.

The results of pyrolysis of 71 in deuterated solvents show very little deuterium incorporation into the products, especially in concentrated solutions. Based on these results the following mechanism is proposed tentatively. (See Scheme 1.)

It is proposed that compound 71 first loses a methyl radical to give pentadienyl radical 85 which may give the ring-opened aromatic radicals 86 or 87 by step a or b respectively.



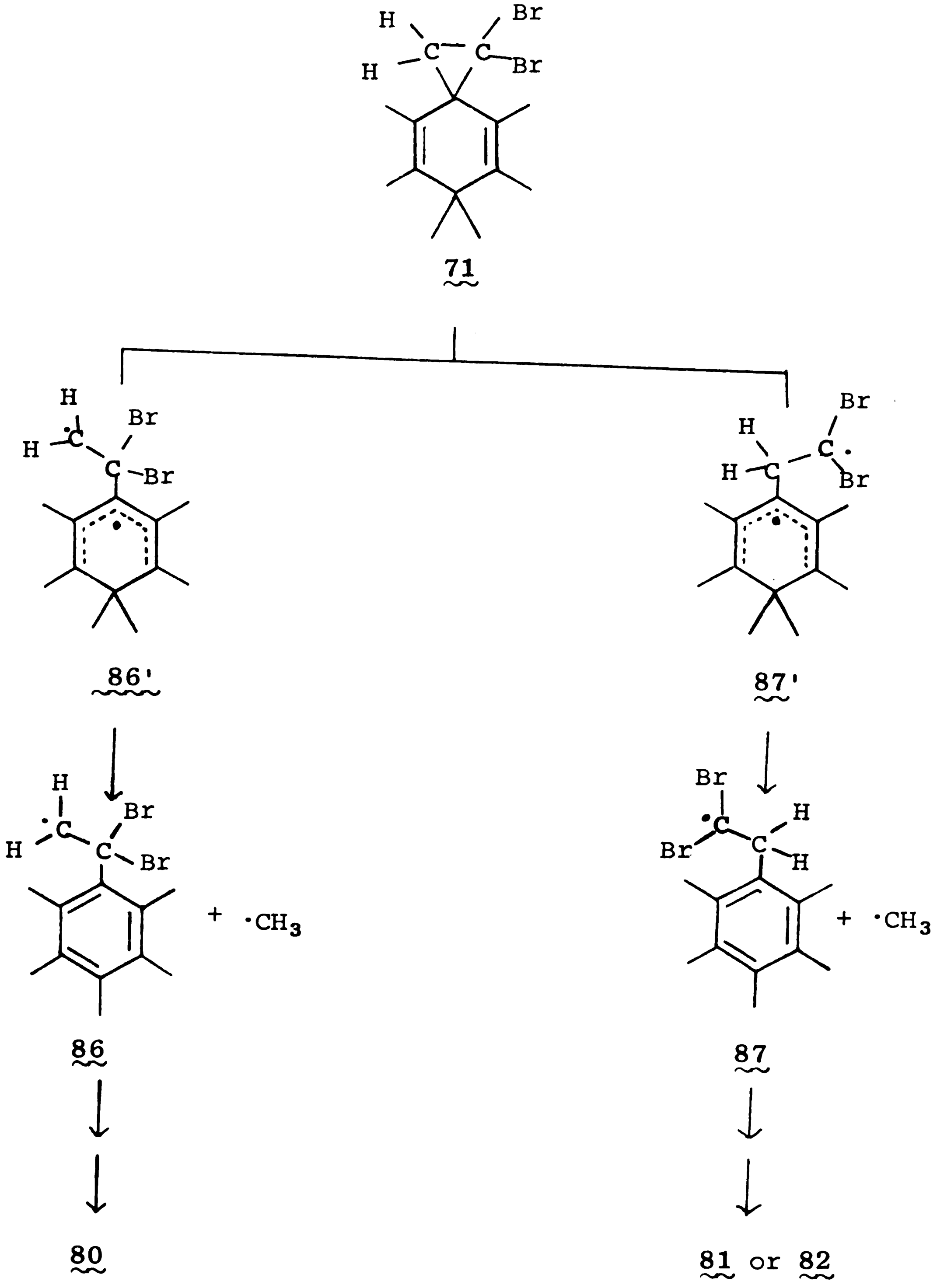
Scheme 1.

Intermediate **86** could lose a bromine atom to give **80** (step *d*) or it could pick up an hydrogen atom from the solvent to give **88** (step *c*) which can give **80** by elimination of hydrogen bromide. Since there is very little deuterium incorporation into the product on pyrolysis in deuterated solvents, step *d* seems to be favored over step *c*.

Intermediate **87** on the other hand probably forms **89** by an intramolecular 1,2-hydrogen migration (step *e*). Compounds **81** or **82** could be formed from **89** by the elimination of a bromine atom. Intermediate **87** could also pick up an hydrogen atom from the solvent to give **90** (step *f*) which could give **81** or **82** by elimination of hydrogen bromide. Again step *e* seems to be favored over step *f* because of low deuterium incorporation in the products.

A second possible route for the thermal rearrangement of **71** is shown in Scheme II. In this case it is suggested that the cyclopropane ring of **71** opens to give two diradicals **86'** and **87'** which give radicals **86** and **87** respectively by the loss of a methyl radical. Radicals **86** and **87** then proceed to the thermal products as in Scheme I.

The effect of a radical source on the reaction of **71** in solution was investigated by pyrolyzing **71** in the presence of benzoyl peroxide. Duplicate samples of benzene solutions containing 0.20*M* **71** and varying concentrations of benzoyl peroxide, 0.01*M*, 0.02*M* and 0.05*M*, were placed in nmr tubes. The nmr tubes were degassed to 0.2 mm of Hg, sealed and pyrolyzed at 110°. Two nmr tubes containing



Scheme II.

0.20*M* solution of 71 in benzene were prepared in the same way and used as the reference solutions. The reaction was followed by nmr. Since the reaction was carried out in an ordinary oil bath the temperature varied by $\pm 1^{0}$, which probably accounts for some difference between the two runs of each solution. The mean of the two runs was plotted and the results are shown in Figure 11.

Benzoyl peroxide accelerates the decomposition of 71 in solution. (The half-life of benzoyl peroxide at 110^{0} is approximately 30 min[59].)

A plot of ln(% of undecomposed 71) *vs* time is shown in Figure 12. Since the conditions were erratic (see the Experimental Section for the conditions which were used) some of the points did not fit the straight line plots. The first order rate constants for the different runs were calculated by the least squares treatment of the data and are shown in Figure 12. The rate of decomposition of 71 at 110^{0} seems to be increased by the increase in concentration of benzoyl peroxide. The benzoyloxy or the phenyl radicals (R•) obtained by the decomposition of benzoyl peroxide may abstract a bromine atom from 71 giving the ring-opened radical 71' which can form 80 by the loss of a methyl radical. However, the other two thermal products 81 and 82 cannot be formed by this route.

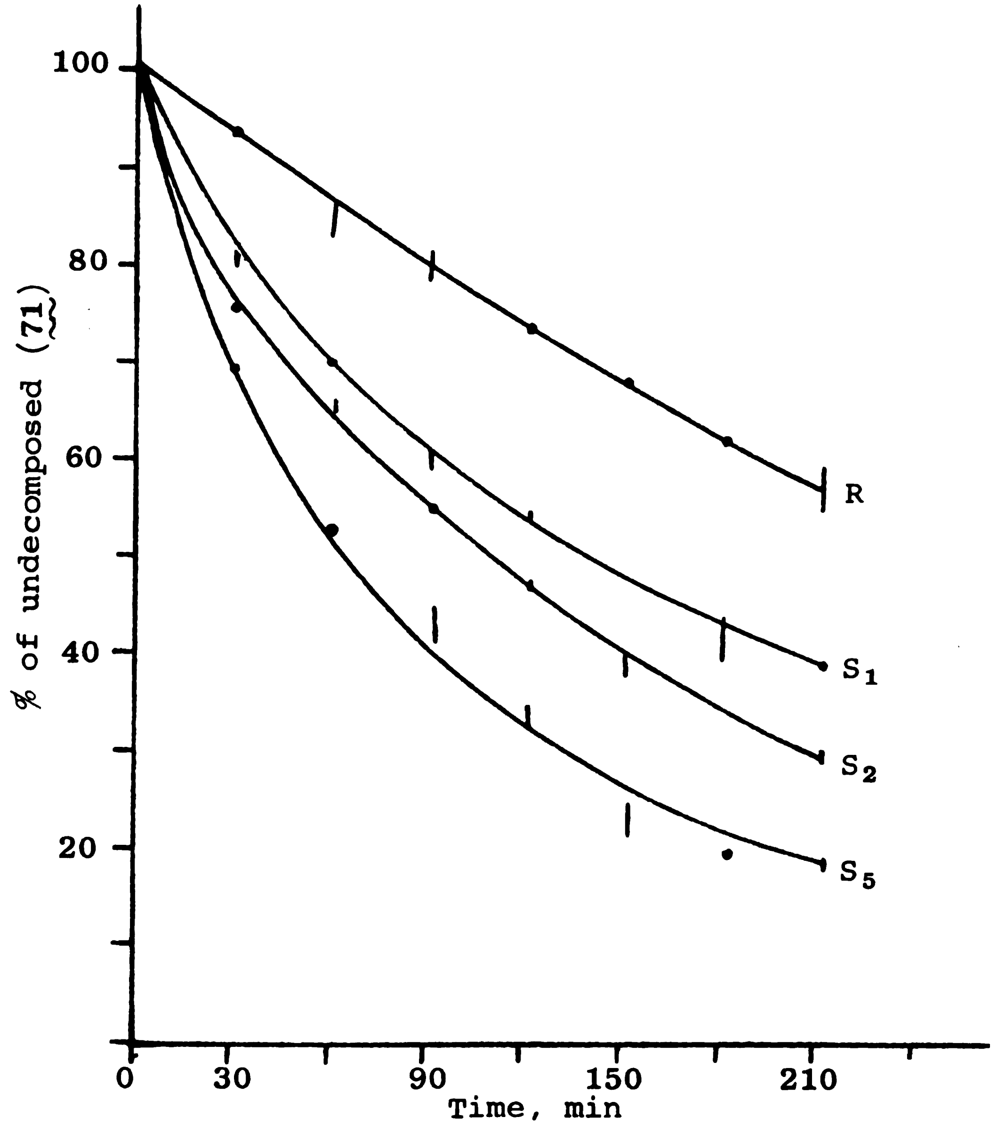


Figure 11. Effect of benzoyl peroxide on the pyrolysis of 71

R Reference solution, 0.2M 71 in benzene.

S_1 Sample solution, 0.2M 71 and 0.01M benzoyl peroxide in benzene.

S_2 Sample solution, 0.2M 71 and 0.02M benzoyl peroxide in benzene.

S_5 Sample solution, 0.2M 71 and 0.05M benzoyl peroxide in benzene.

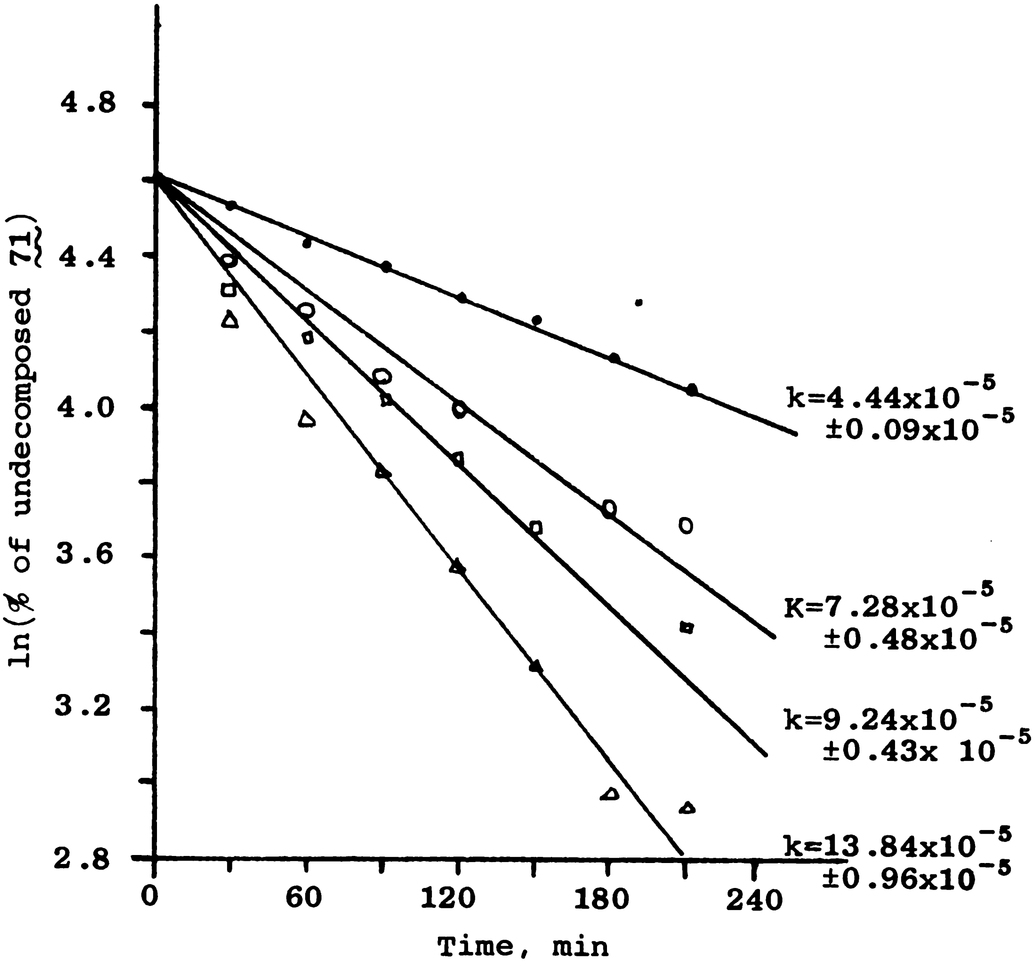


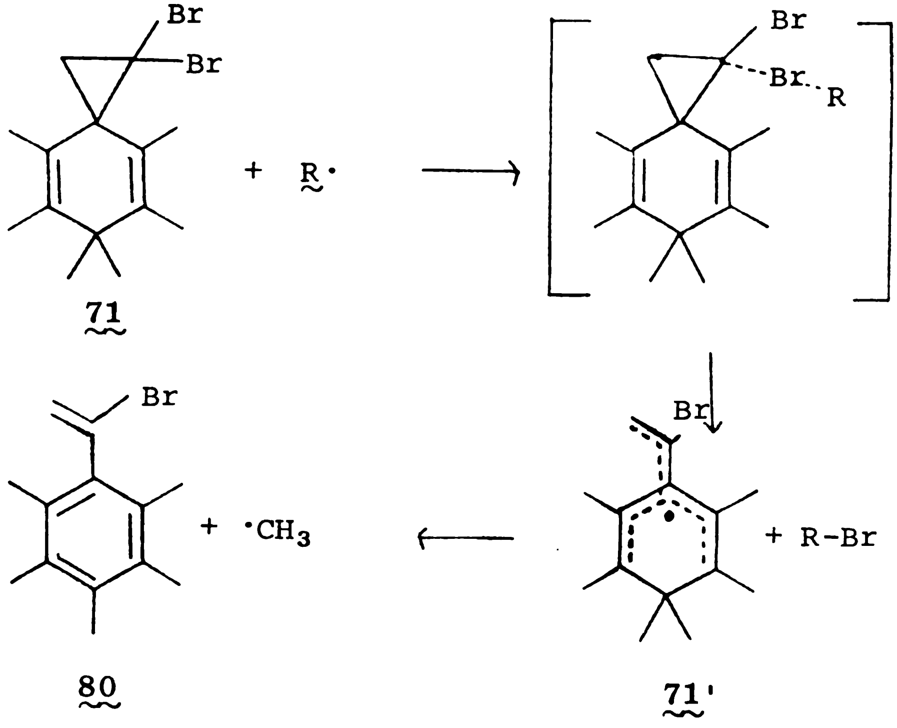
Figure 12. Kinetics of the thermal rearrangement of 71 in benzene at 110°.

● = 0.20M 71 in benzene.

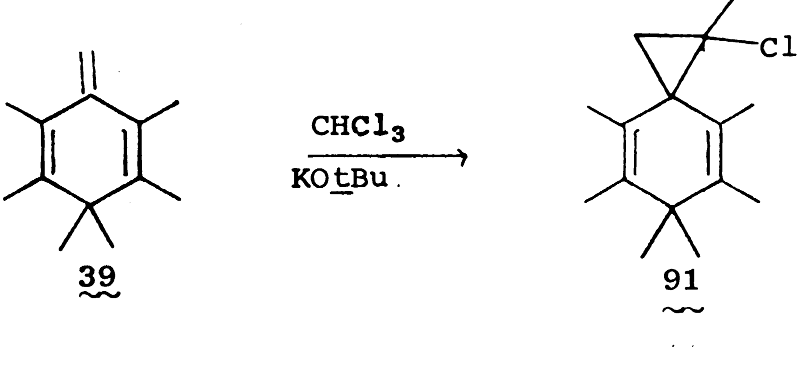
○ = 0.20M 71 and 0.01M benzoyl peroxide in benzene.

□ = 0.20M 71 and 0.02M benzoyl peroxide in benzene.

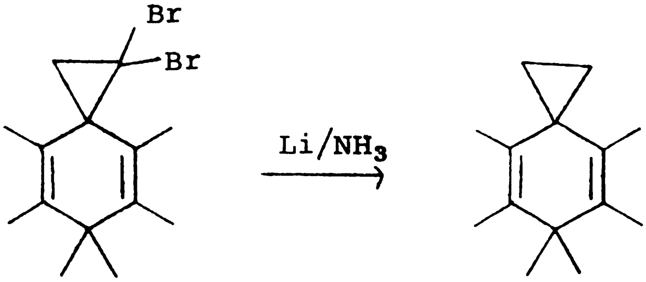
△ = 0.20M 71 and 0.05M benzoyl peroxide in benzene.



2,2-Dichloro-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (**91**) was prepared in the same way as the dibromocarbene adduct **71**, using chloroform, potassium *t*-butoxide and triene **39**. The nmr spectrum (Figure 26) of **91** was very similar to that of **71**. It consisted of singlets at τ 8.91 (3H), 8.73 (3H), 8.45 (6H), 8.30 (6H) and 7.98 (2H). The chemical analysis and the mass spectrum were also in accord with the structure of **91**.



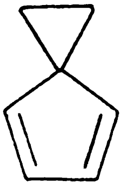
Compound 71 was reduced to the parent hydrocarbon 37 with lithium and liquid ammonia by the procedure used by Birch[60] to reduce 1,1-dihalocyclopropanes. Compound 37 was obtained in a 48% yield.



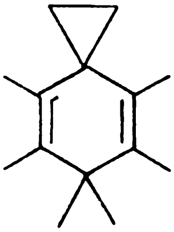
71 37

It is thermally unstable and decomposes to form a yellow oil when exposed to the atmosphere for a few hours. Due to its instability a good elemental analysis could not be obtained. It can be stored in 95% ethanol solution in the refrigerator.

The spectral data are also in accord with the proposed structure of 37. The nmr spectrum (Figure 27) consisted of singlets at τ 9.28 (4H), 8.93 (6H), 8.74 (6H) and 8.40 (6H). The ir spectrum (Figure 14) had bands at 3070 (cyclopropane ring-hydrogen band) and 1635 cm^{-1} (C=C). The uv spectrum (cyclohexane) had a maximum at 213 nm (ε 11,630). This absorption could be compared to the intense absorption of spiro[2.4]hepta-4,6-diene (92) at 223 nm (EtOH, $\varepsilon = 6310$) which appears to arise from the interaction of the 200 nm Rydberg diene transition (R <— N band) with the 190-210 nm cyclopropane transition.[61] It is suggested that with diene 92 the in-plane cyclopropane electronic transition has a direction such that it can couple strongly with the diene 2p → 3s out-of-plane Rydberg transition of appropriate symmetry. Such an interaction is also possible for 37 and the higher intensity of the absorption in 37 may be due to the greater flexibility of the six-membered ring allowing greater interaction of the cyclopropane ring.



92

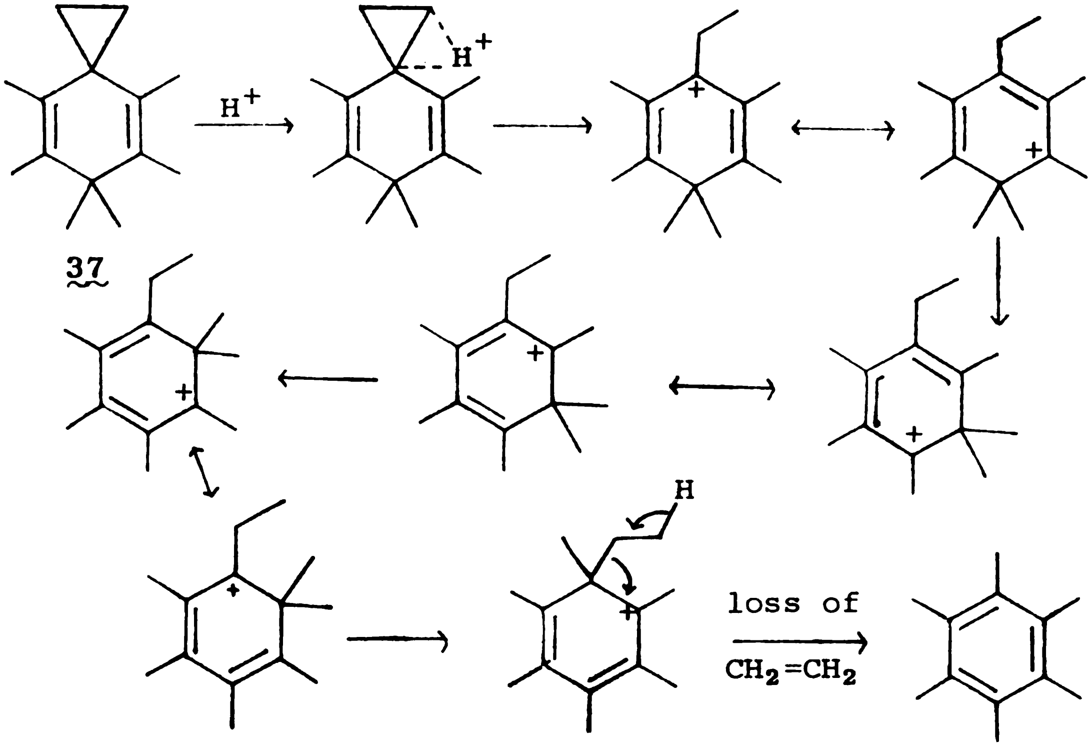


37

Since we had compound 37 in reasonable amounts we could study its chemistry further. For a photochemical investigation a 1% solution of 37 in ether was irradiated through quartz with a 450-watt Hanovia lamp. The nmr spectrum of the material recovered after 22 hr was identical with the starting material. Next an acetone-sensitized photolysis was tried. This time a 1% solution of 37 in acetone was irradiated under similar conditions through Pyrex. Once again the nmr spectrum of the recovered material showed mostly starting material, but a small peak was observed at τ 7.88 which may have been caused by the formation of a small amount of hexamethylbenzene. When the photolysis of 37 was carried out in the vapor phase with mercury sensitization using 2537 A resonance lamps in a Srinivasan-Griffin reactor for 21 hr at 40^0 still no change was observed in the starting material. The problem here is that 37 has a very small vapor pressure. Therefore a very small amount of this compound is present in the vapor phase. The reaction was repeated at 71^{0}, hoping that more of compound 37 may be present in the vapor phase at this temperature. The nmr spectrum of the product showed mostly starting material and a large peak at τ 7.88 indicating the presence of hexamethylbenzene. It is not known whether hexamethylbenzene is a thermal or photo product, because compound 37 had been found to rearrange thermally to hexamethylbenzene.

To investigate the thermal reaction of 37 a 10% solution of 37 in tetrachloroethylene (bp 121^{0}) was refluxed for 36 hr. This solvent was used because it would not interfere with the proton nmr spectrum of the thermal products. The solution was scanned by nmr, which showed the presence of a small amount of starting material and a strong peak at τ 7.84 indicating the presence of hexamethylbenzene. In order to carry out a quantitative determination of the hexamethylbenzene formed, a solution of 0.5 g of 37 in 10 ml of decalin was refluxed for 10 hr. The solution was then concentrated and chromatographed over alumina. A white residue (0.2 g) was obtained. The nmr spectrum showed a singlet at τ 7.84 and signals for the starting material. From the nmr spectrum, a 2.3% contamination of starting material was calculated. The mass spectrum of this residue showed the major peak at 162 (MW of hexamethylbenzene 162) and a small peak at 190 (MW of 37 190). From the relative heights of the peaks it was confirmed that hexamethylbenzene, obtained in 47.5% yield, was contaminated with 2.3% of 37. The mechanism of this reaction was not investigated.

To investigate the behavior of compound 37 in an acidic medium it was added to a 2% solution of *p*-toluenesulfonic acid in carbon tetrachloride and refluxed for 15 hr. The solution was then concentrated and the residue was chromatographed over alumina. A 60% conversion and a 78.7% yield of hexamethylbenzene (93) was obtained. The rest of the material contained polymeric products and was not investigated further. When an nmr spectrum of 37 in trifluoroacetic acid was obtained, a signal at τ 7.84 was observed instantly indicating the rapid formation of hexamethylbenzene. The following mechanism is proposed for this conversion.



37

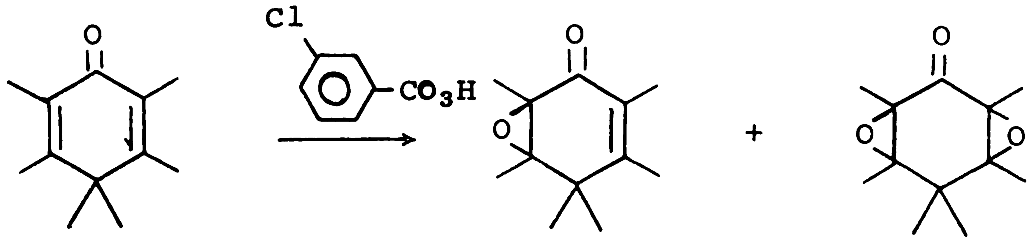
93

In order to justify this mechanism a low temperature study was undertaken. It has been reported that cyclopropane is protonated and cleaved in FSO_3H-SbF_5-SO_2ClF solution above -80° to t-butyl and t-hexyl cations in varying amounts.[62] A solution of 37 in methylene chloride was added slowly to fluorosulfonic acid at -78°. An nmr spectrum was obtained at -80° of the resulting solution and it consisted of multiplets at τ 8.50 and 7.08. There was not much change in the spectrum by raising the temperature from -80° to 45°. Spectra were obtained at various temperatures between these two limits. It appears that the carbonium ion initially formed undergoes dimerization and trimerization, giving a complicated nmr spectrum. We had hoped to observe one of the intermediates at -80° or even a mixture of them. They should be stable since they are tertiary carbonium ions. Also because hexamethylbenzene is formed instantly at room temperature in strong acid solutions, we had hoped to observe the formation of hexamethylbenzene by gradually raising the temperature from -80° to 45°. No signal was found to develop at τ 7.84, indicating that starting material had probably polymerized.

B. Preparation and Photolysis of 2,3-Epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (94) and 2,3:5,6-Diepoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (95)

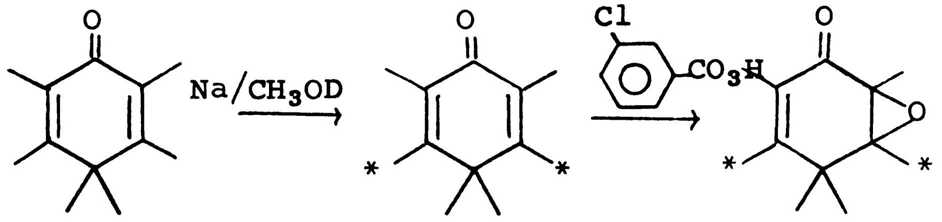
Though some chemistry of 2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (35) had been well studied in our laboratory, it has not been epoxidized before. The resulting

2,3-epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (94), a Δ^2- unsaturated, α,β-epoxyketone, should make an interesting subject for a photochemical study. The sodium salt of hydrogen peroxide or the sodium salt of *t*-butyl hydroperoxide are two reagents which are recommended for the epoxidation of α,β-unsaturated ketones.[63] The reaction is believed to proceed by nucleophilic attack of the hydroperoxide ion on the β-carbon of the unsaturated ketone. But the attempt to prepare 94 from dienone 35 with sodium hydroxide and hydrogen peroxide was unsuccessful. Next hydrogen peroxide with sodium tungstate was used as the epoxidizing reagent. This is a very potent reagent for epoxidation. Payne and Williams[64] found that maleic, fumaric and crotonic acid were very resistant to attack by peracetic or perbenzoic acid but were converted to their epoxides in good yields by hydrogen peroxide-sodium tungstate. However, 35 was not epoxidized by this reagent. Therefore *m*-chloroperbenzoic acid was used next. A vpc analysis of the product mixture showed that it contained two new products. When a mass spectrum was obtained of these compounds, one had a parent peak 16 units above that of the dienone, at mass 194, which indicated it might be epoxide 94. The second compound had a parent peak at mass 210 indicating it might be the diepoxide 95.



35 94 95

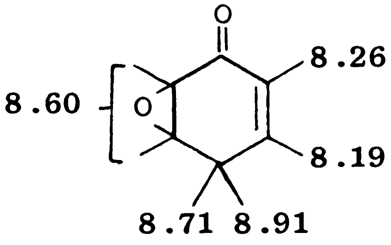
The uv spectrum (cyclohexane) of 94 had maxima at 323 nm (ε 86) and 246 nm (ε 8330). The infrared spectrum (Figure 16) had bands at 1655 (conjugated C=O), 1625 (C=C) and at 1025 cm^{-1} (oxirane ring C-O). The nmr spectrum of 94 (CCl_4, Figure 28) showed gem dimethyls at τ 8.91 (s, 3H) and 8.71 (s, 3H). The allylic methyls were seen at τ 8.26 (s, 3H) and 8.19 (s, 3H), whereas the methyls at C_2 and C_3 appeared as a singlet at τ 8.60 (6H). In order to confirm these assignments 3,5-dimethyl-d_6-2,4,4,6-tetramethyl-2,5-cyclohexadienone (96) was made as described previously.[39] Epoxide 97 was obtained by the oxidation of 96 with m-chloroperbenzoic acid. The nmr spectrum of 97 showed no



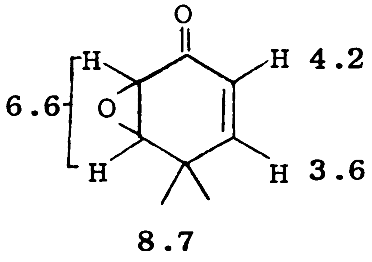
35 96 97

peak at τ 8.19; therefore this signal can be assigned to the allylic methyl at C_5. The signal at τ 8.60 integrated for only 3 hydrogens instead of 6 hydrogens; therefore this signal is rightly assigned to the methyl groups at C_2 and C_3.

2,3-Epoxy-4,4-dimethyl-2,5-cyclohexadienone (98) is a known compound[65] and the nmr spectra of 94 and 98 are given below for comparison.

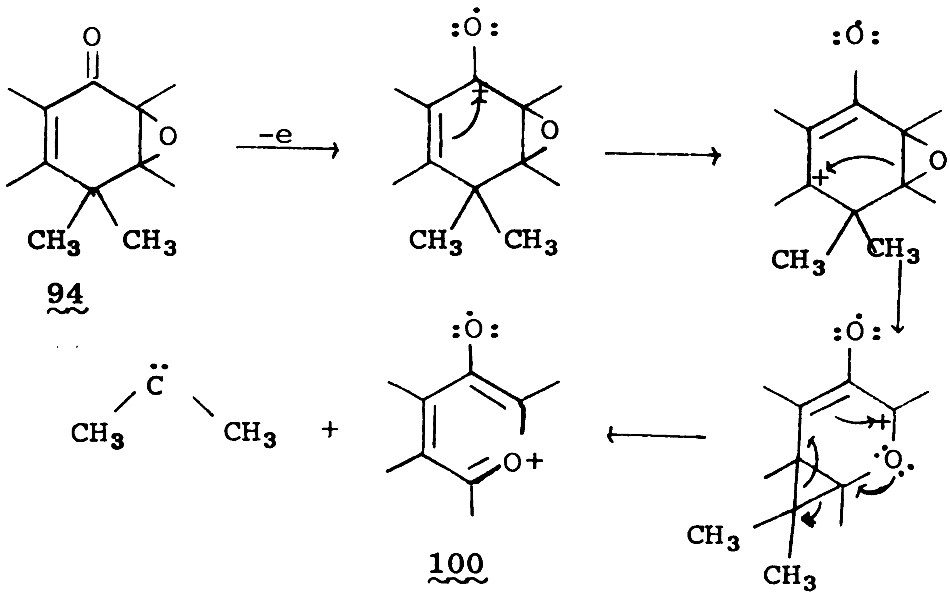


94

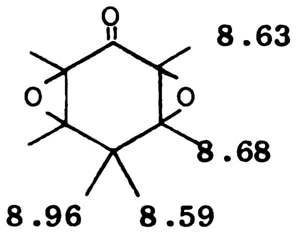


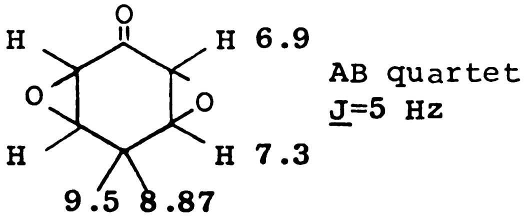
98

The groups at C_5 are deshielded more than the groups at C_6 in both cases. Also the groups at C_2 and C_3 have identical chemical shifts. The mass spectrum of 94 showed the parent peak at mass 194 and a base peak at mass 152. The latter is probably formed from epoxide 94 by the elimination of propylene (42 mass units) as shown below, and may have structure 100. Ion 100 would be expected to be very stable because it is aromatic according to Huckel's 4n + 2π electron rule of aromaticity.



The uv spectrum of diepoxide 95 had maxima at 240 nm (ε 607) and at 217 nm (ε 1960). The ir spectrum (Figure 17) had bands at 1690 (C=O) and 1025 cm^{-1} (oxirane ring C-O). The nmr spectral data for diepoxide 95 and diepoxide 99, which is a known compound,[65] are given below:

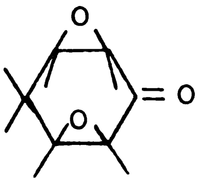




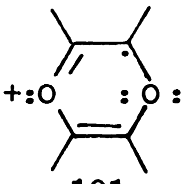
95

99

Since the gem dimethyls of diepoxide 95 do not have identical chemical shifts, the compound probably has the *syn* configuration. If 95 had the *anti* configuration the geminal methyls would be expected to have identical chemical shifts.

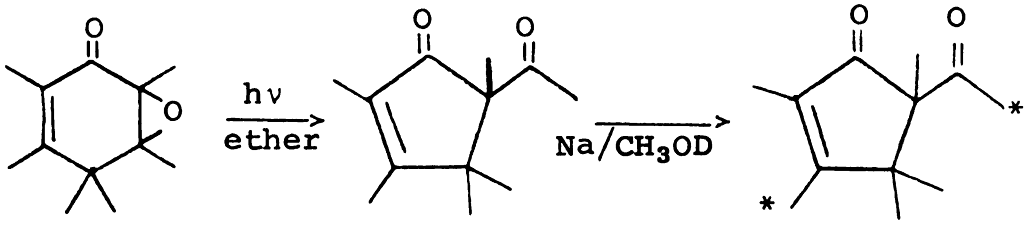


The mass spectrum of 95 showed the parent peak at mass 210 and a base peak at m/e 140, which may represent ion 101 which can be obtained from diepoxide 95 by the elimination of carbon monoxide and propylene (28 + 42 mass units).



101

For the photochemical study a 1% solution of 94 in ether was irradiated through Pyrex with a 450-watt Hanovia lamp. The reaction was monitored by vpc but no change was observed even after 6 hr. When the reaction was repeated using a 1% acetone solution of 94 under similar conditions, still no change was observed. The experiment with a 1% solution of 94 in ether was repeated but with a vycor filter. The reaction was followed by vpc. As the reaction proceeded the peak for 94 became smaller and a new peak which appeared grew larger. The reaction was complete after 10 hr. The photoproduct was collected by preparative vpc as a colorless oil. Elemental analysis and the mass spectrum of the photoproduct showed that it was isomeric with starting material. The photoproduct was identified as 6-acetyl-2,3,4,4,5,-pentamethyl-2-cyclopentenone 102 on the basis of its spectral data.

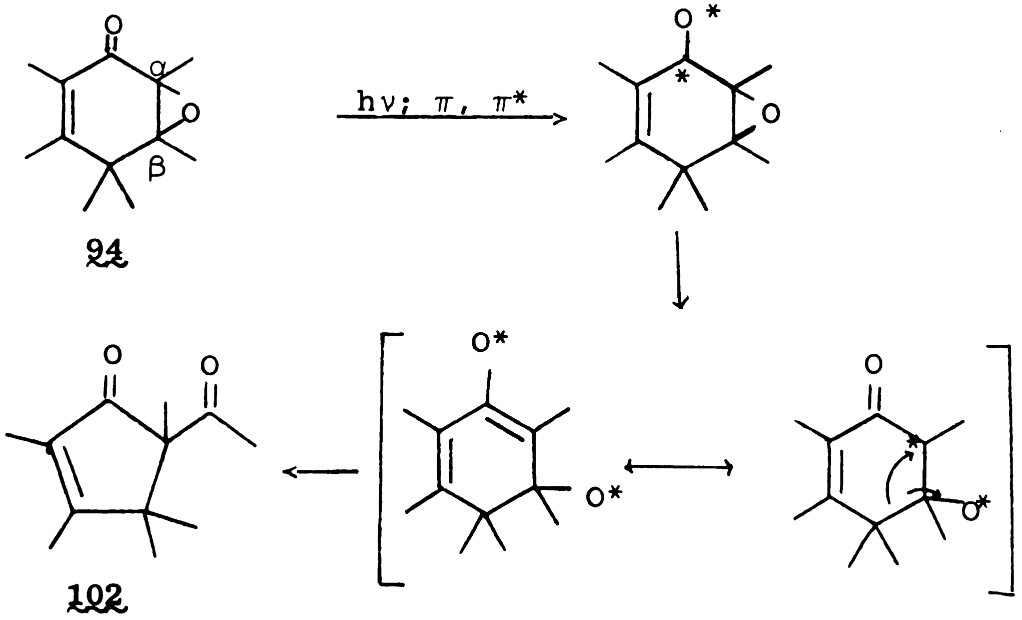


94 102 103

The ir spectrum of 102 (Figure 18) showed bands at 1698 and 1647 cm^{-1} which are assigned to the β-diketonic groups. The uv spectrum (cyclohexane) had a maximum at 233 nm (ε 14750). According to the empirical generalizations derived by Woodward^{66,67} for the effect of substituents on the position of π, π^* absorption in the uv spectrum of α,β-unsaturated ketones, 102 should have an absorption band at 247 nm. This predicted value is for spectra obtained in ethanol. In order to compare the observed value with the predicted value a correction has to be made for the solvent effect. A correction of +7 is recommended for converting spectra from hexane to ethanol.[66] Assuming that this correction should hold for cyclohexane, the observed π, π^* absorption band would appear at 240 nm in ethanol. Though this value is lower than the predicted value (247), it is in keeping with the observations of Gilliam and West[68] that α,β-substituted cyclopentenones absorb at lower wavelengths than predicted by Woodward's rules. Gilliam and West found that substituted cyclopentenones absorb around 232-237 nm, and this value is in better agreement with our observation. The nmr spectrum (CCl_4, Figure 30) of 102 showed the geminal methyls as two singlets at τ 9.0 (3H) and 8.94 (3H). A singlet at τ 8.88 (3H) is assigned to the methyl group at C_5. A multiplet at τ 8.34 (3H) is assigned to the allylic methyl at C_2 and the multiplet at τ 8.06 (6H) represents the allylic methyl at C_3 and the acetyl methyl group.

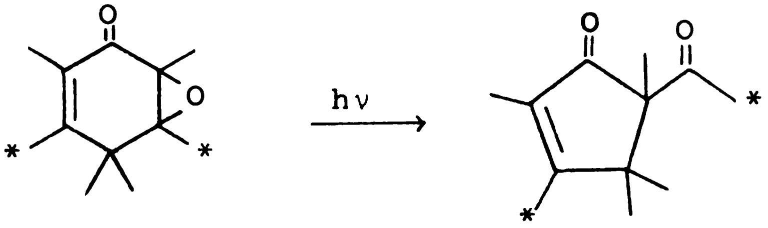
In order to confirm the last assignment 102 was dissolved in 5 ml of 95% methanol-d containing sodium and refluxed for 6 hr to exchange the hydrogens of the allylic methyl at C_3 and the acetyl methyl group. The nmr spectrum of the product showed no signal at τ 8.06; therefore this signal is rightly assigned to the two groups that are capable of exchange.

The results of the photolysis of 94 are in accord with the observations of Jeger and coworkers[51] for the photorearrangement of Δ^2-unsaturated α,β-epoxyketones which were mentioned in the Introduction. Accordingly when 94 was irradiated through Pyrex (>2800 A) no photoreaction was observed but when it was irradiated through Vycor (>2100 A) rearrangement took place. Therefore this reaction probably goes through a π, π^* excited state, most likely the singlet state, because the reaction was not sensitized by acetone.



The preferential migration of the methylene group over the methyl group from the β-position to the α-position is in agreement with the migratory aptitude of the β-substituents found by Reusch and Markos.[50]

To further support the above mechanism and to show that the methyl at C_5 in 94 ends up on the acetyl group of 102, we photolyzed 3,5-dimethyl-d_6-2,3-epoxy-2,4,4,6-tetramethyl-2,5-cyclohexadienone (96) which had been prepared earlier. When 96 was irradiated under the same conditions as 94, the photoproduct obtained had an nmr spectrum identical to that of 103. This supports the proposed mechanism for the photorearrangement by methylene migration.



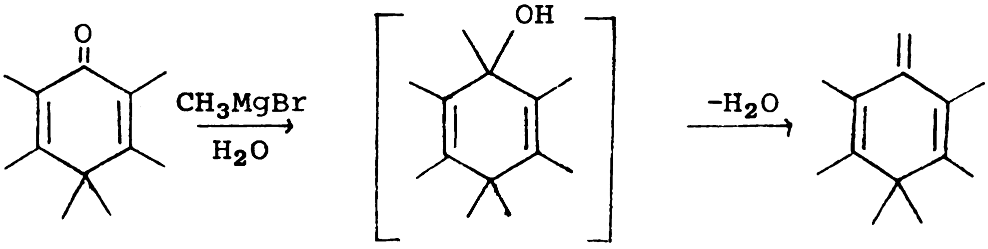
96 103

In order to demonstrate the presence of an unsaturated five membered ring in 102 an attempt was made to hydrogenate 102 to prepare the corresponding saturated cyclopentanone. All attempts to hydrogenate this compound were unsuccessful. Even when 102 was taken in an acidic ethanol solution with palladium on charcoal as the catalyst and subjected to hydrogen at 6 atm pressure, it still could not be hydrogenated.

Diepoxide 95 was irradiated through various filters and finally through quartz using a 450-watt Hanovia lamp, but it remained unchanged. When an acetone solution of 95 was irradiated through Pyrex under the same conditions for 16 hr, the nmr spectrum of the recovered material showed that starting material was still unchanged. Compound 95 seems to act like an ordinary saturated ketone.

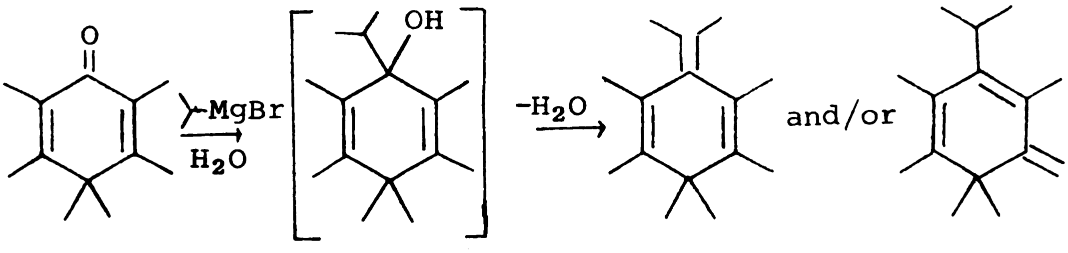
C. Attempted Preparation of 2-Methylene-1,3,3,4,5-pentamethylbicyclo[2.2.2]octa-5,7-diene (**65**)

DeVrieze[41] found that when dienone **35** was treated with methylmagnesium bromide only hydrocarbon **39** was isolated because the initially formed tertiary alcohol **104** dehydrates to give **39**.



35 **104** **39**

Similarly when we treated **35** with isopropylmagnesium bromide a quantitative yield of hydrocarbon with a molecular formula $C_{15}H_{24}$ was obtained. The tertiary alcohol **105** can dehydrate to give two possible products, **106** or **107**.

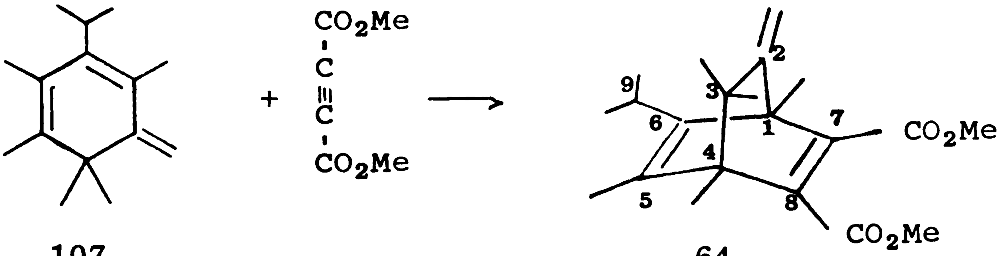


35 **105** **106** **107**

The nmr spectrum of the product showed that only 1-methylene-3-isopropyl-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (**107**) was obtained. The nmr spectrum (Figure 31) included a singlet at τ 8.94 (6H) for the gem dimethyls. Two peaks at τ 8.85 (3H) and 8.71 (3H) probably represent the two methyls of the isopropyl group. A multiplet at τ 8.33-7.71 (9H)represents the three allylic methyls. The multiplet at τ 7.06 (1H) represents the hydrogen of the isopropyl group and the vinylic protons appear at τ 5.10 (2H, *J* = 2.3 Hz) as an AB quartet. In case structure 106 had been obtained, vinylic protons would not be present in the nmr spectrum and six methyl groups would have been obtained in the allylic region instead of the three that were observed. Also the multiplet at τ 7.06 for the tertiary proton of the isopropyl group would not be observed if 106 had been obtained.

The uv spectrum (cyclohexane) had maxima at 310 nm (ε 3260), 255 nm (ε7050) and 220 nm (ε 6800). Using the rules proposed by Fieser and Fieser[69] for the calculation of uv spectra of steriodal dienes and polyenes a value of 318 nm is calculated for structure 107 and 279 nm for 106. The observed maximum at 310 nm is consistent with structure 107 rather than structure 106. The ir spectrum (Figure 19) had bands at 1655 and 1625 cm^{-1} (C=C).

To further confirm that 107 had a conjugated cyclohexadiene structure, an adduct of 107 was made with dimethyl acetylenedicarboxylate. It is assigned structure 64.



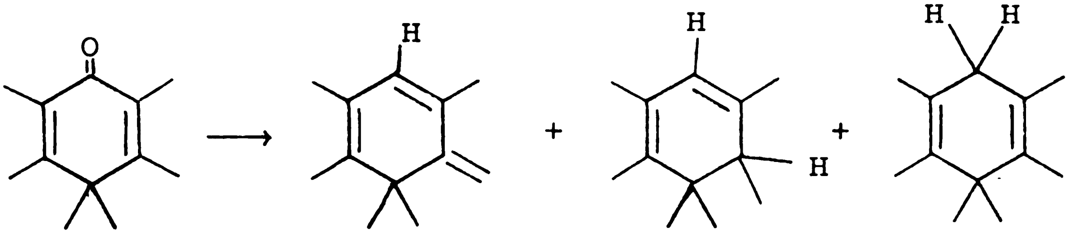
107

64

The chemical analysis and mass spectrum confirmed that 64 had a molecular formula of $C_{21}H_{30}O_4$. The nmr spectrum (Figure 32) consisted of singlets at τ 9.03 (3H), 8.95 (6H), which may be due to the methyl groups at C_3 and one of the methyls at C_9. A doublet was observed at τ 8.84 (3H, J = 1.75 Hz) and probably represents the other methyl group at C_9. Two singlets at τ 8.56 (3H) and 8.45 (3H) are in the range of bridgehead methyls and therefore are assigned to the methyls at C_1 and C_4. The singlet at τ 8.20 (3H) is assigned to the allylic methyl at C_5. The methyls on the ester groups were seen as a singlet at τ 6.40 (6H) and the two vinylic protons appeared at τ 5.30 (s, 1H) and 5.14 (s, 1H).

Compound 64 has a 2-methylenebicyclo[2.2.2]octadiene structure and we were interested in studying the photochemistry of such a system. Since 64 is a very complicated molecule with various substituents we decided to prepare a simpler molecule with the basic 2-methylenebicyclo[2.2.2]-octa-5,7-diene structure. We chose to attempt the synthesis of 2-methylene-1,3,3,4,5-pentamethylbicyclo[2.2.2]-octa-5,7-diene (65) because a possible route for its preparation from 2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (35) could be formulated.

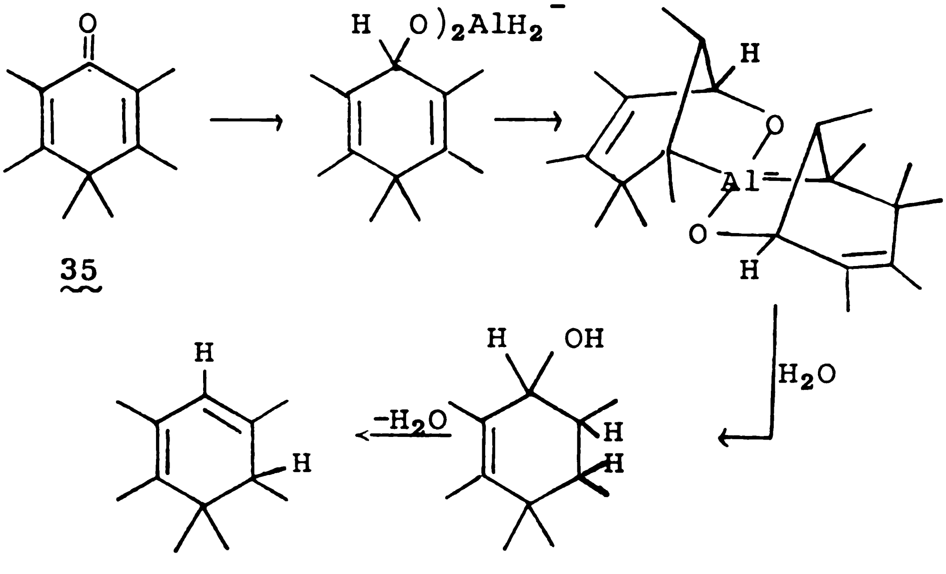
The first step for the synthesis of this bicyclooctadiene was the preparation of 1-methylene-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (108) which had been made in this laboratory by Dr. A. Sheller by the reduction of dienone 35 with lithium aluminum hdyride.[70]



35 108 109 110

Dienone 35 on reduction probably forms the corresponding tertiary alcohol which dehydrates to give triene 108. When we repeated the reduction of 35 with lithium aluminum hydride, the vpc trace of the product mixture showed three peaks with retention times of 6.5, 13 and 17 min. The peak with a retention time of 17 min was the required triene 108. The nmr spectrum of the collected material consisted of peaks at τ 8.9 (s, 6H, gem dimethyls), 8.33 (s, 6H, methyls at C_4 and C_5), 8.13 (d, 3H, J = 1.5 Hz, methyl at C_2), 5.10 (s, 2H methylene group at C_1), 4.56 (m, 1H, vinylic proton at C_3). The nmr spectrum was identical to that obtained by Dr. Sheller for triene 108.

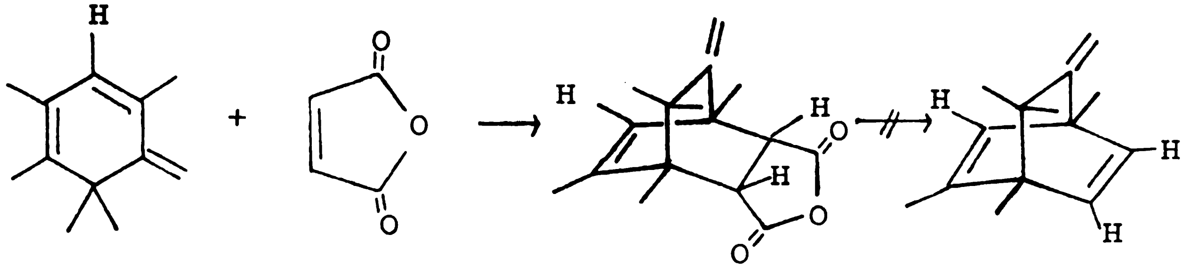
The chemical analysis and the mass spectrum of the compound with a retention time of 6.5 min showed that it had a molecular formula of $C_{12}H_{20}$; that is there were two more hydrogens than in triene 108. This compound is assigned structure 109. The nmr spectrum (Figure 34) of this compound is consistent with this structure, as it showed a doublet at τ 9.21 (3H, J = 7 Hz), two singlets at τ 9.13 (3H) and 9.07 (3H), a multiplet at 8.38-8.30 (10H) and another multiplet in the vinylic region at τ 4.73 (1H). The ir spectrum (Figure 21) had a band at 1663 cm^{-1}. Though double bonds are generally not reduced by lithium aluminum hydride, α,β-unsaturated carbonyl compounds form an exception to this rule.[71] They are first reduced to the corresponding allylic alcohols which are further reduced to saturated alcohols via organoaluminum intermediates. A similar mechanism is used below to explain the formation of 109 from dienone 35.



109

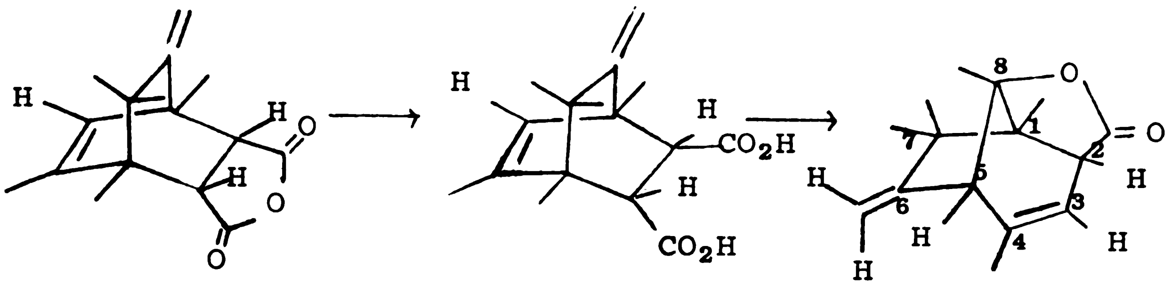
The compound with a retention time of 13 min had an nmr spectrum (Figure 33) which consisted of singlets at τ 8.99 (6H), 8.43 (12 H), 7.60 (2H) and is assigned structure 110. Mass spectrum showed parent peak at 164. This compound was not investigated in great detail because it was a minor side product.

Triene 108 is very reactive and turns yellow on keeping. Therefore it cannot be stored for a long time and must be used as quickly as possible. On adding maleic anhydride to triene **108** an adduct was obtained in 93.5% yield. The adduct was assigned structure **111** on the basis of its nmr spectrum (Figure 35) which consisted of singlets at τ 9.05 (3H), 8.89 (3H), 8.54 (6H) and doublets at τ 8.28 (3H, *J* = 1.7 Hz), 7.34 (1H, *J* = 8.5 Hz), 6.90 (1H, *J* = 8.5 Hz), two more singlets in the vinylic region at τ 5.25 (1H) and 5.06 (1H), and a broad singlet at τ 4.54. A band at 1763 cm^{-1} (C=O), was observed in the ir spectrum (Figure 23). By oxidizing **111** with lead tetraacetate we hoped to obtain the desired compound, 2-methylene-1,3,3,4,5-pentamethylbicyclo[2.2.2]octa)5,7-diene (**65**). However, when **111** was oxidized with lead tetraacetate no reaction was observed and the nmr spectrum of the recovered material showed that it was unchanged starting material.



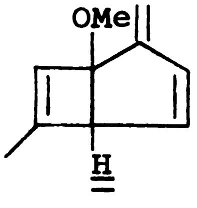
108 **111** **65**

Another attempt was made to prepare **65** by hydrolyzing **111** to the diacid **112** and oxidizing it with lead tetraacetate. The major product, which formed 75% of the volatile products of this reaction, was not the desired compound **65**. The ir spectrum (Figure 24) of this product had a band at 1770 cm^{-1}, which is typical of a γ-lactone.[72] The uv spectrum (cyclohexane) had maxima at 240 nm (ε 8370), 220 (ε 7940) and 214 nm (ε 8370). The chemical analysis and mass spectrum showed that the lactone had a molecular formula of $C_{15}H_{20}O_2$. The nmr spectrum (Figure 36) consisted of singlets at τ 9.06 (3H), 8.93 (3H), 8.78 (3H), 8.64 (3H), doublets at τ 8.30 (3H, *J* = 1.5 Hz) and 7.51 (1H, *J* = 6 Hz) and additional singlets at τ 7.38 (1H), 5.38 (1H), 5.20 (1H) and a multiplet at τ 4.66 (1H). On the basis of the spectral data and mechanistic considerations, the lactone has been assigned structure 113.



111 112 113

The signal at τ 7.38 is assigned to the proton at C_5. Compound 114 has been used as a model for this assignment. The tertiary proton in this compound has a chemical shift of τ 7.31.[73] This eliminates structure 115 in which the tertiary proton is at the C_8 position and should have a chemical shift of about τ 6.2. Structure 116 is eliminated on the basis that the proton at C_1 which can also be assigned the chemical shift of τ 7.38 should be split into a doublet by the proton at C_8 whereas the signal at τ 7.38 appeared as a singlet in the nmr spectrum.



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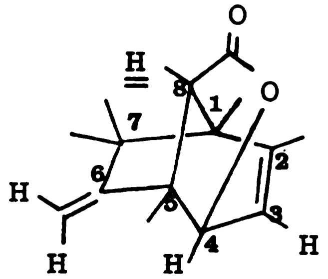
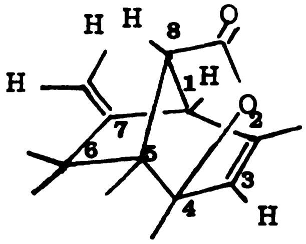
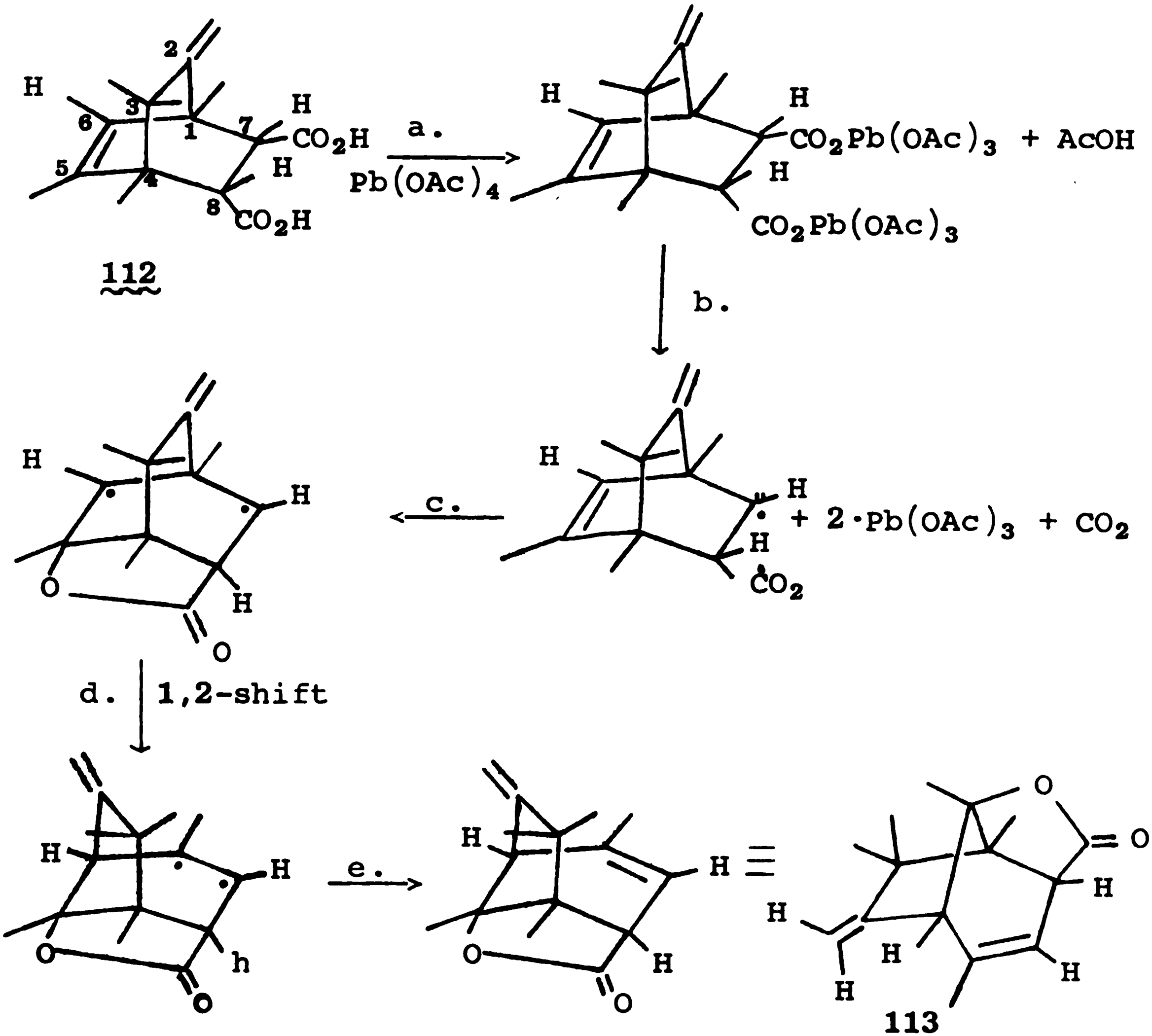


115



116

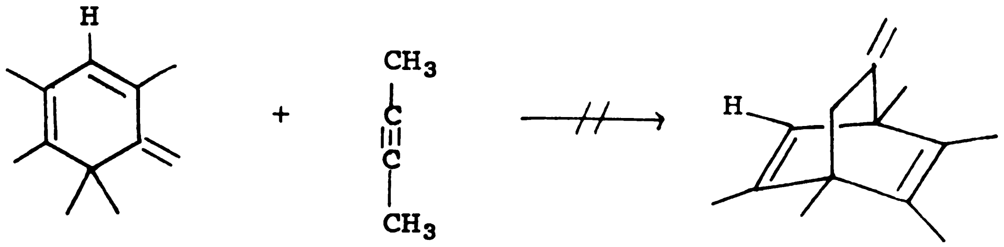
A possible mechanism for the formation of 113 from 112 is presented below.



A 1,2-shift from C_1 to C_7 in step d would result in compound 116 which has been eliminated on the basis of the nmr spectrum.

A γ-lactone can be reduced to the corresponding ether with sodium borohydride and boron trifluoride.[74] When **113** was reduced by these reagents the ir spectrum of the product showed that the carbonyl function was not present. The molecular weight of the product was determined to be 220 from the mass spectrum. This indicated that not only the carbonyl function of the lactone group had been reduced but also one of the double bonds, probably the exocyclic double bond, had been hydrogenated. Since we had only a few milligrams of the γ-lactone an appreciable amount of the reduction product was not obtained to carry out a complete structure determination.

Since the 2-methylenebicyclo[2.2.2]octa-5,7-diene system was not obtained an attempt was made to form an adduct of triene **108** with 2-butyne to form this bicyclic system directly. All attempts to form this adduct **117** were unsuccessful.



108 **117**

EXPERIMENTAL

1. *Microanalyses*: Microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

2. *Nuclear Magnetic Resonance Spectra*: These spectra were recorded on a Varian Model A-60 using CCl_4 solutions with tetramethylsilane as an internal standard.

3. *Infrared Spectra*: Infrared spectra were obtained with a Unicam Sp-200 spectrophotometer in CCl_4 solution (unless otherwise stated).

4. *Ultraviolet Spectra*: These spectra were obtained with a Unicam SP-800 spectrometer.

5. *Mass Spectra*: Mass spectra were obtained by Mrs. R. Guile with a Hitachi-Perkin-Elmer RMU-6 mass spectrometer.

6. *Melting Points*: Melting points were determined with a Gallenkamp Melting Point Apparatus and are uncorrected.

7. *Preparation of **37** from 1-Methylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene (**39**)*: To a vigorously stirred solution of 0.25 g of cupric acetate monohydrate in 15 ml of glacial acetic acid was added 4 g of zinc dust. The Zn-Cu couple formed at once and was allowed to settle for 1 min.

Glacial acetic acid was decanted and the couple was washed with more glacial acetic acid (2 x 15 ml) followed by anhydrous ether (3 x 12 ml). More anhydrous ether (10 ml) was added to the couple. The erlenmeyer flask which contained the couple was fitted with a reflux condenser and a dropping funnel. A few drops of methylene iodide were added to start the reaction. A solution of 4.56 g (0.026 mole) of **39** and 21.44 g (0.0352 mole) of methylene iodide in 25 ml of anhydrous ether was added to the Zn-Cu couple over 1 hr. The resulting solution was refluxed for 30 hr. The ethereal layer was decanted and washed thrice with a solution of 1*N* HCl containing ice cubes and twice with water. The washed ethereal layer was dried (Na_2SO_4), concentrated and analyzed by vpc using a 5-ft 20% SE-30 column at 150° with the flow rate of Helium at 75 ml/min. Three peaks with a retention time of 3, 5 and 14 min represented methylene iodide, triene **39** and compound **37** respectively. From the areas under the peaks a conversion of 61.5% was calculated and **37** was obtained in 95% yield: ir (CCl_4) 1635 cm^{-1} (C=C); nmr (CCl_4) τ 9.28 (s, 4H), 8.90 (s, 6H), 8.74 (s, 6H), 8.40 (s, 6H) and a singlet at τ 7.78.

8. *Preparation of 2,2-Dibromo-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (**71**)*: To a well stirred solution of 15.84 g (0.09 mole) of triene **39** and 15.75 g (0.108 mole, assuming it contains 38% *t*-BuOH) of potassium *t*-butoxide in pentane (100 ml) at 0° was added bromoform (27.9 g,

0.108 mole) over 10 min. The mixture was stirred for 4 hr at room temperature. Water (50 ml) was added to the mixture which was stirred for 10 min. The organic layer was separated and washed with water whereas the aqueous layer was washed with two 30-ml portions of pentane. The combined pentane layers were dried (Na_2SO_4) and concentrated to yield impure product (36 g). The crude product was treated with methanol (10 ml). When the methanol solution was cooled, the dibromocarbene adduct crystallized out to give 14 g (44.7%) of crystals.

Since the methanol solution still contained some unreacted triene 39, it was concentrated and subjected to the reaction again using 12 g of bromoform and 7 g of potassium *t*-butoxide. This time 2.5 g of product was obtained giving an overall yield of 52.75%: mp 88^0; ir spectrum is shown in Figure 13; nmr (CCl_4, Figure 25) τ 8.86 (s, 3H), 8.78 (s, 3H), 8.38 (s, 6H), 8.20 (s, 6H), and 7.81 (s, 2H); mass spectrum (70 ev, inlet temperature 100^0) m/e (rel intensity) 350(10), 348(20), 346(10), 335(4), 333(7), 331 (4), 269(3), 267(3), 254(8), 252(9), 175(100); mass spectrum (inlet temp 250^0) m/e (rel intensity) 269(5), 267(6), 254(12), 252(12), 171(100).

Anal. Calcd for $C_{14}H_{20}Br_2$: C, 48.29; H, 5.79; Br, 45.91.
Found : C, 48.29; H, 5.86; Br, 44.57.

9. *Photolysis of 71*: A 2% solution of 71 in pentane (15 ml) was taken in a quartz test tube. The solution was

irradiated with a 450-watt Hanovia lamp through vycor for 2 hr. At the end of this time the solution had become dark yellow and a black residue had deposited on the walls of the test tube.

The reaction was repeated using a corex filter but the black residue was observed even after 1/2 hr.

10. Reaction of **71** with Methyllithium: To a solution of 0.348 g (0.001 mole) of **71** in 10 ml of anhydrous ether at -78° was added a 0.5 ml of 2*M* solution of methyllithium (0.027 g) in anhydrous ether. The solution was stirred for 30 min and the excess of lithium salt was decomposed with water. The ethereal layer was separated, dried (Na_2SO_4), and concentrated to yield a white residue. The nmr spectrum of the residue showed peaks at τ 8.86 (s, 3H), 8.78 (s, 3H), 8.38 (s, 6H), 8.20 (s, 6H) and 7.81 (s, 2H).

The reaction was rerun at 0°. The nmr spectrum of the product had no peaks in the vinylic region. A vpc analysis with a 5-ft 20% SE-30 column at 160°, with helium flowing through at a rate of 75 ml/min showed a small peak at a retention time of 3 min and a large peak with a retention time of 6 min.

11. Pyrolysis of **71** in solution: A solution of **71** in the required solvent was taken in a Pyrex tube which was degassed, sealed and heated in an oil bath for 3 or 8 hr. The tube was then cooled to -78° and opened. The solution was concentrated and analyzed by vpc using a 5-ft 20% SE-52 column at 180° with helium flowing through at a rate of 75 ml/min.

Compound **80**: mp 74-76°; retention time 37 min; ir (CCl_4) 1625 cm^{-1}; uv max (cyclohexane) 227 nm (ε 1090); nmr (CCl_4): τ 7.84 (s, 9H), 7.74 (s, 6H), 4.42 (d, 1H, *J* = 1.25 Hz), 4.10 (d, 1H, *J* = 1.25 Hz); mass spectrum (70 ev) m/e (rel intensity) 254 (7), 252 (7), 172 (100), 157 (100).

Compound **81**: mp 74-75°; retention time 44 min; ir (CCl_4) 1615 cm^{-1}; uv max (hexane) 214 nm (ε 16580); nmr (CCl_4): τ 7.95 (s, 9H), 7.90 (s, 6H), 3.62 (d, 1H, *J* = 7.5 Hz), 2.99 (d, 1H, J = 7.5 Hz); mass spectrum (56 ev) m/e (rel intensity) 254 (45), 252 (46), 172 (86), 158 (100).

Anal. Calcd for $C_{13}H_{17}Br$: C, 61.66; H, 6.77; Br, 31.56.
Found: C, 61.94; H, 6.82; Br, 30.41.

Compound **82**: mp 76-77°; retention time 51 min; ir (CCl_4) 1610 cm^{-1} (C=C); uv max (hexane) 214 nm (ε 13900); nmr (CCl_4): τ 7.89 (s, 15H), 4.15 (d, 1H, *J* = 14 Hz), 3.11 (d, 1H, *J* = 14 Hz); mass spectrum (56 ev) m/e (rel intensity) 254 (27), 252 (28), 172 (69), 157 (100).

Anal. Calcd for $C_{13}H_{17}Br$: C, 61.66; H, 6.77; Br, 31.56.
Found: C, 61.20; H, 6.67; Br, 30.74.

12. *Preparation of* ***80***: Pentamethylacetophenone (1.0 g, 0.0053 mole) was refluxed with PBr_3 (4.0 ml, 11.4 g, 0.041 mole) for 5 hr. The mixture was poured into a beaker containing water and ice cubes, and extracted with ether. The ethereal extract was dried (Na_2SO_4) and concentrated to yield 0.7 g of a solid. The residue was dissolved in a small amount of acetone and analyzed by vpc using a 5-ft

20% SE-30 column at 135°, with helium flowing through at a rate of 75 ml/min; the retention time of the main peak was 12 min and it amounted to a 59.5% yield: mp 74-76°; ir CCl_4) 1625 cm^{-1} (C=C); uv max (hexane) 227 nm (ε 1090); nmr (CCl_4): τ 7.84 (s, 9H), 7.74 (s, 6H), 4.42 (d, 1H, *J* = 1.25 Hz); 4.10 (d, 1H, *J* = 1.25 Hz).

13. Preparation of 1-Dideuteromethylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene (84): a) Magnesium turnings (1.34 g, 0.055 mole) were taken in a 3-necked 100-ml flask fitted with a condenser and an addition funnel. Methyl-d_3 iodide (8 g, 0.055 mole) in 50 ml of ether was added slowly. The resulting solution was stirred for 2 hr at room temperaature. A solution of 6 g (0.0338 mole) of dienone 35 in 25 ml of ether was added to the Grignard reagent over 30 min and the solution was refluxed for 1.5 hr, cooled in an ice bath and hydrolyzed by 10 ml of D_2O containing 6 drops of D_2SO_4. The ethereal layer was separated, dried ($MgSO_4$) and concentrated to yield 6.0 g of crude product which was crystallized from methanol-d to give 3 g of pure 84: nmr (CCl_4): τ 8.9 (s, 6H), 8.17 (s, 12H) and 5.24 (s, 0.55 H).

b) 1-Methylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene (39, 1 g) was dissolved in 10 ml of carbon tetrachloride and 10 ml of D_2O containing 6 drops of D_2SO_4 was added to this solution and the mixture was stirred for 45 min. At the end of this time the D_2O layer was replaced by a fresh amount of D_2O containing D_2SO_4. The reaction was continued for 5 more hours and the D_2O layer was replaced again. The reaction was stopped after being stirred for 17 more hours, the carbon tetrachloride was separated, dried ($MgSO_4$), and concentrated: mass spectrum (70 ev) m/e (rel intensity) 162(100), 176(12), 177(24), 178(25), 179(16), 180(9), 181(4), 182(2), 183(1).

14. Effect of Benzoyl Peroxide on the Rate of Decomposition of 2,2-Dibromo-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (71): Duplicate samples (0.5 ml) of 0.20*M* 71 containing 0.01*M*, 0.02*M* and 0.05*M* benzoyl peroxide in benzene were taken in nmr tubes and degassed to 0.2 mm of Hg and sealed. These were heated in an oil bath at 110° ± 1°. Every 30 min the tubes were removed from the oil bath and the reaction was quenched by cooling them in a dry ice-acetone bath. The nmr spectrum was recorded and the tubes reheated for another 30 min. The results are shown in Figure 11.

Two 0.5-ml samples of 0.20*M* 71 in benzene were taken in nmr tubes which were degassed to 0.2 mm of Hg and sealed. These were heated in an oil bath at 110° ± 2° and the reaction was followed by nmr as above. The results are shown in Figure 11.

15. Preparation of 2,2-Dichloro-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (91): Compound 91 was made by the same procedure used for the dibromo compound 71, using triene 39, chloroform and potassium *t*-butoxide: mp 100-101.5°; yield 44%; the ir spectrum is shown in Figure 14; uv max (cyclohexane)

234 nm (ε 5850) and 206 nm (ε 5540); nmr (CCl_4, Figure 26): τ 8.91 (s, 3H), 8.73 (s, 3H), 8.45 (6H), 8.30 (s, 6H) and 7.98 (s, 2H).

Anal. Calcd for $C_{14}H_{20}Cl_2$: C, 64.86; H, 7.78; Cl, 27.32.
Found: C, 64.29; H, 7.66; Cl, 26.40.

16. Reduction of 71 to 4,5,6,6,7,8-Hexamethylspiro[2.5]octa-4,7-diene (37): To a blue solution of 2.0 g (0.284 atom) of lithium in 300 ml of ammonia was added a solution of 8.0 g (0.023 mole) of 71 in 80 ml of anhydrous ether, over 30 min. The resulting solution was stirred for an additional 2 hr. Then 14.98 g (0.28 mole) of ammonium chloride was added to the solution, whereupon the blue color disappeared. Ammonia was evaporated and the residue was treated with 30 ml of water and extracted with three 20-ml portions of ether. The ethereal extract was dried (Na_2SO_4) and concentrated to give 3 g of crude product which was crystallized from 95% ethanol to give 2.1 g (47.9%) of pure product: mp 65-67^0; ir spectrum is shown in Figure 15; uv (hexane) 213 nm (ε 11630); nmr (CCl_4, Figure 27): τ 9.28 (s, 4H), 8.93 (s, 6H), 8.74 (s, 6H), and 8.40 (s, 6H); mass spectrum (70 ev) m/e (rel intensity), 81(22), 119(39), 133(25), 147(65), 161(42), 162(46), 175(100), 190(81).

17. Photolysis of 37: A 1% solution of 37 in anhydrous ether was irradiated with a 450-watt Hanovia lamp through quartz for 22 hr. An nmr spectrum of the solid recovered from the ether solution showed singlets at τ 9.28 (s, 4H), 8.93 (s, 6H), 8.74 (s, 6H), and 8.40 (s, 6H).

18. Acetone-sensitized Photolysis of **37**: A 1% solution of **37** in acetone was irradiated through Pyrex under the same conditions as above for 16 hr. The nmr spectrum obtained was the same as above except for an additional peak at τ 7.88.

19. Mercury-sensitized photolysis of **37**: Compound **37** together with a drop of mercury, was placed in a long quartz tube. This was cooled to -78° and evacuated. Next dry nitrogen was let into the tube and it was allowed to warm up slowly to room temperature. This procedure was repeated two more times and the quartz was finally evacuated to a 0.1 mm pressure. The evacuated tube was irradiated in a Srinivasan-Griffin reactor using 2537 A resonance lamps for 21 hr at 40°. At the end of this time the tube was removed from the reactor and cooled to -78°. Dry air was let into the tube and the residue was extracted with pentane. The nmr spectrum of the product showed singlets at τ 9.28 (s, 4H), 8.93 (s, 6H), 8.74 (s, 6H), 8.40 (s, 6H) and 7.88 (s).

The whole procedure was repeated but this time the reactor temperature was maintained at 71°. The nmr spectrum obtained was identical with the one obtained when the reaction was carried out at 40°.

20. Pyrolysis of **37** in Solution: a) A 10% solution of **37** in tetrachloroethylene was heated for 36 hr at 121°. This solution was scanned directly by nmr and the spectrum showed small singlets at τ 9.28, 8.93, 8.74, 8.40 and a very large singlet at τ 7.88.

b) A solution of 0.5 g (0.0026 mole) of 37 in 10 ml of decalin was refluxed for 10 hr. The decalin solution was concentrated and chromatographed over 25 g of alumina. The column was eluted with 120 ml of pentane. A white residue (0.2 g) was obtained from the pentane solution; nmr (CCl_4): small peaks at τ 9.28, 8.93, 8.74, 8.40 and a large peak at τ 7.88; mass spectrum (70 ev) m/e (rel intensity) 147(100), 162(53), 190(2).

21. Acid-catalyzed Rearrangement of 37: Compound 37 (0.5 g, 0.0026 mole) was dissolved in 25 ml of a 2% solution of *p*-toluenesulphonic acid in carbon tetrachloride. The resulting solution was refluxed for 15 hr, and then washed with two 10-ml portions of water, dried (Na_2SO_4) and concentrated to yield 0.6 g of a black residue. The residue was chromatographed over a column of alumina which was eluted with pentane. Hexamethylbenzene (0.2 g) and 37 (0.2 g) were obtained from the pentane solutions giving 60% conversion and 78.7% yield of hexamethylbenzene.

22. Low Temperature nmr Study of 37: To 1 ml of FSO_3H at -78^0 was added a solution of 0.10 g of 37 in methylene chloride dropwise and the solution was stirred vigorously. The acid layer was pipetted into an nmr tube containing 0.006 g tetramethylammonium fluoroborate. The nmr spectra were obtained at -80^0 to 45^0 at 10^0 intervals: nmr (FSO_3H) τ 8.50 (m), 7.05 (m).

23. Attempted Preparation of 94 Using Sodium Hydroxide and Hydrogen Peroxide: In a 3-necked 100-ml flask equipped with a mechanical stirrer, thermometer and dropping funnel was placed a solution of 1.78 g (0.01 mole) of dienone 35 and 2.9 ml (0.03 mole) of 30% hydrogen peroxide in 10 ml of methanol. The flask was cooled to 15° and a solution of 0.2 g (0.005 mole) of sodium hydroxide in 0.5 ml of water was added slowly over 15 min. The mixture was stirred for an additional 3 hr at 20-25°, then poured into 200 ml of cold water. The aqueous solution was extracted with three 50-ml portions of ether. The ethereal solution was dried (Na_2SO_4) and concentrated. The residue consisted of 1.78 g of a white material: nmr: τ 8.82 (s, 6H), 8.18 (s, 6H), 8.05 (s, 6H).

24. Attempted Preparation of 94 Using Sodium Tungstate and Hydrogen Peroxide: A solution of 1.78 g (0.01 mole) of dienone 35 and 1.65 g (0.005 mole) of sodium tungstate dihydrate in 20 ml of ether was placed in a 3-necked, 100-ml flask fitted with a reflux condenser, dropping funnel and a magnetic stirring bar. The solution was stirred vigorously and 20 ml (0.208 mole) of 30% hydrogen peroxide was added to it over 45 min at room temperature. The resulting solution was refluxed for 45 min, then poured into 100 ml of cold water. The aqueous solution was treated with ether as above and 1.78 g of a white material was recovered from the ethereal extract: nmr (CCl_4): τ 8.82 (s, 6H), 8.18 (s, 6H), 8.05 (s, 6H).

25. Preparation of **94** using m-Chloroperbenzoic Acid: To a well-stirred solution of 3.58 g (0.02 mole) of dienone **35** in 60 ml of benzene at 0° was added 5.75 g (0.03 mole) of m-chloroperbenzoic acid. The solution was further stirred for 1 hr at 0° and then at room temperature for 24 hr. At the end of this time the benzene solution was washed with three 30-ml portions of 10% sodium hydroxide solution and with three 30-ml portions of water. It was then dried (Na_2SO_4) and concentrated to give 3.2 g of a white solid. This solid was dissolved in a small amount of acetone and analyzed by vpc using a 10-ft column of 20% DEGS on chromosorb 60/80 at 150°. The flow rate of helium was 170 ml/min and the injector temperature was 180°. Three peaks in a ratio of 1:19:10 were observed. The first peak had a retention time of 8 min which is identical with that of dienone **35**. The second peak had a retention time of 11 min and was found to be the epoxide **94**, while the third peak had a retention time of 18 min and was found to be the diepoxide **95**.

Spectral data and analysis of **94**: mp 48-48.5°; the ir spectrum is shown in Figure 16; nmr (CCl_4, Figure 28): τ 8.91 (s, 3H), 8.71 (s, 3H), 8.26 (s, 3H), 8.19 (s, 3H), 8.60 (s, 6H); uv max (cyclohexane) 323 nm (ε 86) and 246 nm (ε 8330); mass spectrum (70 ev) m/e (rel intensity) 194(5), 188(4), 152(100), 137(78).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34.

Found: C, 73.93; H, 9.29.

Spectral data and analysis of 95: mp 80-81°; the ir spectrum is shown in Figure 17; nmr (CCl_4, Figure 29): τ 8.96 (s, 3H), 8.59 (s, 3H), 8.68 (s, 6H), and 8.63 (s, 6H); uv max (cyclohexane): 240 nm (ε 607), 217 (ε 1960); mass spectrum (70 ev), m/e (rel intensity): 210 (4), 140 (100), 168 (28).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63

Found: C, 68.39; H, 8.59.

26. *Photolysis of 2,3-Epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (94)*: A 2% solution of 94 was prepared by dissolving 0.6 g of 94 in 30 ml of ether. The solution was irradiated through vycor with a 450-watt Hanovia lamp. The photolysis was followed by vpc. A 5-ft column of 20% SE-30 on chromosorb 60/80 at 144° was used for vpc analysis. The flow rate of helium was 150 ml/min. As the reaction proceeded the peak for the starting material at a retention time of 9.5 min decreased and a new peak appeared at a retention time of 7.5 min. After 10 hr the starting material had disappeared and the photoproduct was collected by preparative vpc: the ir spectrum is shown in Figure 18; nmr (CCl_4, Figure 30): τ 9.0 (s, 3H), 8.94 (s, 3H), 8.88 (s, 3H), 8.34 (m, 3H), and 8.06 (m, 6H); uv max (cyclohexane): 233 nm (ε 14750); mass spectrum (70 ev) m/e (rel intensity): 194 (3), 152 (82), 137 (100).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34.

Found: C, 74.23; H, 9.33.

27. Preparation of 6-Acetyl-d$_3$-3-methyl-d$_3$-2,4,4,5-tetramethyl-2-cyclopentenone (103): To a solution of 100 mg of 6-acetyl-2,3,4,4,5-pentamethyl-2-cyclopentenone (102) in 5 ml of 95% methanol-d was added 50 mg of sodium. The solution was refluxed for 6 hr under anhydrous conditions. At the end of this time the solution was analyzed by nmr which showed that the multiplet at τ 8.06 (6H) had disappeared; nmr (CCl$_4$): τ 9.0 (s, 3H), 8.94 (s, 3H), 8.88 (s, 3H), and 8.34 (m, 3H).

28. Preparation and Photolysis of 3,5-Dimethyl-d$_6$-2,3-epoxy-2,4,4,6-tetramethyl-2,5-cyclohexadienone (97): 3,5-Dimethyl-d$_6$-2,4,4,6-tetramethyl-2,5-cyclohexadienone (96) was prepared as described previously.[39] Next, 96 was oxidized by *m*-chloroperbenxoic acid as described for dienone 35, and 97 was collected by vpc: nmr (CCl$_4$): τ 8.92 (s, 3H), 8.71 (s, 3H), 8.60 (s, 3H), 8.26 (s, 3H).

Compound 97 was photolyzed under the same conditions as those used for the nondeuterated compound. The photoproduct was collected by vpc: nmr (CCl$_4$): τ 9.0 (s, 3H), 8.94 (s, 3H), 8.88 (s, 3H), and 8.34 (s, 3H).

29. Attempted Hydrogenation of 6-Acetyl-2,3,4,4,5-pentamethyl-2-cyclopentenone (102): To a solution of 0.4 g (0.00206 mole) of 102 in 4 ml of ethanol was added 3 drops of hydrochloric acid. The solution was taken in a Parr hydrogenator and subjected to hydrogen at a pressure of 6 atm for 24 hr. The ethanol solution was neutralized (NaHCO$_3$), dried (Na$_2$SO$_4$) and filtered. A vpc analysis with

a 5-ft column of 20% SE-30 on chromosorb 60/80 at 150°, with a flow rate of helium at 200 ml/min showed that the filtrate contained only starting material.

30. Attempted Photolysis of 2,3;5,6-Diepoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (95): A 1% solution of 95 in ether (100 mg in 10 ml) was irradiated through quartz with a 450-watt Hanovia lamp for 9 hr. The ethereal solution was evaporated and the residue was dissolved in carbon tetrachloride. An nmr analysis of this solution showed that the starting material remained unchanged.

A 1% solution of 95 in acetone was irradiated for 16 hr through Pyrex with a 450-watt Hanovia lamp. When the solution was analyzed by nmr the starting material was found to be unchanged under these conditions.

31. Preparation of 1-Methylene-3-isopropyl-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (107): In a 3-necked 100-ml flask fitted with a condenser and an additional funnel was placed 0.972 g (0.04 atom) of magnesium. A solution of 4.92 g (0.04 mole) of isopropyl bromide in 20 ml of anhydrous ether was added slowly. The resulting solution was stirred for 2 hr at room temperature. Next, a solution of 3.56 g (0.02 mole) of dienone 35 in 50 ml of anhydrous ether was added slowly to the Grignard reagent. The solution was refluxed for 1.5 hr, cooled in an ice bath and hydrolyzed with 20 ml of 10% aqueous ammonium chloride solution. The ethereal layer was separated, washed with water, dried

(Na_2SO_4) and concentrated giving 4.08 g (100%) of 107. A small amount was purified by vpc using a 5-ft column of 20% SE-30 on chromosorb 60/80 at 145⁰ with the flow rate of helium at 150 ml/min: uv max (cyclohexane): 310 nm (ε 3260), 255 nm (ε 7050), 220 nm (ε 6800); ir (CCl_4, Figure 19): 1655 and 1625 cm^{-1}, (C=C); nmr in CCl_4 (Figure 31): τ 8.94 (s, 6H), 8.85 (s, 3H), 8.71 (s, 3H), 8.33-7.71 (m, 9H), 7.06 (m, 1H), and 5.10 (AB q, 2H, *J* = 2.3 Hz).

Anal. Calcd for $C_{15}H_{24}$: C, 88.22; H, 11.84.

Found: C, 88.04; H, 11.91.

32. Preparation of the Adduct 64 of 107 with Dimethyl Acetylenedicarboxylate: A solution of 2.04 g (0.01 mole) of 107 and 1.42 g (0.01 mole) of dimethyl acetylenedicarboxylate in 25 ml of benzene was refluxed for 12 hr. The solution was concentrated and distilled giving 1.8 g (52%) of the adduct. A sample was prepared for analysis by injecting a small amount of the adduct on to a 5-ft column of 20% SE-30 on chromosorb 60/80 at 205⁰ with helium flowing through at a rate of 75 ml/min: bp 137-139⁰ (0.07 mm); ir (CCl_4, Figure 20): 1615 (C=C), 1630 (C=C), 1715 (C=O) and 893 cm^{-1} (=CH_2); nmr in CCl_4 (Figure 32): τ 9.03 (s, 3H), 8.95 (s, 6H), 8.84 (d, 3H, *J* = 1.75 Hz), 8.56 (s, 3H), 8.45 (s, 3H), 8.20 (s, 3H), 6.40 (s, 6H), 5.30 (s, 1H) and 5.14 (s, 1H); mass spectrum (70 ev) m/e (relative intensity): 346(16), 246(100).

Anal. Calcd for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73.

Found: C, 72.71; H, 8.68.

33. Preparation of 1-Methylene-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (108): In a 3-necked, 100-ml flask fitted with a mechanical stirrer, reflux condenser and dropping funnel was placed 0.6 g (0.0158 mole) of lithium aluminum hydride. A solution of 5.0 g (0.0281 mole) of dienone 35 in 50 ml of ether was added over 30 min to the lithium aluminum hydride. The solution was further refluxed for 1 hr and then cooled in an ice bath. Water (1.3 ml) was added to the solution to destroy the excess of lithium aluminum hydride. The ethereal solution was dried (Na_2SO_4) and concentrated to yield 4 g (79%) of a colorless oil. The oil was analyzed by vpc using a 10-ft column of 20% Carbowax on chromosorb 60/80 at 180^0 with helium flowing through at a rate of 75 ml/min, injector temp 240^0. Three peaks with a retention time of 6.5, 13 and 17 min with a relative ratio of 2.8:1:2.3 were observed. The first peak was due to a new compound 109 which was characterized by spectral data and chemical analysis. The second peak was due to diene 110 and the third peak was due to the desired triene 108.

Spectral data and analysis of 109: ir (CCl_4, Figure 21): 1663 cm^{-1} (C=C); nmr in CCl_4 (Figure 34): τ 9.21 (d, 3H, *J* = 7 Hz), 9.13 (s, 3H), 9.07 (s, 3H), 8.38-8.30 (m, 10H), 4.73 (m, 1H); mass spectrum (70 ev) m/e (rel intensity): 164(67), 149(77), 124(83), 123(100).

Anal. Calcd for $C_{12}H_{20}$: C, 87.78; H, 12.27.
Found: C, 87.81; H, 12.12.

Spectral data of 110: ir (CCl_4, Figure 22): 3400 (OH) and 1640 cm^{-1} (C=C); nmr (CCl_4, Figure 33): τ 8.99 (s, 6H), 8.43 (s, 12H), 7.60 (broad s, 2H); mass spectrum (70 ev) m/e (rel intensity): 164(6), 149(100), 134(16), 133(17), 119(13).

Nmr spectrum of **108**: (CCl_4): τ 8.9 (s, 6H), 8.33 (s, 6H), 8.13 (d, 3H, *J* = 1.5 Hz), 5.10 (s, 2H), 4.56 (m, 1H).

34. Preparation of Adduct **111** of **108** with Maleic Anhydride: A solution of 0.2 g (0.00124 mole) of triene **108** in 15 ml of carbon tetrachloride was placed in a 100-ml 3-necked flask at 0°. A solution of 0.121 g (0.00124 mole) of maleic anhydride in 5 ml of carbon tetrachloride was added slowly with the help of a dropping funnel. The resulting solution was stirred for 0.5 hr, and concentrated giving 0.3 g (93.5%) of residue. The residue was crystallized from pentane: mp 125-127°; ir (CCl_4, Figure 23): 1763 (C=O), 1635 (C=C), and 940 cm^{-1} ($=CH_2$); nmr (CCl_4, Figure 35): τ 9.05 (s, 3H), 8.89 (s, 3H), 8.54 (s, 6H), 8.28 (d, 3H, *J* = 1.7 Hz), 7.34 (d, 1H, *J* = 8.5 Hz), 6.90 (d, 1H, *J* = 8.5 Hz), 5.25 (s, 1H), 5.06 (s, 1H), and 4.54 (broad s, 1H).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74.
Found: C, 73.70; H, 7.71.

35. Attempted Oxidation of Adduct **111**: Oxygen was bubbled through a solution of 0.5 g (0.00192 mole) of **111** in 5 ml of pyridine. To this solution was added 1.28 g (0.00288 mole) of lead tetraacetate and the solution was heated in an oil bath at 67° until the evolution of carbon dioxide ceased. The flask was then immersed in an ice bath and 5 ml of cold methylene chloride was added to the solution.

The resulting solution was poured into a 200-ml beaker and 15 ml of 50:50 mixture of nitric acid and water was added. This solution was extracted with five 10-ml portions of methylene chloride. The methylene chloride extract was washed with 50 ml of 5% aqueous sodium bicarbonate solution, dried (Na_2SO_4) and concentrated giving 0.2 g of material: nmr (CCl_4): τ 9.05 (s, 3H), 8.89 (s, 3H), 8.54 (s, 6H), 8.28 (d, 3H, J = 1.7 Hz), 7.34 (d, 1H, J = 8.5 Hz), 6.90 (d, 1H, J = 8.5 Hz), 5.25 (s, 1H), 5.06 (s, 1H), and 4.54 (broad s, 1H).

36. *Preparation of Diacid **112**:* A suspension of 1.0 g (0.00384 mole) of anhydride **111** in 100 ml of 5% aqueous sodium bicarbonate was refluxed for 24 hr. At the end of this time the insoluble anhydride was filtered (0.5 g), the solution was acidified and the diacid **112** (0.535 g, 50% conversion, 100% yield) precipitated from the solution: ir (nujol), 1730 (C=O), 1690 (C=O), and 895 cm^{-1} (=CH_2).

37. *Oxidation of Diacid **112**:* Compound 112 (0.5 g, 0.001798 mole) was oxidized with lead tetraacetate by the same procedure described for anhydride **111**. The product was a yellow oil (0.3 g) and was analyzed by vpc using a 5-ft column of 20% SE-30 on chromosorb 60/80 at 175^0 with a flow rate of helium at 75 ml/min. The vpc chromatogram indicated that 75% of the product consisted of a compound with a retention time of 6 min. The spectral data and chemical analysis indicate that this compound is **113**: ir

(CCl_4, Figure 24): 1770 cm^{-1} (C=O); nmr in CCl_4 (Figure 36): τ 9.06 (s, 3H), 8.93 (s, 3H), 8.78 (s, 3H), 8.64 (s, 3H), 8.30 (d, 3H, *J* = 1.5 Hz), 7.51 (d, 1H, *J* = 6 Hz), 7.38 (s, 1H), 5.38 (s, 1H), 5.20 (s, 1H), 4.66 (m, 1H); uv max (cyclohexane): 240 nm (ε 8370), 220 nm (ε 7940), 214 (ε 8370); mass spectrum (70 ev) m/e (relative intensity): 232(2), 188(10), 173(100).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55, H, 8.68.
Found: C, 76.82, H, 8.59.

38. Reduction of γ-Lactone 113: γ-Lactone 113 (0.030 g, 0.129 mmole) in 1 ml of boron trifluoride etherate was added to a well-stirred solution of 0.02 g (0.555 mmole) of sodium borohydride in 10 ml of anhydrous ether, at 0°. The solution was stirred further for 45 min at 0° and then refluxed for 2 hr. The ethereal solution was washed with 10 ml of 5% aqueous sodium bicarbonate solution, dried (Na_2SO_4) and concentrated giving a small amount of white solid: ir (CCl_4): 2960, 1380, 1260, 1100, 1020 and 823 cm^{-1}; mass spectrum (70 ev), m/e (relative intensity): 220(13), 147(100).

39. Attempted Preparation of Adduct 117 of 108 with 2-Butyne: Triene 108 (0.5 g, 0.00308 mole) together with an excess of 2-butyne (0.65 g, 0.94 ml, 0.0154 mole) were placed in a metal bomb at -78°. The two compounds were allowed to react at 0° for 24 hr. At the end of this time the bomb was opened and 2-butyne was allowed to evaporate. The nmr

spectrum of the product showed signals at τ 8.9 (s, 6H), 8.13 (d, 3H, $\underline{J}$ = 1.5 Hz), 5.10 (s, 2H), 4.56 (m, 1H). The reaction was carried out at room temperature for 24 hr and the same results obtained. The reaction was repeated once again at 160^0 for 8 hr. A black tar was obtained as the product.

SPECTRA

NMR Spectra

The nmr spectra presented here were obtained using CCl_4 solutions with tetramethylsilane as an internal standard.

IR Spectra

The ir spectra presented here were also obtained using CCl_4 solutions.

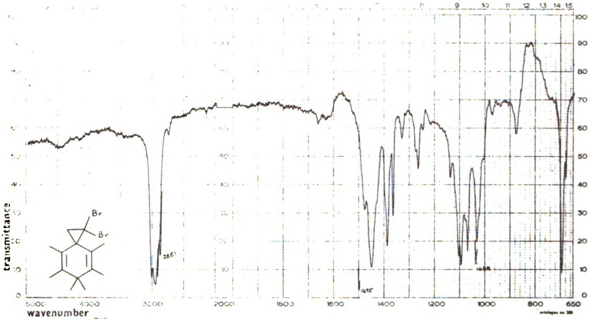


Figure 13. IR spectrum of 2,2-dibromo-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (71)

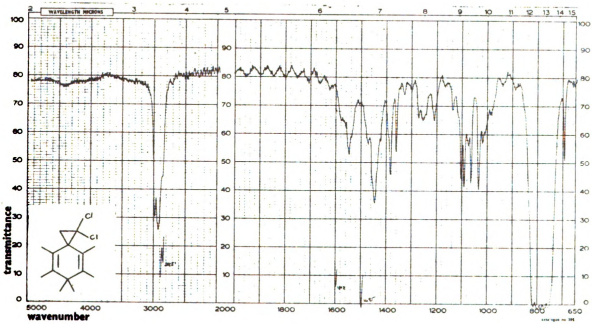


Figure 14. Ir spectrum of 2,2-dichloro-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (91).

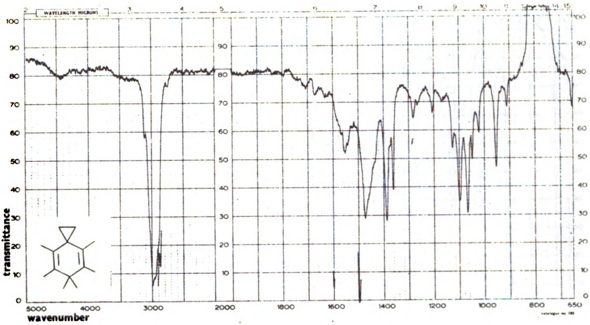


Figure 15. IR spectrum of 4,5,6,6,7,8-hexamethylspiro-[2.5]octa-4,7-diene (37).

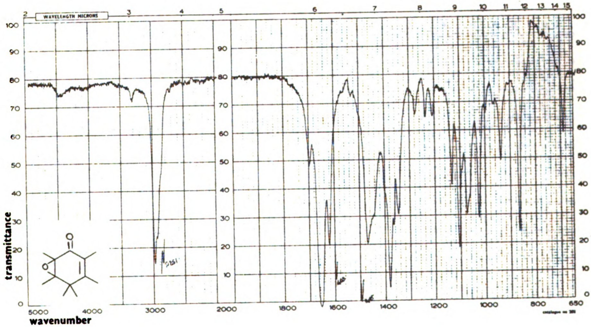


Figure 16. IR spectrum of 2,3-epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (94)

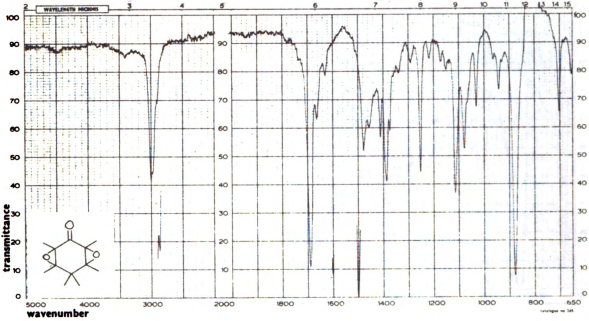


Figure 17. IR spectrum of 2,3;5,6-diepoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (95).

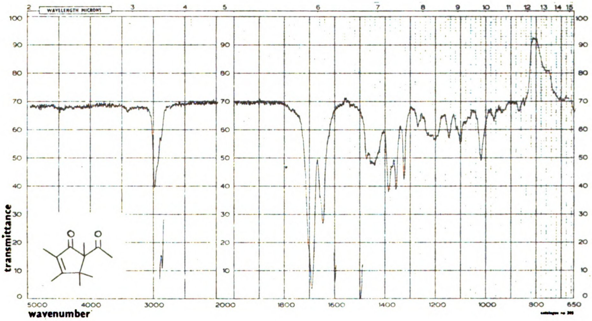


Figure 18. IR spectrum of 6-acetyl-2,3,4,4,5-pentamethyl-2-cyclopentenone (102).

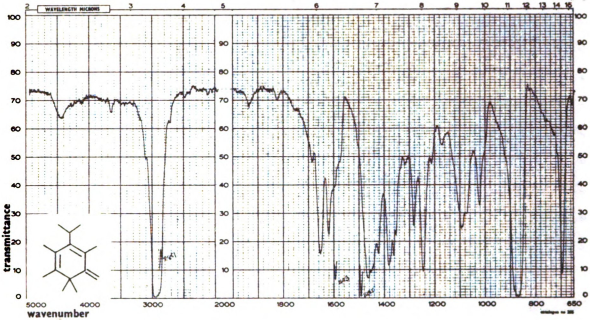


Figure 19. IR spectrum of 1-methylene-3-isopropyl-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (107).

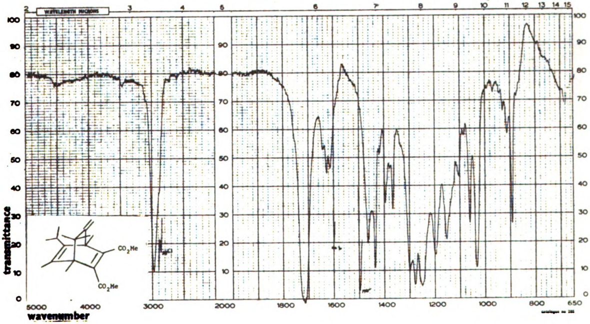


Figure 20. IR spectrum of adduct 64.

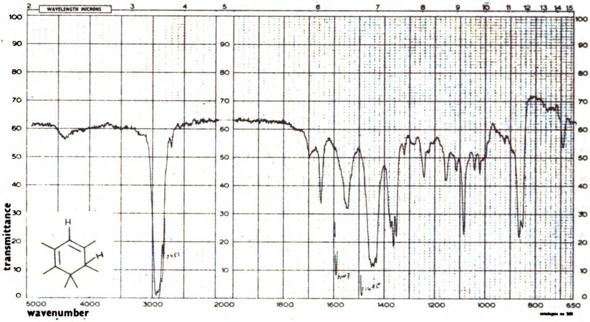


Figure 21. IR spectrum of 1,3,4,5,5,6-hexamethyl-1,3-cyclohexadiene (109).

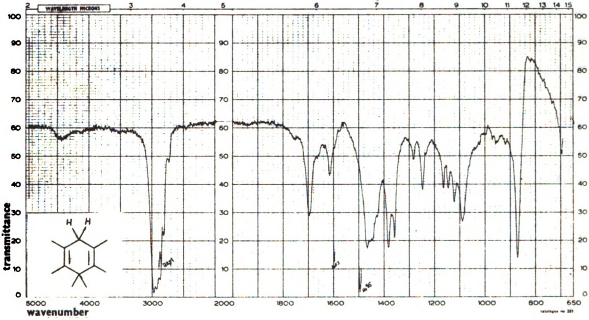


Figure 22. IR spectrum of 1,2,3,3,4,5-hexamethyl-1,4-cyclohexadiene (110).

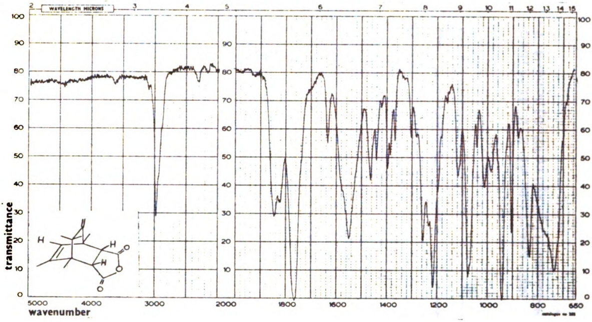


Figure 23. IR spectrum of adduct 111.

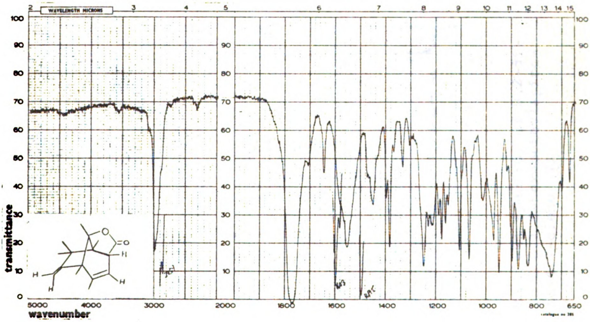


Figure 24. Ir spectrum of γ-lactone 113.

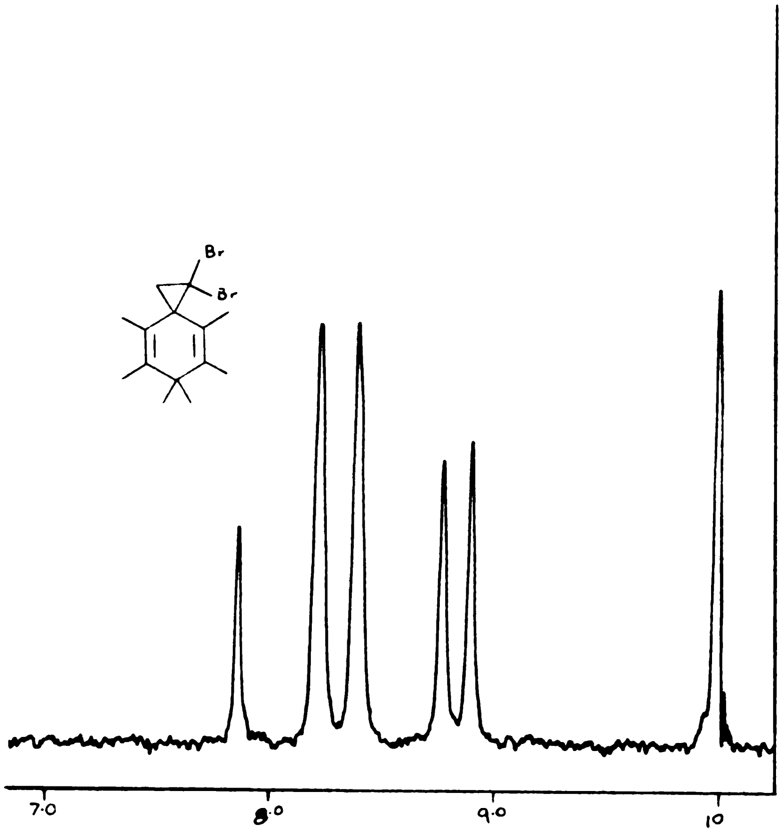


Figure 25. NMR spectrum of 2,2-dibromo-4,5,6,6,7,8-hexamethylspiro-[2.5]octa-4,7-diene (71).

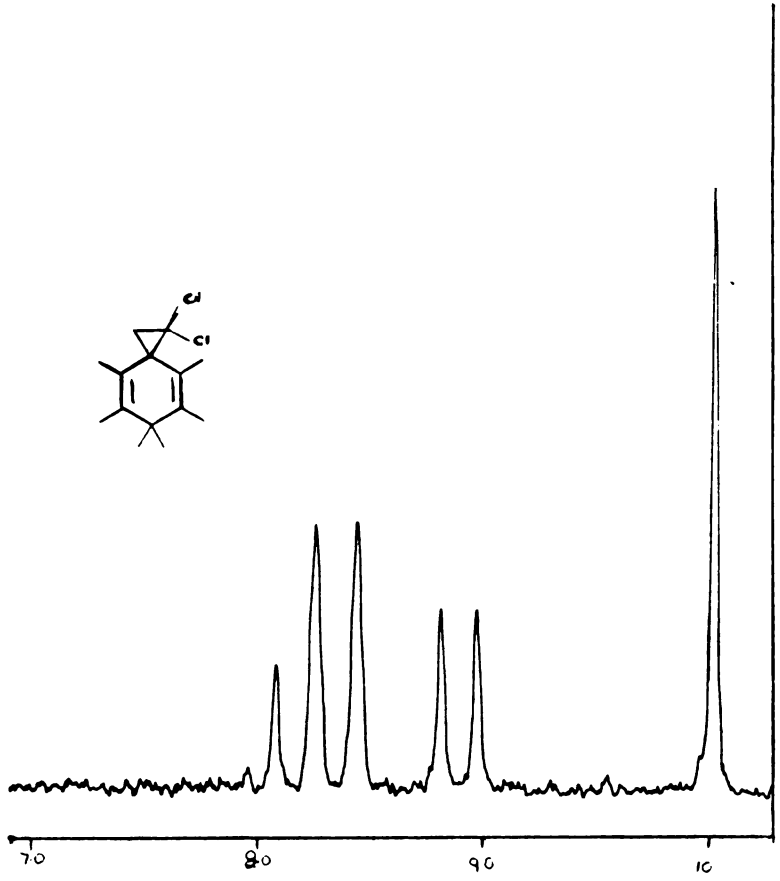


Figure 26. NMR spectrum of 2,2-dichloro-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (91).

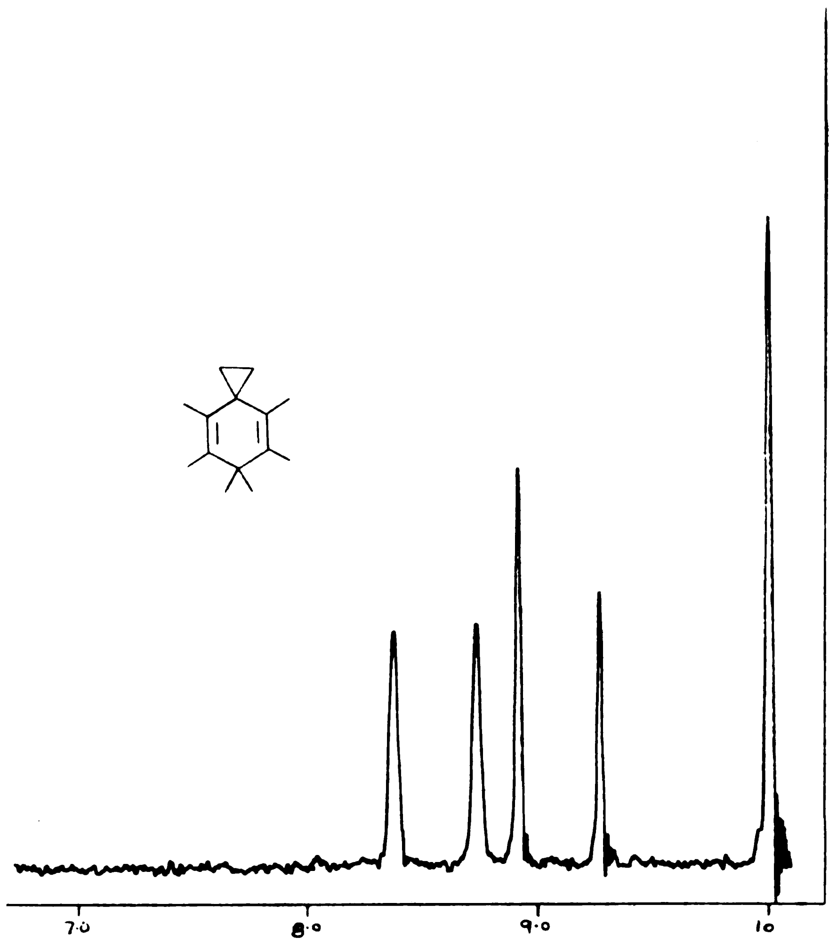


Figure 27. NMR spectrum of 4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (37).

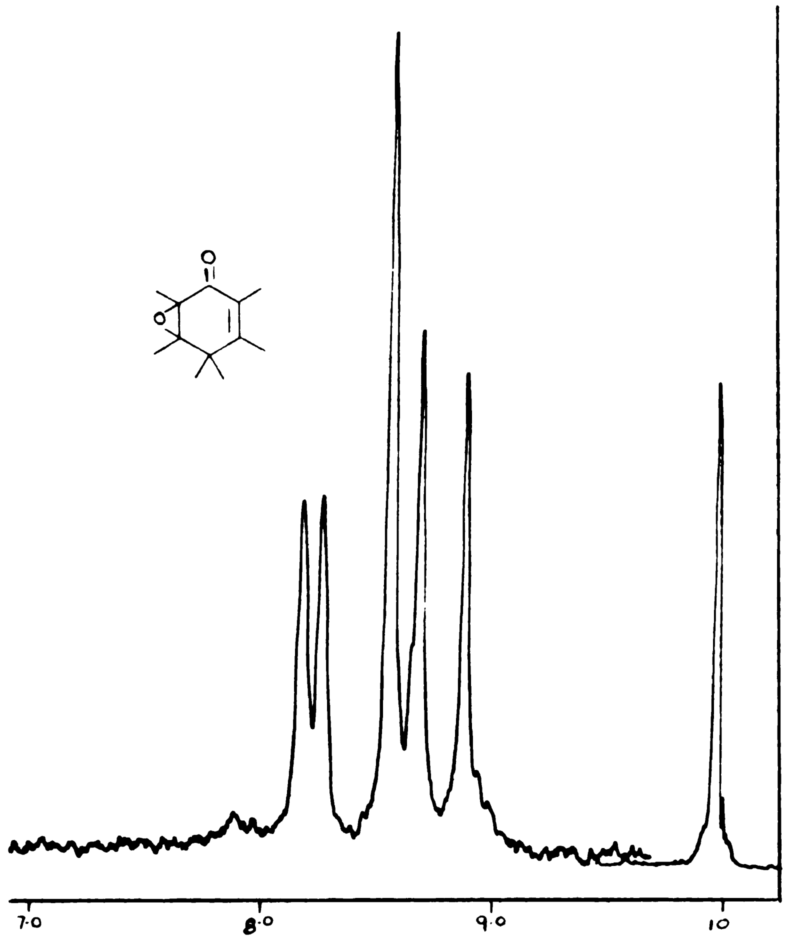


Figure 28. NMR spectrum of 2,3-epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (94).

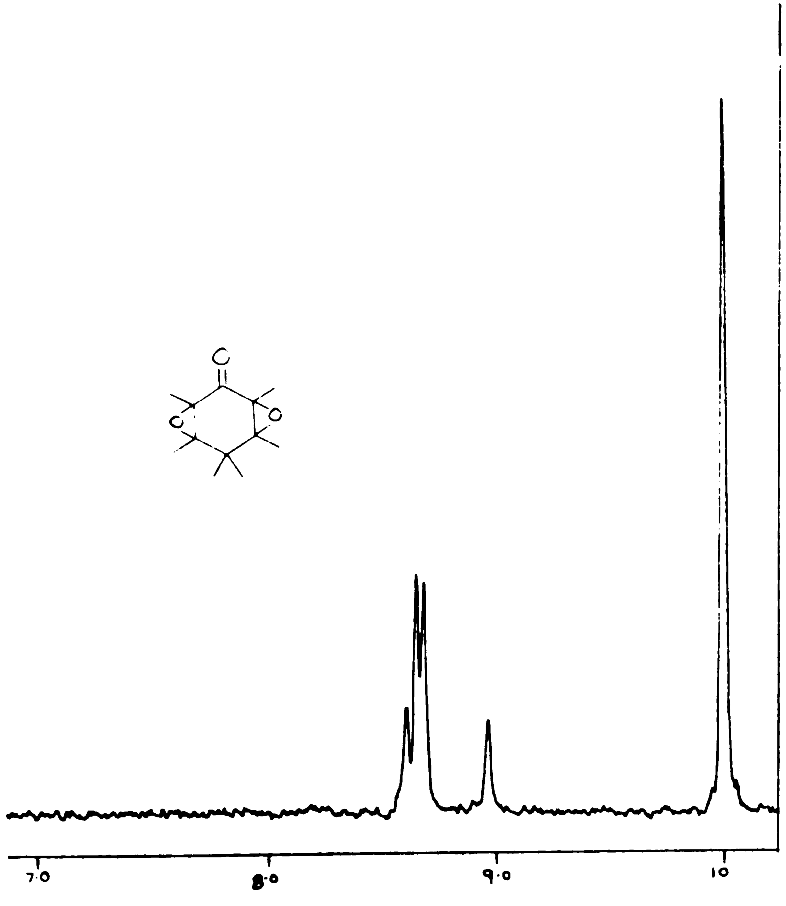


Figure 29. NMR spectrum of 2,3;5,6-diepoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (95).

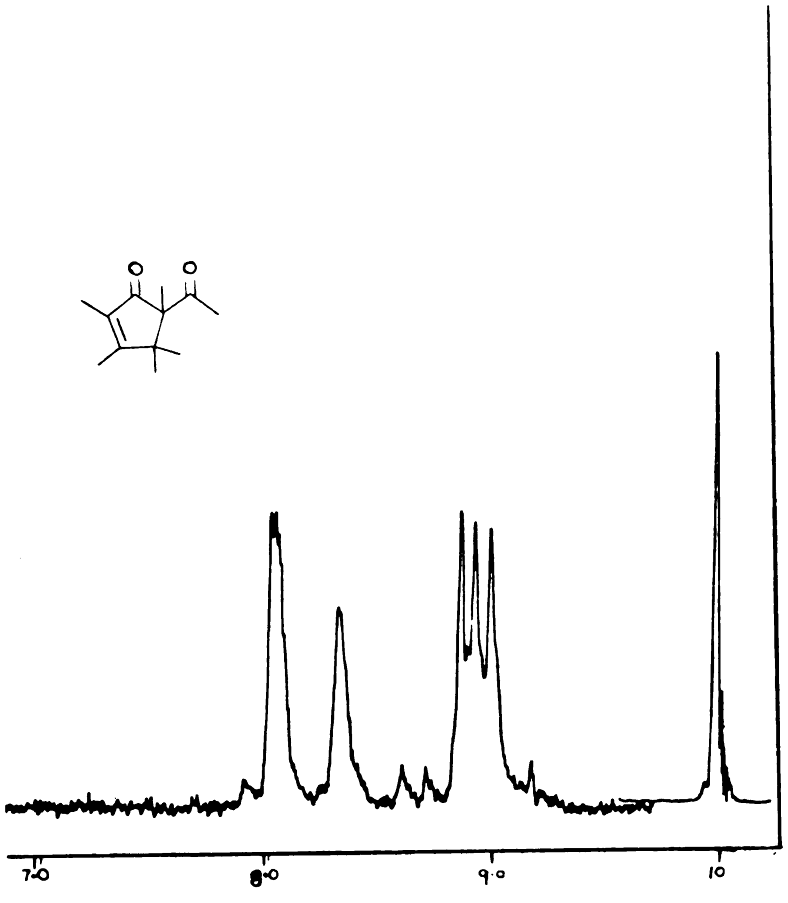


Figure 30. NMR spectrum of 6-acetyl-2,3,4,4,5-pentamethyl-2-cyclopentenone (102).

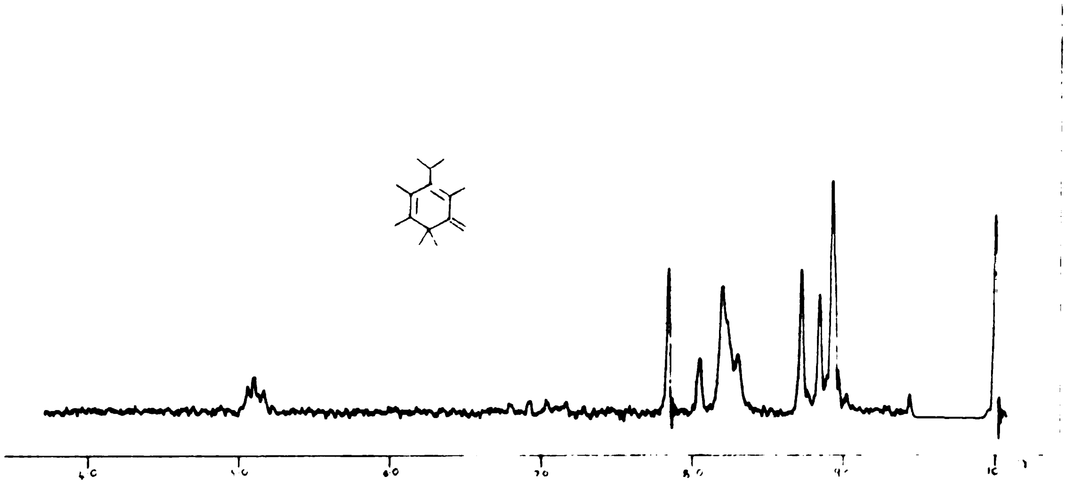


Figure 31. NMR spectrum of 1-methylene-3-isopropyl-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (107).

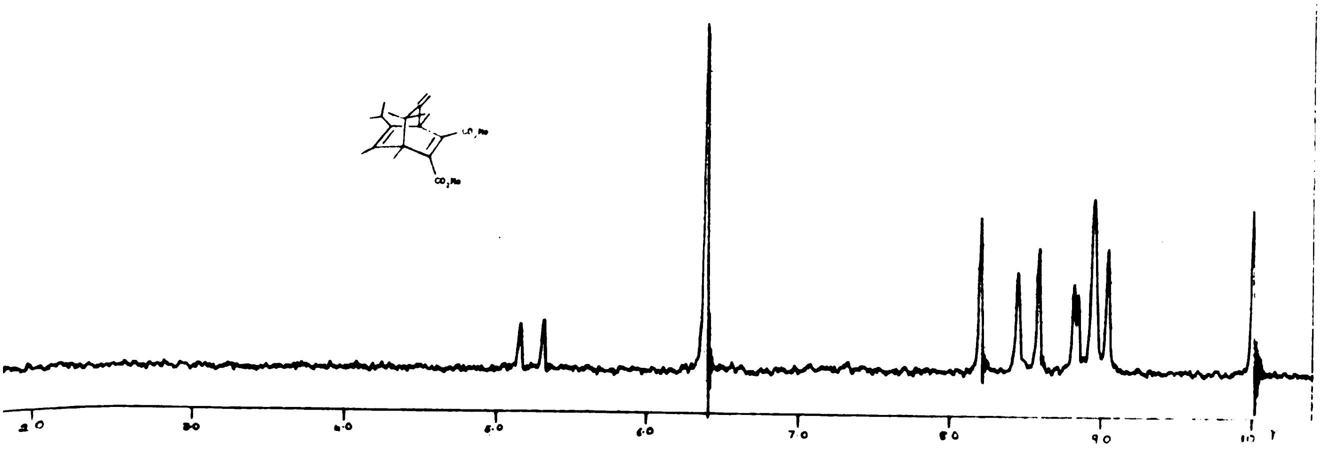


Figure 32. NMR spectrum of adduct 64.

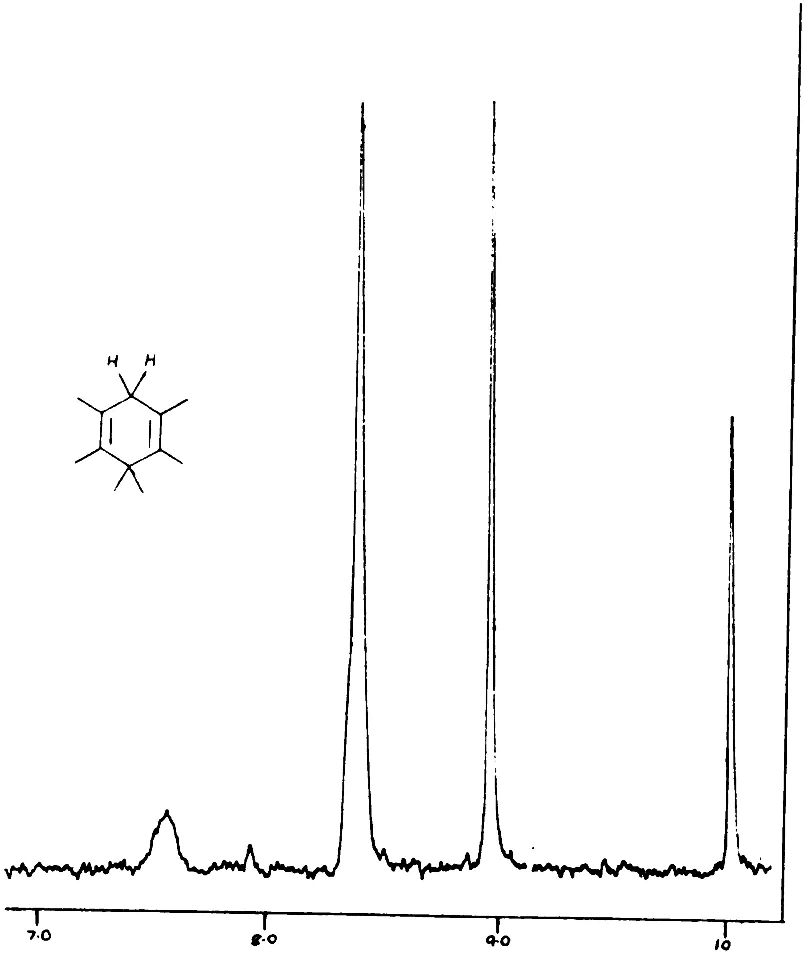


Figure 33. NMR spectrum of 1,2,3,3,4,5-hexamethyl-1,4-cyclohexadiene (110).

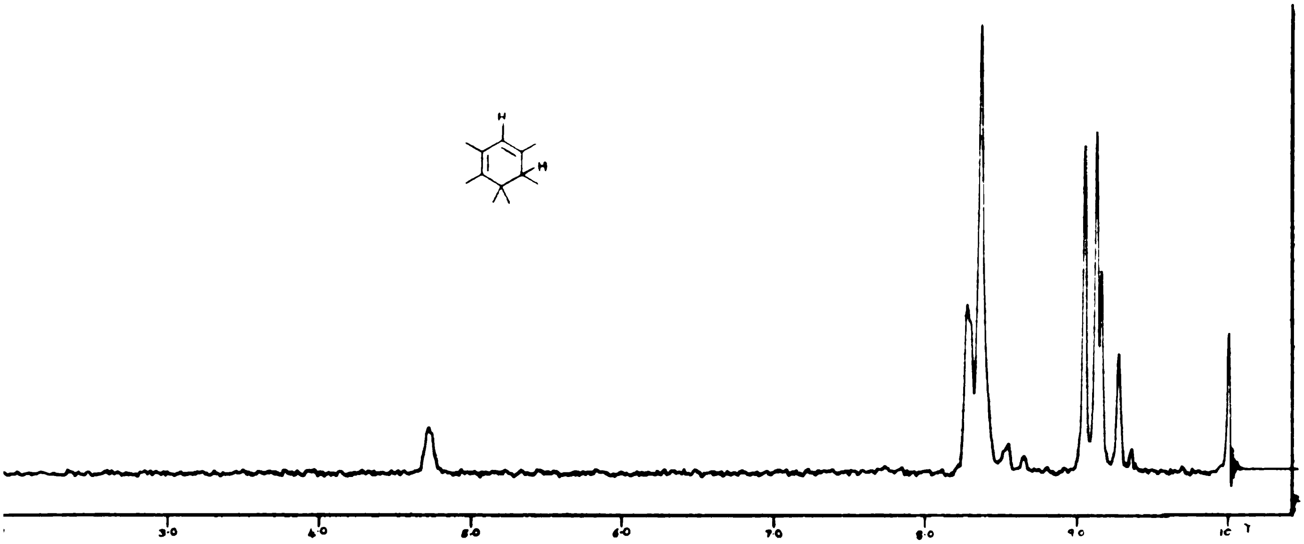


Figure 34. NMR spectrum of 1,3,4,5,5,6-hexamethyl-1,3-cyclohexadiene (109).

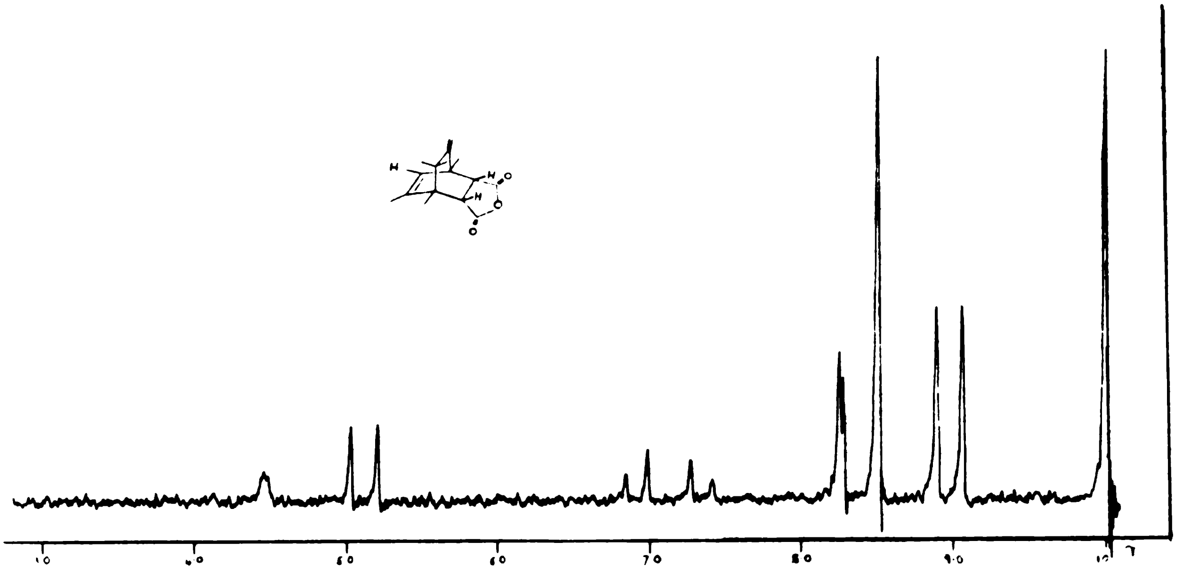


Figure 35. NMR spectrum of adduct 111.

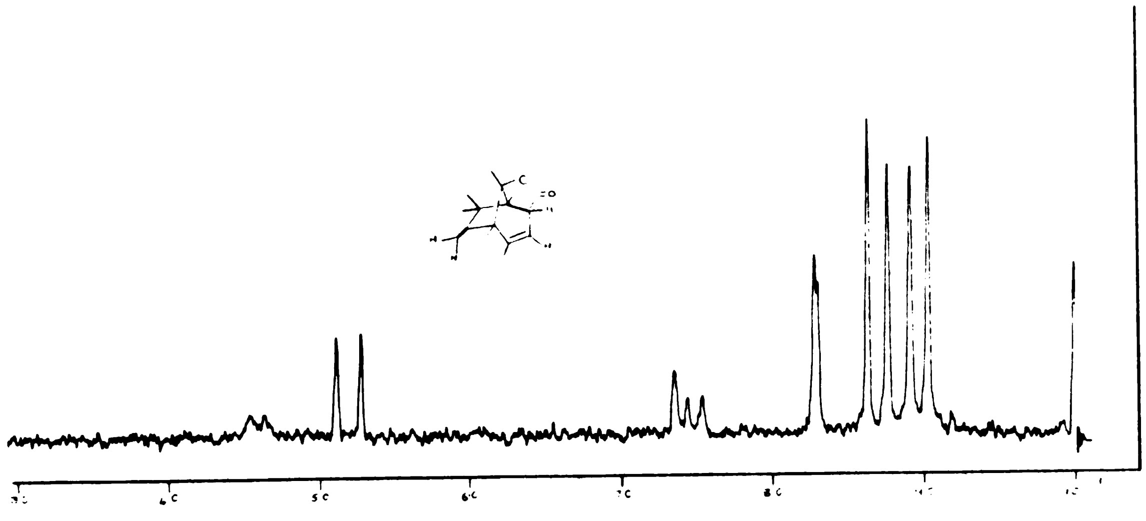


Figure 36. NMR spectrum of γ-lactone **113**.

SUMMARY

1. 2,2-Dibromo-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (**71**) was prepared by the addition of dibromocarbene to 1-methylene-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadiene (**39**). Compound **71** underwent polymerization on photolysis. Treatment of **71** with methyllithium did not yield an allene.

2. Pyrolysis of **71** in solution gave three isomeric products, α-bromopentamethylstyrene (**80**), cis-β-bromo-pentamethylstyrene (**81**), and trans-β-bromo-pentamethylstyrene (**82**). Pyrolysis of **71** in deuterated solvents showed very little deuterium incorporation into the products. Based on these results a possible mechanism was proposed for this reaction. Benzoyl peroxide accelerates the decomposition of **71**. The rate of decomposition was found to be proportional to the concentration of benzoyl peroxide.

3. Addition of dichlorocarbene to (**39**) gave 2,2-dichloro-4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (**91**).

4. Reduction of **71** with lithium and liquid ammonia gave 4,5,6,6,7,8-hexamethylspiro[2.5]octa-4,7-diene (**37**). Pyrolysis of **37** in solution produced mainly hexamethylbenzene. Compound **37** was observed to rearrange to hexamethylbenzene in acidic media.

5. Oxidation of 2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (**35**) with *m*-chloroperbenzoic acid gave 2,3-epoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (**94**) and 2,3;5,6-diepoxy-2,3,4,4,5,6-hexamethyl-2,5-cyclohexadienone (**95**). Photolysis of a 1% solution of epoxide **94** in ether with 450-watt Hanovia lamp through vycor for 10 hr gave 6-acetyl-2,3,4,4,5-pentamethyl-2-cyclopentenone (**102**). Diepoxide **95** was found to be photochemically stable.

6. 1-Methylene-3-isopropyl-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (**107**) was prepared from dienone **35** and isopropylmagnesium bromide. Addition of dimethyl acetylenedicarboxylate to triene **107** gave adduct **64**.

7. Reduction of dienone **35** with lithium aluminum hydride gave 1-methylene-2,4,5,6,6-pentamethyl-2,4-cyclohexadiene (**108**), 1,3,4,5,5,6-hexamethyl-1,3-cyclohexadiene (**109**) and 1,2,3,3,4,5-hexamethyl-1,4-cyclohexadiene (**110**). Addition of maleic anhydride to triene **108** gave adduct **111**. Oxidation of **111** with lead tetraacetate did not give 2-methylene-1,3,3,4,5-pentamethylbicyclo[2.2.2]-octa-5,7-diene (**65**). Hydrolysis of **111** gave diacid **112** which on oxidation with lead tetraacetate gave lactone **113**. 2-Butyne did not add to triene **108** to form an adduct.

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