1984

Characterization and chemistry of vinylketene prepared by flash vacuum pyrolysisstudy of the flash vacuum pyrolysis of hydroaromatic compounds: 5,8-diphenyltetralin and the parent and substituted 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctenes

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CHARACTERIZATION AND CHEMISTRY OF VINYLKETENE PREPARED BY FLASH VACUUM PYROLYSIS. STUDY OF THE FLASH VACUUM PYROLYSIS OF HYDROAROMATIC COMPOUNDS: 5,8-DIPHENYLTETRALIN AND THE PARENT AND SUBSTITUTED 5,6,11,12-TETRAHYDRODIBENZO(A,E)CYCLOOCTENES

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by

Bruce Warren Surber

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GENERAL INTRODUCTION

Flash vacuum pyrolysis (FVP) is a pyrolysis technique whereby the substrate is volatilized under vacuum and passes in the gas phase into a hot zone where pyrolysis occurs. The products then pass out of the hot zone and condense in a cold zone. Because compounds are generated in the gas phase and quickly cooled, secondary reactions are minimized. Thus, two important uses of FVP have developed: (1) to prepare very reactive compounds which are stable only at low temperatures, and (2) to study, by product analysis, fundamental thermal reactions. This thesis is in three parts; in each part, FVP is used in one of these two ways.

Parts I and III are studies on the thermal chemistry of hydroaromatic compounds. In part II, vinylketene, a very reactive compound, is prepared by FVP, characterized by Low-Temperature NMR, and allowed to react with itself and with cyclopentadiene.

Explanation of Dissertation Format

Each part is in the form of a full paper, suitable for publication in a professional journal. As such, each part has its own numbering system and each part's references follow it. The research described in the Results and Experimental sections was done by the author.

PART I. FORMATION OF ANTHRACENES IN THE FLASH VACUUM PYROLYSIS OF BENZOCYCLOBUTENES AND DIMERS OF ORTHO-QUINODIMETHANES AND ITS IMPLICATIONS FOR THE DIENE MECHANISM OF AROMATIZATION IN HYDROCARBON PYROLYSIS

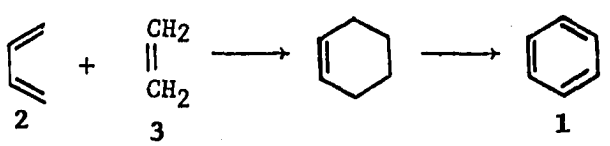
INTRODUCTION

It is generally held that aromatic compounds are formed in the pyrolysis of hydrocarbons by the breakdown of the feedstock to small molecules which condense to form the aromatic rings.[1-4] Several theories have been advanced through the years to explain how the aromatic rings are formed.[5-9] Central to every theory is the explanation of benzene (1) since it is generally the major product of aromatization and one

1

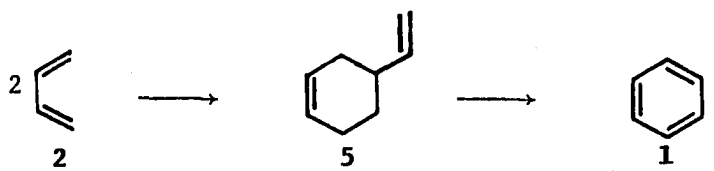
of the first formed. Also, it is the simplest aromatic compound.

One theory of aromatization, which was advanced early and still enjoys wide acceptance, is the diene-synthesis theory.[5] It states that aromatic rings are formed by Diels-Alder reactions followed by dehydrogenation. Butadiene (2), which is produced early in hydrocarbon pyrolysis and is quickly consumed as arenes are formed, is believed to play a key role.[4,6,7] According to this theory, benzene was first thought to arise by a Diels-Alder reaction between butadiene and ethylene (3) followed by dehydrogenation (reaction 1). However, evidence to the



2 + 3 → 1 1.

contrary has accumulated which suggests that benzene is formed from the dimer of butadiene, 4-vinylcyclohexene (**5**, reaction 2).[6,7] It is the major component (43%) of the tar formed in the nitrogen flow pyrolysis of **5**.[8]



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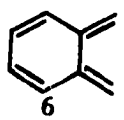
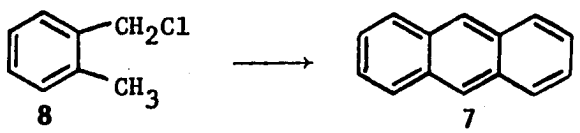
Recently, a rather intriguing aromatization has surfaced whereby compounds related to o-quinodimethane (o-xylylene) (**6**) pyrolytically



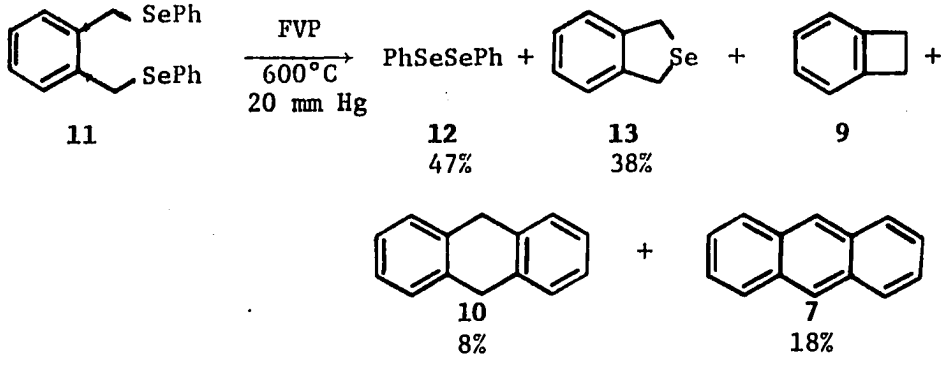
form anthracene (**7**). The first report appeared in 1969, where **7** was formed as a minor product in the later stages of the static gas-phase pyrolysis of α-chloro-o-xylene (**8**) at 430°C (reaction 3).[10] We found



3.

that **8** also gives **7** by flash vacuum pyrolysis (FVP) (see Results). Recently, a report of a new synthon of benzocyclobutene (**9**) (the

valence tautomer of **6**) described the formation of **7** and dihydroanthracene (**10**) in 18% and 8% yields, respectively, in the FVP of 1,2-bis(phenylselenomethyl)benzene (**11**) at 600°C and 20 mm Hg (reaction 4).[11]



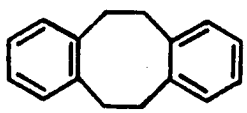
11 **12** 47% **13** 38% **9**

10 8% **7** 18%

4.

These results suggest that anthracene might be formed pyrolytically from **6** and/or **9**. There are three reasons why this is intriguing. First, anthracene formation in hydrocarbon pyrolysis is of particular interest and this is a new and unexpected way to anthracene.[12-19] How two molecules lose two carbon atoms towards formation of the central aromatic ring is not at all clear. Second, **6** and **9** have never before been implicated in the formation of a polycyclic aromatic compound. It would be interesting to determine to what extent these basic units are involved in arene formation in hydrocarbon pyrolysis. Third, since **6** can be regarded as a diene, its condensation to anthracene would be analogous to butadiene (**2**) going to benzene (**1**). So what we learn about this reaction may be applicable to the formation of benzene in hydrocarbon pyrolysis. Therefore, this study was undertaken to examine anthracene

formation in the pyrolysis of such hydrocarbons as **9** and **14**, the [4+4] dimer of **6**.

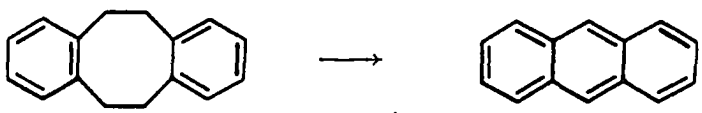


14

RESULTS

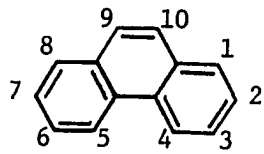
Anthracene (**7**) was formed in 1-2% yield in the preparation of benzocyclobutene (**9**) by the flash vacuum pyrolysis (FVP) of α-chloro-o-xylene (**8**) (reaction 3).[10,20] It was deposited just outside the oven and was contaminated with minor amounts of dimeric compounds.

FVP of **14**, prepared by thermal dimerization of 9 at 210°C,[21] gave several isomers of **14** and a good yield of **7** depending on the pyrolysis temperature (reaction 5). Also, two minor products of molecular weight



14 **7** 5.

192 (methylanthracenes?) (**15** and **16**) were also formed. The NMR of the pyrolyzate from FVP at 920°C showed that virtually no phenanthrene (**17**) was produced since there was no absorption around δ 8.62 where its 4-



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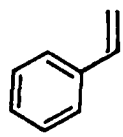


18

and 5-protons resonate.[22] Also, gas chromatography (gc) analysis showed that virtually no **9** or styrene (**18**) (the major product of pyrolysis of

9)[23] was produced. Formation of **17** was not determined by gc since it has about the same retention time as anthracene. The product distribution as a function of FVP temperature is tabulated (Table 1) and depicted graphically in Figure 1. As Figure 1 illustrates, the yields of most of the isomers of **14** peak at 920°, then drop off quickly. This is in contrast to the yields of anthracene (**7**) and the two minor products of M.W. 192 (**15** and **16**) which peak at 980° and are slow to taper off. Also, Figure 1 illustrates how clearly dominant anthracene (**7**) is in the product mixture.

Benzocyclobutene (**9**) was pyrolyzed at 770°C very rapidly to maximize bimolecular reactions in the hot zone. NMR and gc analysis indicated the presence of ethylene (**3**) in the pyrolyzate. Several light compounds were produced such as styrene (**18**) which was the major component of these in 3.8% yield. Also, many "dimeric" compounds were formed which were obviously the result of condensation of two molecules but not necessarily having twice the molecular weight of benzocyclobutene (**9**). The major ones are listed in Table 1 by their retention times in the gc and correlated with the products of the pyrolysis of the [4+4] dimer (**14**). In contrast to the FVP of **14**, which gave essentially only those compounds listed in Table 1, benzocyclobutene (**9**) gave numerous minor dimeric products not listed. Of the compounds listed, many appear to be the same compounds that are formed in the FVP of the [4+4] dimer (**14**) and these are listed as such. However, four major dimeric compounds (**19**, **21**, **28**, and **29**) formed in the pyrolysis of benzocyclobutene (**9**) do not appear in the pyrolysis of the [4+4] dimer

Table 1. Yields of products[a] in the FVP of benzocyclobutene (**9**) and of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (**14**)

Compound	Retention time, min	Molecular weight, m/e[b]	Absolute yields, %					
			From **9**,	From **14**				
			770°	720°	805°	902°	980°	1030°
19	11.70	?	1.0	--	--	--	--	--
20	11.90	208	0.2	--	1.1	4.4	0.9	0.7
21	12.20	?	0.6	--	--	--	--	--
22	12.70	208	0.3	--	1.5	2.6	0.6	--
23	13.20	208	0.3	1.8	3.7	1.0	--	--
24	14.15	208	0 ?	--	1.0	3.2	0.8	0.5
14	14.70	208	5.5	75.3	58.8	9.5	--	--
7	15.15	178	6.4	--	4.9	25.1	33.0	31.3
25	15.85	208	0.2	--	0.5	4.8	2.3	1.5
26	16.82	208	0.5	3.8	5.7	6.6	--	--
27	17.48	208	0.9	--	4.3	9.0	3.7	3.0
15	18.60	192	1.3	--	1.1	8.1	8.8	8.4
28	19.44	?	2.1	--	--	--	--	--
16	19.62	192	0.2	--	--	1.0	1.7	1.5
29	19.71	?	0.4	--	--	--	--	--
30	20.55	206	0.2	--	--	0.6	--	--

[a]Determined by gc by comparison of peak area to biphenyl internal standard.

[b]Determined by gc/ms analysis of the pyrolyzate from FVP of **14** at 920°C.

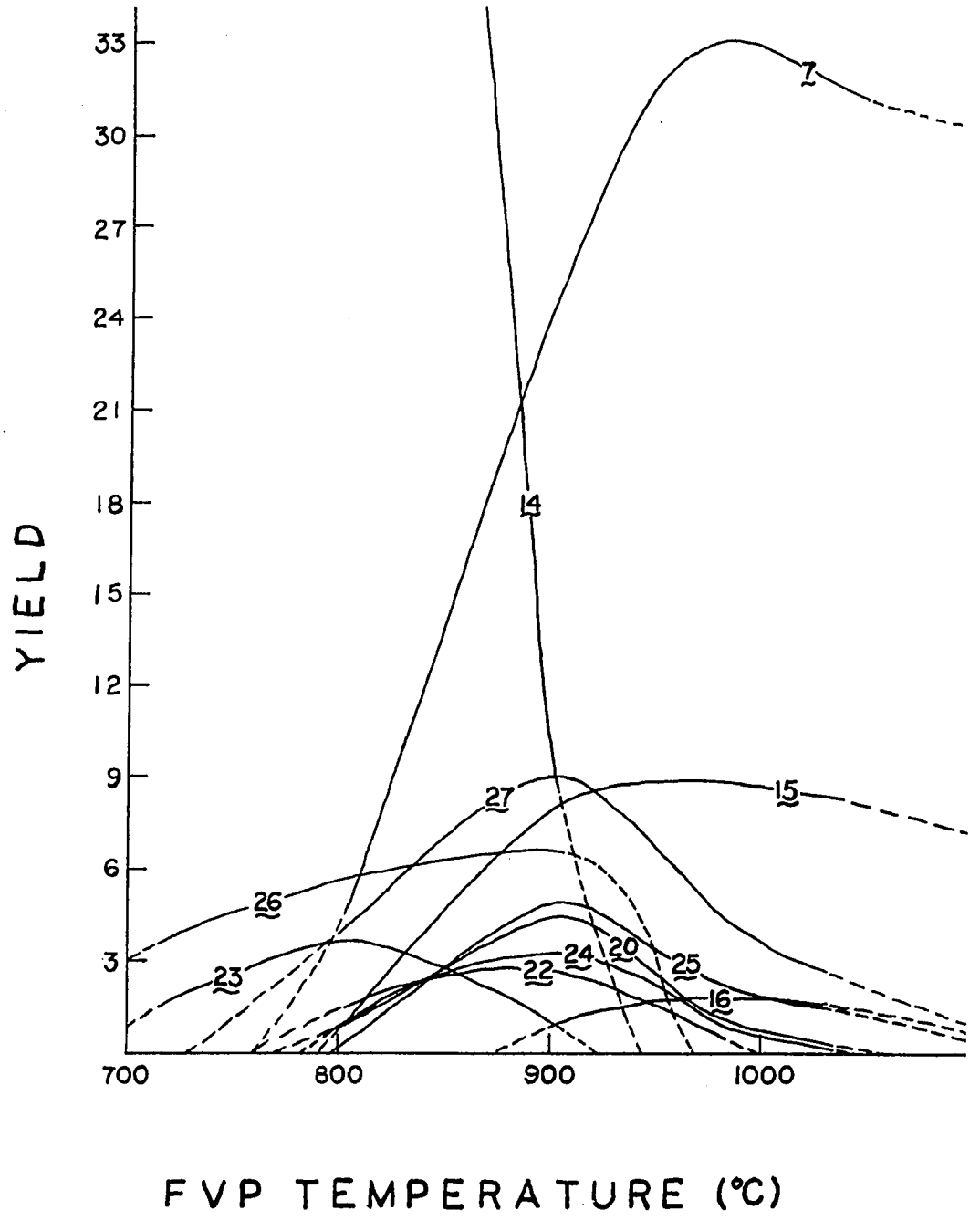
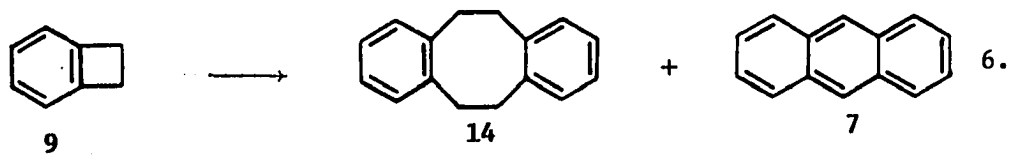


Figure 1. Yields of products as a function of FVP temperature in the FVP of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (14). Data are from Table 1

(14) at any temperature. The major "dimeric" products of the pyrolysis of benzocyclobutene (9) are the [4+4] dimer (14) (5.5%) and anthracene (7) (reaction 6).



Of the products common to both pyrolyses, the ratios of the yields to that of 14 were calculated for each pyrolysis. It was found that the ratio of each component from the pyrolysis of 9 generally lies between the corresponding ratios from the pyrolyses of 14 at 805° and 920°C (Table 2).

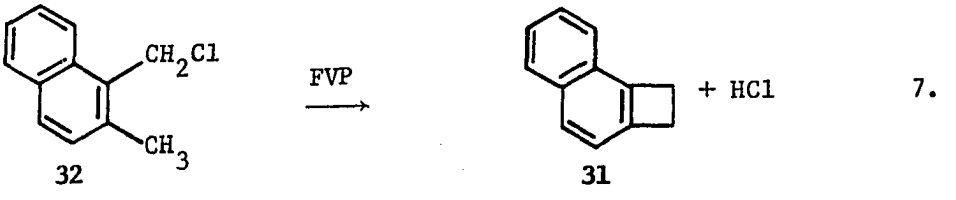
Table 2. Ratios of yields of selected products[a] to that of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene in the FVP of benzocyclobutene (9) and of the [4+4] dimer (14) at 720°, 805° and 920°C

Compound	Retention time, min[b]	Yield of compound/yield of 14			
		From 9,	From 14		
		770°	720°	805°	920°
20	11.90	0.04	0	0.02	0.46
23	13.20	0.05	0.02	0.06	0.10
26	16.82	0.09	0.05	0.10	0.69
27	17.48	0.16	0	0.07	0.95
15	18.60	0.24	0	0.02	0.85
7	15.15	1.16	0	0.08	2.64

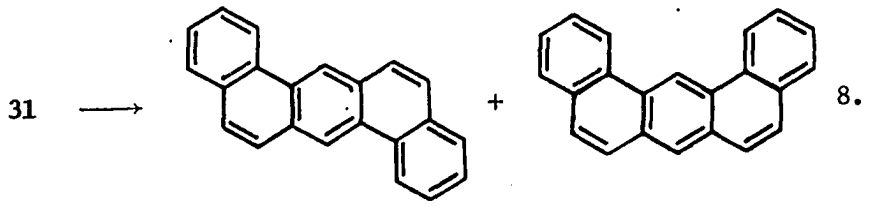
[a]Products were selected because they were major products in the FVP of 9 and of 14.

[b]Retention time in the gc trace.

To test the generality and the regioselectivity of the benzocyclobutene condensation, 1,2-naphthocyclobutene (31), prepared by FVP of 1-chloromethyl-2-methylnaphthalene (32, reaction 7),[24] was pyrolyzed at 890°C. A solid condensed just outside the hot zone which was shown by NMR and gc/ms to be a 1:1 mixture of dibenz[a,h]anthracene (33) and dibenz[a,j]anthracene (34) (reaction 8).



32 31 7.

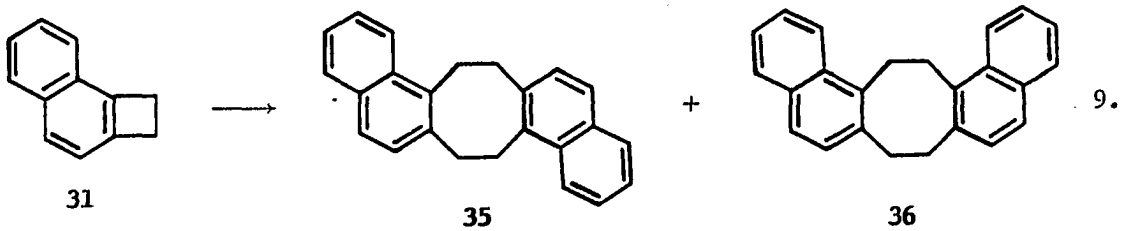


33 34 8.

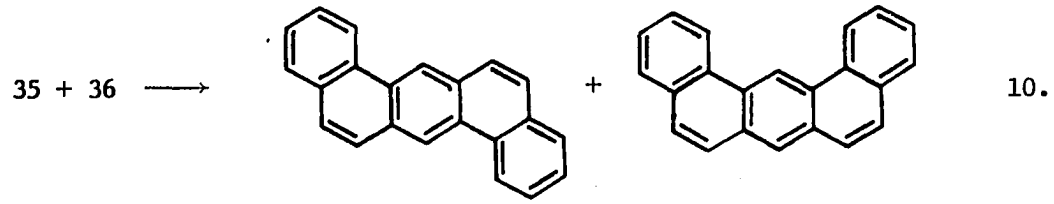
The gc trace of the solid contained essentially just two peaks of nearly equal areas which were shown by gc/ms to each have the molecular weight of a dibenzanthracene. The NMR spectrum of the mixture identified the two compounds. It contained only aromatic resonances. Of these, the downfield absorptions (>δ8.0) fit exactly what one would expect for a mixture of dibenz[a,h]anthracene (33) and dibenz[a,j]anthracene (34) since these compounds have very characteristic absorptions in this region.[22,25]

In a fashion analogous to the preparation of the [4+4] dimer (14),

naphthocyclobutene (**31**) was converted to a mixture of [4+4] dimers (**35** and **36**, reaction 9). These gave **33** and **34** in 21% yield by FVP at 800° (reaction 10).

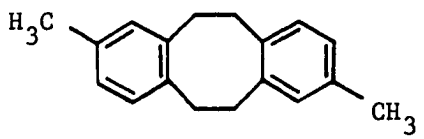


31 **35** **36** 9.



35 + 36 **33** **34** 10.

As a probe into the mechanism of anthracene formation in the pyrolysis of **14**, **37** and **38** were prepared and pyrolyzed separately to



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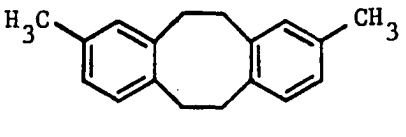
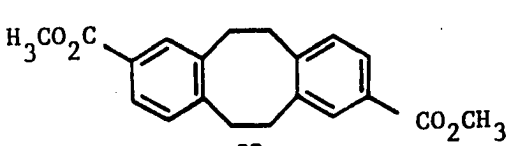


38

determine the regiochemistry of anthracene formation. The methyl groups were chosen as labels since it was expected that they would not alter the chemistry of the dibenzocyclooctene nucleus.

The strategy in the synthesis of **37** and **38** was to prepare, by dimerization of the appropriate benzocyclobutene, a mixture of isomeric precursors which could easily be separated and then convert each isomer to the desired dimethyl derivative. The transoid and the cisoid diesters (**39** and **40**, respectively) were deemed suitable precursors since the ester groups, by virtue of their polarity, were expected to render them separable and be conveniently transformed to methyls.



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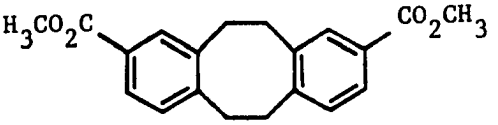


40

Compounds **39** and **40** were obtained as a 45:55 mixture starting from p-toluic acid (**41**). This was chloromethylated[26] and esterified to give ester **43**. This compound was then pyrolyzed to form the carbomethoxy-substituted benzocyclobutene (**44**) which was dimerized in refluxing diphenylether to afford the mixture of **39** and **40** (scheme 1). After purifying the mixture by distillation and column chromatography, **39** and **40** were separated by fractional crystallization.

Analysis by high-field NMR allowed the positive identification of both isomers. The dibenzyl linkages in the transoid isomer (**39**), which are identical to each other, showed an AA'BB' pattern (Figures 2 and 3) while the same linkages in the cisoid isomer (**40**), which are different from each other, showed two singlets since all the protons on each linkage are equivalent to one another on the NMR time scale (Figures 4 and 5).

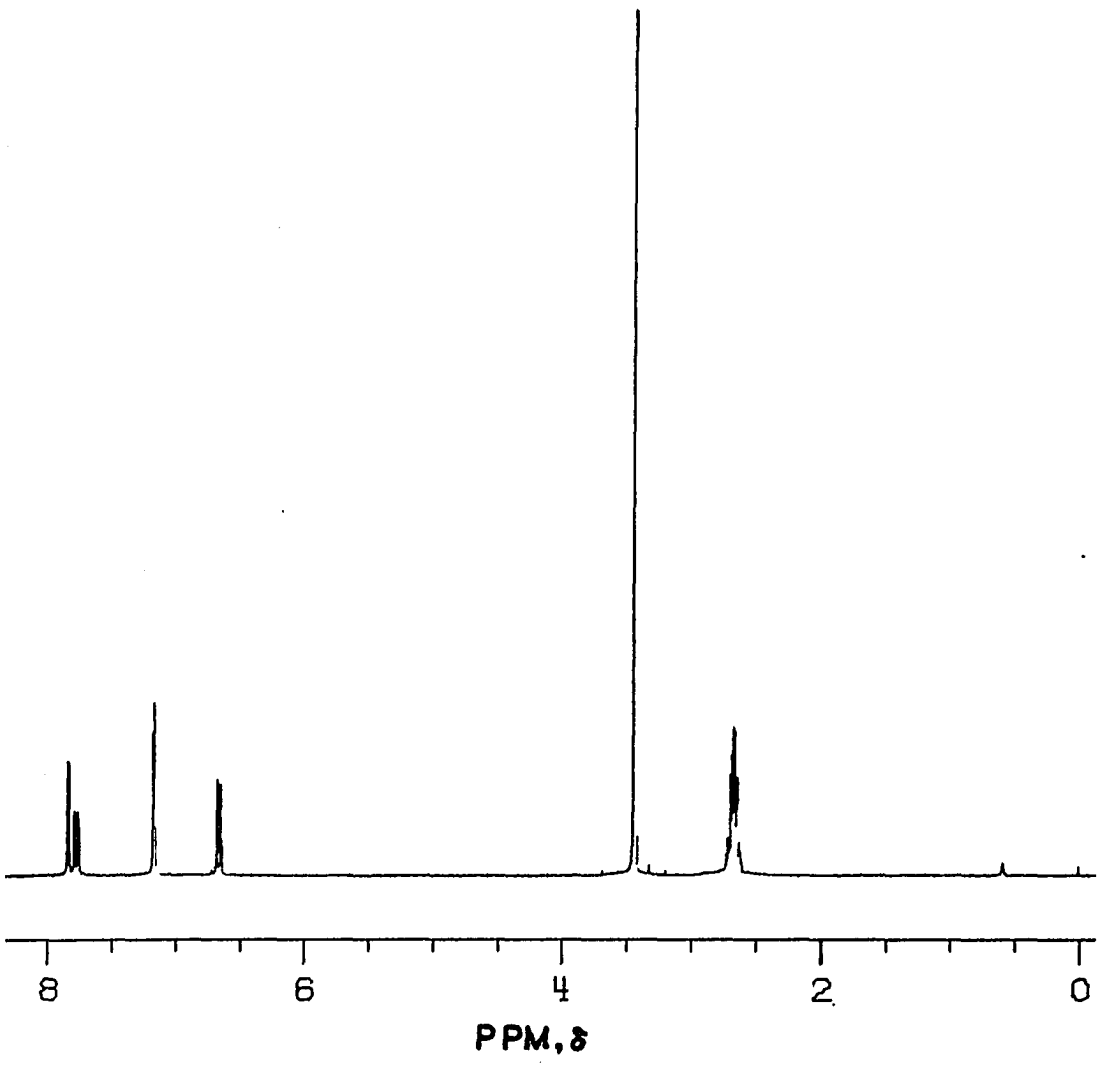


Figure 2. Proton NMR spectrum (300 MHz) of 2,8-dicarbomethoxy-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (39)

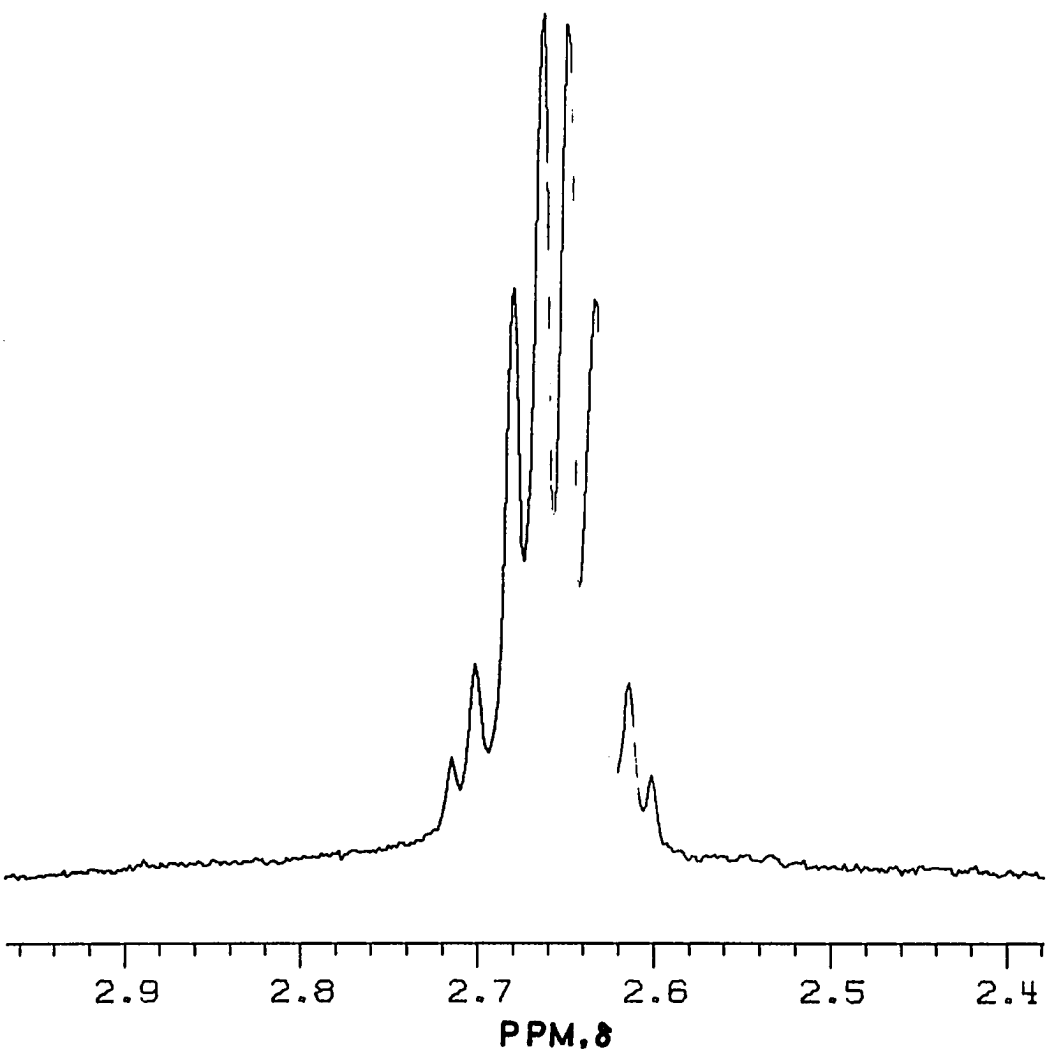


Figure 3. Closeup of the AA'BB' pattern of the dimethylene bridges of 2,8-dicarbomethoxy-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (**39**) in the proton NMR spectrum (300 MHz)

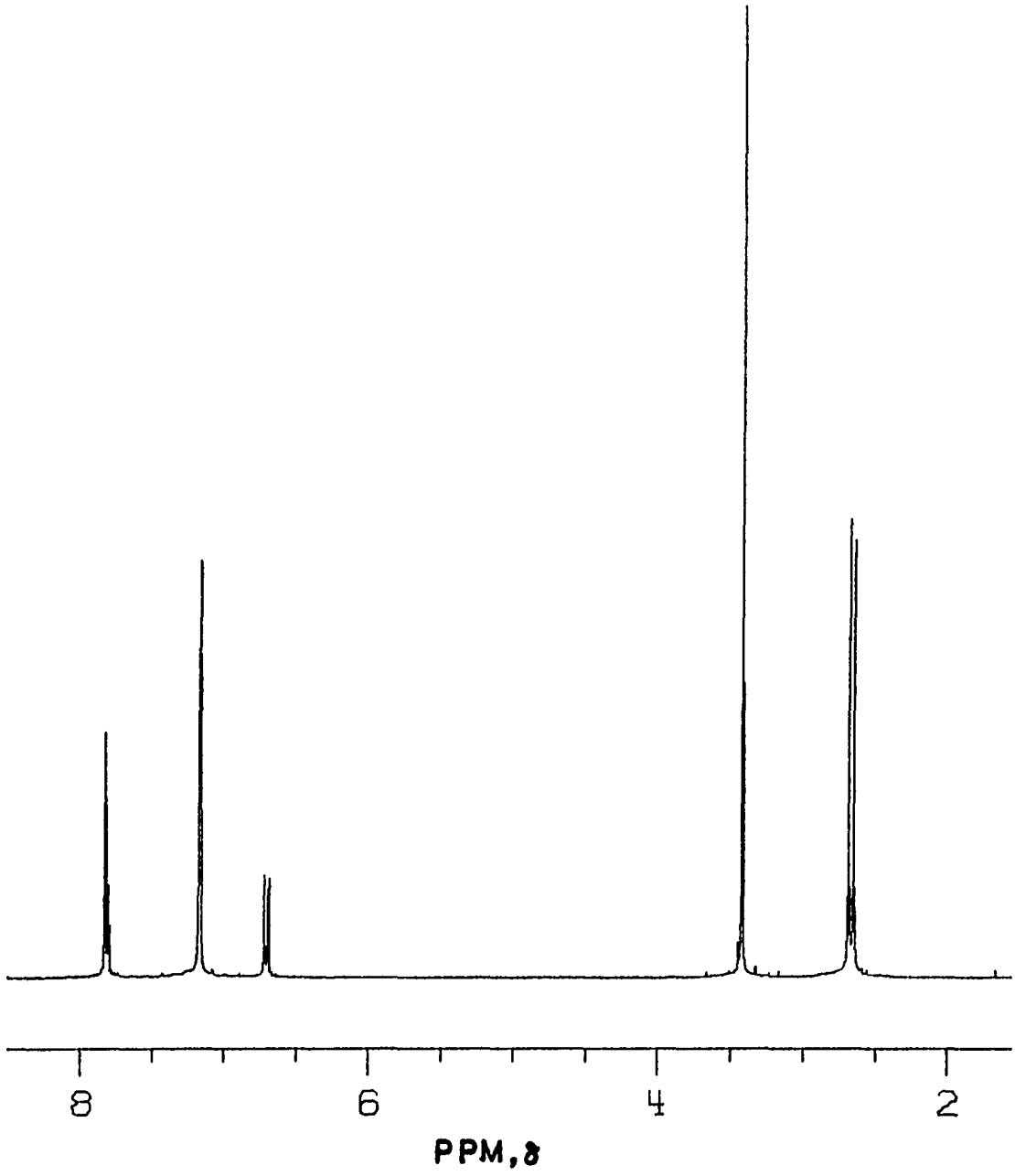


Figure 4. Proton NMR spectrum (300 MHz) of 2,9-dicarbomethoxy-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (**40**)

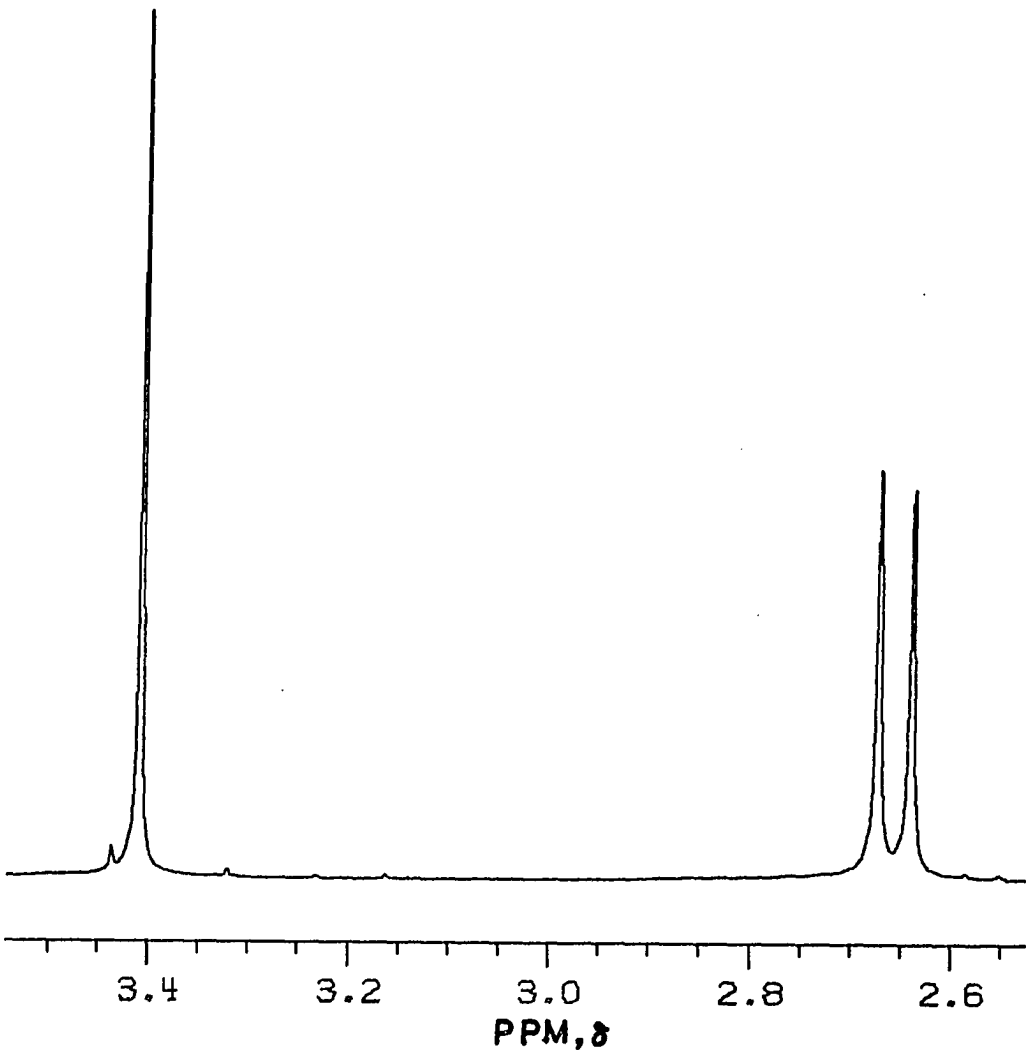
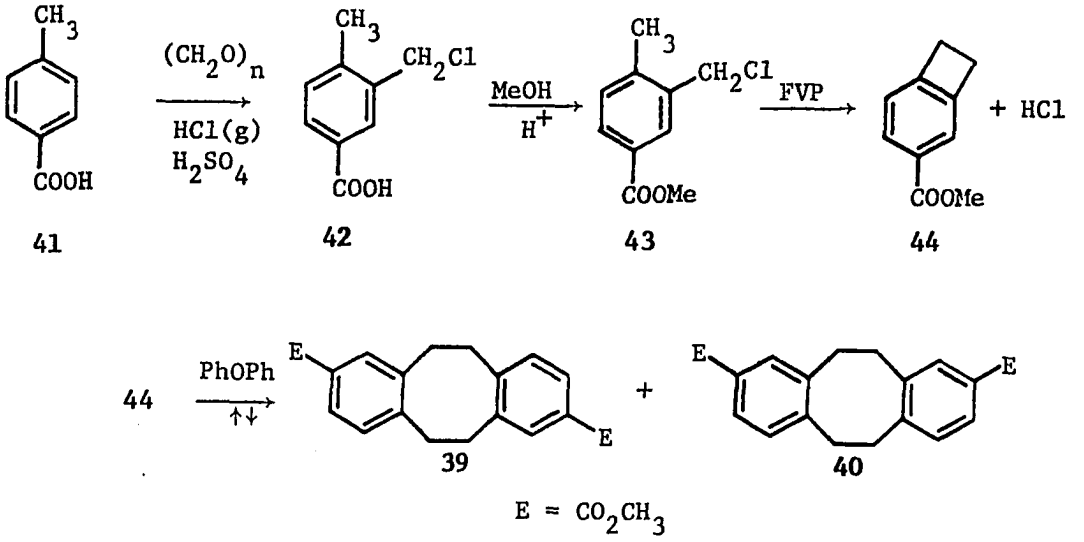


Figure 5. Closeup of the aliphatic region of the proton NMR (300 MHz) of 2,9-dicarbomethoxy-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (**40**) showing the singlets for the two dimethylene bridges and the carbomethoxy groups. The singlet due to the carbomethoxy groups of the other isomer (**39**) appears just downfield of the carbomethoxy signal of **40**

Scheme 1:

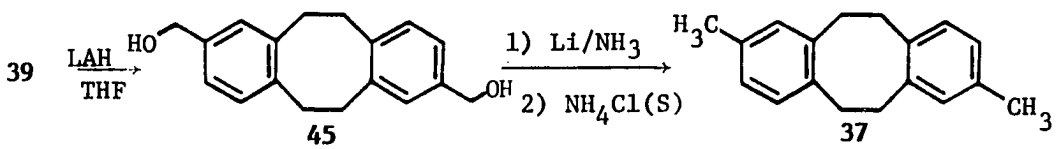


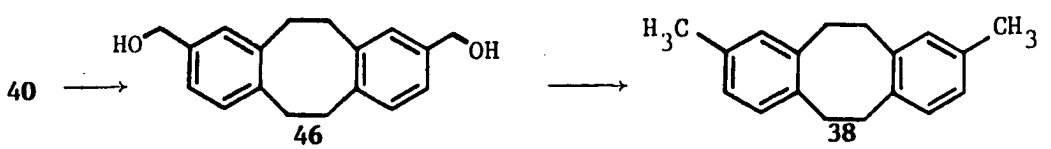
The NMR spectra of the diesters provided a check of the isomeric purity determined by gc since the carbomethoxy signals for the two isomers have different chemical shifts. In the NMR of the cisoid diester (40), the signal for the carbomethoxy groups of the transoid impurity (39) appears as a tiny singlet at δ3.433, just downfield of the signal for the carbomethoxy groups of 40 at δ3.407 (Figure 5). The isomeric purity of this sample of the cisoid diester (40), determined from the ratio of these peaks, was >99% which agreed with the gc results. The sample of the cisoid diester transformed to the dimethyl derivative (38) was 92% pure by gc. Likewise, the NMR spectrum of the transoid diester (39) contains a small singlet just upfield from the signal of the carbomethoxy groups of 39 (Figure 2). The sample of transoid diester (39) converted to the dimethyl derivative (37) was actually purer by gc

(>99.2%) than the NMR sample (>99%).

Reduction of the diesters was accomplished using established general procedures. Treatment of **39** and **40** with lithium aluminum hydride (LAH)[27] afforded the corresponding diols (**45** and **46**) which were converted to the desired dimethyl compounds (**37** and **38**) by lithium and ammonia[28] (Scheme 2).

Scheme 2:





The dimethyl compounds (**37** and **38**) could not be distinguished by ^{1}H NMR (Figure 6), ^{13}C NMR (Figure 7) or gc. There were slight differences in the melting points and infrared spectra. The isomeric purity of these compounds was assumed to be the same as the diesters (**39** and **40**) whence they came.

FVP of the transoid dimethyldibenzocyclooctene (**37**) at 920° gave a product mixture which was indistinguishable from the parent system by gc except that the retention times were longer due to the added methyl

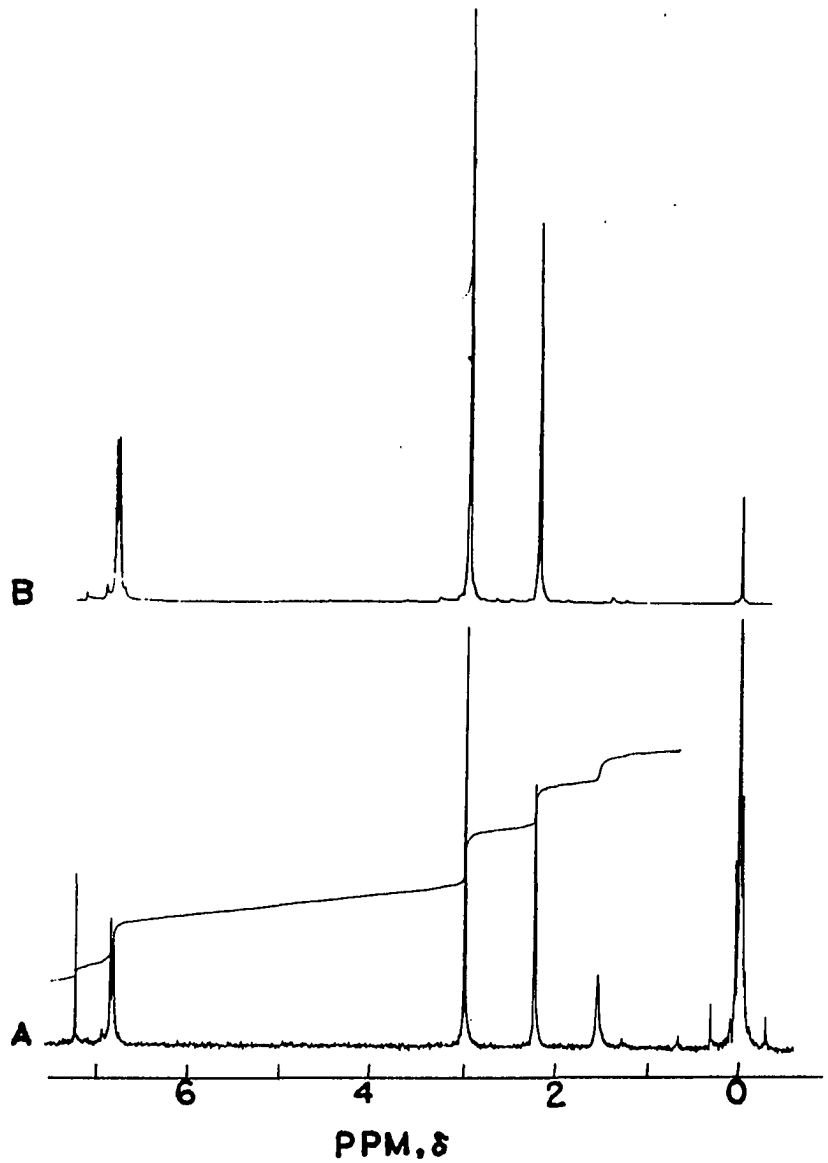


Figure 6. Proton NMR spectra (90 MHz) of (a) 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (37) and (b) 2,9-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (38)

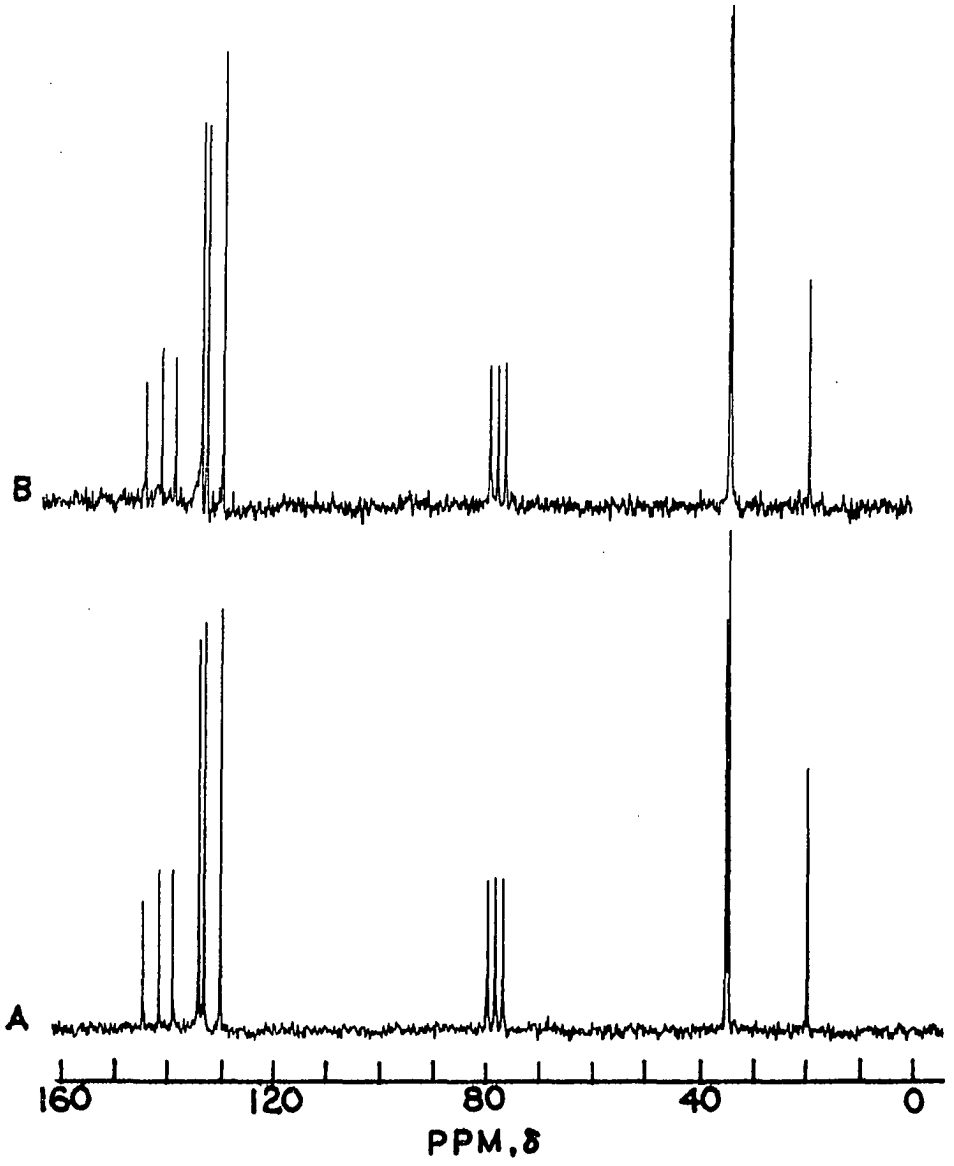


Figure 7. Carbon-13 NMR spectra (22.5 MHz) of (a) 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (37) and (b) 2,9-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (38)

groups. Preparative thin layer chromatography (TLC) on alumina separated the anthracene products from the rest of the pyrolyzate. ^{1}H NMR analysis of this material showed it to be mostly 2,7-dimethylanthracene (**47**) with some 2,6-dimethylanthracene (**48**) in a 96:4 mole ratio[29] and another minor product (possibly a trimethylanthracene by analogy to the parent system) (Figures 8 and 9). The two isomers (**47** and **48**) were distinguished by their 9- and 10-protons in the NMR spectrum.[29] Whereas **47** showed two singlets at δ8.20 and 8.30 (1H each), 48 showed one singlet at δ8.25 (2H) since its 9- and 10-protons are equivalent. The isomer ratio was determined by integration of these signals. The cisoid dimethyldibenzocyclooctene (**38**) (92% isomeric purity) gave mostly the transoid dimethylanthracene (**48**) in a fashion identical to the pyrolysis of the transoid isomer (**37**). The dimethylanthracenes (**47** and **48**) are distinguished by their ^{13}C NMR spectra as well as their ^{1}H spectra since **47** has 8 different aromatic carbons while **48** has 7. Comparison of the ^{1}H NMR (Figure 10) and the ^{13}C NMR (Figure 11) of the TLC purified anthracenes clearly showed which isomer was the major product of each pyrolysis. Also, after recrystallization, melting points[30] and IR spectra[31] (Table 3) agreed with literature values. Thus, the formation of anthracenes in the pyrolysis of dibenzocyclooctenes is highly regiospecific (Scheme 3).

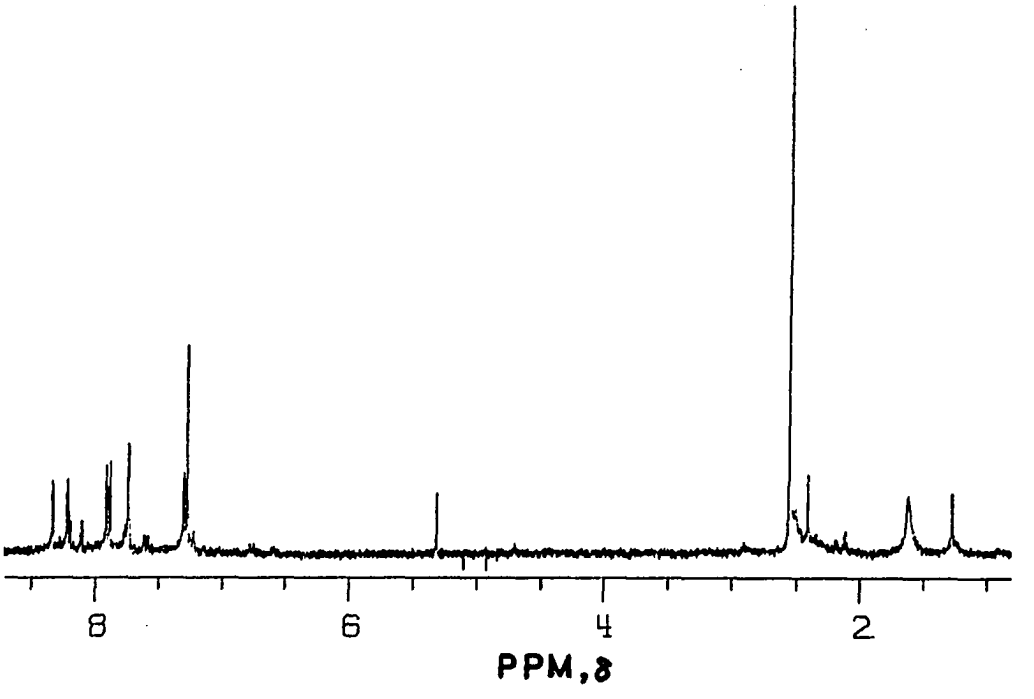


Figure 8. Proton NMR spectrum (300 MHz) of the anthracene products from the FVP of 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (37). 2,7-Dimethylanthracene (47) is the major component

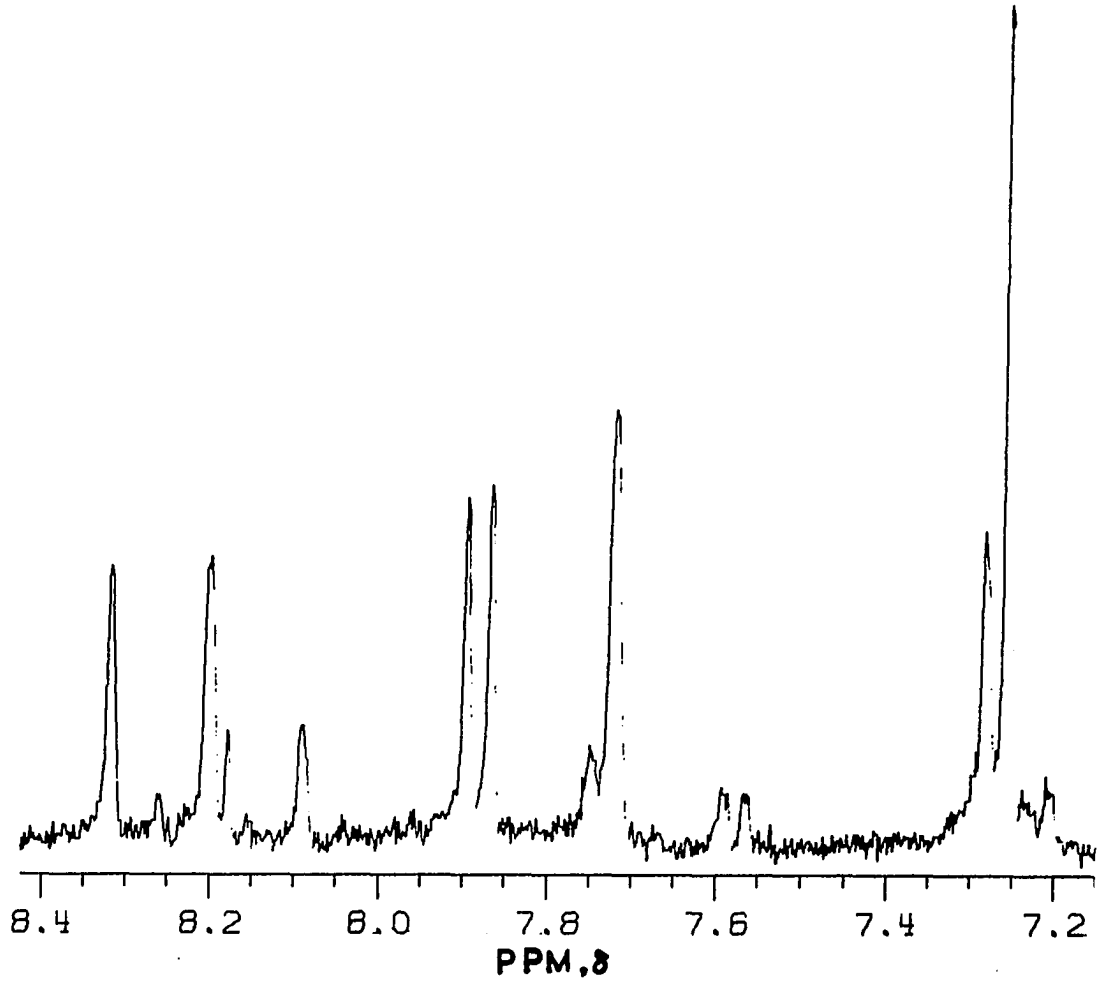


Figure 9. Closeup of the aromatic region of the proton NMR spectrum (300 MHz) of the anthracene products from the FVP of 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (37). The major component is 2,7-dimethylanthracene (47)

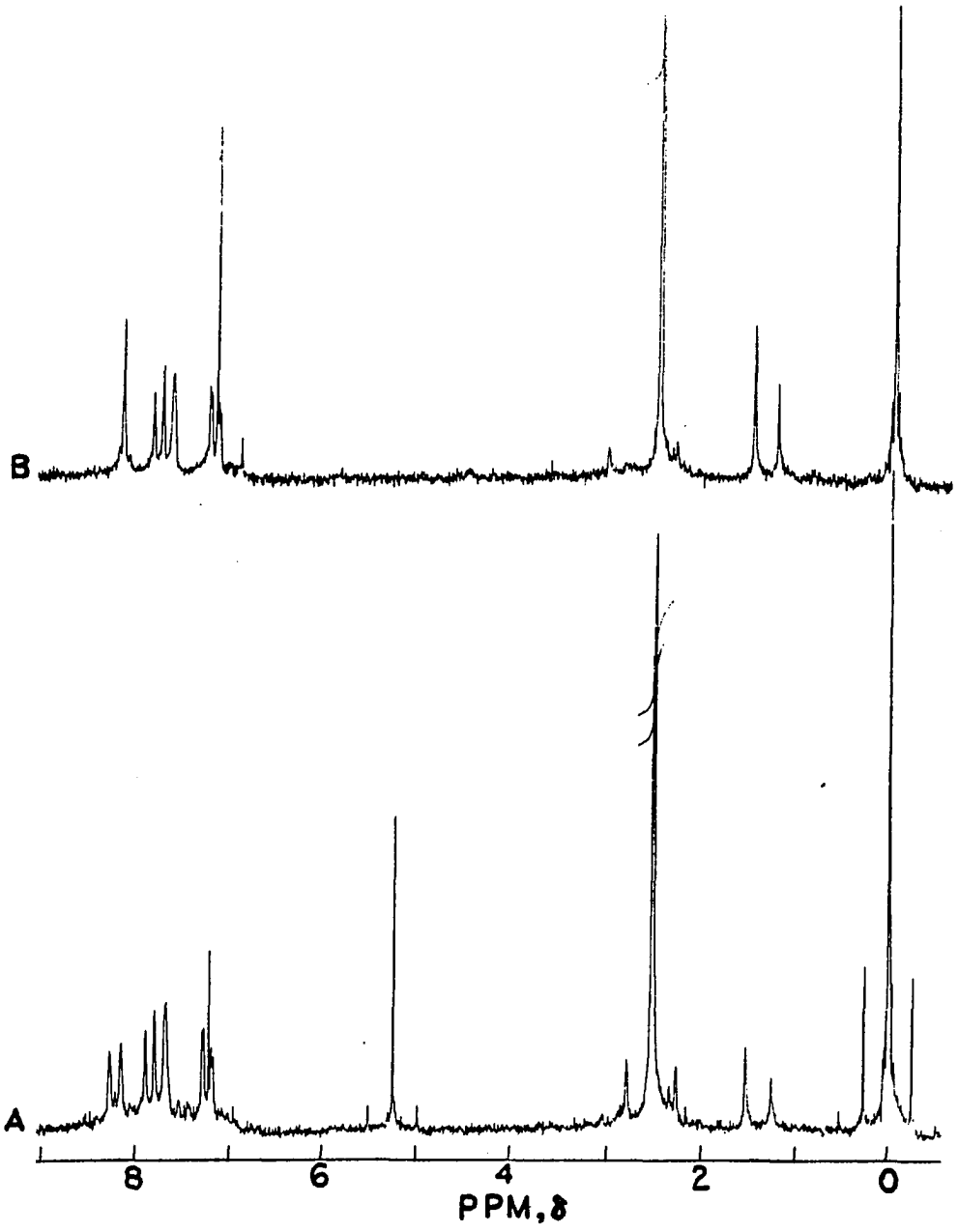


Figure 10. Proton NMR spectra (90 MHz) of the anthracene products from the FVP of (a) 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]-cyclooctene (**37**) (the major component is 2,7-dimethylanthracene (**47**)) and (b) 2,9-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (**38**) (the major component is 2,6-dimethylanthracene (**48**))

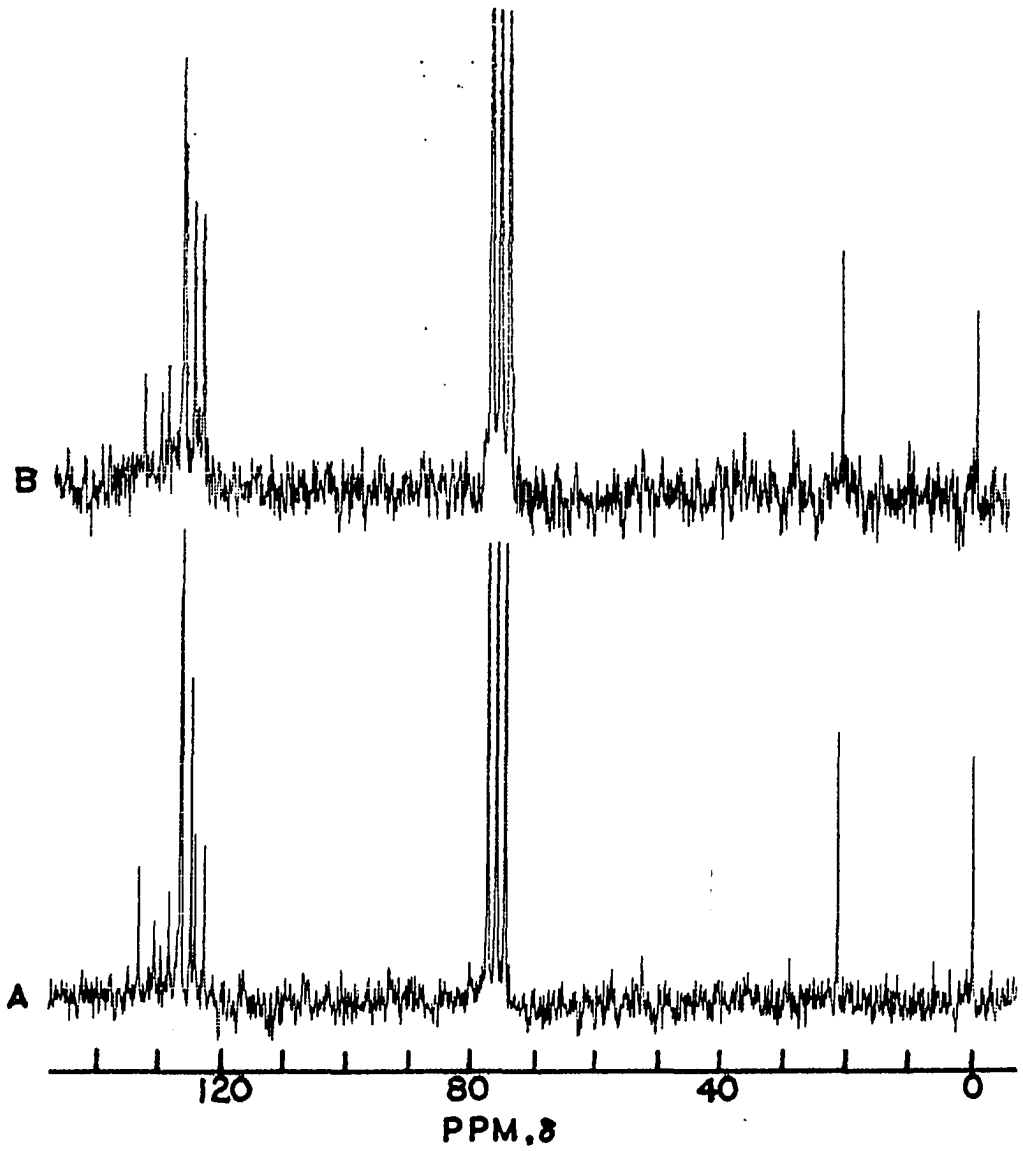


Figure 11. Carbon-13 NMR spectra (22.5 MHz) of the anthracene products from the FVP of (a) 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (37) (the major component is 2,7-dimethylanthracene (47)) and (b) 2,9-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (38) (the major component is 2,6-dimethylanthracene (48))

Scheme 3:

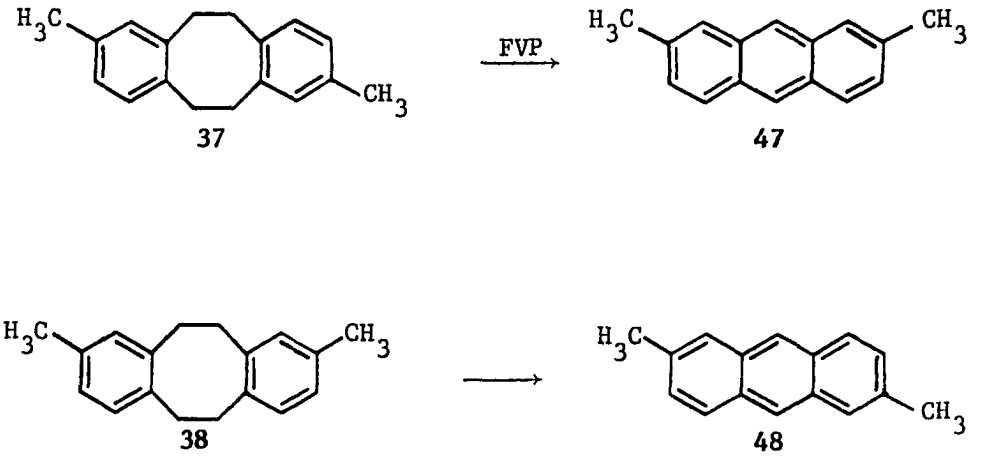


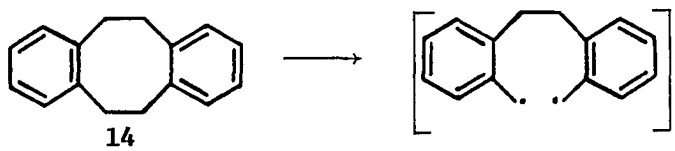
Table 3. Comparison of IR data for 2,7- and 2,6-dimethylanthracenes (**47** and **48**) obtained by FVP of dimethyldibenzocyclooctenes (**37** and **38**) to literature values[a]

2,7-dimethylanthracene (47)			2,6-dimethylanthracene (48)		
a exptl. cm^{-1} (int.)	b lit. values[a] cm^{-1} (int.)	Difference (b-a) cm^{-1}	a exptl. cm^{-1} (int.)	b lit. values[a] cm^{-1} (int.)	Difference (b-a) cm^{-1}
1442 (m)	1463 (s)	21	1462 (m)	1474 (m)	12
1363 (m)	1379 (m)	16	1442 (m)	1460 (m)	17
1292 (m)	1310 (m)	18	1365 (m)	1378 (m)	13
1257 (m)	1273 (m)	16	1292 (m)	1305 (m)	13
1157 (m)	1174 (m)	17	1260 (m)	1273 (m)	13
1100 (w)	1120 (w)	20	1160 (m)	1171 (m)	11
1018 (m)	1040 (m)	22	1128 (w)	1139 (w)	11
943 (s)	962 (s)	19	1023 (m)	1041 (m)	18
922 (w)	941 (w)	19	949 (s)	963 (s)	14
896 (s)	916 (s)	20	929 (m)	942 (m)	13
874 (vs)	896 (vs)	22	888 (vs)	905 (vs)	17
839 (m)	861 (m)	22	858 (s)	873 (s)	15
770 (vs)	791 (vs)	21	777 (s)	793 (s)	16
750 (m)	771 (m)	21			

[a]Reference 31.

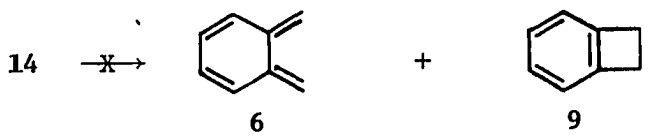
DISCUSSION

Almost certainly the pyrolysis of **14** begins with homolysis of one of the bibenzyl bonds giving two benzylic radicals (reaction 11). Bibenzyl is known to readily cleave this way.[32-34] What happens after that must be the cause of the many isomers of **14**. One can imagine a



11.

number of hydrogen abstraction and ring formations that would isomerize **14**. It is somewhat surprising that there was very little reversion back to **6** and **9** (reaction 12).

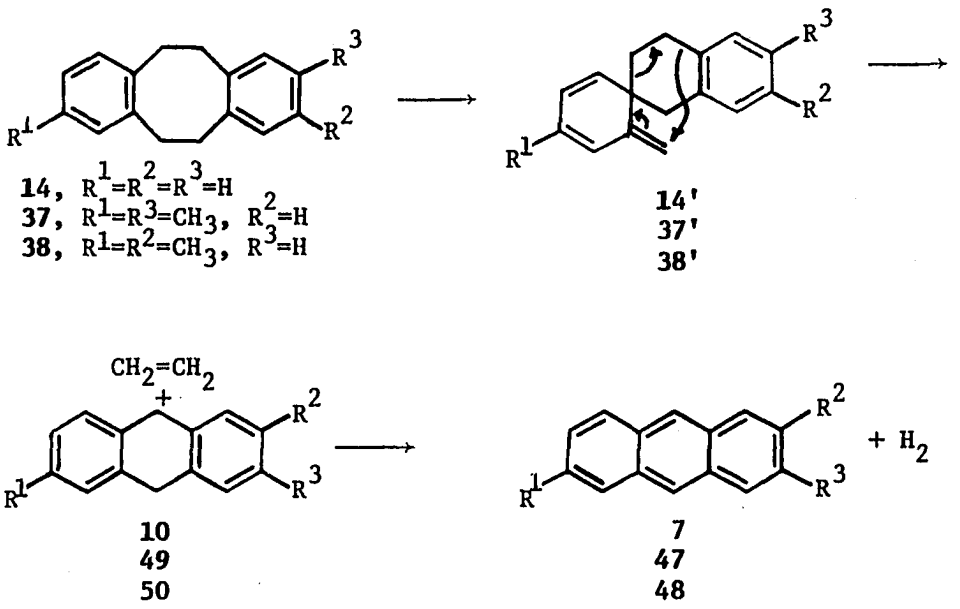


12.

The reaction that leads to anthracene is clearly favored over the others (Figure 1). A clue as to the nature of this reaction is found in the pyrolysis of **37** and **38**. When these form the anthracenes, one of their aromatic rings is flipped 180° relative to the other. A reasonable way to account for this is by the intermediacy of the o-xylylene spirodimer (**14'**, **37'**, **38'**) in which 90° of the ring flip has occurred. Fragmentation of the spirodimer completes the ring flip, giving

ethylene with formation of a new phenyl-methylene bond and rearomatization to give the 9,10-dihydroanthracene (**10**, **49**, **50**). A 1,4-elimination of H_2, a well-known facile thermal reaction,[16,35] completes the formation of anthracenes (**7**, **47**, **48**, Scheme 4).

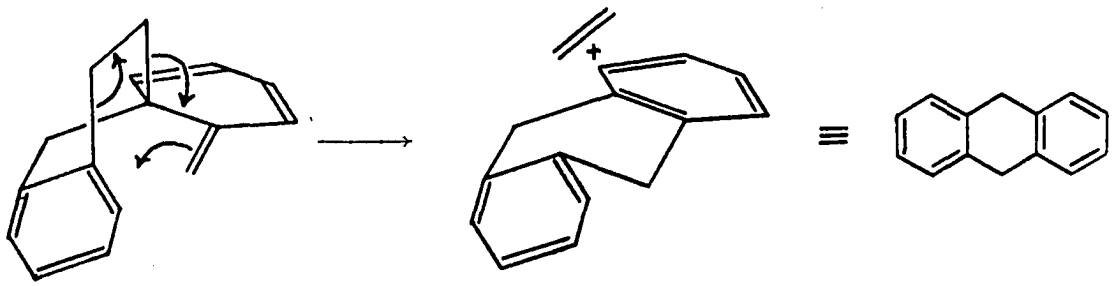
Scheme 4:



One reason why anthracene is the major product of the pyrolysis of **14** must be that isomerization to **14'** is preferred over other isomerizations. This is probably because both radical centers are satisfied in one step and, in fact, it might even be concerted since it is a 1,3-shift of carbon which is thermally allowed by Woodward-Hoffmann rules.[36] This is the first evidence that the two well-known dimers of o-quinodimethane (**14** and **14'**) can interconvert.

Another reason why anthracene predominates is that there is considerable driving force in the irreversible fragmentation since a small closed-shell molecule is split off and the aromatic ring is regenerated. A model of **14'** indicates that there are basically two conformations of the central ring and in one of these, the exo-methylene group is directly above the carbon atom of the aromatic ring with which it forms a new bond. Indeed, in this conformation, the six atoms involved in the fragmentation-phenyl migration are oriented in roughly a boat form of a six-membered ring. This would facilitate a concerted reaction (Scheme 5).[36] On the other hand, in this conformation there appear

Scheme 5:

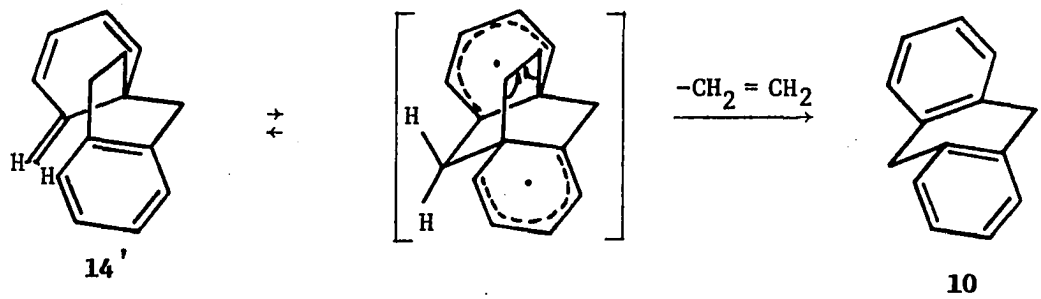


14' **10** **10**

to be considerable van der Waals forces which are relieved by a twist of the double bond to the exo methylene, enhancing its radical nature and promoting bonding to the aromatic ring. This would result in the diradical pictured in Scheme 6 which should quickly lose ethylene.

The fragmentation-phenyl migration is analogous topologically to the

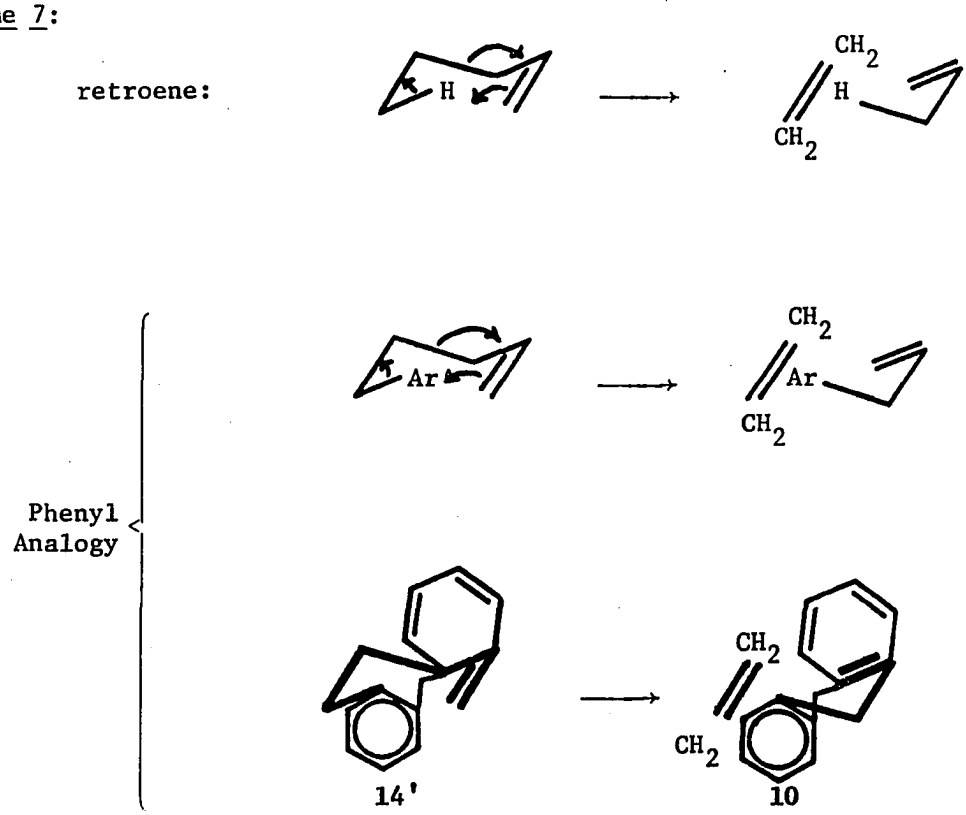
Scheme 6:



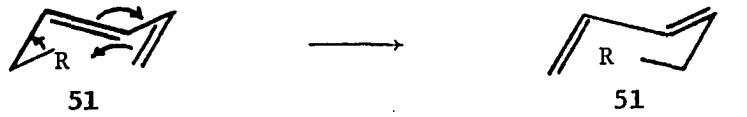
14' 10

retroene reaction in which the fragmentation is accompanied by a hydrogen migration (Scheme 7).[37] In this regard, it is interesting to note that, for

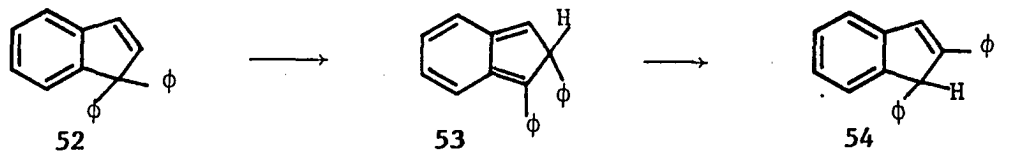
Scheme 7:



the related 1,5-shift (reaction 13), the order of reactivity is hydrogen (R=H) > phenyl (R=Ar) > alkyl ($R=CH_3$) in the only system in which a sigmatropic phenyl shift has been observed (phenylindenes) (reaction 14).[38]



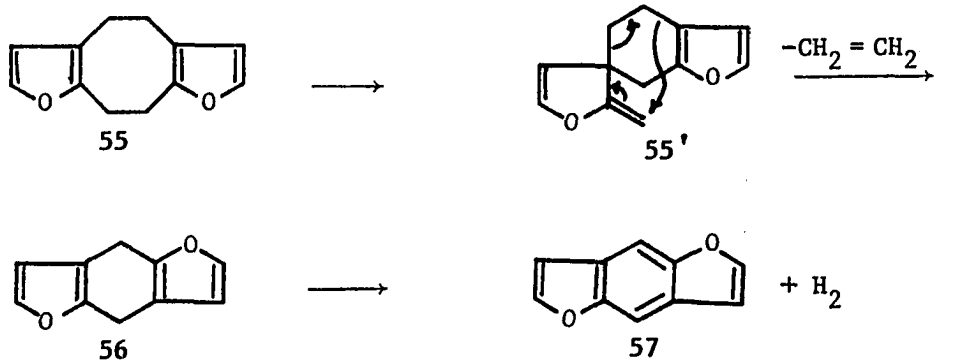
51 51 13.



52 53 54 14.

This is the first time such a fragmentation has been recognized but it may be quite general, operating in heterocyclic chemistry as well as carbocyclic chemistry. In this laboratory, it has been shown to occur in the FVP of the difurano-analogue of **14** (**55**, Scheme 8).[39] In the

Scheme 8:

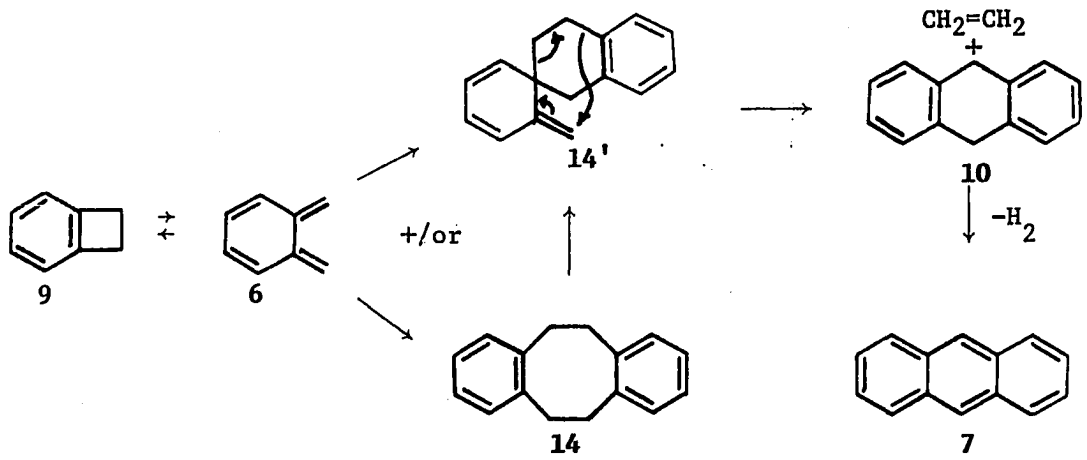


55 55' 56 57

literature, there are several reports of heterocyclic reactions which could be going by the same mechanism (see the Appendix). It will be shown later how this fragmentation may be operating in general hydrocarbon pyrolysis.

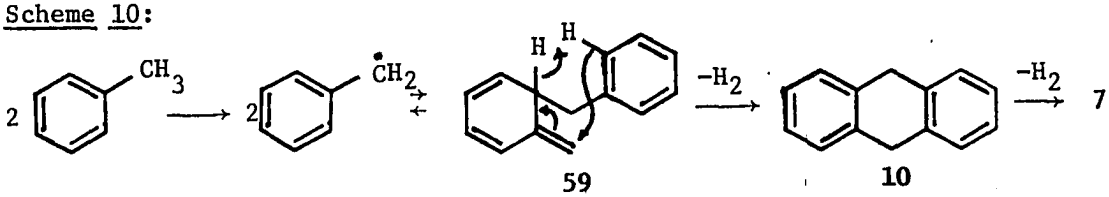
Benzocyclobutene (**9**) seems to be giving anthracene by essentially the same mechanism. The results in Table 1 indicate that most of the major "dimeric" products of pyrolysis of **9** are the same compounds obtained in the FVP of **14**. Also, the ratios of these products to **14** in the pyrolysis of **9** are about what one would expect if they were formed by pyrolysis of first-formed **14**, anthracene being no exception (Table 2). Of course, it is possible that the spirodimer (**14'**) that leads to anthracene is formed directly from **6**, the open form of **9**. Thus, a unified mechanism is proposed whereby both substrates form anthracene through the spirodimer of **6** (**14'**, Scheme 9).

Scheme 9:



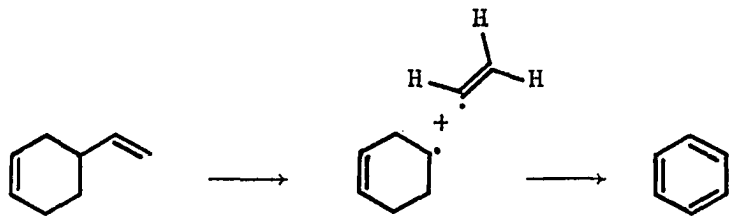
Even though this is a new way to anthracene, the mechanism may be analogous to the way toluene (**58**) gives anthracene. While the details of this transformation are unclear, it is thought to occur by a combination of benzyl radicals.[17,40,41] To give anthracene, two benzyl radicals would first combine to give 6-benzyl-5-methano-1,3-cyclohexadiene (59). This compound is analogous to 14' and may eliminate H_2 to form **10** in a fashion analogous to the fragmentation of **14'**(Scheme 10).

Scheme 10:



59 10

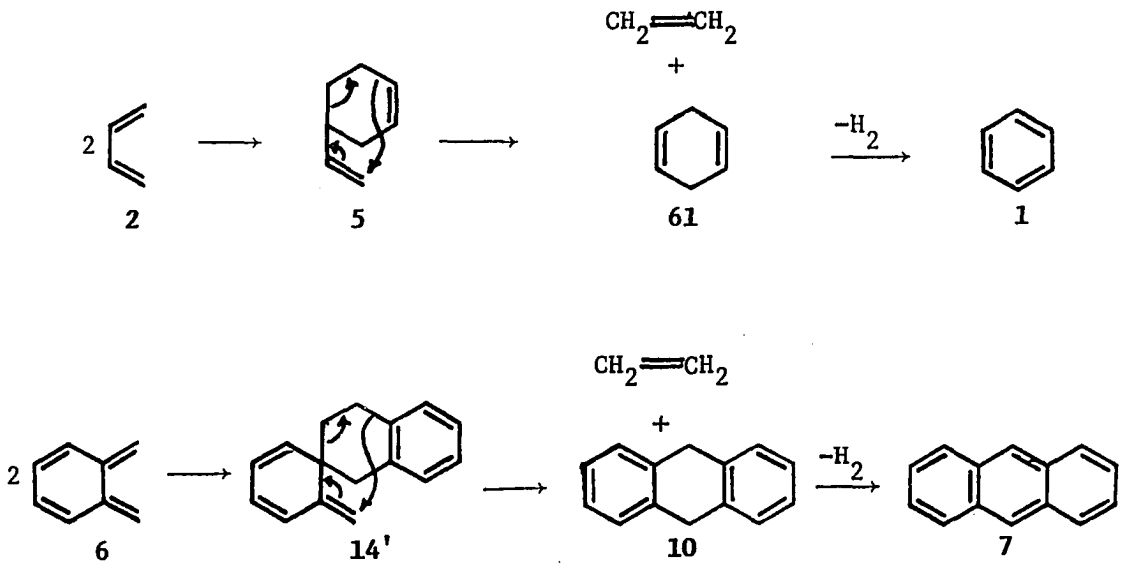
As noted earlier, benzene (**1**) is thought to arise in hydrocarbon pyrolysis through the intermediacy of 4-vinylcyclohexene[6-8] (**5**, reaction 2). Badger and Novotny,[8] who studied the pyrolysis of **5**, favored a simple homolytic cleavage of the vinyl group to generate a cyclohexenyl radical (**60**) which would give benzene by dehydrogenation (reaction 15). They also suggested that just about every conceivable ring fragmentation probably occurs under their conditions(700°, N_2 flow)



5 60 1 15.

forming radical and diradical fragments. Some of these would be expected to give benzene by cyclization and dehydrogenation. Gil-Av and coworkers[6] proposed mechanisms similar to reaction 15. This was only speculation on the part of these authors and until now there has not been any experiment reported which has a direct bearing on the mechanism of this transformation. Well, butadiene (2) → 5 → benzene (1) (reaction 2) is analogous to o-xylylene (6) → spirodimer (14') → anthracene (7) (Scheme 9), so perhaps benzene is formed from 5 by the same fragmentation (Scheme 11).

Scheme 11:

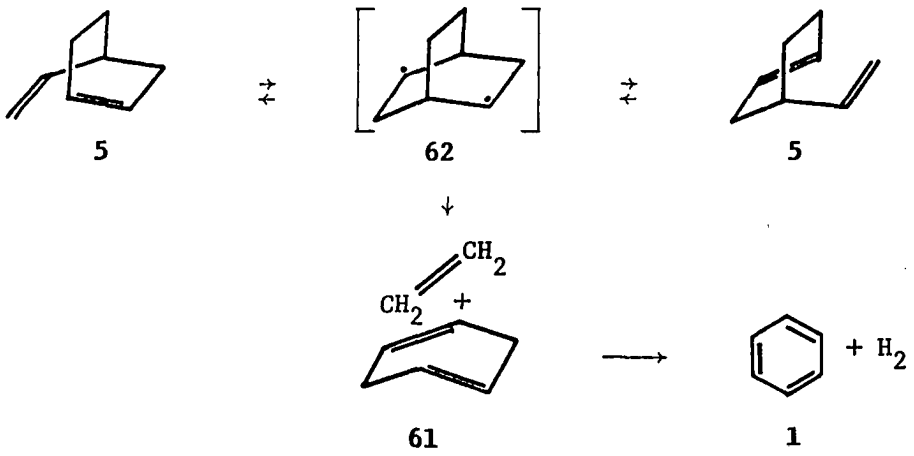


Not only does this mechanism explain the facile loss of two carbon atoms in going from 5 to **1**, but the loss of H_2 from **61** is also facile.[35] One of the problems with the original theory of benzene formation

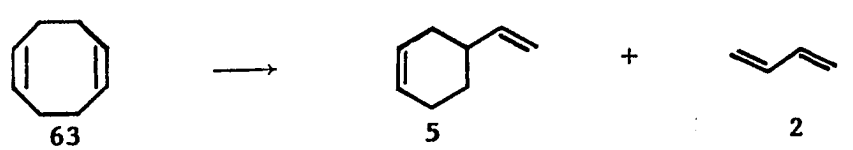
(reaction 1) is that direct dehydrogenation of cyclohexenes to aromatics has not been established.[6,35]

It is interesting that one extreme of the diradical transition state for the degenerate Cope rearrangement of **5** (**62**)[42] is the same diradical one would draw for the formation of **61** by analogy to the fragmentation of **14'** seen in Scheme 6. One could imagine that **5** undergoes several reversible Cope rearrangements until fragmentation occurs (Scheme 12).

Scheme 12:



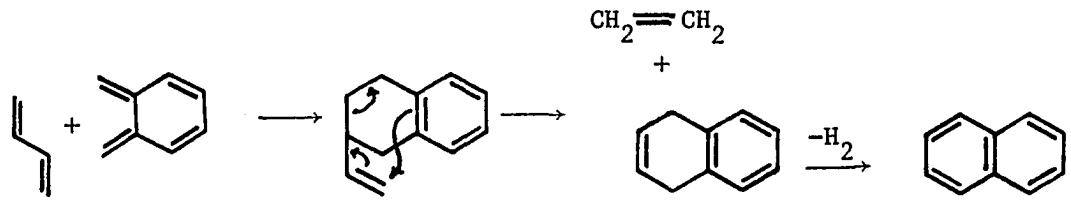
The proposed transformation of dibenzocyclooctene (**14**) to the spirodimer (**14'**) also has its analogy in the parent system. Cyclooctadiene (**63**) gives by pyrolysis primarily vinylcyclohexene (**5**) with some butadiene (**2**) (reaction 16)[43]



16.

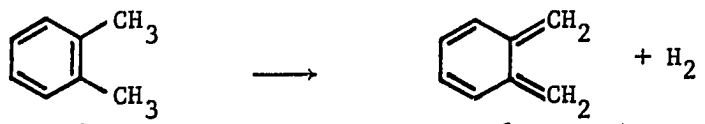
Another major product of hydrocarbon thermal aromatization is naphthalene (64).[4,8] One can imagine this compound arising by the same mechanism provided a substantial amount of o-xylylene (6) is formed (Scheme 13). Formation of o-xylylene in hydrocarbon pyrolysis is not out

Scheme 13:



2 6 65 66 64

of the question. In the pyrolysis of butadiene (2) at 550°C, xylenes are major products. At 700°C, there is a 62% decrease in the yield of o-xylene (67).[6] This is coincident with dramatic increases in the yields of benzene and polycyclic aromatics (probably mostly naphthalene)[8] and lesser reductions in the yields of other C_8 aromatics. It seems likely that some of the polycyclic aromatics are the result of pyrolysis of o-xylene (67) possibly by the intermediacy of 6 (reaction 17, Scheme 13).



67 6 17.

EXPERIMENTAL SECTION

General

The flash vacuum pyrolysis (FVP) apparatus was patterned after the one described by Trahanovsky et al.[32] Central to the apparatus was a vycor tube, 2.5 cm x 30 cm, packed in the central 10 cm with 1 cm x 8 mm pieces of vycor tubing and heated by a Lindberg furnace. At one end of the tube was the sample chamber attached by a 40/35 ground glass joint and containing the sample in a glass boat. At the other end, attached by o-ring joints was the product condenser: a u-tube immersed in a liquid nitrogen bath. Attached to the other end of the u-tube was an oil diffusion pumping system, nitrogen inlet and cold cathode vacuum gauge. The temperature of the hot zone was measured by a thermocouple touching the outside of the tube at the center and connected to an Omega chromel-alumel model 199 potentiometer with digital readout. When HCl was generated, a basket of KOH pellets was placed in the exit end of the u-tube (Figure 12).

Gas chromatographic (gc) analysis was performed on a Hewlett Packard 5840A gas chromatograph with a glass capillary column coated with methylsilicon fluid and a flame ionization detector. Retention times were reproducible to ±0.1 minute during the course of the study of benzocyclobutene (9) and dibenzocyclooctene (14).

Gas chromatography/mass spectrometry analysis was with a Finnigan 4000 gc/ms with INCOS Data system and Finnigan 9610 gc. Double Focusing mass spectra were obtained on an AEI MS902 high resolution ms. NMR

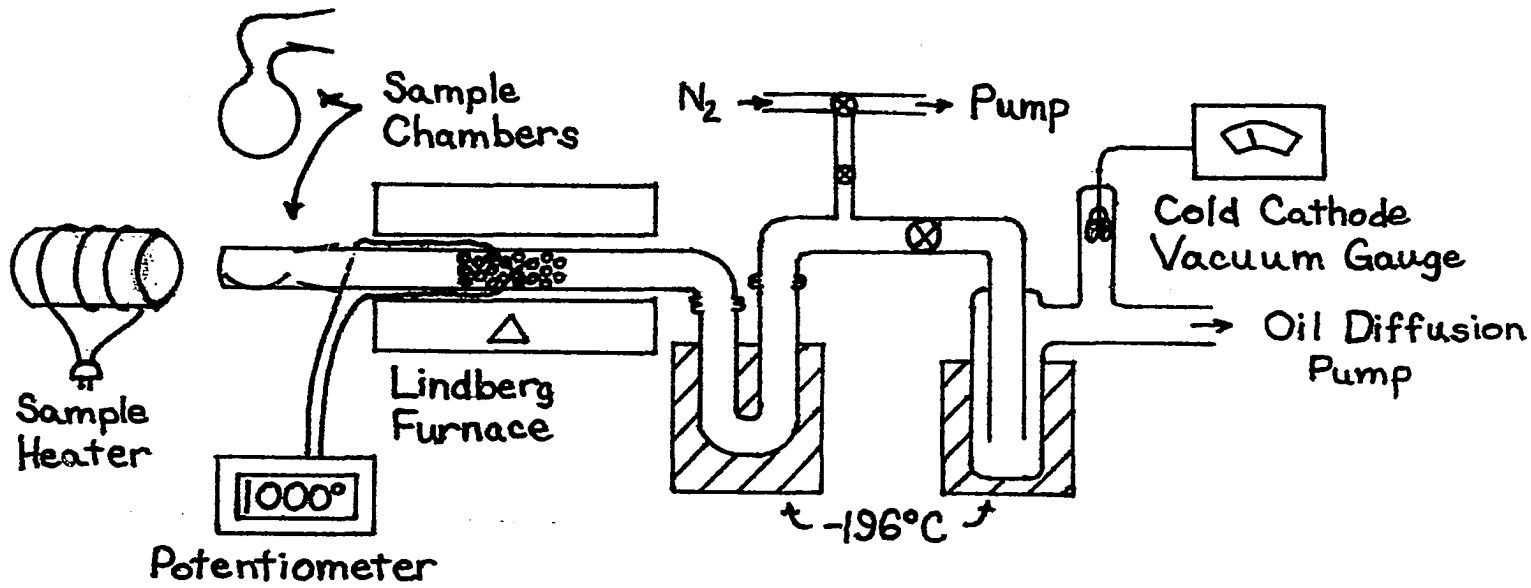


Figure 12. The flash vacuum pyrolysis (FVP) apparatus

spectra were recorded on either a Varian EM360, a JEOL FX90Q or a Nicolet NT300. Chemical shifts are reported in δ values downfield from tetramethylsilane as an internal standard. Infrared spectra were recorded on a Beckman Acculab II with neat films or KBr pellets. Melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected. The commercially available chemicals used are listed in Table 4.

Benzocyclobutene (9)

This compound was prepared according to the method of Morello.[20] α-Chloro-o-xylene (7.25 g) was pyrolyzed by FVP at 765°C and 7×10^{-4} torr. After warming the contents of the u-tube under nitrogen to room temperature, the walls were rinsed down with pyridine (stored over KOH). The white precipitate which formed was filtered and the supernatant pyridine solution (30 mL) was heated for 1.5 h to destroy excess starting material, then shaken with HCl (10%, 520 mL). The aqueous solution was extracted with pentane and the organic layer was washed with HCl (10%, 9x50 mL) and $CuSO_4$ (sat., 3x50 mL) and dried over $MgSO_4$. The solvent was removed by distillation and the product was distilled under reduced pressure to give 3.05 g of **9** (57%): bp 64° (34 mm Hg) [lit.[43] bp 94.5°C (142 mm Hg)]; IR (neat) 1450, 1088, 992, 773, 700 cm^{-1} (lit. IR[44] 10.03, 12.8, 14.0 μ); ^1H NMR (60 MHz, $CDCl_3$) δ 7.05 (m, 4H), 3.17 (s, 4H) (lit.[20] NMR δ 7.0 (m, 4H); MS (70 eV) 104 (100), 103 (55), 78 (65), 77 (30) [lit.[20] MS 104 (100), 103 (54), 78 (63), 77 (28), 63 (14)]. Just outside the oven, a solid was deposited which was scraped out of the tube and washed with

Table 4. Commercially available compounds

Compound	Source
Acetone	Fisher Scientific Co.
Acetone-d_6	Norell, Inc.
Alumina (neutral powder)	J. T. Baker Chemical Co.
Alumina TLC plates	Eastman Kodak Co.
Ammonia (anhydrous)	Matheson Division of Searle Medical Products USA, Inc.
Ammonium chloride	J. T. Baker
Anthracene	MCB Manufacturing Chemists, Inc.
Benzene	Fisher
Benzene-d_6	Cambridge Isotope Laboratories
Biphenyl	Eastman Kodak
Carbon dioxide (s) (dry ice)	Heller Carbonic
Carbon disulfide	Fisher
Carbon tetrachloride	Fisher
Chloroform	Fisher
Chloroform-d	Aldrich Chemical Co.
1-Chloromethyl-2-methyl-naphthalene	Aldrich
α-Chloro-o-xylene	Aldrich
Copper (II) sulfate	J. T. Baker
Diethylphthalate	The Matheson Co., Inc.
Dimethylsulfoxide-d_6 (DMSO-d_6)	Columbia Organic Chemicals
Ethanol (absolute)	Worum Chemical Co.
Ether	Fisher
Ethyl acetate	Fisher
Ethylene	Matheson
Ethylene glycol	Mallinckrodt, Inc.
Hexanes	Fisher
Hydrochloric acid	Mallinckrodt
Hydrogen chloride	Matheson
Isopropanol	Mallinckrodt
Lithium	Morton Thiokol, Inc.
Lithium tetrahydroaluminate (LAH)	Morton Thiokol, Inc.
Magnesium sulfate	J. T. Baker
Methanol	Fisher
Methylene chloride	Fisher
Nitrogen (g)	Quickway, Inc.
Nitrogen (l)	Air Products and Chemicals, Inc.
Paraformaldehyde	Eastman Kodak
Pentane	Mallinckrodt
Phenyl ether	J. T. Baker
Potassium hydroxide	J. T. Baker
Pyridine	J. T. Baker

Table 4. (Continued)

Compound	Source
Silica gel 60 (230-400 mesh)	E. Merck, Darmstadt, Germany
Silica gel TLC plates	Eastman Kodak
Sodium bicarbonate	J. T. Baker
Sodium chloride	J. T. Baker
Sodium hydroxide	J. T. Baker
Sulfuric acid	Captree Chemical Corp.
Tetrahydrofuran	Fisher
Tetramethylsilane (TMS)	Norell, Inc.
Toluene	Fisher
p-Toluic acid	Aldrich

acetone to yield 66.8 mg (1.5%). This was shown by gc and NMR to be mostly anthracene (96% pure by gc): ^{1}H NMR (60 MHz, $CDCl_3$)δ 8.44 (s, 2H), 8.10-7.94 (m, 4H), 7.58-7.37 (m, 4H) [lit.[22] NMR δ 8.36 (2H), 7.93 (4H), 7.39 (4H)].

5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene (**14**)

This compound was prepared according to the method of Jensen *et al.*[21] Benzocyclobutene (**9**) (2.5 g) was placed in a constricted test tube and degassed by 3 freeze-pump-thaw cycles. The tube was sealed under vacuum and heated for 5 days at 210°C during which a green fluorescent color developed. Upon cooling, the reaction mixture became quite viscous. It was dissolved in benzene and analyzed by gc/ms which indicated only a trace of benzocyclobutene (**9**), two dimeric components in the ratio of 5:2 and several trimers. Distillation (Kugelrohr, pot 100-130°, 0.15 torr) afforded a white crystalline product mixed with a lesser amount of liquid (0.7 g). Washing the solid with hexanes provided 0.36 g of

14 (14.4%) which was 97.7% pure by gc: mp 106-108°C (lit.[45] mp 109.4-109.9°C); IR (KBr) 1470, 1435, 1318, 1290, 1210, 1145, 1070, 1030, 915, 848, 730 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$)δ 7.00 (s, 8H), 3.05 (s, 8H) [lit.[46] NMR (CCl_4)δ 6.88 (s, 8H), 3.02 (s, 8H)]; ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 140.58, 129.64, 126.06, 35.16; MS (70 eV) 208 (67), 193 (100), 179 (20), 178 (37), 117 (23), 116 (36), 115 (34), 104 (60), 103 (41), 91 (21), 89 (13), 78 (40), 77 (21), 51 (13).

1,2-Naphthocyclobutene (31)

This compound was prepared following the procedure of Ewing and Boekelheide.[24] 1-Chloromethyl-2-methylnaphthalene (**32**) (4.7 g) was pyrolyzed by FVP at 725°C and $2x10^{-4}$ torr. The sample chamber was heated to 80°C to volatilize the substrate. After most of the sample had transferred, the u-tube was warmed to room temperature under N_2 and rinsed down with CH_2Cl_2. Some of the product was a rubbery, sticky insoluble mass. The soluble product was coated on alumina, then eluted through a column of alumina. The fractions containing **31** were concentrated to give 2.0 g. Distillation (Kugelrohr, pot 85-115°, 0.11 mm Hg) afforded only 1.0 g (26%) [lit.[47] bp 98° (1-2 mm Hg)]: ^1H NMR (60 MHz, $CDCl_3$)δ 7.87-7.11 (m, 6H), 3.41-3.12 (m, 4H) [lit.[24] NMR (100 MHz, $CDCl_3$)δ 7.90-7.14 (m, 6H), 3.46-3.20 (m, 4H)].

1,2,7,8- and 1,2,9,10-Dibenzo-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (35 and 36)

The [4+4] dimers of 1,2-naphthocyclobutene (**31**) were prepared by an adaptation of Cava and Deana's method of solution pyrolysis[48] by

heating a solution of **31** (0.59 g) in diethylphthalate (10 mL) to reflux under N_2 for 1h. The solution was then stirred with NaOH (15%, 50 mL) at 40° for 12 h. The resulting mixture was extracted with toluene and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was chromatographed on alumina (neutral) (10% benzene in hexanes elution) and the fractions containing **35** and **36** were combined and concentrated to give 110 mg (18%). Gc analysis showed a 49:51 ratio of isomers (86% pure): ^1H NMR (60 MHz, $CDCl_3$)δ 8.2-6.7 (m, 12H), 3.7-1.9 (m, 8H).

Methyl 3-chloromethyl-4-methylbenzoate (**43**)

The acid (**42**) was prepared by chloromethylation of p-toluic acid (**41**) following the procedure of Matsukawa et al.[26] Acid **41** (78 g, 0.57 mole) was added over a period of 0.5 h to a stirred solution of paraformaldehyde (18 g, 0.6 mole CH_2O) in H_2SO_4 (400 mL) as HCl (g) was bubbled through the solution. The temperature was maintained between 30° and 40°C during addition and for one h after. The solution was then poured onto 2 L ice-water discharging the dark color that had developed and forming a white solid. The solid was filtered, washed 3 times with H_2O and dried in a vacuum desiccator to give 161 g of crude **42**. The acid was esterified without purification by mixing with methanol (1 L) and H_2SO_4 (3 mL) and heating on the steam bath under N_2 to reflux for 10 h which caused dissolution of the solid. The resulting solution was partitioned between water (2 L) and ether. The organic layer was washed with NaOH (1 M) and brine, dried over $MgSO_4$, filtered and concentrated. Fractional distillation and recrystallization

afforded 18.1 g of **43** (16%): bp 85-98°C (0.1 mm Hg); m.p. 56-62°C; IR (KBr) 1710, 1425, 1285, 1250, 1208, 1180, 1108, 990, 750, 723, 657 cm^{-1}; ^1H NMR (60 MHz, CCl_4)δ 7.90 (br. s, 1H), overlapping with 7.84 (d of d, J_1 = 8 Hz, J_2 = 2 Hz, 1H), 7.18 (d, J = 8 Hz, 1H), 4.57 (s, 2H), 3.85 (s, 3H), 2.48 (s, 3H); MS (70 eV) 200 (19), 198 (38), 167 (57), 163 (100), 139 (31), 135 (32), 104 (32), 103 (56), 78 (32), 77 (52); $C_{10}H_{11}ClO_2$: calculate 198.04476, measure 198.04450 (error: -1.3 ppm).

3-Carbomethoxybicyclo[4.2.0]octa-1,3,5-triene (**44**)

Methyl 3-chloromethyl-4-methylbenzoate (**43**) (15 g) was pyrolyzed by FVP at 785°C and $7x10^{-4}$ torr. The product was taken up in ether, washed with $NaHCO_3$ (sat.) and brine, dried over $MgSO_4$, filtered and concentrated. Distillation afforded 8.84 g of **44** (72%) as a yellow liquid: bp 75°C (3 mm Hg); IR (neat) 1710, 1430, 1322, 1270, 1238, 1183, 1130, 1090, 762, 722; ^1H NMR (60 MHz, $CDCl_3$)δ 7.95 (d of d, J_1 = 8 Hz, J_2 = 2 Hz, 1H), 7.72 (br. s, 1H), 7.10 (d, J = 8 Hz, 1H), 3.88 (s, 3H), 3.12 (s, 4H), MS (70 eV) 162 (78), 131 (100), 103 (70), 102 (31), 77 (70); $C_{10}H_{10}O_2$: calculated 162.06808, measured 162.06788 (error: -1.2 ppm).

2,8- and 2,9-Dicarbomethoxy-5,6,11,12-tetrahydro-dibenzo[a,e]cyclooctene (**39** and **40**)

The carbomethoxybenzocyclobutene (**44**) (8 g) was added to a N_2-flushed flask with phenyl ether (100 mL) which was passed through a column of alumina directly into the flask. The solution was heated to

reflux under N_2 for 2 h and allowed to cool. The solvent was removed by distillation under reduced pressure and the dimeric products were distilled (Kugelrohr, pot 225-275°C, 0.001 mm Hg) affording 4.0 g of a viscous fluorescent liquid. A 25% solution in hexanes-ethyl acetate was prepared from which precipitated crystals of 39 and 40. The mother liquor was chromatographed on silica gel (elution with 10% ethyl acetate in hexanes) to isolate the rest of 39 and 40. A benzene solution of 39 and 40 was swirled with alumina to remove a fluorescent contaminant. The isomers were separated by fractional crystallization from hexanes-ethyl acetate. The transoid isomer (39) was the first to crystallize in tiny round clusters which firmly held to the glass surface of the flask. The cisoid isomer (40) crystallized later in large fluffy clusters which were easily separated from those of 39. Repeated fractional crystallizations of the separated isomers improved the purity to the desired degree. The purity of each isomer was determined by gc. For pyrolysis studies, the transoid diester (39) was prepared in >99.2% isomeric purity and the cisoid diester (40) was prepared in 92% isomeric purity. Analytical samples were prepared in >99% purity. Isomer 39: mp 177.5-178.5°C; IR (KBr) 1705, 1605, 1570, 1490, 1459, 1430, 1410, 1295, 1265, 1200, 1165, 1115, 1078, 988, 931, 899, 850, 832, 787, 757, 738, 722 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6)δ 7.828 (d, J = 1.75 Hz, 2H), 7.763 (d of d, J_1 = 1.75 Hz, J_2 = 7.83 Hz, 2H), 6.652 (d, J = 7.83 Hz, 2H) 3.433 (s, 6H), 2.714-2.600 (AA'BB' pattern, 8H) (Figures 2 and 3); MS (70 eV) 324 (100), 309 (23), 293 (84), 265 (86), 206 (25), 162 (19), 131 (60); $C_{20}H_{20}O_4$: calculated 324.13616, measured 324.13683 (Error:

+2.1 ppm).

Isomer 40: mp 145-146°C, IR (KBr) 1722, 1708, 1607, 1571, 1435, 1412, 1379, 1360, 1209, 1194, 1169, 1127, 1095, 1090, 982, 925, 911, 845, 786, 767, 743 cm^{-1}; ^1H NMR (300 MHz, benzene-d_6) δ 7.815-7.788 (m, 4H), 6.693 (d, J = 8.36 Hz, 2H), 3.407 (s, 6H), 2.671 (s, 4H), 2.638 (s, 4H) (Figures 4 and 5); MS (70 eV) 324 (73), 309 (16), 293 (48), 265 (100), 206 (32), 162 (24), 131 (79); $C_{20}H_{20}O_4$: calculated 324.13616, measured 324.13716 (Error: +3.1 ppm).

2,8-Dihydroxymethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (45)

The transoid diester (39) (>99.2% isomeric purity) was reduced according to the general procedure of Fieser and Fieser.[27] It was dried in a vacuum desiccator, dissolved in dry THF (5 mL) (freshly distilled under N_2 from LAH) and added to LAH (350 mg) in 10 mL THF. The mixture was heated to reflux and stirred for 1 h under N_2. After cooling, the reaction was carefully quenched by adding dropwise with shaking 350 µL water, 350 µL NaOH (15%) and 1050 µL water. The solid was filtered and washed with ethyl acetate. The filtrate was washed with HCl (10%), $NaHCO_3$ (sat.) and NaCl (sat.), dried over $MgSO_4$, filtered and concentrated. Upon cooling, 142.2 mg of crystalline 45 precipitated (94.6%): mp 180.5-186°C; IR (KBr) 3350 (broad), 1492, 1447, 1415, 1355, 1017, 820 cm^{-1}; ^1H NMR (90 MHz, DMSO-d_6) δ 6.90 (s, 6H), 4.94 (br. s, 2H), 4.32 (s, 4H), 3.02 (s, 8H); ^{13}C-NMR (22.5 MHz, DMSO-d_6) δ 139.82, 139.55, 138.25, 129.31, 127.85, 124.11, 62.68, 34.56, 33.97; MS (70 eV) 268 (16), 251 (31), 250 (100), 235 (74), 221 (74), 207 (91), 206 (52), 205 (32),

192 (36), 134 (30), 91 (73), 77 (33); $C_{18}H_{20}O_2$: calculated 268.14633, measured 268.14723 (error +3.4 ppm).

2,8-Dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (37)

The transoid diol (39) was reduced using the general procedure of Small et al.[28] A lithium-ammonia mixture was prepared under N_2 by condensing NH_3 (5-6 mL) into a flask containing Li wire (0.8 cm long), which had been washed with hexanes, and stirring for 1 h while NH_3 refluxed. After cooling the mixture to -78°C with a dry ice-isopropanol bath, 39 (135.4 mg) was added as a THF solution (5 mL). The resulting mixture was allowed to warm and was stirred for 1.5 h as NH_3 refluxed. Very carefully, the reaction was quenched with NH_4Cl (s) until the deep blue color was discharged. The NH_3 was allowed to evaporate and the residue was partitioned between brine and ether. The organic layer was separated, dried over $MgSO_4$ and concentrated to about 1 mL. Upon cooling, 101.4 mg of crystalline 37 precipitated (85%, 100% pure by gc): mp 141.5-144.5°; IR (KBr) 1492, 1445, 1430, 1325, 1296, 1083, 1027, 938, 914, 887, 852, 808 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$)δ 6.85 (s, 6H), 2.99 (s, 8H), 2.21 (s, 6H); ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 140.76, 137.78, 135.34, 130.58, 129.66, 126.68, 35.50, 35.07, 20.82; MS (70 eV) 236 (68), 221 (100), 206 (24), 130 (18), 118 (33), 91 (15); $C_{18}H_{20}$: calculated 236.15650, measured 236.15662 (error: +0.5 ppm).

2,9-Dihydroxymethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (**46**)

The cisoid diester (**40**) (92% isomeric purity) (162.4 mg) was reduced by the same procedure as described for **39** using 325 mg LAH to give 122.6 mg of **46** (93%): mp 154-156°C; IR (KBr) 3310 (broad), 1496, 1447, 1255, 1053, 1027, 818 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$)δ 6.95 (s, 6H), 4.51 (s, 4H), 3.06 (s, 8H); ^{13}C NMR (22.5 MHz, acetone-d_6)δ 140.91 (2C), 139.72, 130.40, 128.99, 125.20, 64.42, 35.70, 35.38; MS (70 eV) 268 (10), 266 (9), 251 (28), 250 (100), 237 (41), 236 (21), 235 (83), 232 (37), 221 (49), 220 (26), 219 (25), 207 (78), 206 (20), 205 (23), 134 (20), 133 (16), 71 (43), 57 (70), 55 (52); $C_{18}H_{20}O_2$: calculated 268.14633, measured 268.14696 (error +2.4 ppm).

2,9-Dimethyl-5,6,11,12-tetrahydrodibenzo-[a,e]cyclooctene (**38**)

The cisoid diol (**40**) (122.6 mg) was treated essentially the same way as the transoid diol (**39**), but some unreacted starting material remained after workup. Recrystallization from ethanol (absolute) gave 52.2 mg of **38** (95% pure by gc). An additional 12.7 mg was provided by thin layer chromatography of the mother liquor (silica gel, hexanes elution) to yield 64.9 mg of **38** (60%): mp 130.5-134°C; IR (KBr) 1498, 1450, 1433, 1328, 1295, 1083, 1030, 922, 884, 809; ^{1}H NMR (90 MHz, $CDCl_3$)δ 6.87-6.84 (m, 6H), 2.99 (s, 8H), 2.22 (s, 6H); ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 140.77 (s), 137.90 (s), 135.40 (s), 130.64 (d, J_{CH} = 156 Hz), 35.46 (t, J_{CH} = 128 Hz), 35.13 (t, J_{CH} = 128 Hz), 20.88 (q, J_{CH} = 126 Hz); MS (70 eV) 236 (79), 221 (100), 206 (37), 130 (18),

118 (35), 91 (16); $C_{18}H_{20}$: calculated 236.15650, measured 236.15655 (error: +0.2 ppm).

Determination of Yields in Hydrocarbon Pyrolysis

The yields of products and recovered starting material in the pyrolyses of **9** and **14** were determined by gc by adding a weighed internal standard (biphenyl) to a solution of the pyrolyzate. The amount of each product (mg P) was then calculated from the weight of the internal standard (mg IS), the area of the peak of the internal standard (AIS) and the area of the product peak (AP) in the gc trace (equation 18):

$$\text{mg P} = \text{mg IS} \left(\frac{\text{AP}}{\text{AIS}}\right) \times \text{res. f.} \qquad 18.$$

A response factor (res. f.) was included to correct for the difference in the response of the detector to the two compounds being compared. The response factor determined by Trahanovsky and Swenson[49] for benzocyclobutene (**90** vs. biphenyl (0.99) on a weight-to-weight basis) was used for **9** and for the [4+4] dimer (**14**) and its isomers. For this study, the response factor for anthracene (**7**) vs. biphenyl was determined. The response factors for other products were assumed to be 1.0 on a weight-to-weight basis.

Determination of the Response Factor for Anthracene (**7**)

Anthracene (**7**) was purified by the method of Orchin[50] by two co-distillations with ethylene glycol and two recrystallizations from benzene. It was 100% pure by gc. Biphenyl was reagent grade and used without purification. It was 99% pure by gc with an unknown impurity which was very close to it in the gc. The weight of this impurity and

its area in the gc were included with those of biphenyl. Three solutions of accurately weighed anthracene (~10 mg) and biphenyl (~8 mg) in benzene were prepared and analyzed by gc. The response factor was determined in each case and an average taken: res. f. for anthracene vs. biphenyl = 1.01 ± 0.02.

FVP of Benzocyclobutene (**9**) at 770°C

Benzocyclobutene (**9**) (533 mg) was placed in the sample chamber and preheated under a nitrogen atmosphere. The u-tube was precooled by liquid nitrogen and the system was evacuated. Immediately, the pyrolyzate was seen exiting from the hot zone as a fog. After transfer was complete, the u-tube was transferred to a dry ice-isopropanol bath and the contents which deposited furthest from the oven were taken up in CS_2 and analyzed by ^1H NMR and gc. These indicated the presence of ethylene by a singlet in the NMR at δ5.29 (lit.[51] NMR δ5.28) and a peak in the gc trace with the same retention time as an authentic sample. Other absorptions in the NMR were aromatic resonances, a singlet for $-CH_2-CH_2-$ of **9**, a singlet at δ2.28 assigned to o-xylene (lit.[20] NMR δ2.28) and 3 minor singlets at δ2.17, 1.01 and 1.00. The NMR sample was mixed with the rest of the u-tube contents, dissolved in acetone with biphenyl (17.1 mg) and analyzed by gc. The product that condensed between the oven and the u-tube was dissolved in THF and analyzed by gc with biphenyl added (44.3 mg). Anthracene and **14** were identified by gc retention times. Yields of products are listed in Table 1. The mass of the product mixture by gc was 73% of the mass of starting material.

FVP of 5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene (**14**)

For the FVP of **14** (41.9 mg) at 920°C, transfer took about 2 h. The vacuum measured was 7×10^{-5} torr during pyrolysis and 1.5×10^{-5} torr afterwards. After 2 h, a residue remained in the sample chamber, even after heating to 136° for several hours. The pyrolyzate was taken up in benzene, added to biphenyl and analyzed by gc. Compound **14** was identified in the product mixture by gc peak enhancement. The solution was then analyzed by gc/ms. After evaporation of the solvent, analysis of the residue by NMR revealed the characteristic downfield signal of the 9- and 10-protons of anthracene: δ 8.36 (s) ($CDCl_3$) [lit.[22] NMR (CCl_4) δ 8.36]. Mass recovery was 95% by gc.

Compound **14** was pyrolyzed at four other temperatures and the pyrolyzates analyzed by gc. The sample chamber was not heated in any of these reactions. The data are tabulated in Table 5. Yields are listed in Table 1.

Table 5. Data for the pyrolyses of 5,6,11,12-tetrahydrodibenzo[a,e]-cyclooctene (**14**)

Oven temp., °C	Vacuum during FVP, torr	Time for transfer, h	Weight of **14**, mg	Weight of biphenyl, mg	Method of anthracene identification[a]	Mass recovery, % by gc[b]
720	1.6×10^{-6}	5	21.9	37.0	a	90
805	5.5×10^{-6}	4	23.8	15.0	a	77
920	7.0×10^{-5}	2	41.9	23.6	a,b,c	95
980	1.0×10^{-6}	2.5	22.3	17.3	a,d	53
1030	3.5×10^{-6}	3.5	22.0	30.9	a,b	43

[a]Anthracene (**7**) was identified in the product mixture four different ways. Method a: by its retention time in the gc; Method b: by its NMR signal at δ 8.36; Method c: by its molecular weight by gc/ms; Method d: the peak assigned to **7** in the gc of the product mixture was enhanced by addition of authentic **7**.

[b]The mass of the product mixture determined by gc divided by the mass of the starting material.

FVP of 1,2-Naphthocyclobutene (31)

Compound **31** (158 mg) was pyrolyzed at 890° with a measured vacuum of $2x10^{-4}$ torr. The sample was heated to 60°, causing it to transfer in about 0.5 h. The crystalline material that deposited just outside the oven was analyzed by gc, gc/ms, and ^1H NMR. Gas chromatography showed this to be two compounds (A and B) in the ratio of 55:45. Gc/ms analysis showed these were isomers of molecular weight 278 g/mole. Compound A: MS (70 eV) 278 (100), 139 (82), 125 (21), 113 (9); Compound B: MS (70 eV) 278 (100), 139 (86), 125 (20), 113 (11). This and the NMR data indicated a mixture of dibenzanthracenes: ^1H NMR (90 MHz, $CDCl_3$)δ 10.01 (s, 1H), 9.08 (s, 2H), 8.91 (d, J = 12.2 Hz, 2H), 8.83 (d, J = 12.4 Hz, 2H), 8.29 (s, 1H), 7.95-7.45 (m, 20H) [dibenz[a,h]-anthracene, lit.[22,25] NMR δ 9.08 (2H), 8.81 (2H), 7.88-7.55 (10H)] [dibenz[a,j]anthracene, lit.[22] NMR δ 9.98 (1H), 8.96 (2H), 8.29 (1H), 7.80-7.56 (10H)].

FVP of 1,2,7,8- and 1,2,9,10-Dibenzo-5,6,11,12-tetrahydro-dibenzo[a,e]cyclooctene (35 and 36)

The mixture of isomers (33.8 mg) was pyrolyzed at 800°C in 2 h. The sample was heated to 112-140°C. The measured vacuum was $1.0x10^{-5}$ torr during pyrolysis. A white crystalline solid deposited just outside the oven which was taken up in acetone for gc analysis. Comparison of retention times to the pyrolyzate of 1,2-naphthocyclobutene (**31**) indicated a very pure mixture of dibenzanthracenes (**33** and **34**). Evaporation of the solvent afforded 6.3 mg (21%): ^1H NMR (90 MHz, $CDCl_3$)δ 10.01 (s, 1H), 9.08 (s, 2H), 8.91 (d, J = 12.2 Hz, 2H), 8.83

(d, J = 12.4 Hz, 2H), 8.29 (s, 1H), 7.95-7.45 (m, 20H) was identical to that of the mixture obtained by FVP of 1,2-naphthocyclobutene (31).

FVP of 2,8-Dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]-cyclooctene (37)

Compound 37 (52.2 mg) (>99.2% isomeric purity by gc of the diester precursor (39)) was pyrolyzed in 3 h at 920°C. The sample chamber was warmed by insulation. The pyrolyzate was taken up in CH_2Cl_2 for gc analysis. The solvent was evaporated and the residue (41.1 mg) was analyzed by ^1H NMR, then separated by TLC on activated alumina (hexane elution). The anthracene band was washed from the alumina with chloroform (15 mL) and analyzed by gc and NMR. Gc and NMR analysis before and after chromatography showed that the major pyrolyzate was in this band. ^1H and ^{13}C NMR analysis showed that 2,7-dimethylanthracene (47) was the major pyrolyzate contaminated by 2,6-dimethylanthracene (48) (96:4 mole ratio)[29] and another minor component with spectral characteristics of an anthracene (Figures 8, 9, 10 and 11). Evaporation of the solvent afforded 9.8 mg of a crystalline solid. Compound 47 was recrystallized from benzene: mp 235-237°C (lit.[30] mp 241°C); IR (KBr) 1442 (m), 1363 (m), 1292 (m), 1257 (m), 1157 (m), 1100 (w), 1018 (m), 943 (s), 922 (w), 896 (s), 874 (vs), 839 (m), 770 (vs), 750 (m) cm^{-1} [lit.[31] IR 1463 (s), 1379 (m), 1310 (m), 1273 (m), 1197 (w), 1174 (m), 1120 (w), 1040 (m), 1016 (w), 962 (s), 941 (w), 916 (s), 896 (vs), 861 (m), 791 (vs), 771 (m) cm^{-1}]; ^1H NMR (300 MHz, $CDCl_3$)δ 8.31 (s, 1H), 8.20 (s, 1H), 7.88 (d, J = 9.7 Hz, 2H), 7.71 (s, 2H), 7.26 (d, J = 9.7 Hz, 2H), 2.53 (s, 6H) [lit.[29] NMR (100 MHz, $CDCl_3$)δ 8.26 (s, 1H),

8.14 (s, 1H), 7.84 (d, J = 9.0 Hz, 2H), 7.68 (s, 2H), 7.24 (d of d, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 2H), 2.50 (s, 6H)]; ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 134.79, 132.18, 129.91, 127.96, 127.80, 126.23, 125.68, 124.11, 21.94; MS (70 eV) 206 (100), 205 (38), 191 (39), 189 (33); $C_{16}H_{14}$: calculated 206.10955, measured 206.10975 (error: +1.0 ppm) (lit.[29] MS 206, 205, 191, 189, 102).

FVP of 2,9-Dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (38)

Compound **38** (59.2 mg) (92% isomeric purity by gc of the diester precursor (**40**)) was pyrolyzed as the transoid isomer (**37**) affording, after workup, 11.9 mg of a solid which was mostly 2,6-dimethylanthracene (**48**). This was analyzed by ^{1}H and ^{13}C NMR (Figures 10 and 11) and recrystallized from benzene: mp 236-243°C (lit.[30] mp 248°C); IR 1462 (m), 1442 (m), 1365 (m), 1292 (m), 1260 (m), 1160 (m), 1128 (w), 1023 (m), 999 (w), 949 (s), 929 (m), 888 (vs), 858 (s), 777 (s) cm^{-1} [lit.[31] IR 1474 (m), 1460 (m), 1449 (sh), 1378 (m), 1305 (m), 1273 (m), 1171 (m), 1139 (w), 1041 (m), 963 (s), 942 (m), 905 (vs), 873 (s), 793 (s) cm^{-1}]; ^{1}H NMR (90 MHz, $CDCl_3$)δ 8.25 (s, 2H), 7.87 (d, J = 8.5 Hz, 2H), 7.71 (br. s, 2H), 7.27 (d of d, J_1 = 8.5 Hz, J_2 = 1.7 Hz, 2H), 2.53 (s, 6H) (lit.[29] NMR as a 1:2 mixture with 47, the singlet for the 9- and 10-protons is reported to be between those for the 9- and 10-protons of 47); ^{13}C NMR (22.5 MHz)δ 134.41, 131.59, 130.51, 128.12, 127.85, 126.33, 124.93, 21.94; MS (70 eV) 206 (100), 205 (34), 191 (13); $C_{16}H_{14}$: calculated 206.10955, measured 206.10917 (error: -1.8 ppm).

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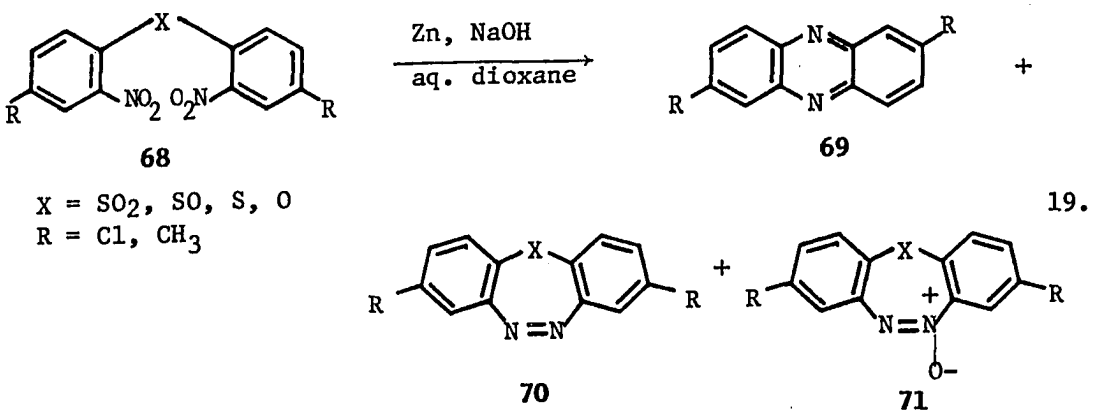
APPENDIX

In part I of this thesis, an aryl analogue to the retroene reaction has been proposed for the first time to account for observed chemistry (Scheme 7, page 30). How this mechanism might apply to hydrocarbon pyrolysis has been addressed (pp. 35-38). This appendix shows how analogous heterocyclic chemistry reported in the literature might go by this mechanism.

A reaction which appeared in 1963[52] stands out because it is the only one found where the aromatic rings are labeled like those of the dimethyldibenzocyclooctenes (**37** and **38**). As for **37** and **38**, a ring flip accompanies formation of the central aromatic ring. It is the reduction of dinitrodiaryl sulfones, sulfoxides, sulfides, and ethers (**68**, X = SO_2, SO, S, O) in which 7-40% of the product mixture is a phenazine derivative (**69**) (reaction 19).[52,53]



68

X = SO_2, SO, S, O
R = Cl, CH_3

69

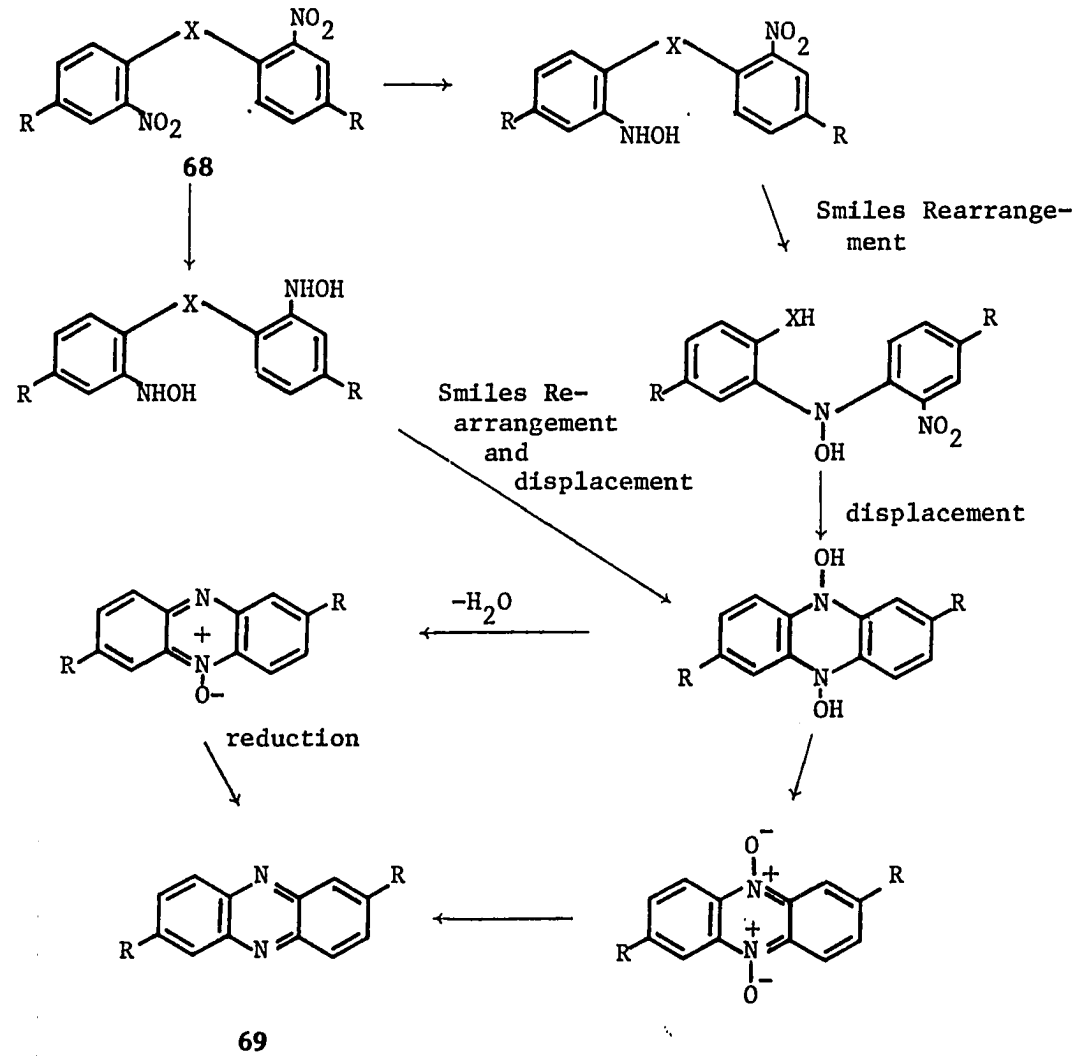
70

71

19.

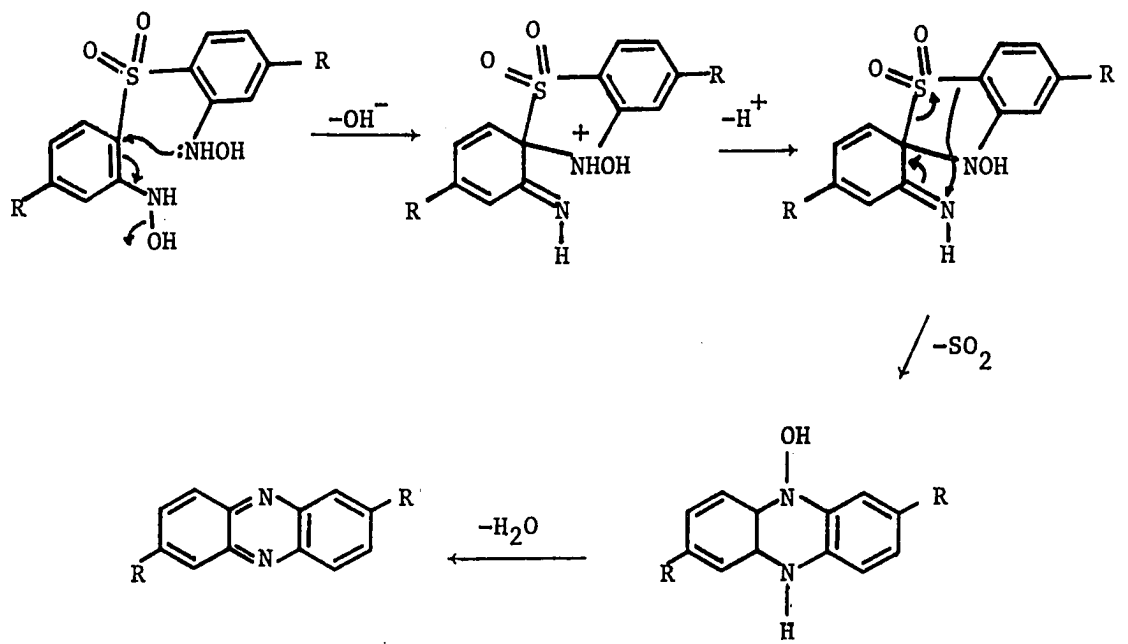
Compound **69** is believed to arise by a Smiles rearrangement of a reduction product followed by displacement of X (Scheme 14).

Scheme 14:



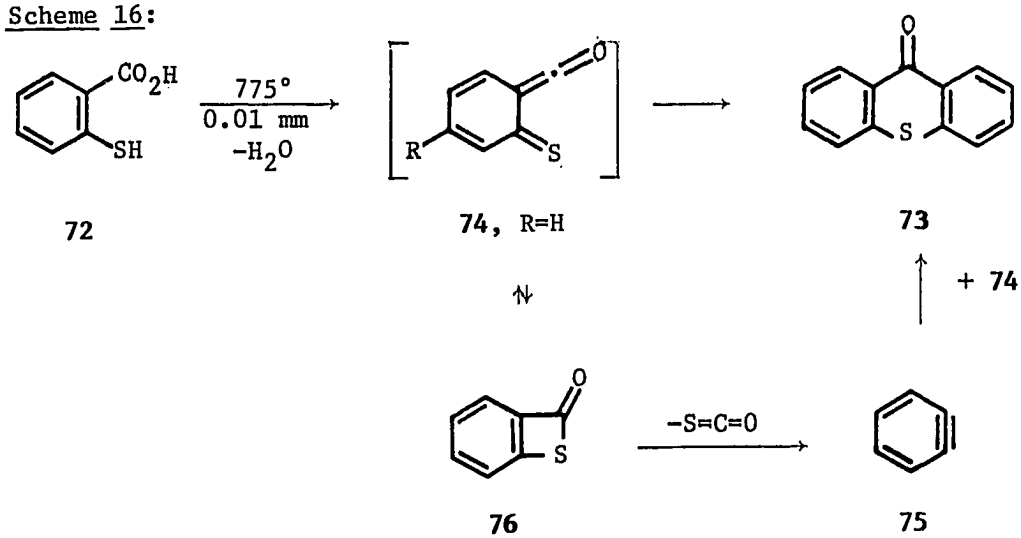
Labeling of the aromatic rings (R = Cl,CH_3) produces the same regiochemical results as the pyrolysis of dimethyldibenzocyclooctenes (37 and 38, Scheme 3, p. 26). Even though this reaction probably does go by a Smiles rearrangement, especially when X = O or S, one can picture it as going by this new mechanism (Scheme 7, p. 30), especially for the sulfoxides and sulfones (X = SO or SO_2) (Scheme 15).

Scheme 15:

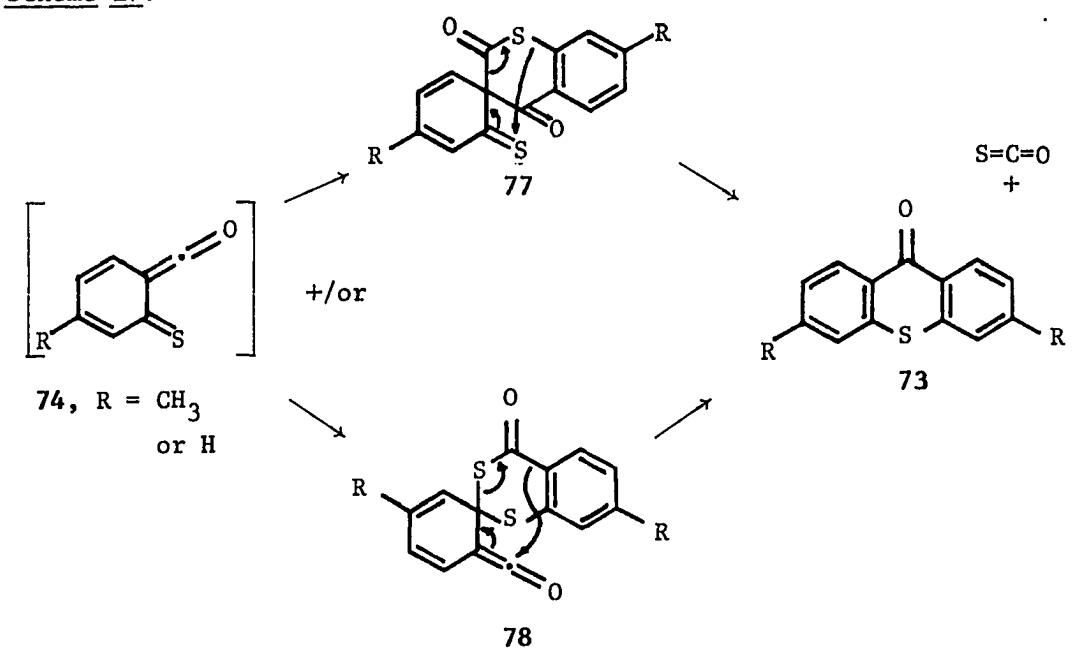


A closer analogy yet is seen in the FVP of thiosalicylic acid (**72**) which forms thioxanthone **73** in 32% yield presumably via the ketene **74**,[54] The rationalization provided by the authors invokes a Diels-Alder reaction between **74** (R=H) and benzyne (**75**), formed by loss of CSO from the closed form of **74** (**76**) (Scheme 16). The new mechanism provides a better explanation since it doesn't require two reactive species (Scheme 17). A labeling experiment, where a methyl group is attached to the aromatic ring (**74**, R=CH_3), would easily distinguish between the two mechanisms since both possible spirodimers (**77** and **78**) would give only one thioxanthone (**73**) whereas a benzyne reaction would be expected to give two isomers.

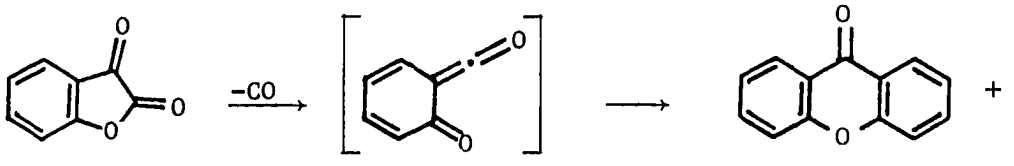
Scheme 16:



Scheme 17:



The α-ketolactone **79**, by decarbonylation, gives xanthone (**80**) presumably via the ketoketene (**81**).[55] This reaction also gives polymer and 3,4-benzocoumarin (**82**) (reaction 20). The formation of **80** can be



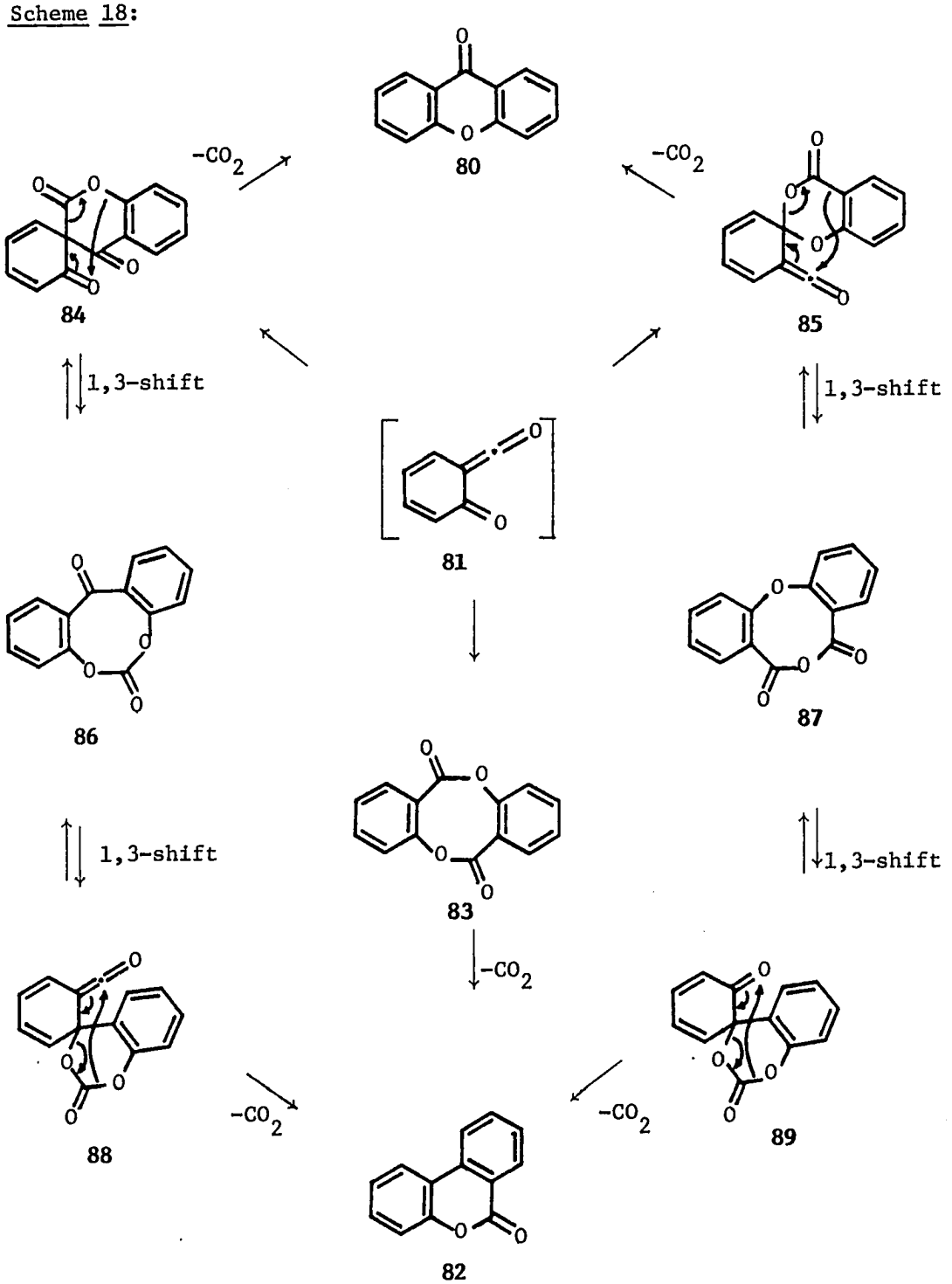
79 **81** **80** + **82** + polymer 20.

explained by the new mechanism by analogy to formation of thioxanthone (**73**) but the appearance of **82** is somewhat puzzling. It could come from direct loss of CO_2 from the head-to-tail [4+4] dimer of **81** (**83**) or from a spirodimer (**84** or **85**) by a series of 1,3-shifts and elimination of CO_2 (Scheme 18).

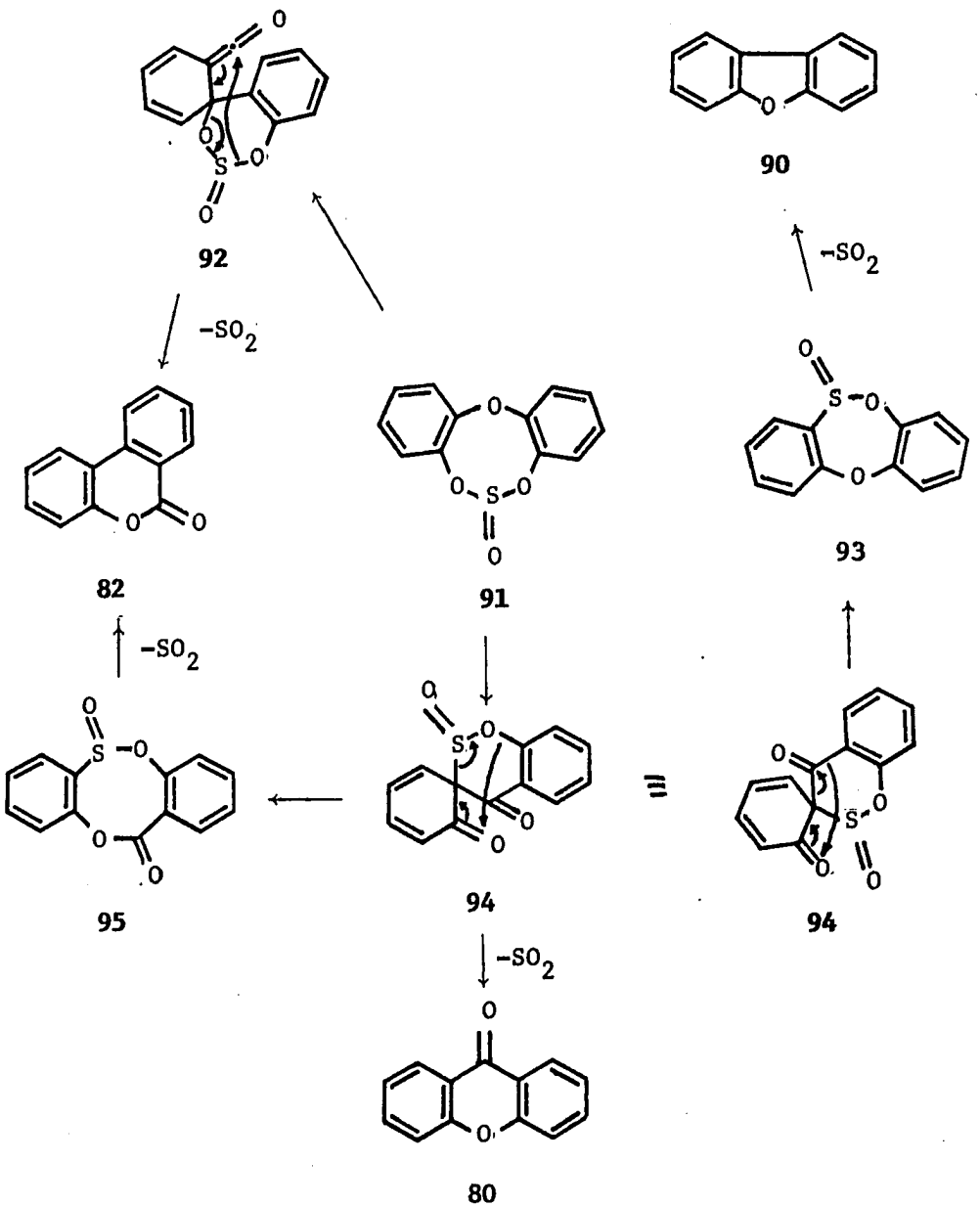
Compounds **80** and **82** were also formed along with dibenzofuran (**90**) in the pyrolysis of ketosulfite **91**.[56] These can all be pictured as arising by this same mechanism (Scheme 19).

Other reactions that appear to be simple displacements can be pictured as going by this mechanism. For example, biphenylene-2,2'-carbonate (**96**) is thought to give **90** by a simple displacement in the first-formed diradical (Scheme 20),[57] but one cannot help but wonder

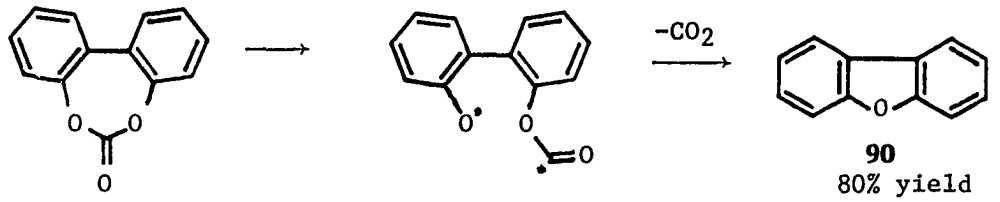
Scheme 18:


80
-CO2
-CO2
84
85
1,3-shift
1,3-shift
81
86
87
1,3-shift
1,3-shift
83
-CO2
88
89
-CO2
-CO2
82

Scheme 19:



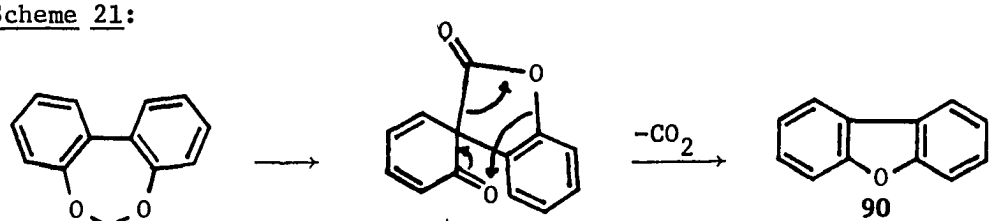
Scheme 20:



96 **90** 80% yield

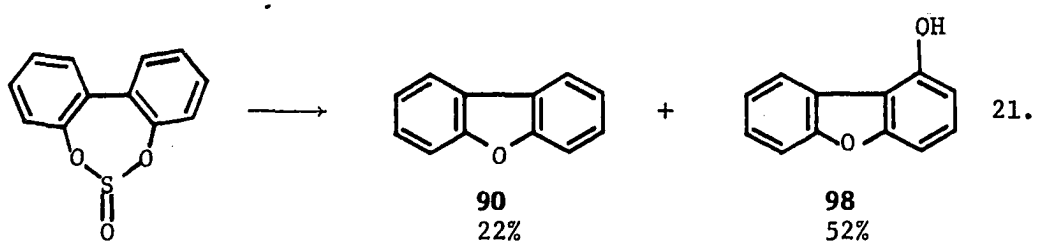
if the retroene mechanism is operating (Scheme 21). Similarly, the

Scheme 21:



96 **90**

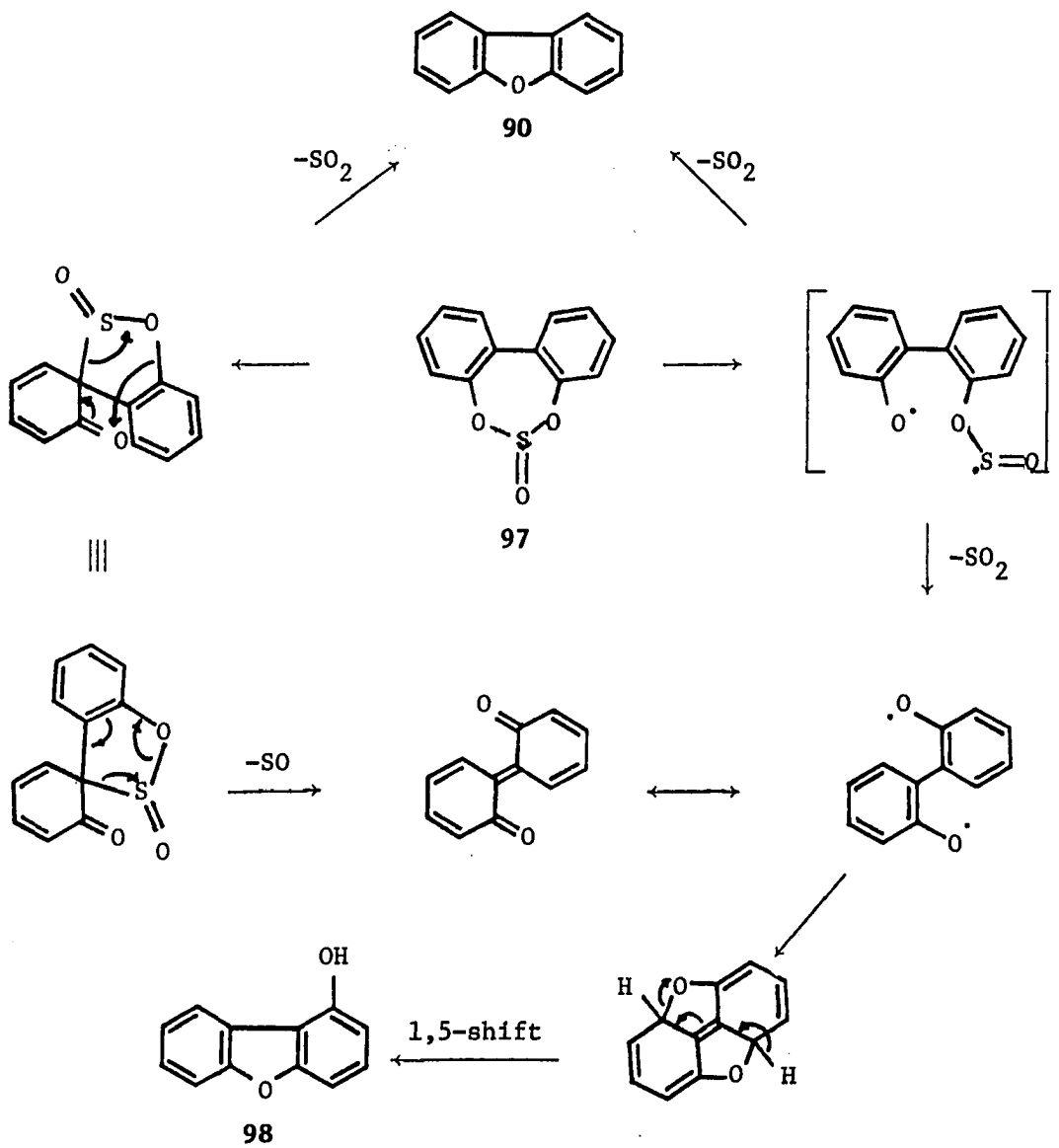
sulfite (**97**) gives **90** but only in 22% yield.[58] The major product is 5-hydroxydibenzofuran (**98**) (52%) (reaction 21). Again, the retroene



90 22% **98** 52% 21.

fragmentation of a spiro-intermediate seems to be a viable alternative to direct displacement (Scheme 22).

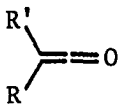
Scheme 22:



PART II. ^{1}H AND ^{13}C NMR OF VINYLKETENE AND ITS DIMERIZATION BY [4+2] CYCLOADDITION. SYNTHESIS OF SIBIRINONE AND BICYCLO[4.2.1]-NONA-3,7-DIEN-2-ONE

INTRODUCTION

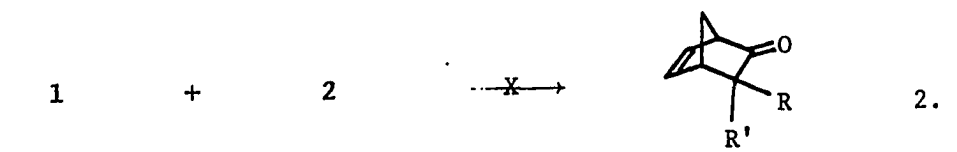
Because of their unusual chemistry and reactivity, ketenes (1) have held the interest of organic chemists since the pioneering work of Staudinger.[1] The chemistry of ketenes is unusual because the carbon-



1

carbon double bond is very electrophilic.[2] This results in a strong tendency towards [2+2] cycloaddition reactions (reaction 1) even when given the opportunity to react by the more common Diels-Alder reaction (reaction 2).[2] Tetrafluoroethylene (5) and allene (6) also display this tendency.[3] The [2+2] cycloaddition reaction has been widely studied and

1 2 3 1.



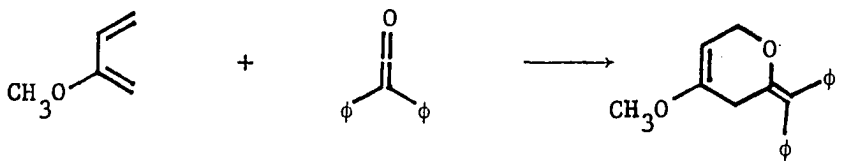
1 2 4 2.

$CF_2=CF_2$ (5) $CH_2=C=CH_2$ (6)

and found to be consistently suprafacial with respect to the ketenophile, polarly directed, and stereoselective with respect to the R groups of the

ketene such that the largest is directed toward the endo face of the adduct.[2,4,5,6] The selectivity approaches 100% when R=H and R'=Methyl or larger.

Exceptions to this rule are rare. Certain ketenophiles elicit deviant behavior as in reaction 3 where the carbonyl group of diphenylketene (7) reacts with the ketenophile (8).[7] The structure of the ketene can



3.

8 7 9

also lead to exceptional chemistry, as will be seen later.

Another result of the ketene's electrophilicity is their ability to add HX (10) to the carbon-carbon double bond where X=OR,NR_2, halide, O_2CR to give esters, amides, acid halides and anhydrides (11) (reaction 4).[2]

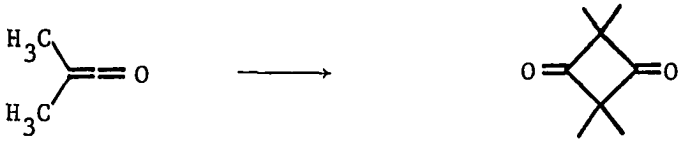
4.

1 10 11

X=OR, NR_2, halide, O_2CR

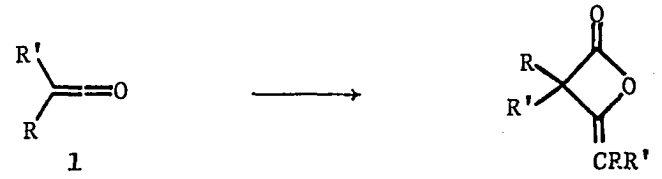
If a suitable ketenophile is not present, most ketenes dimerize by one of two ways. How the ketene dimerizes and the temperature at which it dimerizes are dependent on the substituents (R and R' in 1). For

example, diphenylketene (**7**) does not dimerize at all, even upon heating, while dimethylketene (**12**) dimerizes so readily it is only useful when generated <u>in situ</u> (reaction 5).[7] One mode of dimerization is seen in reaction 5 where a cyclobutadione (**13**) is formed. This is typical of



12 **13** 5.

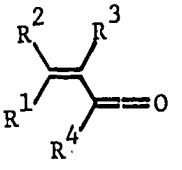
ketenes where neither substituent is a hydrogen (R and R' ≠ H in **1**).[8] If one or both substituents are hydrogen (R and/or R' = H in **1**), a β-lactone (**14**) is formed (reaction 6).[8]



1
R and/or R'=H

14 6.

One class of ketene which has appeared in the literature is vinylketenes (**15**). The first was methylvinylketene (**16**) from the pyrolysis of carvone (**17**) (reaction 7).[1] A double bond conjugated to the ketene



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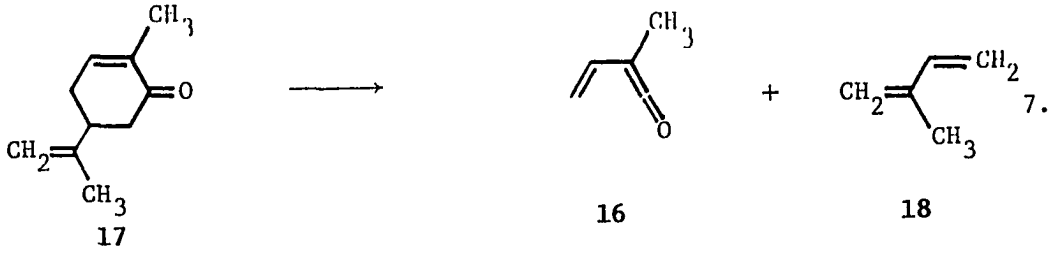
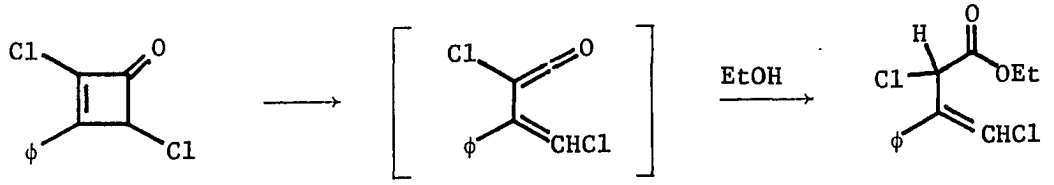


17 16 18 7.

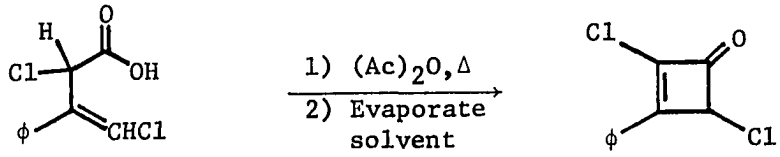
provides some interesting alternatives to its chemistry. For example, the early work of Roberts and co-workers addressed the possibility of an electrocyclic ring closure which should be possible by analogy to the facile [2+2] cycloaddition reaction.[9] Ring opening of a cyclobutenone (19) to the vinylketene (20) was shown by trapping with ethanol (Scheme 1). Ring closure of 20 was shown by dehydration of the

Scheme 1:



19 20 21

corresponding acid (22) (reaction 8).



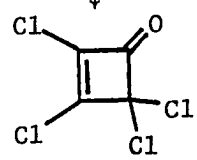
22 19 8.

While many thermal and photochemical ring openings of cyclobutenones (Scheme 1) are known,[10,11,12,13,14,15] the ring closure is not a general reaction and not until 1963 was another example found (Scheme 2).[16] The only other example, one in which the driving force is

Scheme 2:

$$Cl_2C{=}CCl{-}CCl{=}CCl{-}OEt \xrightarrow{200°} Cl_2C{=}CCl{-}CCl{=}C{=}O + ClCH_2CH_3$$

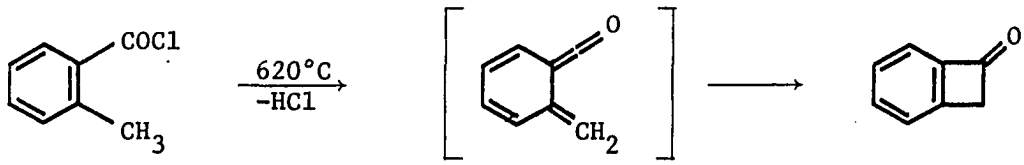
23 24 25



26

aromatization, is the formation of benzocyclobutenone (27) in the pyrolysis of o-toluyl chloride (28) (Scheme 3).[17]

Scheme 3:

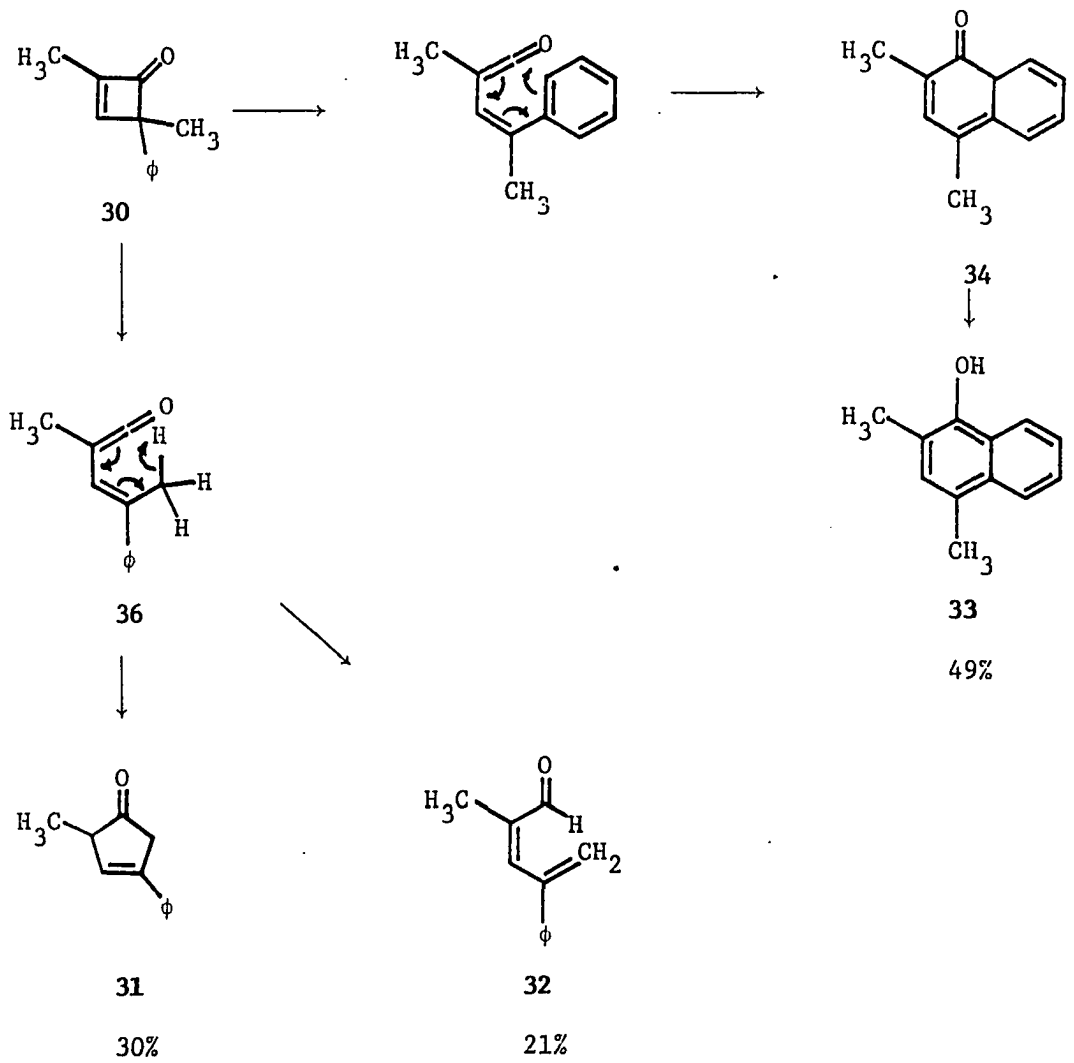


28 29 27

Many vinylketenes are reported as reactive intermediates which generally undergo rearrangements to stable compounds by electrocyclic ring closures or hydrogen migrations.[9,11,13,16-25] A prime example is the pyrolysis of cyclobutenone 30 in which both types of reaction are seen

as well as an unusual rearrangement to a cyclopentenone (31) (Scheme 4).[11]

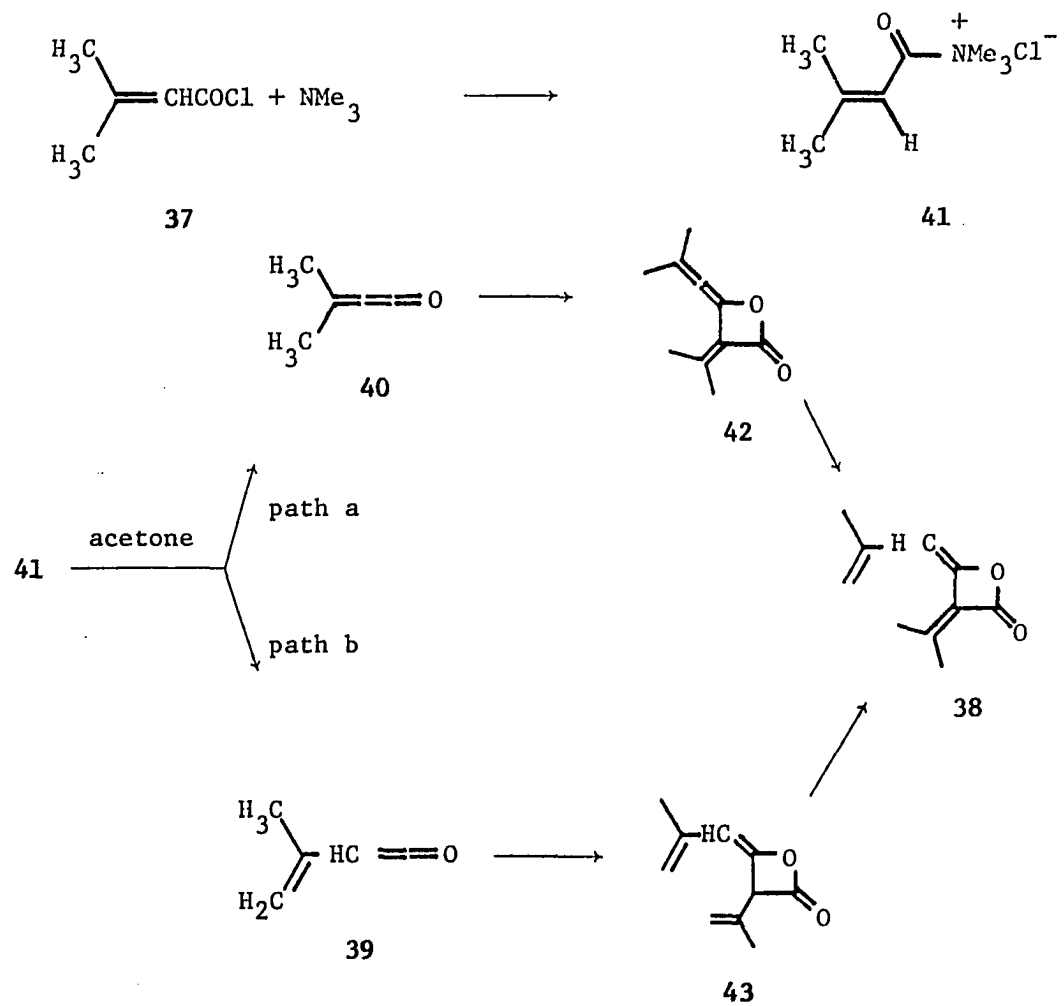
Scheme 4:

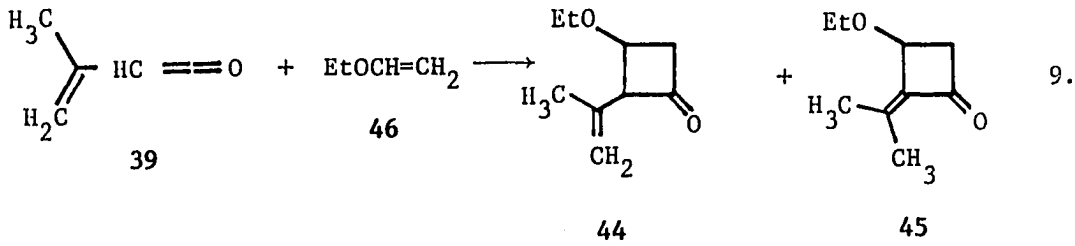


The only report of a vinylketene dimerization appears in Payne's study of base-induced generation of vinylketenes from α,β-unsaturated acid chlorides (37).[26] In this study, a β-lactone (38) was formed

which he concluded was formed to a large extent if not exclusively from isopropenylketene (**39**) rather than from isopropylideneketene (**40**) (Scheme 5). This followed from the [2+2] cycloadduct (**44**) which was obtained by distillation as a 1:1 mixture with its conjugated isomer (**45**) when the decomposition was carried out in the presence of ethyl vinyl ether (**46**) (reaction 9). Compound **45** was shown to isomerize to **46** slowly at room temperature.

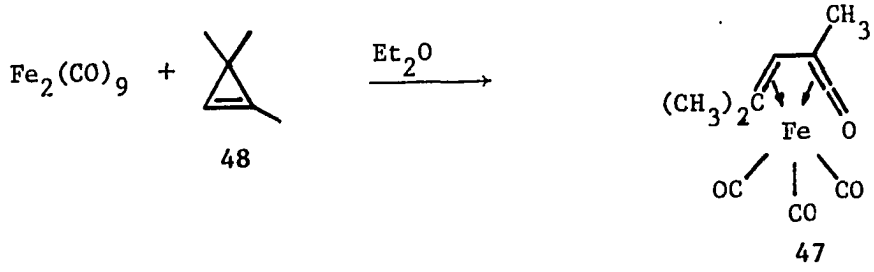
Scheme 5:





9.

One result of the many reports of vinylketenes as reactive intermediates is the effort to synthesize relatively stable vinylketenes. One way in which stable vinylketenes have been formed is by coordination in a stable iron complex (47) (reaction 10).[27] The first of these started from an η^3 vinyl carbene iron complex (49) (reaction 11).[28]



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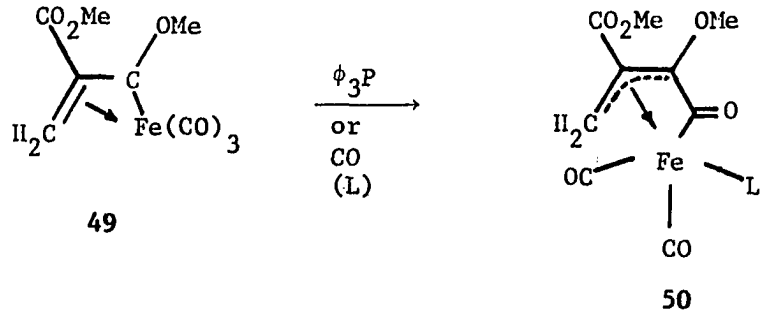
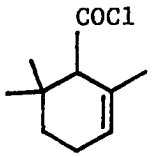


11.

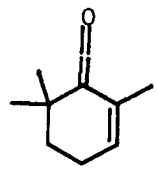
The first stable vinylketene reported (51)[20] appears to derive its stability from the steric interference of the methyl groups towards

dimerization. This is probably the same reason that rather drastic conditions were required for its formation (reaction 12). Other stable vinylketenes are the bis(trimethylsilyl)ketene (**53**) and its tricarbonylchromium complex (**54**) (reaction 13).[28] In a later synthesis, the



52

$\xrightarrow[160°C\ \text{sealed tube}\ 62\%]{NEt_3}$



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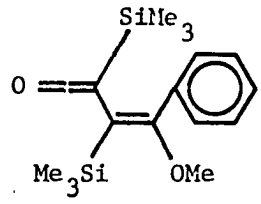
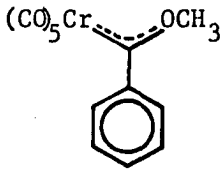
12.



53

13.



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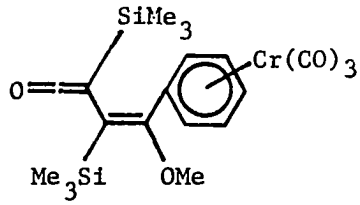
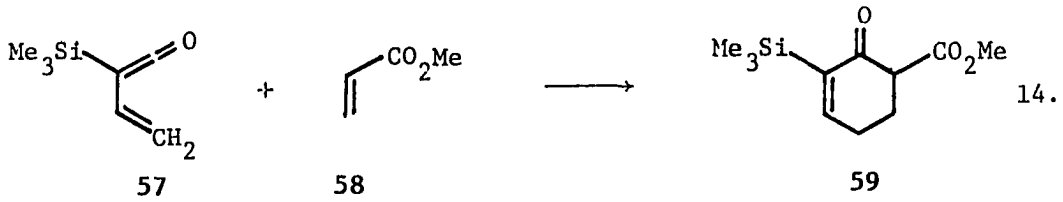
+ $Me_3Si{-}{\equiv}{-}SiMe_3$ **56**

$\xrightarrow[50°C]{(n\text{-}Bu)_2O}$



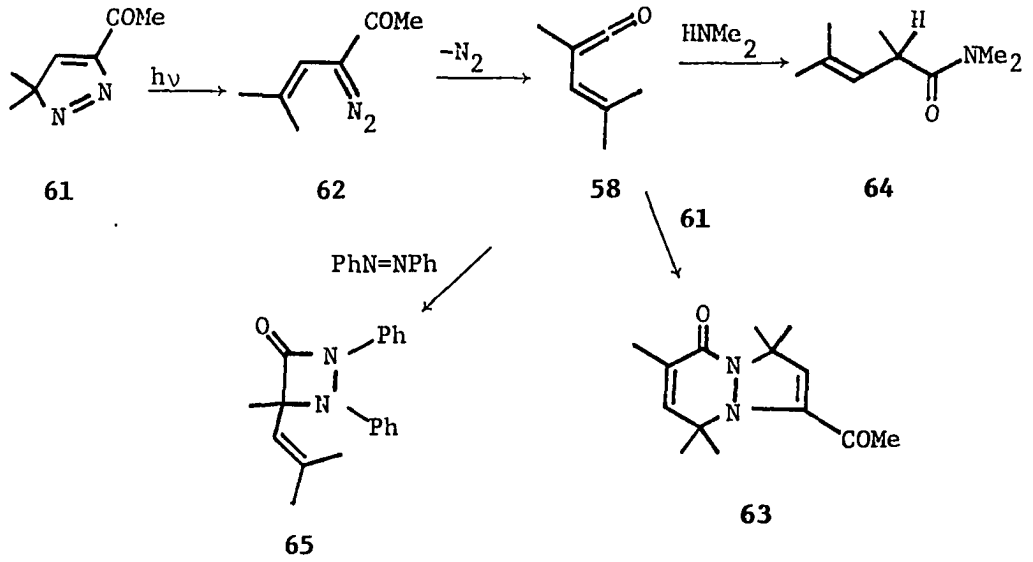
54

trimethylsilyl group was used to stabilize a vinylketene (**57**) which could then effectively participate as a diene in a Diels-Alder reaction (reaction 14).[29] Only one other vinylketene Diels-Alder reaction is known. This was a special case where the ketene (**60**) reacted with the pyrazole precursor (**61**). Other diazo compounds did not react the same way (Scheme 6).[30]



57 58 59 14.

Scheme 6:



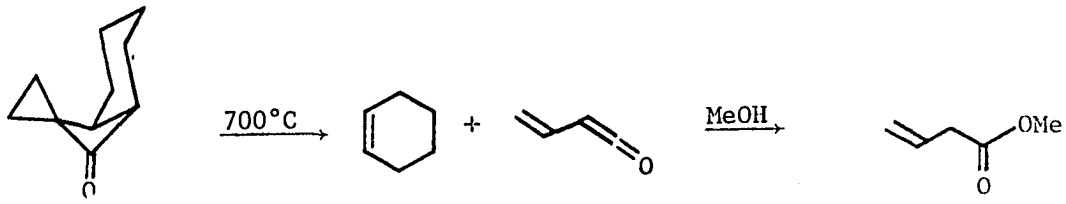
Another result of the reports of vinylketenes as reactive intermediates was the study of the parent compound (**66**). It was first

$$CH_2{=}CH{-}CH{=}{=}O$$

66

generated by the pyrolysis of spiro[2.3]hexane-4-one (**67**) (Scheme 7).[31] The product, described as a red liquid stable up to -160°C, was

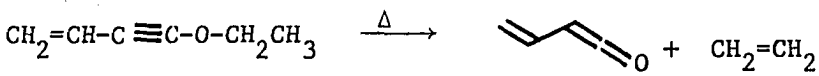
Scheme 7:



67 **69** **66** **68**

identified by mixing with methanol which gave methyl vinylacetate (**68**). Vinylketene (**66**) was also proposed as an intermediate in [2+2] cycloaddition reactions of cyclopentadiene (**2**) with the dehydrochlorination product of crotonyl chloride (**70**) and but-3-enoyl chloride (**71**).[32,33] The initial adduct (**72**) could only be obtained with difficulty since it isomerized in the basic medium (Scheme 8). Vinylketene (**66**) was also postulated as the product of pyrolysis of ethylidenemalonate (**75**) on the basis of trapping with aniline vapor (Scheme 9).[34]

More recent studies of vinylketene focused on its spectral identification. The first such study dealt with its mass spectral identification in the pyrolysis of 1-ethoxybut-3-en-1-yne (**77**) (reaction 15).[35]

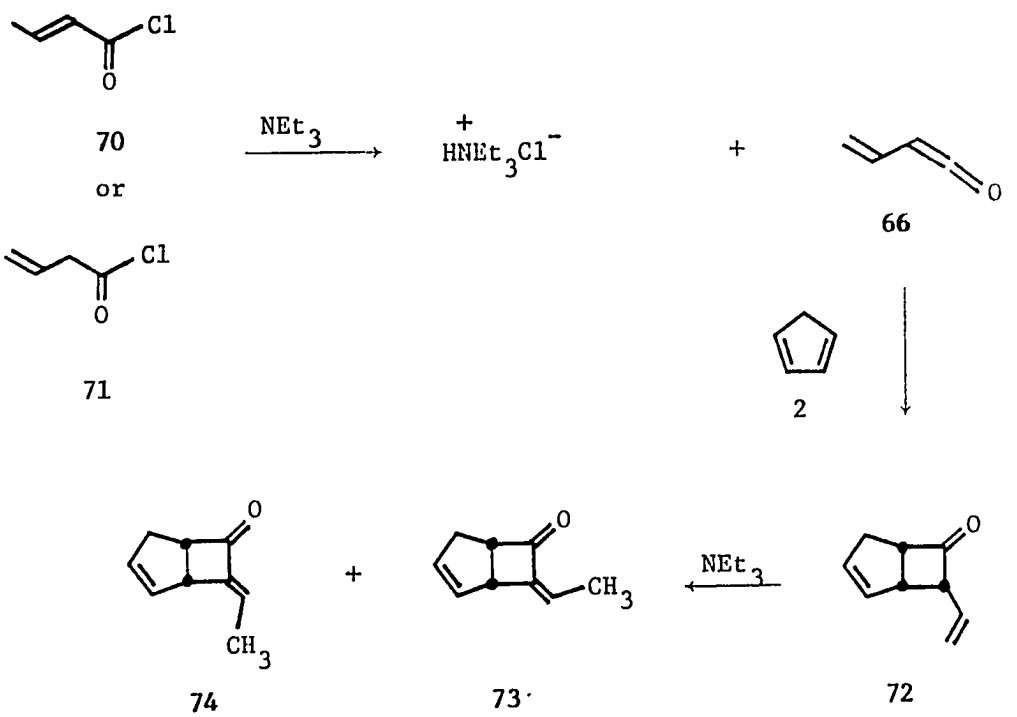


15.

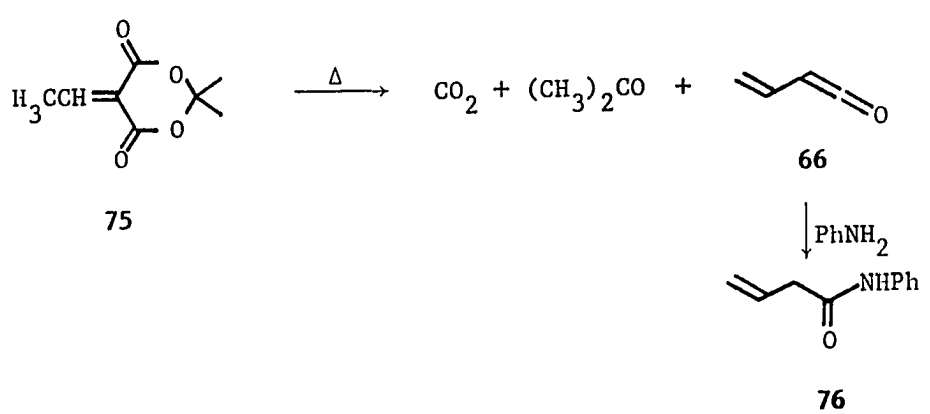
77 **66**

In the same year, two papers appeared which identified vinylketene (**66**) by microwave spectroscopy in one case[36] and by microwave and infrared

Scheme 8:

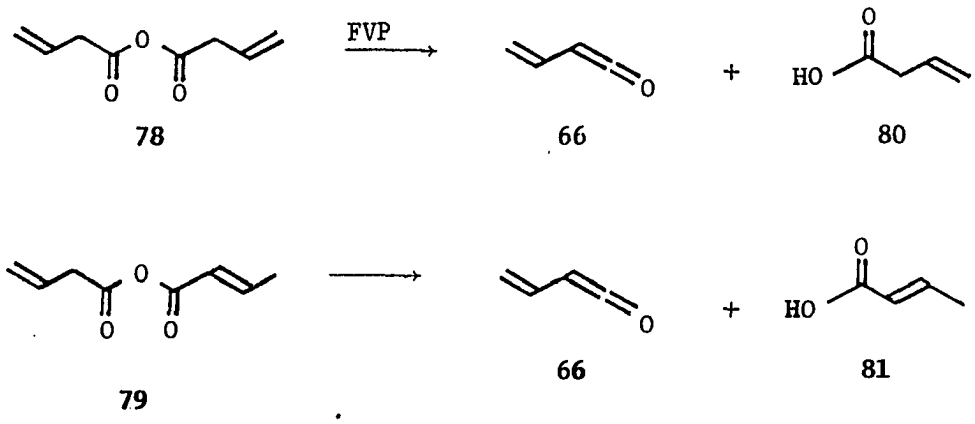


Scheme 9:



spectroscopy in the second case.[37] In both studies, the vinylketene (66) was formed by acid anhydride pyrolysis (78 in the first case, 79 in the second) and was analyzed in the gas phase (Scheme 10).

Scheme 10:



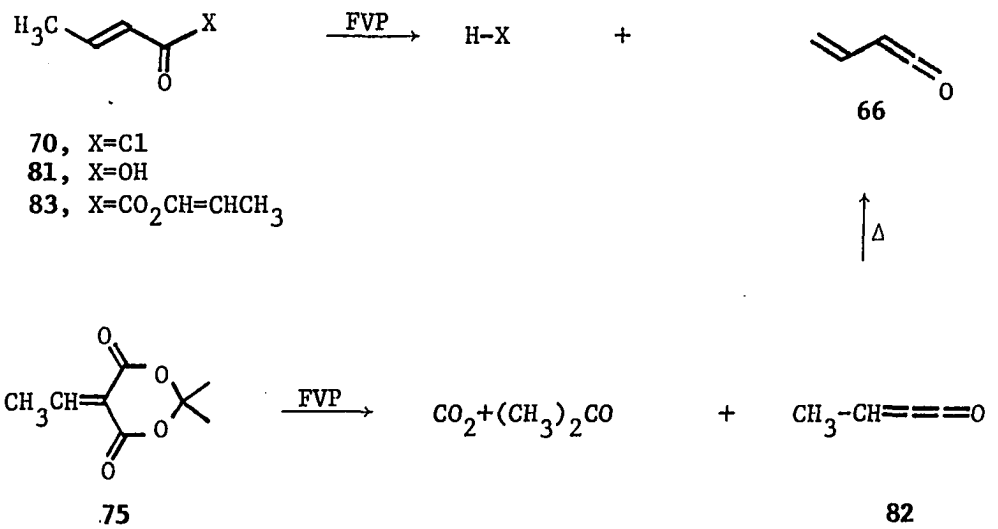
78 66 80

79 66 81

Since Payne's study, there was the question of whether 1,4-elimination or 1,2-elimination of HX took place in compounds such as crotonyl chloride (70) (X=Cl) to give vinylketene (66) in the first case or ethylideneketene (82) in the latter. This question was answered by Bock and co-workers who studied thermal HX elimination from α,β-unsaturated carboxylic acid derivatives (H_3C-CR=CH-COX with R=H,CH_3).[38] The temperature dependent changes of amounts of products in the heated flow system were analyzed by photoelectron spectroscopy. Based on MNDO calculations and literature data, the vinylketene structure (66) was assigned to the pyrolysis product (Scheme 11). The isomeric ethylideneketene (82) was produced in the 760K short path pyrolysis of ethylidene

malonate (**75**) and rearranged on prolonged residence time in the hot zone into the thermodynamically more stable vinylketene (**64**) (Scheme 11).

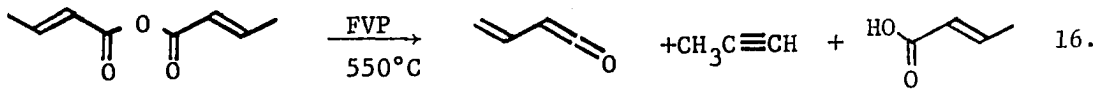
Scheme 11:



To complete the spectral characterization of vinylketene, UV and NMR spectra are required. Because of a good body of data on ketene NMR chemical shifts, the NMR of vinylketene should provide a very clear and unambiguous identification of this reactive compound. Also, a better understanding of its reactivity and chemistry is desirable. This part of the thesis describes the low temperature ^{1}H and ^{13}NMR spectra of vinylketene (**66**) and some of its low-temperature thermal chemistry. Also described is some chemistry of the dimer of vinylketene and of the vinylketene-cyclopentadiene adduct (**72**). This work has been briefly described in a published communication.[39]

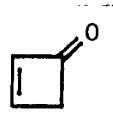
RESULTS

Vinylketene (**66**) was prepared by the flash vacuum pyrolysis (FVP) of crotonic acid anhydride (**83**) (reaction 16). Methyl acetylene (**84**)



83 **66** **84** **81** 16.

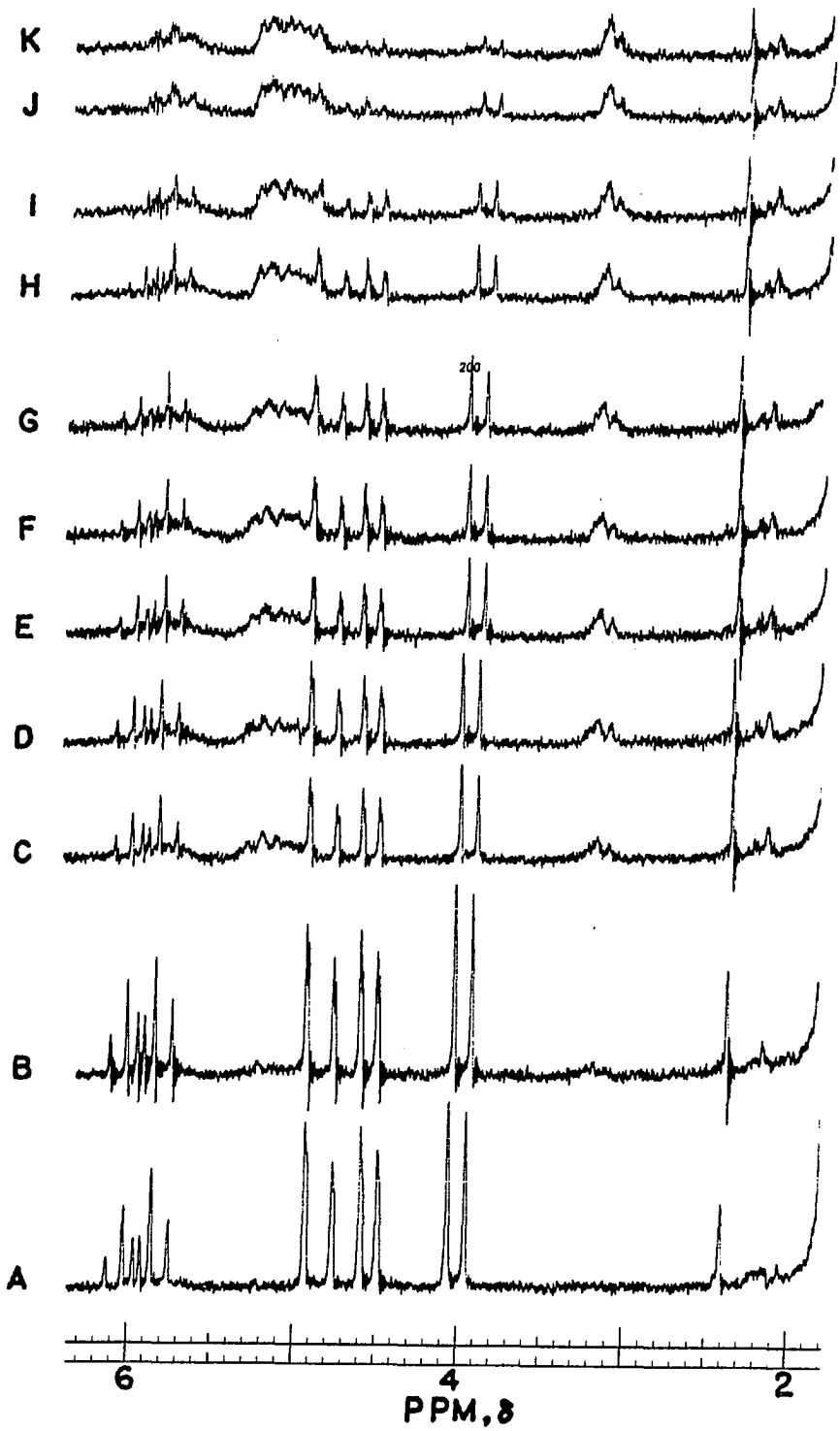
was also formed by a secondary reaction. The crotonic acid produced (**81**) was separated from the more volatile products by using an apparatus with two product condensers, the first cooled to -20°C and the second cooled to -196°C. Vinylketene (**66**) and methylacetylene (**84**) were identified by ^{1}H and ^{13}C NMR by distilling a solvent into the -196°C condenser and allowing the mixture to warm to -78°C which produced a bright yellow solution. The ^{1}H-NMR spectrum of this solution at -70°C showed by an internal standard a 22% yield of vinylketene (**66**) and a 40% yield of methylacetylene (**84**). Only 5% of minor products were present (Figure 1a). No evidence for the cyclic isomer of **66**, cyclobutenone (**85**) was obtained.



85

The ^{1}H-NMR spectrum clearly shows the structure of vinylketene (**66**) (Figure 1a). The ketenic hydrogen (H_a) has about the same chemical

Figure 1. Proton NMR spectra (100 MHz) of (a) vinylketene (64) at -70°C, (b) 64 after 2 hours at -70°C, (c) -50°C, (d) -50°C 30 min after spectrum c, (e) -30°C, (f) -30°C 20 min after spectrum e, (g) -30°C 30 min after spectrum e, (h) -10°C, (i) -10°C 20 min after spectrum h, (j) +10°C, (k) +10°C 10 min after spectrum j


K
J
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200
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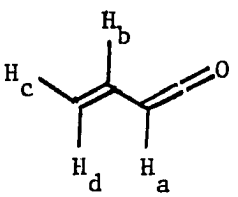
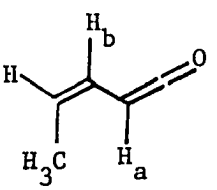
2
PPM, δ

shift and coupling constant as those for the corresponding hydrogens of cis- and trans-(1-propenyl)ketene (86 and 87) (Table 1).[22] The rest of the spectrum fits the vinyl group perfectly. The terminal



66



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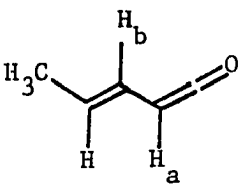


87

Table 1. Chemical shifts (δ) and coupling constants (J) for ketenic hydrogens (H_a)[a]

Compound	Temperature, °C	δ for H_a, ppm	J_{ab}, Hz
64	-70	4.02	11
86	-80	3.93	10
87	-80	4.05	10

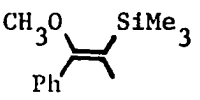
[a]Data for 86 and 87 are from reference 22.

protons (H_c and H_d) show the geminal splitting and coupling to H_b which is also coupled to H_a. The coupling constants J_{ab} and J_{bc} are equal (11 Hz) so the pattern for H_b appears as a doublet of triplets. Not seen in Figure 1 are the strong absorptions of methylacetylene (84) at δ 1.9. The ketene showed little polymerization after two hours at -70° (Figure 1a, b). However, upon warming, the disappearance of vinylketene (66) was observed coincident with the appearance of oligomeric signals (Figure 1c-1k). If the solution was warmed quickly, a much cleaner

spectrum of the dimer appeared (70% yield) (Figure 2). This effect was also seen by ^{13}C-NMR (Figure 3).

Vinylketene was also characterized by ^{13}C NMR at -70° as a mixture with methylacetylene (84) (Figure 4). The signals of methylacetylene appear at 80.4 (s), 68.4 (s) and 3.7 (q). The ketene group is evident in the absorptions at 200.2 (s) and 28.6 (d, J_{CH} 173 Hz) by comparison to literature values (Table 2). The peaks at 121.9 (d) and 109.1 (d of d) are due to the vinyl group.

Table 2. Carbon-13 NMR data of ketenes ($R_1R_2C_1=C_2=O$)

R_1	R_2	δ for C_1, ppm	δ for C_2, ppm	J_{CH}, Hz	Reference
H	H	2.5	194.0	171.5	40
CH_3	H	10.9	200.0		40
	$SiMe_3$	18.0	183.1		28
C_2H_5	H	18.6	200.0		40
CH_2=CH	$SiMe_3$	22.3	183.7		29
C_2H_5	CH_3	26.9	206.1		40
C_6H_5	CH_3	33.8	205.6		40
C_6H_5	C_2H_5	42.1	205.6		40
C_6H_5	C_6H_5	47.0	201.3		40

The ^{13}C-NMR spectrum of the dimer (Figure 3) ruled out the β-lactone structure (**88**) and the 1,3-cyclobutadione structure (**89**) by the

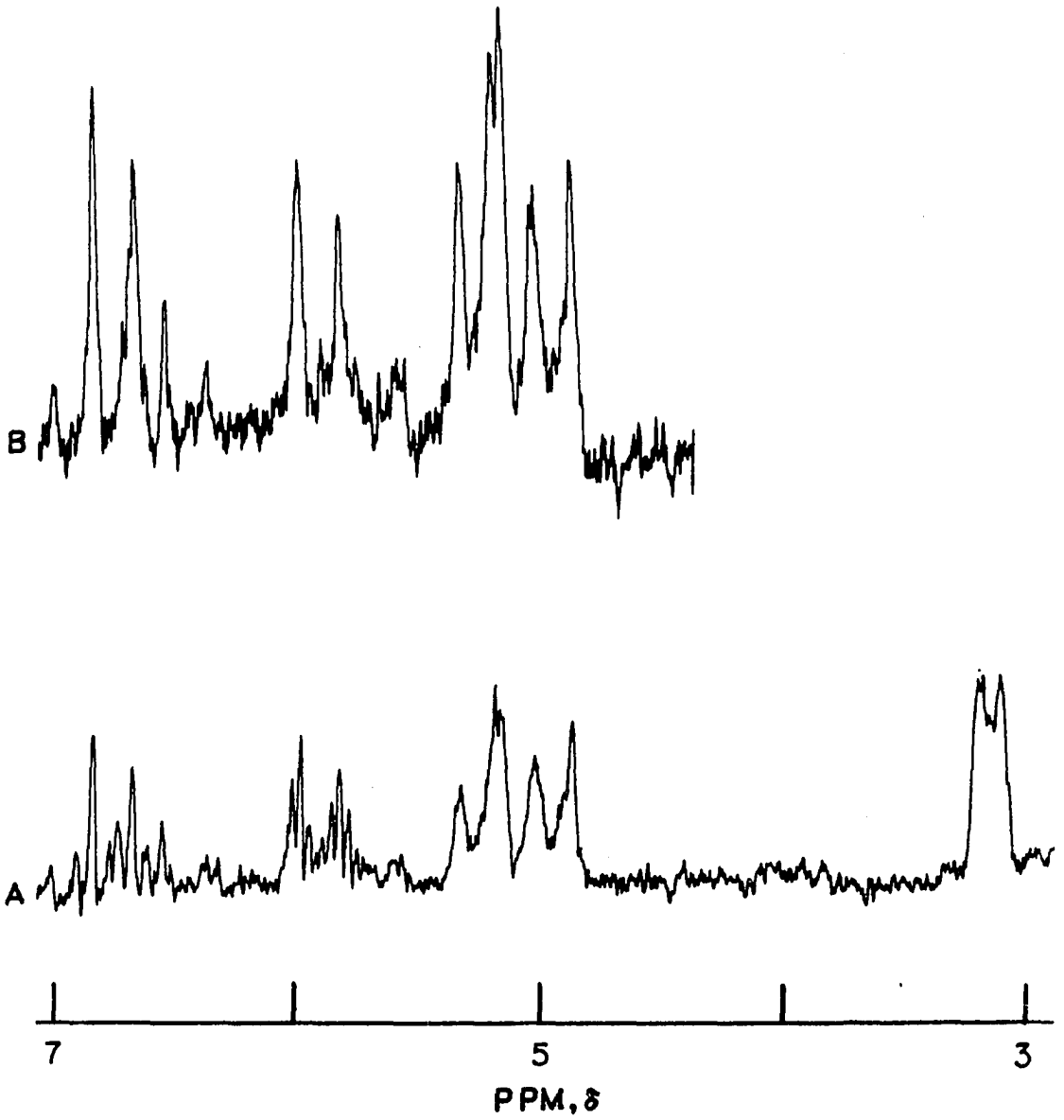
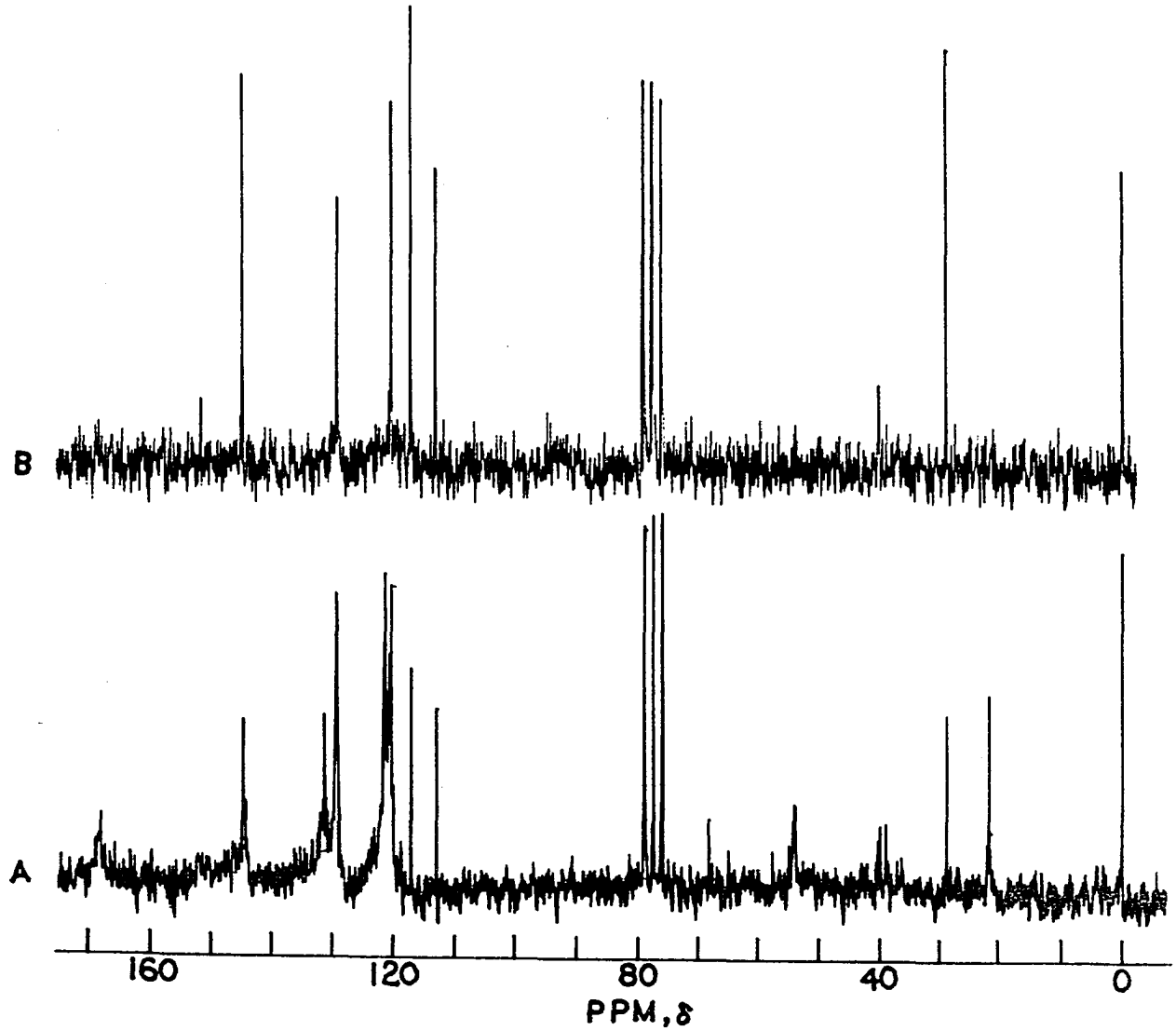


Figure 2. Proton NMR spectrum (60 MHz) of 2,5,6-trihydro-6-allylidenepyran-2-one (**90**): (a) normal, (b) spin-spin decoupled with irradiation at $\delta \approx 3.2$

Figure 3. Carbon-13 NMR spectra (22.5 MHz) of the products from warming vinylketene (**66**): (a) slow warm-up, (b) fast warm-up showing fairly clean formation of 2,5,6-trihydro-6-allylidenepyran-2-one (**90**)


B
A
160
120
80
40
0
PPM, δ

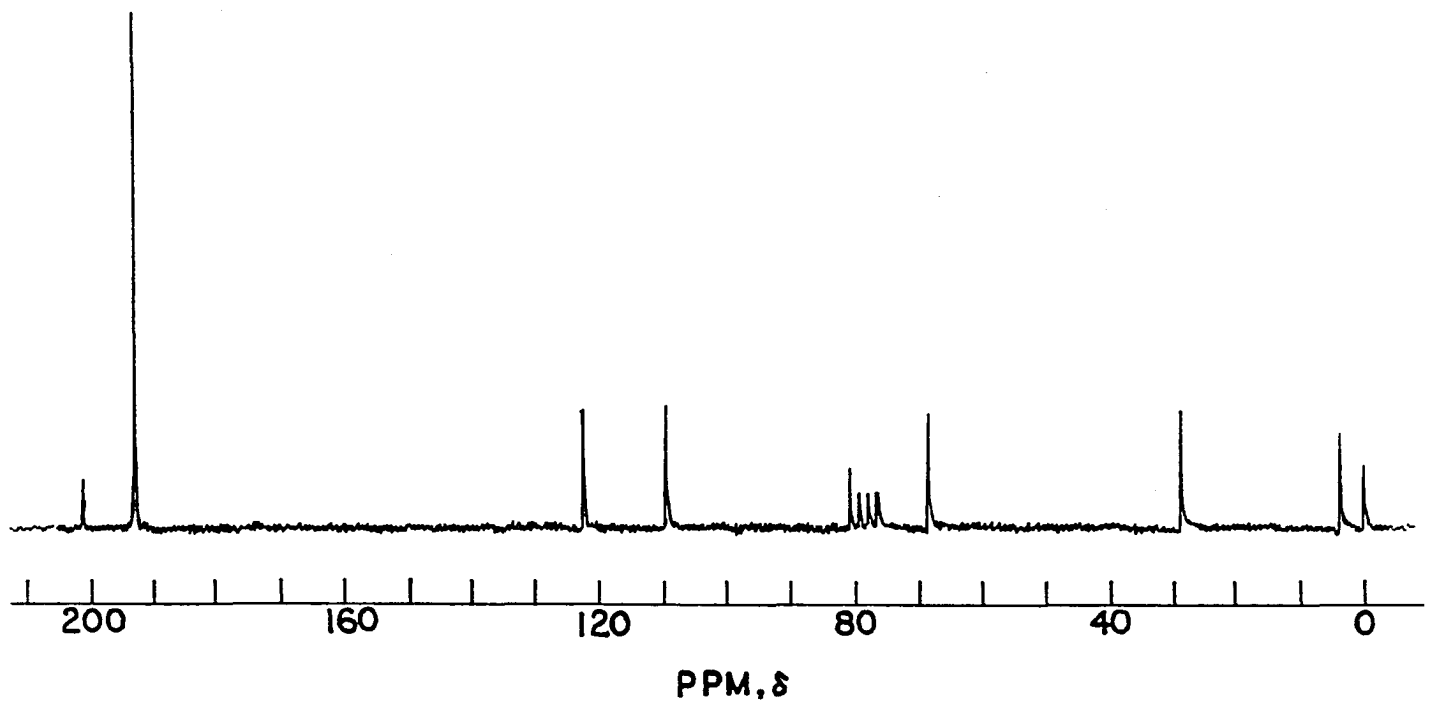
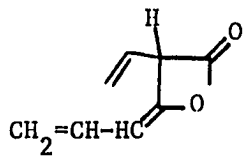
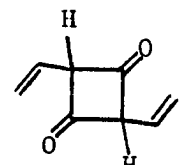


Figure 4. Carbon-13 NMR spectrum (22.5 MHz) at -70°C of vinylketene (66) and methylacetylene (84)

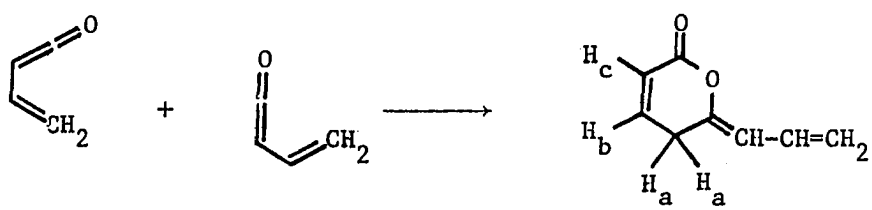


88



89

multiplicity of the aliphatic signal at δ 28.6 in the gated-decoupled spectrum - a triplet. Also, as seen in a double irradiation NMR experiment (Figure 2b), the protons on this carbon (δ 3.25, H_a) are coupled with olefinic protons of a double bond conjugated to the carbonyl group since the signals at δ 6.9 (doublet of triplets, H_b) and δ 6.0 (doublet of triplets, H_c) collapse to doublets when the methylene protons are irradiated. The lactone structure is evident in the IR (C=O stretch, 1760 cm^{-1}; C(O)O-C stretch 1240, 1125 cm^{-1}) and ^{13}C NMR (δ 176.1 (s), 160.7 (s), not obvious in Figure 3b) spectra of the dimer and the vinyl group is apparent in the ^{1}H (Figure 2) and gated-decoupled ^{13}C NMR (not shown). Thus, the structure of the major vinylketene dimer is the δ-lactone (**90**) (reaction 17). A minor component is formed even



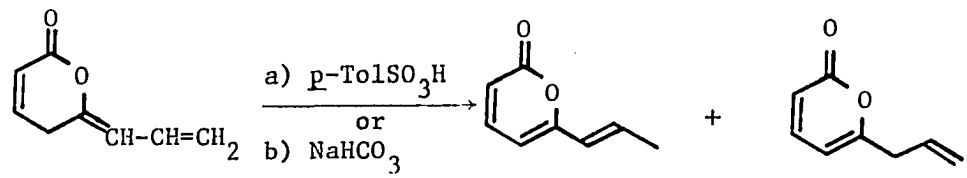
17.

66 66 90

in the fast warm-up mixture as indicated by a small aliphatic signal at δ 38.9 in Figure 3b. The chemical shift suggests it is either **88** or **89**.

Attempts to purify the dimer (**90**) by either chromatography or distillation caused isomerization and decomposition so **90** was isomerized to a mixture of α-pyrones (**91** and **92**) without purification. Acid-catalyzed isomerization resulted in a 9:1 mixture of **91** and **92** (50% yield). When isomerization was effected by base, a 1:3 mixture was obtained (50-60%) (Scheme 12). Formation of these pyrones serves as additional proof of the dimer's structure.

Scheme 12:



90 **91** **92**

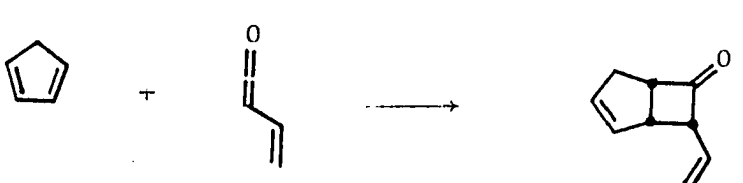
a)	9	:	1
b)	1	:	3

Compound **91** is sibirinone, a recently discovered metabolite of Hypomyces semitranslucens G. Arnold.[41] Its spectral data were consistent with the structure and agreed with the literature data. Most notable is a strong ring breathing band in the infrared spectrum at 1540 cm^{-1}. Also indicative of the pyrone ring are lactone carbons (C(O)-O-C) in the ^{13}C NMR and a doublet of doublets at δ 7.47 in the ^{1}H NMR for the

hydrogen β to the carbonyl (Figure 5). Figure 5 also shows the methyl group as a doublet at δ 1.9 coupled to the olefinic hydrogen at δ 6.71 which appears as a doublet of quartets since it is coupled to the other olefinic hydrogen of the side chain. Close inspection of the overlapping patterns of the other 3 protons between δ 6.14 and 5.99 allows one to discern the 3 doublets there by their long-range coupling patterns and their coupling constants.

Compound **92** is a new pyrone and was identified by its spectral data. It had all the characteristics of a pyrone mentioned above for sibirinone (**91**) in addition to NMR signals for the allyl side chain. The methylene protons appear as a doublet in the ^{1}H NMR (Figure 6) and are coupled to the only aliphatic carbon giving rise to a triplet in the gated-decoupled ^{13}C NMR. The rest of the allyl group is apparent in the vinyl pattern in the ^{1}H NMR (Figure 6) and an olefinic triplet in the gated-decoupled ^{13}C NMR.

When cyclopentadiene (2) was distilled into the -196°C condenser containing vinylketene and the mixture was allowed to warm up, a bright yellow solution was obtained which lost its color before reaching room temperature. The result was adduct **72** obtained in 23% yield from the anhydride (reaction 18). The structure of **72**, the expected structure



2 **66** **72** 18.

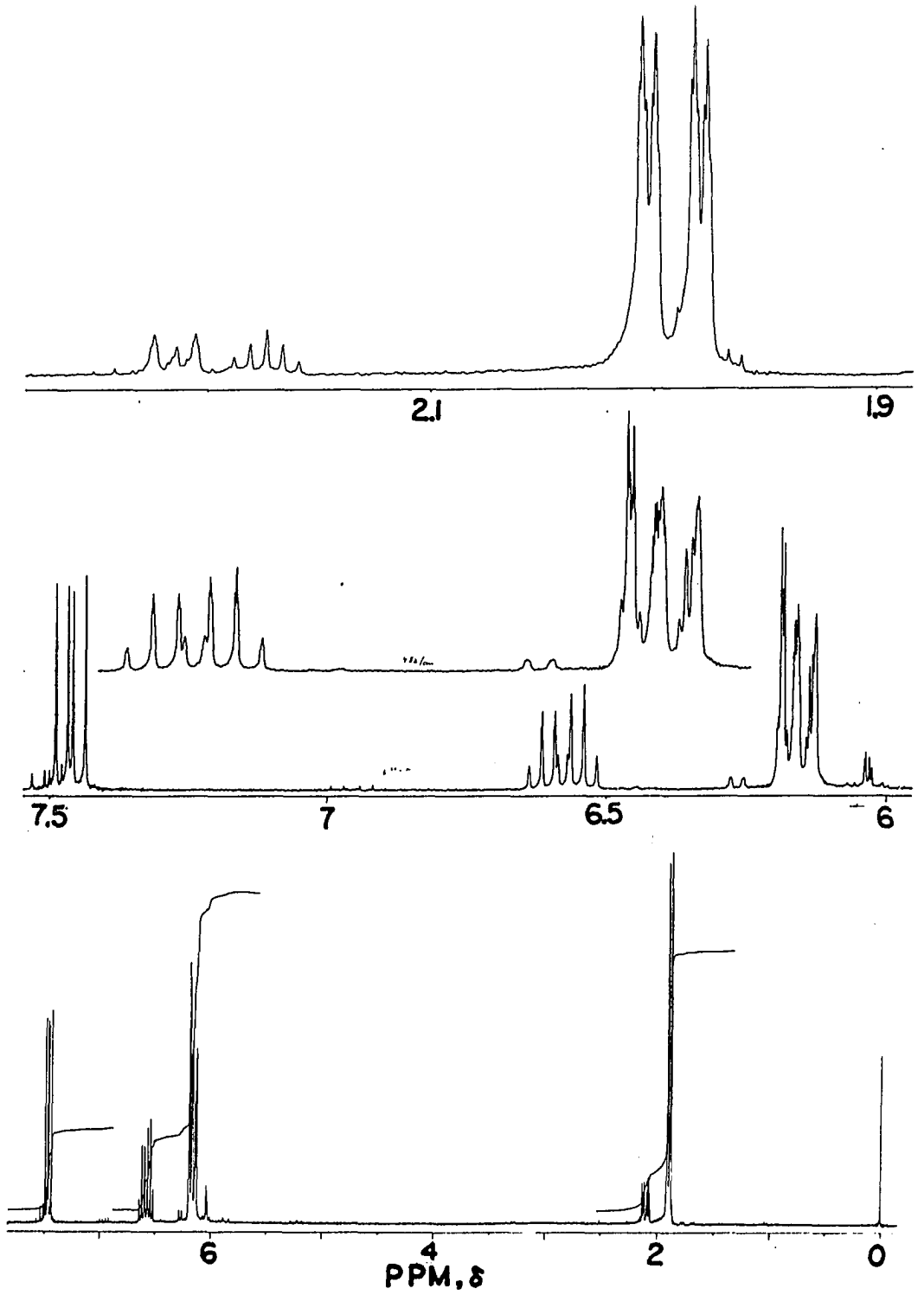


Figure 5. Proton NMR spectrum (400 MHz) of sibirinone (91)

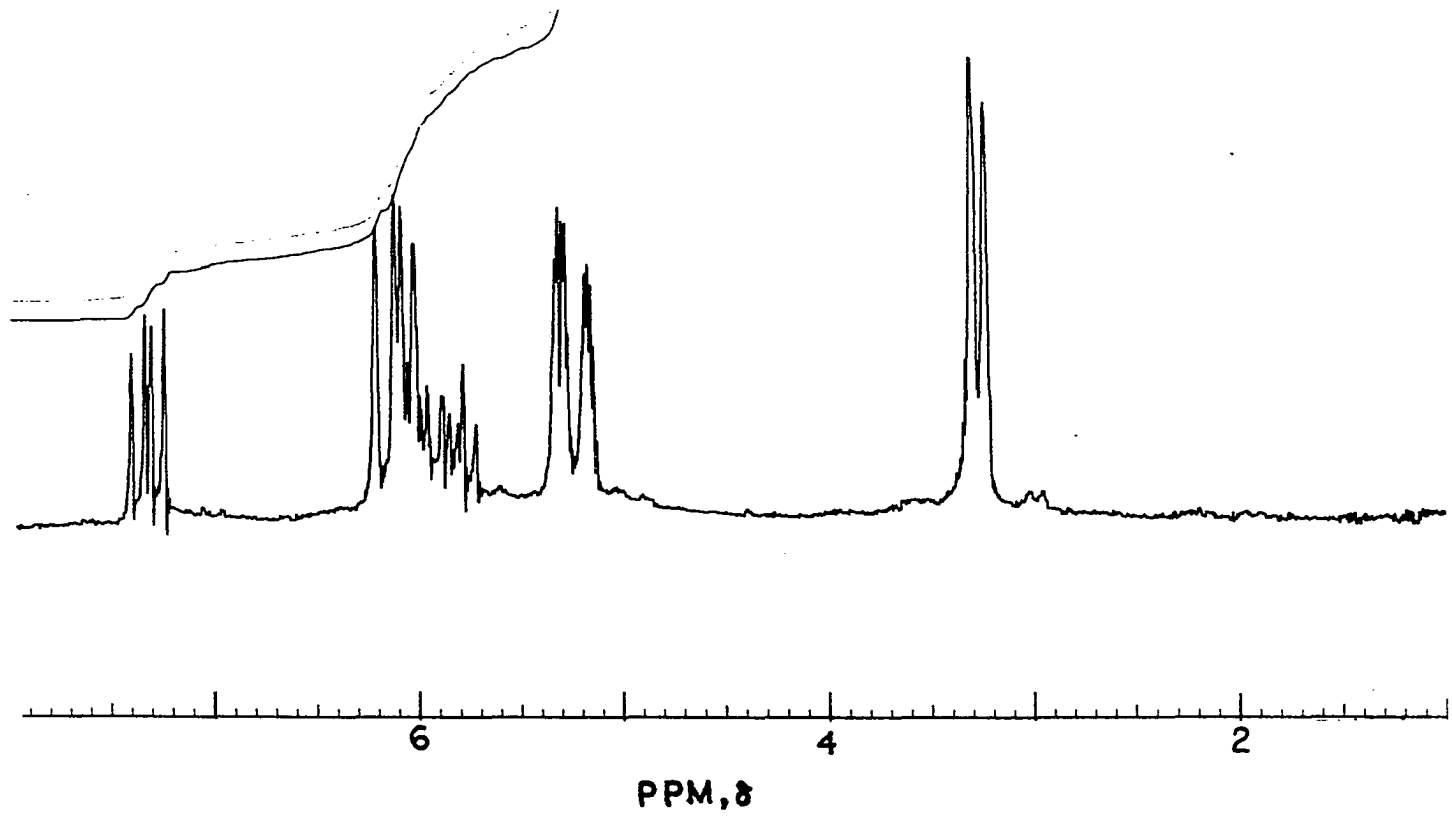
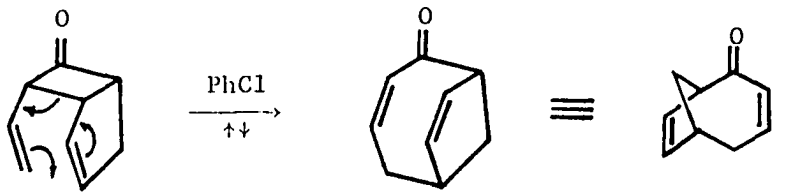


Figure 6. Proton NMR spectrum (100 MHz) of 6-allyl-α-pyrone (92)

based on previous studies of ketene cycloadditions,[2,4-6,32,33] was indicated by its spectral properties which agree with the literature data.[33] The cyclobutanone ring of **72** was indicated by the carbonyl stretching band at 1780 cm^{-1} in the IR and the vinyl group was obvious from the ^{1}H-NMR (Figure 7). No other isomer was detected in the ^{13}C NMR spectrum (Figure 8). In this spectrum, only 8 peaks are observed (theoretical number is 9) since 2 carbons have the same chemical shift. The same result is obtained at 64 MHz.[33] Attempts to react vinylketene with other substrates (acetyl chloride (**93**), butadiene (**94**), cyclohexadiene (**95**), methylacrylate (**96**)) resulted in dimerization of the ketene (reaction 27).

Compound **72** was isomerized to bicyclo[4.2.1]nona-3,7-dien-2-one (**97**) in refluxing chlorobenzene (40% yield) (reaction 19). The



72 **97** **97** 19.

structure of **97** followed from its spectral properties. The UV and IR spectra showed a carbonyl group which was now conjugated to a double bond. The gated-decoupled ^{13}C NMR indicated no methyl group. Only two possible structures that are isomers of **72** will accommodate these data: **97** and the product of a 1,3-sigmatropic shift (**98**). Of these, only **97** fits the ^{13}C-NMR data. This spectrum contains two aliphatic doublets

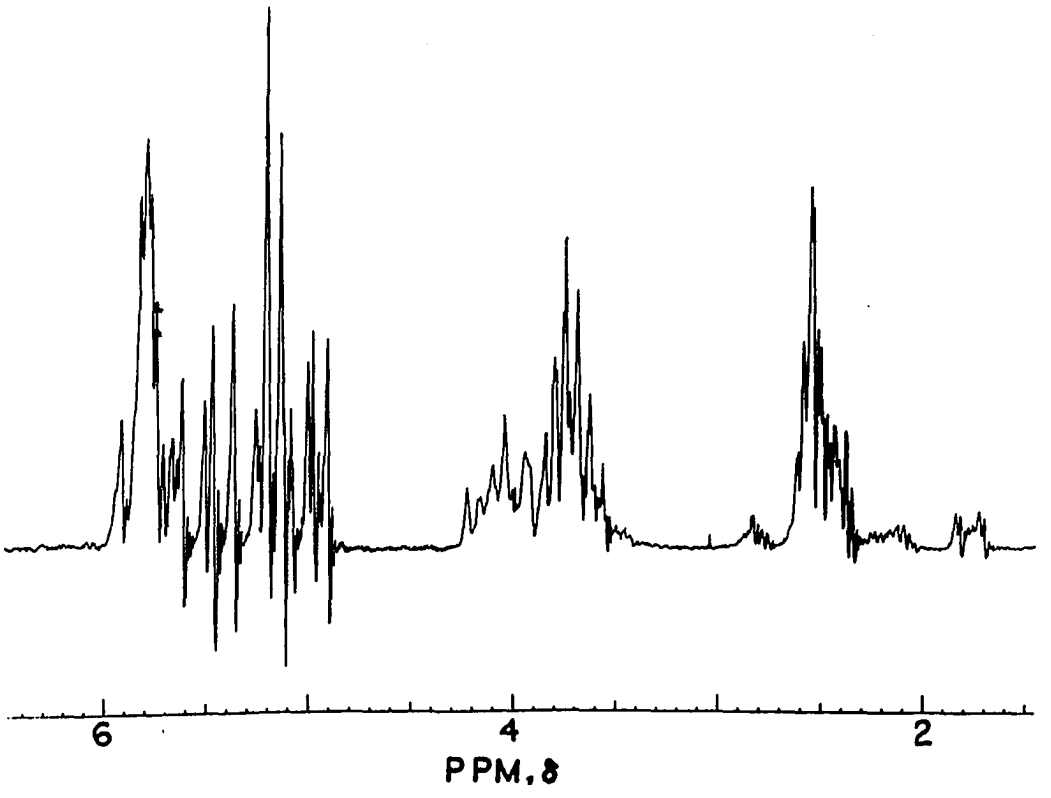


Figure 7. Proton NMR spectrum (60 MHz) of endo-7-vinylbicyclo [3.2.0]hept-2-en-6-one (72)

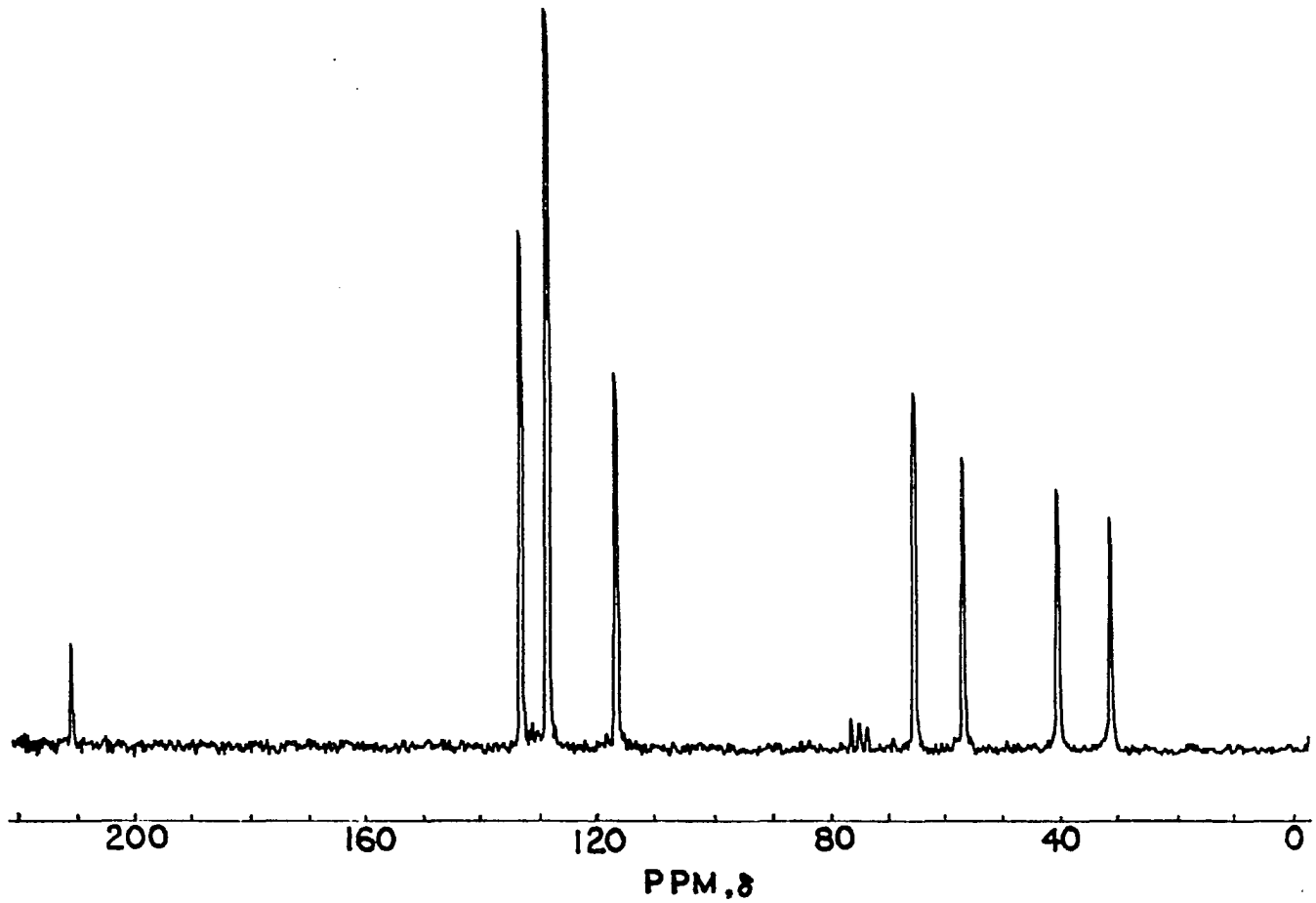
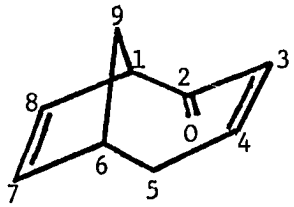
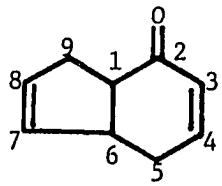


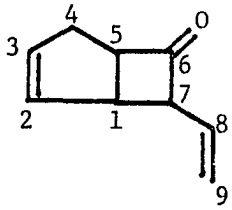
Figure 8. Carbon-13 NMR spectrum (22.5 MHz) of endo-7-vinylbicyclo[3.2.0]hept-2-en-6-one (72)



97

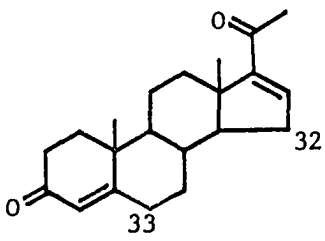


98



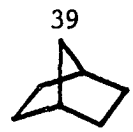
72

(the bridgehead carbons) and two aliphatic triplets at δ 39 and 32 ppm. Of the triplets, the one at δ 32 is assigned to C-5 by comparison to steroid **99**.[42] Of course, C-5 of **98** would also be expected to have this chemical shift. The triplet at δ 39 is too far downfield to be C-9 of **98** which should have a chemical shift similar to C-4 of **72** (δ 34 ppm). On the other hand, 39 ppm is about right for C-9 of **97** by comparison to chemical shifts for bridging carbons of norbornene (**100**, δ 49) and norbornane (**101**, δ 39).[42] The ^{1}H-NMR spectrum was complex but fit the structure well (Figure 9).



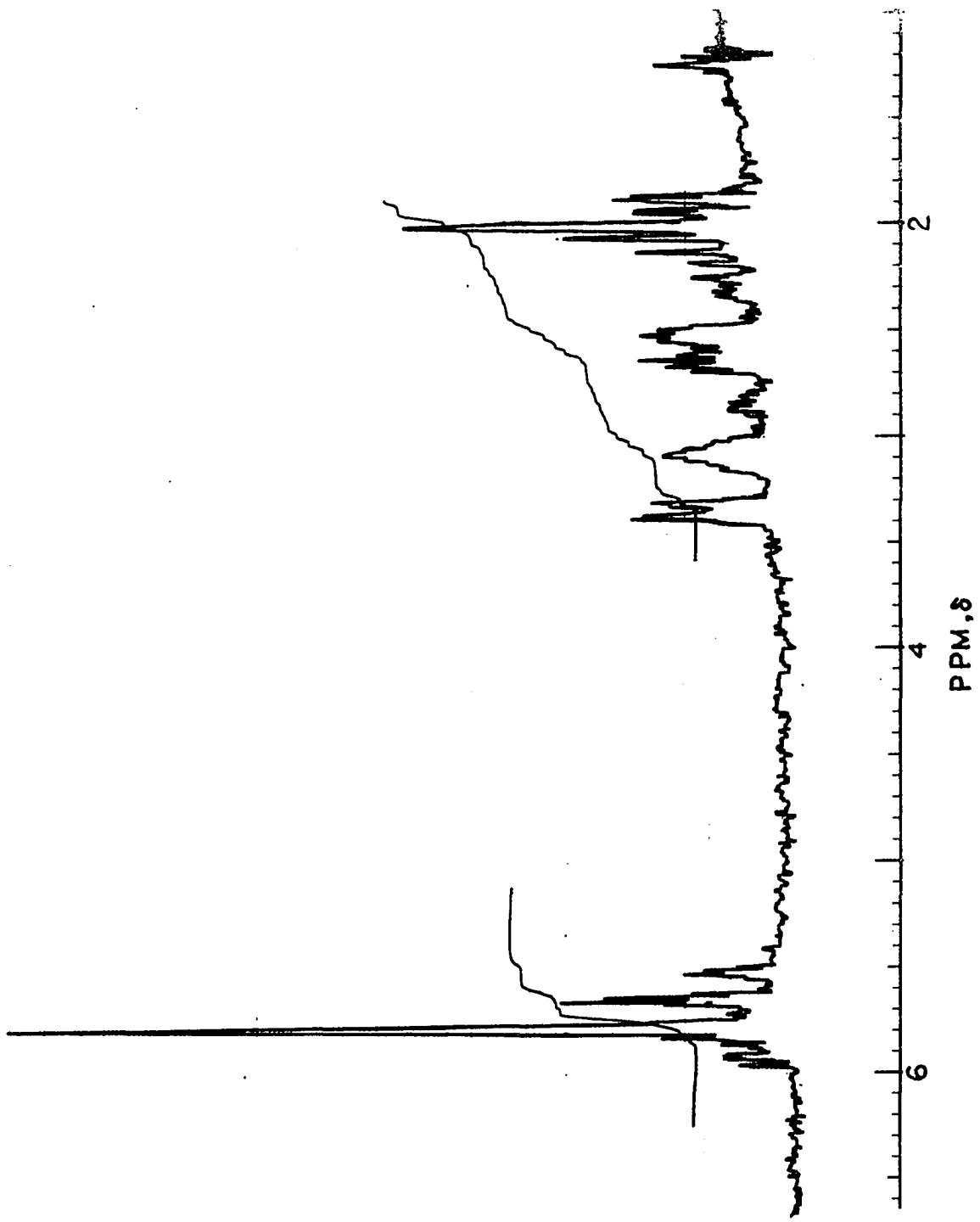
99

100



101

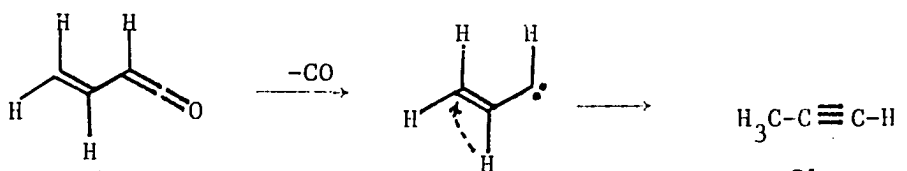
Figure 9. Proton NMR spectrum (100 MHz) of bicyclo[4.2.1]nona-3,7-dien-2-one (97)


6
4
2
PPM, δ

DISCUSSION

Methylacetylene (**84**) is a well-known by-product in pyrolytic formations of vinylketene.[36,37] It is believed to arise by loss of CO from vinylketene followed by hydrogen migration in the resulting carbene (Scheme 13).[43,44]

Scheme 13:



66 **84**

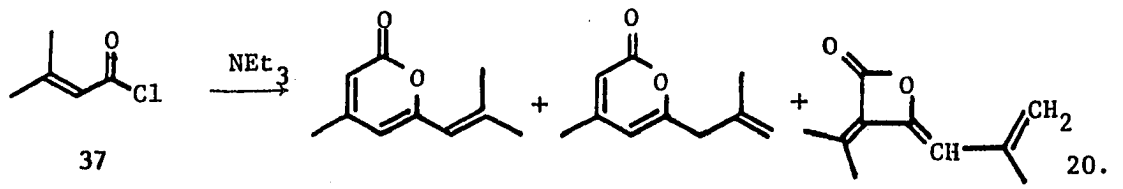
Obtaining spectra of vinylketene in solution at low temperature is quite satisfying because it puts us on firm ground when discussing its chemistry. For instance, we know for a fact that the compound obtained upon warming the solution (**90**) is truly the dimer of vinylketene (reaction 27) and that the adduct (**72**) obtained with cyclopentadiene (2) is formed from vinylketene (reaction 28).

The δ-lactone structure of the dimer (**90**) was totally unexpected. This is the first time a ketene dimerization went by a Diels-Alder reaction. The carbonyl group of ketenes has been shown to react as dienophiles with certain dienes (reaction 3)[7] and some vinylketenes have reacted as dienes (reaction 24[29] and Scheme 6[30]). The only other vinylketene dimerization reported gave a β-lactone (Scheme 5).[26]

The isomer ratios in the isomerization of the dimer to pyrones

(Scheme 12) can be rationalized by the mechanisms shown in Scheme 14. Acid-catalyzed isomerization would yield a neutral intermediate (**102**) which would give the protonated isomers (**91**-H^+ and **92**-H^+) in a slow, reversible reaction. These would in turn deprotonate in a fast but reversible reaction. Thus, the thermodynamically more favorable isomer (**91**) is formed to a greater extent. On the other hand, base-catalyzed isomerization gives an anionic intermediate (**104**) in a reversible reaction which gives the isomeric pyrones in a fast neutralization. This should be an irreversible reaction since protons on **91** and **92** are not especially acidic. Thus, a kinetically-controlled product ratio results. Since there is some freedom of rotation in the sigma bond to the terminal vinyl group of **104**, and since there would be some coordination to the oxygen in the ring, path a is the favorite path of neutralization resulting in a larger amount of **92**.

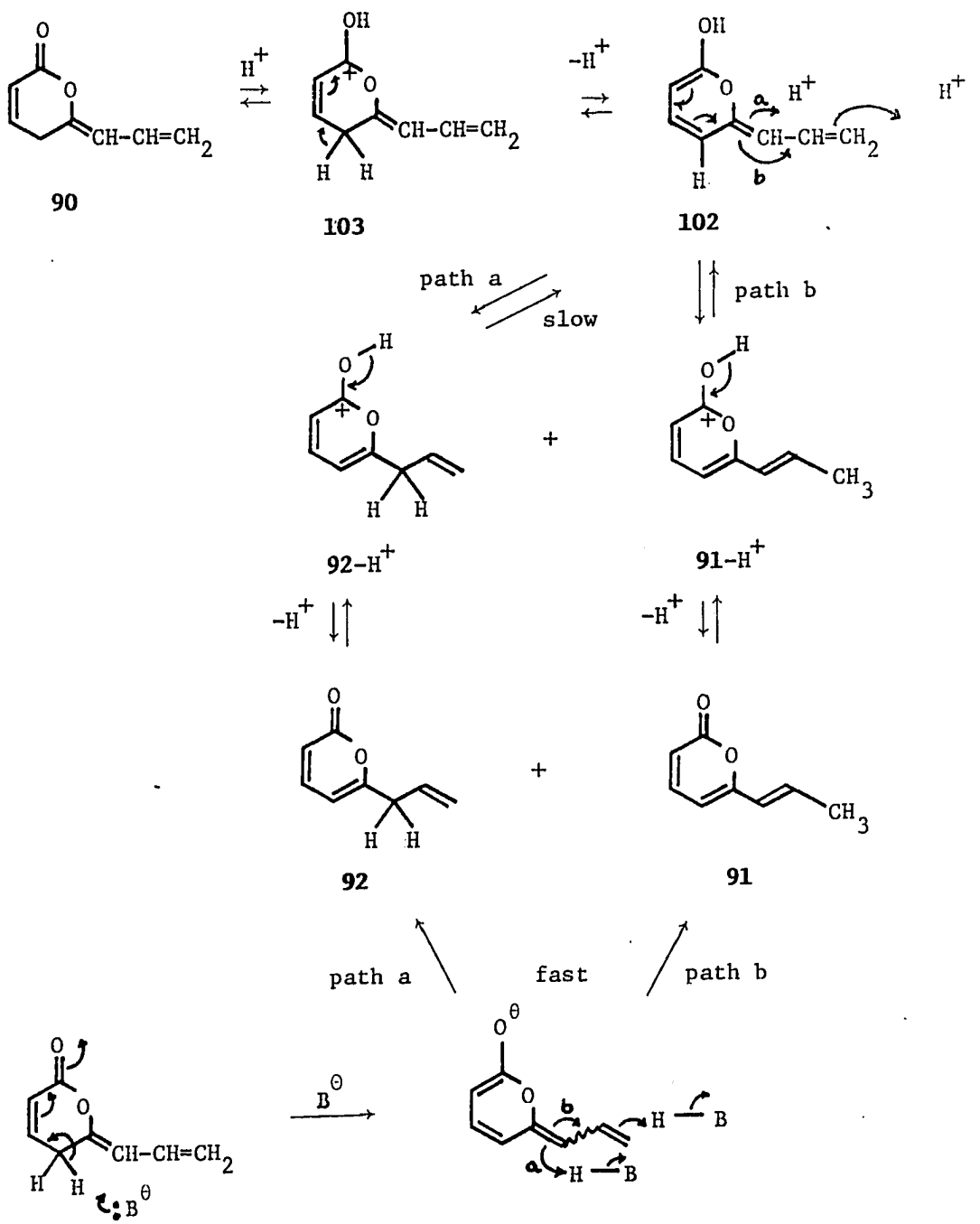
The formation of these pyrones is interesting because it complements the method of Rey *et al.* for the preparation of pyrones by the action of tertiary amines on α,β-unsaturated acid chlorides (reaction 20).[45] Their efforts to obtain the parent system (**91** and **92**) failed.



37 **105** **106** **38** 20.

The failure of vinylketene (**66**) to react with butadiene (**94**) or cyclohexadiene (**95**) was not too surprising, since these are not nearly as

Scheme 14:

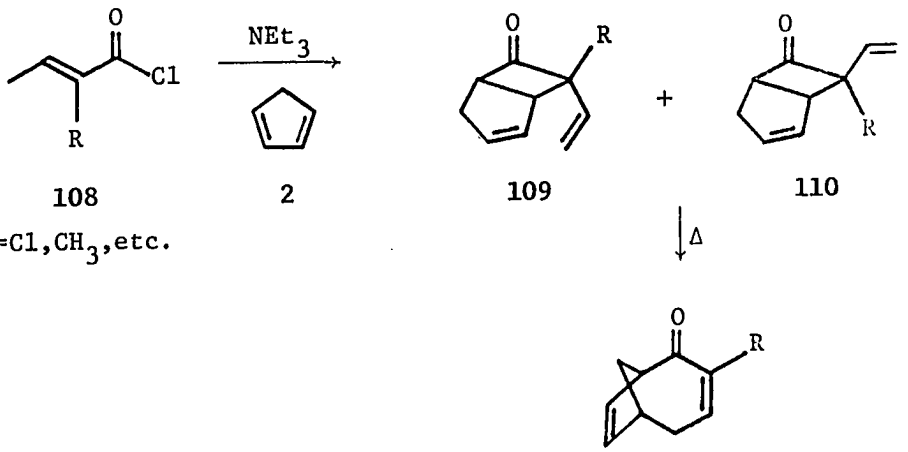


reactive as cyclopentadiene (**2**).[46] The experiments with methyl acrylate **96** and acetyl chloride **93** were attempts to find a carbonyl compound that would react with the diene portion of the ketene (**66**) in the same manner that **66** itself does in dimerization (reaction 27) in hopes that a new general synthesis of pyrones would be found.

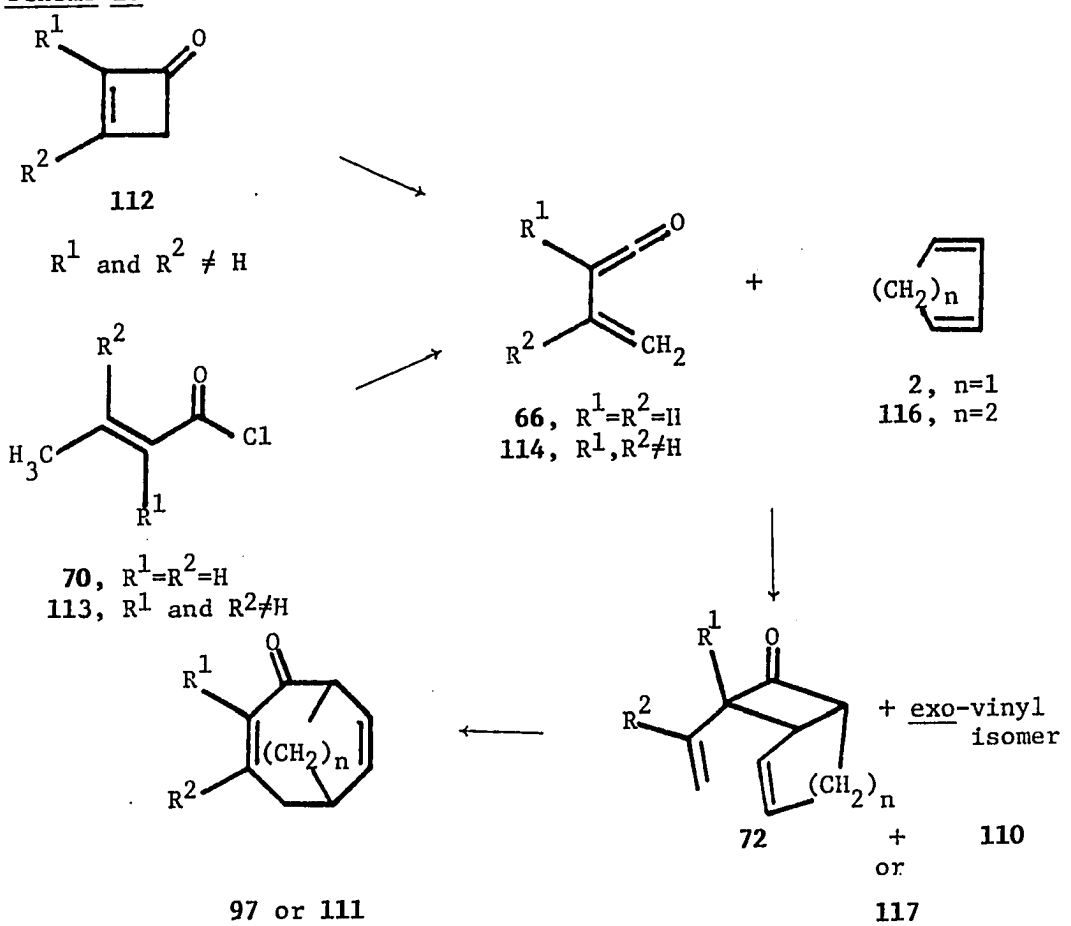
The [2+2] cycloaddition between a diene (**2**) and vinylketene (**66**) (reaction 28) followed by a Cope rearrangement to form the bicyclo-[4.2.1]dienone (**97**) (reaction 29) represents a new synthetic strategy. Huston, Rey and Dreiding recently employed this strategy towards the synthesis of derivatives of **97** (**107**) (Scheme 15).[47] They generated substituted vinylketenes <u>in situ</u> from α,β-unsaturated acid chlorides (**108**) and base and trapped them with cyclopentadiene (**2**). The α-position of **108** had to be a group other than hydrogen to prevent conjugation of the double bond in the basic medium. So, like the pyrone synthesis, the parent system (**97**) was inaccessible by their method. Both stereoisomeric adducts (**109** and **110**) were converted to the target molecule (**107**) although the <u>exo</u>-vinyl isomer (**110**) reacted slower than the <u>endo</u>-vinyl isomer (**109**). Danheiser and co-workers recently developed this approach for the synthesis of cycloctadienones (**111**) from cyclobutenones (**112**) or α,β-unsaturated acid chlorides (**113**) (Scheme 16).[15] They were able to control the conditions for the preparation of **72** and the <u>exo</u>-vinyl isomer (**110**, R=H) and prepared **97** in 18% overall yield from crotonyl chloride (**70**).

One reason why the yield of **97** in reaction 29 is not very good (40%) is suggested in the isolation of α-pyrone **92** from the product mixture

Scheme 15:

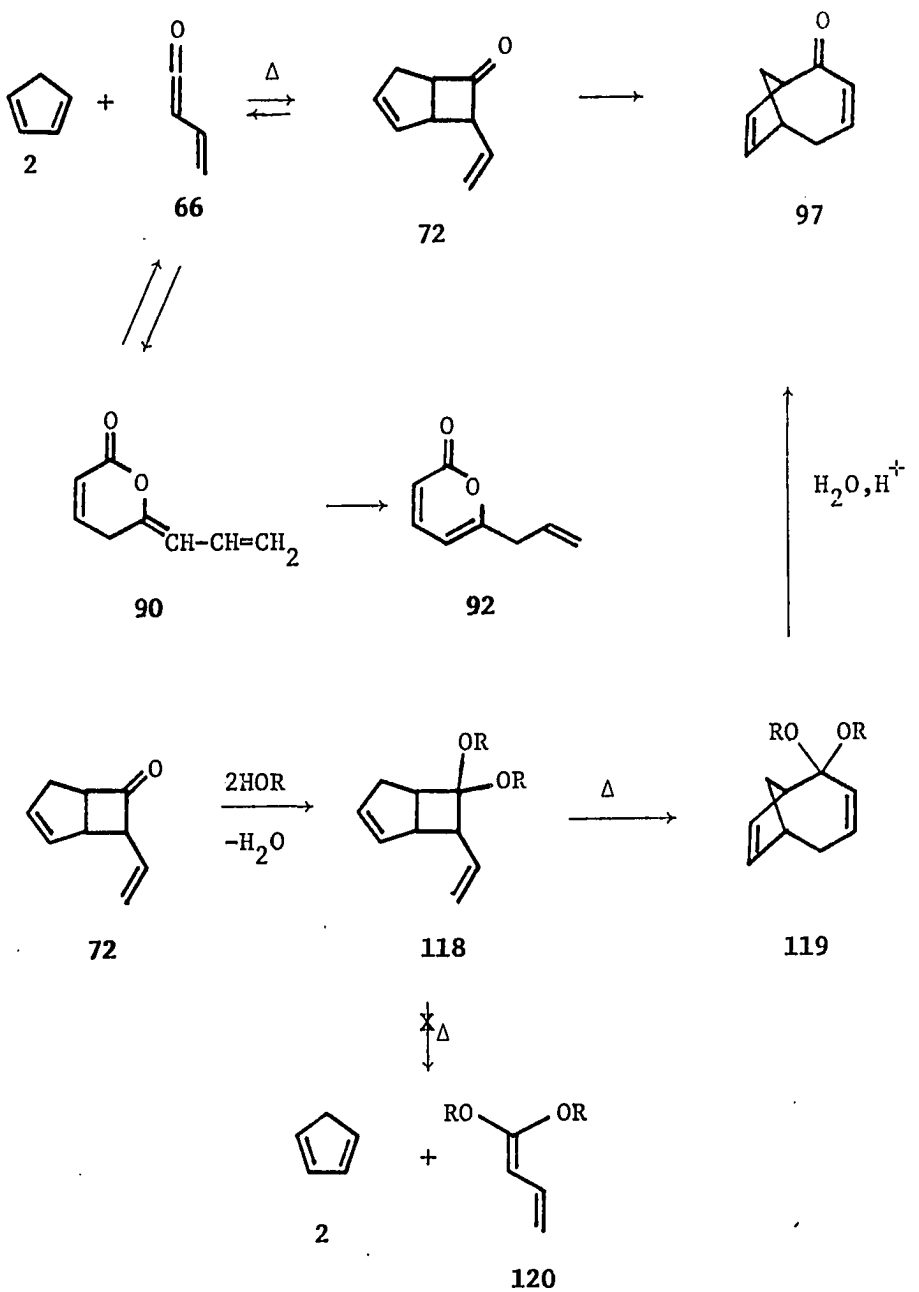


Scheme 16:



and by seeing cyclopentadiene (2) in the gc trace of the product mixture. These products suggest there is competition between the Cope rearrangement and a retro-[2+2]cycloaddition which gives vinylketene (66) and 2. A possible solution to this problem is ketalization of the cyclobutanone (72) prior to heating (Scheme 17).

Scheme 17:



EXPERIMENTAL

General

The basic flash vacuum pyrolysis (FVP) apparatus was described in part I of this thesis (pp. 39a-39b). It was patterned after the one described by Trahanovsky *et al.*[48] In addition to the basic unit, a second condenser was placed between the oven and the -196°C condenser. This condenser was cooled to -20°C by pumping through it isopropanol which had passed through a dry ice/isopropanol bath. A peristaltic pump was used to pump the isopropanol.

Infrared spectra were recorded on either a Beckman Model 4250, a Model 19A, or an Acculab II spectrophotometer. Proton NMR spectra were obtained on either a Varian A60, an EM360, a Hitachi R-20B, a JEOL FX-90Q, a Varian HA-100 or a Bruker NH-400. Carbon-13 NMR spectra were recorded on either the JEOL FX-90Q or a Bruker HX-90 with a Nicolet 1089 computer. Chemical shifts are reported in δ units down field from TMS (δ 0.00). Gas chromatography/mass spectrometry analysis was performed on a Finnigan Model 4023 gc/ms data system. Exact mass was determined on an AEI MS-902 high-resolution spectrometer. The ultraviolet spectrum was obtained with a Cary 14 UV-Vis spectrophotometer. The melting point was determined using a Thomas-Hoover capillary melting-point apparatus. Gas chromatography (gc) was performed on a Varian Aerograph series 1700 gc equipped with a thermal conductivity detector. Commercially available chemicals used and their sources are listed in Table 3.

Table 3. Commercially available compounds

Compound	Source
Acetic anhydride	Fisher Scientific Co.
Acetyl chloride	Fisher
Acetone-d_6	Norell, Inc.
Benzene	Fisher
Butadiene	Matheson Division of Searle Medical Products USA, Inc.
Calcium chloride	J. T. Baker Chemical Co.
Carbon dioxide(s)	Heller Carbonic
Carbon disulfide	Fisher
Carbon tetrachloride	Fisher
Chlorobenzene	Fisher
Chloroform-d	Aldrich Chemical Co.
Crotonic acid	Aldrich
Cyclohexadiene	Columbia Organic Chemicals
Dibromoethane	J. T. Baker
Dicyclopentadiene	The Matheson Co., Inc.
Diethyl ether	Fisher
Hexanes	Fisher
Isopropanol	Fisher
Magnesium sulfate	J. T. Baker
Methylacrylate	Aldrich
Nitrogen (g)	Quickway, Inc.
Nitrogen (l)	Air Products and Chemicals, Inc.
Silica gel	E. Merck, Darmstadt, Germany
Sodium bicarbonate	J. T. Baker
Sodium chloride	J. T. Baker
Tetramethylsilane (TMS)	Norell, Inc.
p-Toluenesulfonic acid	J. T. Baker

Cyclopentadiene (2)

This was prepared from dicyclopentadiene using an adaptation of the method of Mardanov *et al.*[49] The dimer was heated to 160-170°C with stirring and the monomer thus formed was distilled through a 6" fractionating column into an ice-cooled receiver: ^{1}H NMR (60 MHz, CCl_4) δ 5.6 (m, 4 H), 2.3 (m, 2 H).

Crotonic Anhydride (**83**)

This compound was prepared following the procedure described by Clover and Richmond.[50] In a 1-L flask equipped with a reflux condenser and a drying tube filled with $CaCl_2$, crotonic acid (85 g, 0.99 mole) and acetic anhydride (300 g, 2.9 mole) were heated to a vigorous reflux for 24 h. Acetic acid and excess anhydride were removed by distillation under reduced pressure and the residue was fractionally distilled (1' column packed with glass helices) to afford 59 g of **83** (99.9% pure by gc: 10% ov-1 on chromosorb w, 7.5' x 1/8"): bp 85-90°C (6 mm Hg) [lit.[50] bp 128-130° (19 mm Hg)]; IR (neat) 1790, 1725, 1655, 1085, 965 cm^{-1}; ^1H NMR (60 MHz, CCl_4)δ 7.05 (d of q, J_d=15 Hz, Jq=7.0 Hz, 2 H), 5.8 (d of q, J_d=15 Hz, J_q=2.1 Hz, 2 H), 1.9 (d of d, J_d=2.1 Hz, J_d=7.0 Hz, 6 H).

Vinylketene (**66**)

Solutions of this compound were prepared by pyrolyzing crotonic anhydride (**83**) at 530°C and 0.01-0.1 torr at a rate of about 1 g per h. The solvent was distilled into the -196°C condenser before, during and after pyrolysis. Best results were obtained when the level of $N_2(\ell)$ was raised while solvent was introduced, then lowered so that the ketene was deposited on a layer of solid solvent. At the end of the pyrolysis, solvent was distilled in fast enough that it ran down into the ketene before freezing. In this way, when the frozen solution was later melted, no ketene was left on the walls of the condenser to polymerize. The amount of **83** pyrolyzed and the amount and type of solvent used depended

on the experiment to be performed. For NMR experiments, 100 mg of **83** was pyrolyzed and 5 mL of solvent was used. For ^{1}H NMR on the HA 100 spectrometer, CS_2 was used and after the solution had been warmed to -78°C in a dry ice/isopropanol bath, an internal standard ($BrCH_2CH_2Br$) for the yield determination was added. Then part of the solution was transferred via pipette to an NMR tube and TMS was added. The ^{13}C-NMR experiment required $CDCl_3$ for an internal deuterium lock so a 1:1 mixture of $CDCl_3$ and CS_2 was used so that at -78°C a liquid solution was obtained. The NMR spectra showed **66** (22% yield) and methylacetylene (**84**) (40% yield). Compound **66**: ^{1}H NMR (100 MHz, CS_2)δ 5.95 (H_b, d of d of d, J_{ab} = 11 Hz, J_{bc} = 11 Hz, J_{bd} = 18 Hz, 1 H), 4.86 (H_d, d of d, J_{bd} = 18 Hz, J_{cd} = 1.5 Hz, 1 H), 4.55 (H_c, d of d, J_{bc} = 11 Hz, J_{cd} = 1.5 Hz, 1 H), 4.02 (H_a, d, J_{ab} = 11 Hz, 1 H); ^{13}C NMR (22.5 MHz, $CDCl_3$/CS_2)δ 200.2 (s), 121.9 (d, J_{CH} = 155 Hz), 109.1 (d of d, J_{CH} = 154, 162 Hz), 28.6 (d, J_{CH} = 173 Hz). Compound **84**: ^{1}H NMR (100 MHz, CS_2)δ 1.89 (s, 1 H), 1.88 (s, 3 H) [lit.[51] NMR (60 MHz)δ 1.9 (s)]; ^{13}C NMR (22.5 MHz, $CDCl_3/CS_2$)δ 80.4 (s), 68.3 (d, J_{CH} = 248 Hz), 3.7 (q, J_{CH} = 132 Hz).

2,5,6-Trihydro-6-allylidenepyran-2-one (**90**)

Vinylketene (**66**) was prepared from crotonic anhydride (**83**) (3.5 g, 23 mmole). Before, during and after pyrolysis, $CDCl_3$ and CS_2 (1:1, 20 mL) was distilled into the -196°C condenser. After pyrolysis, the contents of the -196°C condenser were warmed quickly to -78°C under N_2, then shaken occasionally until the mixture was homogeneous. It was

removed from the dry ice/isopropanol bath and allowed to warm to room temperature which discharged the bright yellow color. The solution was analyzed by infrared and ^{13}C-NMR spectroscopy, then an internal standard was added ($BrCH_2CH_2Br$) and a ^{1}H-NMR spectrum was obtained which showed a clean formation of **90** (22% yield from **83**): IR (neat) 1760, 1680, 1240, 1125 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3/CS_2$)δ 6.81 (d of t, J_d = 9.8 Hz, J_t = 4.2 Hz, 1 H), 6.70 (d of d of d, J_1 = 17.5 Hz, J_2 = J_3 = 10.7 Hz, 1 H), 5.95 (d of t, J_d = 9.8 Hz, J_t = 2.4 Hz, 1 H), 5.40-4.90 (m, 3 H), 3.20 (m, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3/CS_2$)δ 176.1 (s), 160.7 (s), 145.0 (d, J_{CH} = 170 Hz), 128.7 (d, J_{CH} = 156 Hz), 119.3 (d, J_{CH} = 175 Hz), 116.5 (t, J_{CH} = 160 H_z), 112.3 (d, J_{CH} = 156 Hz), 28.6 (t, J_{CH} = 132 Hz).

Sibirinone (**91**)

The crude dimer (**90**) (0.68 g) was dissolved in benzene (3 mL) and added to a solution of p-toluenesulfonic acid (21 mg) in benzene/ether (2:1, 1 mL). The resulting solution was stirred at 58°C for 20 h. The solution was diluted with ether and washed with $NaHCO_3$ (sat.) and brine. The aqueous washings were extracted with ether and the ether solutions were combined and dried over $MgSO_4$. Distillation of the solvent afforded a yellow oil which by ^{1}H NMR was a mixture of **91** and the allylpyrone (**92**) (9:1 mole ratio). The yield of **91** was 45% by NMR integration vs. an internal standard ($BrCH_2CH_2Br$). Crystallization from ether - hexanes afforded pure **91**: mp 55.0-55.3°C (lit. mp 58-59°C), IR (mull) 1735, 1660, 1540, 1095, 820, 790 cm^{-1} (lit.[41] IR 1740, 1715, 1653, 1605, 1550

cm^{-1}); ^1H NMR (300 MHz, acetone-d_6)δ 7.25 (d of d, J_1 = 9.5 Hz, J_2 = 6.5 Hz, 1 H), 6.71 (d of q, J_d = 15 Hz, J_q 7.0 Hz, 1 H), 6.14 (d, J = 9.5 Hz, 1 H), 6.03 (d, J = 6.5 Hz, 1 H), 5.99 (d of q, J_d = 15 Hz, J_q = 1.2 Hz, 1 H), 1.92 (d of d, J_1 = 7.0 Hz, J_2 = 1.2 Hz, 3 H) [lit.[41] ^1H NMR δ 7.28 (d of d, J_1 = 9.5 Hz, J_2 = 6.5 Hz, 1 H), 6.67 (d of q, J_d = 15 Hz, J_q = 7.0 Hz, 1 H), 6.12 (d, J = 9.5 Hz, 1 H), 6.03 (d of q, J_d = 15 Hz, J_q = 1.2 Hz, 1 H), 5.97 (d, J = 6.5 Hz, 1 H), 1.87 (d of d, J_1 = 7.0 Hz, J_2 = 1.2 Hz, 3H)]; ^{13}C NMR (22.2 MHz, acetone-d_6)δ 161.4 (s), 160.1 (s), 144.8 (d, J_{CH} = 163 Hz), 133.9 (d, J_{CH} = 157 Hz), 124.1 (d, J_{CH} = 160 Hz), 114.1 (d, J_{CH} = 171 Hz), 103.7 (d, J_{CH} = 170 Hz), 18.3 (q J_{CH} = 127 Hz); MS (70 eV) 136 (59), 108 (100), 95 (34), 79 (98), 67 (23), 51 (16) [lit.[41] MS 136 (50), 108 (95), 95 (40), 89 (100)].[52]

6-Allyl-α-pyrone (**92**)

The crude dimer (**90**) (0.5 g) was dissolved in ether (2 mL) and stirred with $NaHCO_3$ (sat.) (2 mL) overnight. The layers were separated and the aqueous layer was washed with ether. The organic parts were combined, dried over $MgSO_4$ and filtered. Removal of the solvent by distillation afforded a yellow oil. ^1H NMR indicated a mixture of **92** and **91** (3:1 mole ratio). The yield of **92** was 42% and that of **91** was 13% by integration vs. an internal standard ($BrCH_2CH_2Br$). The isomeric pyrones were subjected to thin layer chromatography (silica gel, ether elution) which failed to separate them. An analytical sample of **92** was obtained by gc prep (1/8" x 4', 3% OV-17, 115°C): IR (neat) 1745, 1648, 1570, 1098, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)δ 7.28 (d of d, J_1 = 6 Hz, J_2 = 9 Hz, 1 H), 6.17 (d, J = 9 Hz, 1 H), 5.99 (d, J = 6 Hz, 1 H), 5.88 (d of d of t, J_{cis} = 10 Hz, J_{trans} = 16 Hz, J_t = 8 Hz, 1 H), 5.23

(geminal vinyl protons) (two overlapping d of d, J_{trans} = 16 Hz, J_{cis} = 10 Hz, J_{gem} = 2 Hz, 2 H), 3.25 (d, J = 8 Hz, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 164.3 (s), 162.3 (s), 143.7 (d, J_{CH} = 162 Hz), 131.2 (d, J_{CH} = 161 Hz), 119.2 (t, J_{CH} = 154 Hz), 113.3 (d, J_{CH} = 172 Hz), 102.8 (d, J_{CH} = 171 Hz), 38.0 (t, J_{CH} = 128 Hz); MS (70 eV) 136 (27), 108 (6), 95 (100), 79 (5), 77 (5), 67 (4), 53 (5); $C_8H_8O_2$, calculate 136.05243, measure 136.05206, error: 2.7 ppm.

7-Vinylbicyclo[3.2.0]hept-2-en-6-one (**72**)

Vinylketene (**66**) was prepared from crotonic anhydride (**83**) (4.0 g, 26 mmole). Before, during and after pyrolysis, freshly prepared cyclopentadiene (2) (10 mL) was distilled into the -196°C condenser. After pyrolysis was complete, the contents of this condenser was shaken and warmed to room temperature. The bright yellow color of the solution at low temperatures was discharged before it reached 0°C. After distillation of the excess **2**, the residue was chromatographed on silica gel. Fractions containing **72** were combined and concentrated to afford 1.0 g. Vacuum distillation afforded 0.8 g of **72** which was isomerically pure by ^1H and ^{13}C NMR (23% yield based on anhydride): bp 44-45° (0.1 mm Hg); IR (neat) 1780, 1645, 1445, 1355, 1245, 1165, 1145, 1030, 990, 925, 795, 710 cm^{-1} [lit.[33] IR 1770, 1630, 1435, 1350, 1235, 1135, 980, 915, 795, 710 cm^{-1}]; ^1H NMR (60 MHz, CCl_4)δ 5.8 (m, 2 H), 5.6-4.9 (m, 3 H), 4.1 (m, 1 H), 3.7 (m, 2 H), 2.5 (m, 2 H) [lit.[33] ^1H NMR (250 MHz, $CDCl_3$) δ 5.91-5.88 (m, 1 H), 5.80-5.75 (m, 1 H), 5.56 (d of d of d, J = 7.5, 10.3, 17.3 Hz, 1 H) 5.22-5.12 (m, 2H), 4.13 (d of d of d, J = 1.1, 7.5,

8.3 Hz, 1 H) 3.89-3.81 (m, 1 H), 3.77-3.68 (m, 1 H), 2.69 (d of t, J = 4.4, 17.0 Hz, 1 H), 2.44 (d of d of d of d, J = 2.0, 4.2, 9.0, 1.70 Hz, 1 H)]; ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 211.2 (s), 134.0 (d, J_{CH} = 163.6 Hz), 129.7 (d, J_{CH} = 159.6 Hz, 2 C) 118.1 (t, J_{CH} = 158.8 Hz), 67.6 (d, J_{CH} = 127.9 Hz), 59.3 (d, J_{CH} = 141.9 Hz), 42.9 (d, J_{CH} = 150.7 Hz), 33.9 (t, J_{CH} = 132.3 Hz) [lit.[33] ^{13}C NMR (62.8 MHz, $CDCl_3$)δ 212.2, 134.5, 129.9 (2 C), 118.6, 68.0, 59.6, 43.1, 34.2]; MS (70 eV) 134 (11), 106 (18), 105 (17), 91 (40), 79 (34), 68 (99), 66 (100) [lit.[33] MS 134 (M^+)]; $C_9H_{10}O$, calculated 134.07317, measured 134.07366, error: 3.7 ppm.

Bicyclo[4.2.1]nona-3,7-dien-2-one (97)

A 5% solution of the vinylcyclobutanone (72) was purged with nitrogen, then heated to reflux under N_2 for 2 h. After gc analysis, which showed the presence of cyclopentadiene, the solvent was distilled under reduced pressure and the residue was chromatographed on silica gel (5% ether in hexanes elution). The fractions containing 97 were combined and concentrated to afford 0.38 g. Distillation afforded 0.32 g of 97 (40% yield): bp 65°C (0.5 mm Hg); IR (neat) 1675, 880 cm^{-1}; UV (EtOH) 277 nm (log ε 4.22), 327 (2.32); ^{1}H NMR (100 MHz, CCl_4) δ 5.97-5.50 (m, 4 H), 3.37 (m, 1 H), 3.09 (m, 1 H), 2.90-2.50 (m, 2 H), 2.37-1.87 (m, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 205.3 (s), 139.9 (d, J_{CH} = 153.7 Hz), 135.5 (d, J_{CH} = 164.0 Hz), 131.7 (d, J_{CH} = 168.4 Hz), 127.0 (d, J_{CH} = 159.6 Hz), 57.5 (d, J_{CH} = 135.3 Hz), 41.1 (d, J_{CH} = 133.1 Hz), 38.8 (t, J_{CH} = 131.6 Hz), 32.4 (t, J_{CH} = 130.9 Hz); MS (70 eV) 134 (34),

106 (5), 105 (4), 91 (8), 79 (7), 68 (100), 66 (69), 40 (17), 39 (27); $C_9H_{10}O$, calculated 134.07317, measured 134.07302, error: 1.1 ppm. Allylpyrone (**92**) was also isolated from the reaction mixture and was identified by IR and NMR.

Attempted Reactions of Vinylketene with Potential Ketenophiles

Vinylketene **66** was prepared in the usual way from 1.0 g of anhydride. In separate experiments, acetyl chloride (**93**) (10 mL), butadiene (**94**) as a 1:1 solution in CS_2 (10 mL), cyclohexadiene (**95**) (10 mL), and methyl acrylate **96** (10 mL) were distilled into the -196°C condenser before, during, and after pyrolysis. In each case, the major product isolated after distillation of excess reagent and chromatography was dimeric material (**90** and its isomers) characterized by TLC, NMR and IR: the mixture had the same characteristics when a solution of vinylketene in CS_2 is treated the same way.

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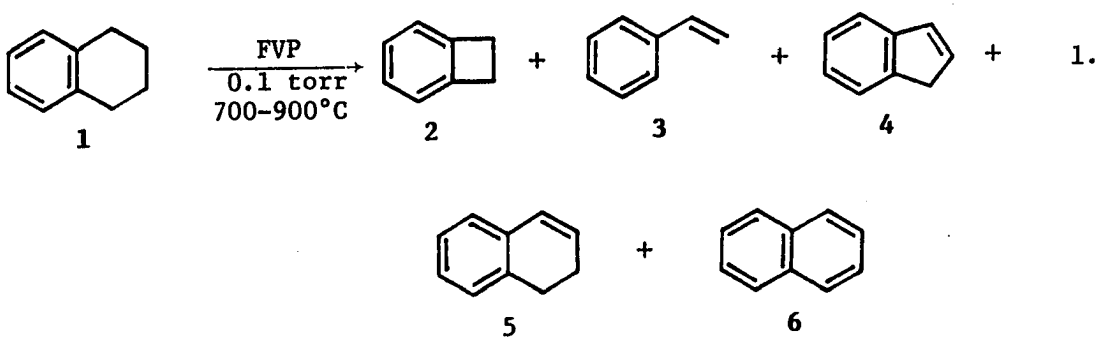
52. In reference 41, the m/e value of the (M-CO-CHO) peak should be 79 instead of 89.

PART III. SYNTHESIS AND FLASH VACUUM PYROLYSIS OF 5,8-DIPHENYLTETRALIN

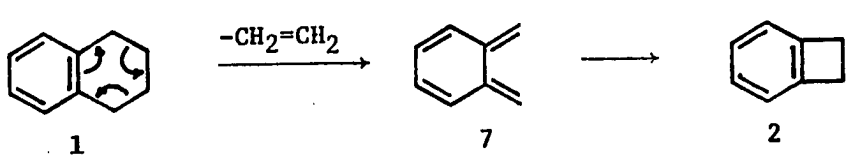
INTRODUCTION

Recently, there has been considerable interest in the thermal chemistry of tetralin (1)[1-9] because it is used as a hydrogen-donor solvent in coal liquifaction[10] and as a model of one of the important structural features of coal.[11] In the flash vacuum pyrolysis (FVP) of 1, the major products are benzocyclobutene (2), styrene (3), indene (4), 1,2-dihydronaphthalene (5), and naphthalene (6) (reaction 1).[1,3]

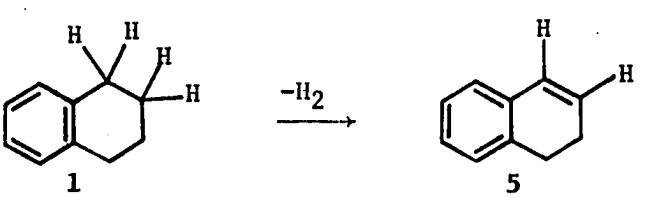


1 2 3 4 5 6 1.

Compound 2 is formed by a retro-Diels-Alder reaction (reaction 2)[1] and Compound 5 is the result of 1,2-elimination of hydrogen (reaction 3).[3]



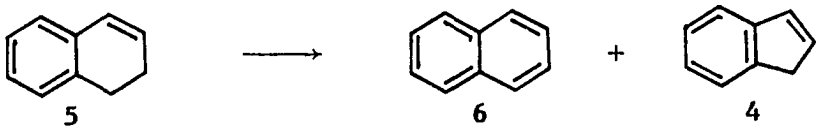
1 7 2 2.



1 5 3.

Styrene (3) is believed to arise primarily by isomerization of 2 (reaction 4)[3] while compounds 4 and 6 are believed to be secondary products of pyrolysis of 5 (reaction 5).[3]

2 3 4.



5 6 4 5.

The ratios of these products in the pyrolysis of **1** are strongly dependent on the conditions of the pyrolysis.[3] Generally, naphthalene (**6**) is the major product, especially at high conversions. It is believed that dehydrogenation that leads to **5** and **6** is catalyzed by collisions with the surfaces of the reactor and that the lowest energy homogeneous thermal reaction of tetralin (**1**) is the retro-Diels-Alder reaction that leads to benzocyclobutene (**2**) (reaction 2).[3] This follows from experiments in which the decomposition of tetralin is laser-induced.[3] When tetralin is decomposed this way, both by direct multiphoton irradiation and by SiF_4-sensitiziation, benzocyclobutene (**2**) and styrene (**3**) are the

major products (Table 1). Under these conditions, surface chemistry has been eliminated. Table 1 also shows how increasing the vacuum in FVP affects the outcome. At the lowest pressure, loss of ethylene becomes comparable to loss of hydrogen. This is probably the result of shorter residence time in the hot zone.

Table 1. Product distribution for thermolysis of tetralin (**1**)

Conditions	Products, %[a]						Conversion, %	Reference
	2	**3**	**4**	**5**	**6**	Other		
1. Flow pyrolysis, latm N_2, 750°C[b]	2.4	18.3	17.5	10.7	45.8	4.7	74.8	3
2. FVP, 0.1 torr, 737°C[b]	6	10	5	55	10	13	6	1
3. FVP, 0.1 torr, 888°C[b]	6	23	15	5	31	20	89	1
4. FVP, 0.05 torr, 750°C[b]	34.7	9.9	4.1	31.8	8.2	11.3	3.7	3
5. Multiphoton excitation[c]	54.8	19.7	5.5	9.0	Trace	11.0	0.8	3
6. SiF_4-sensitization, T_{max}-1490°C[d]	38.2	20.1	9.4	15.5	5.6	11.2	7.7	3

[a]Numbers are percent of total product found.

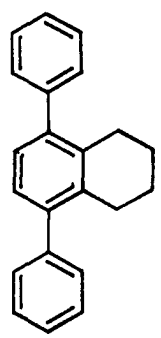
[b]All pyrolyses (entries 1-4) were carried out in quartz reactors.

[c]Multiphoton excitation was accomplished with a pulsed CO_2 TEA laser tuned to 945.99 cm^{-1}, energy/pulse 0.8 J, 2790 pulses, 0.325 torr **1**.

[d]Compound **1** (0.325 torr) and SiF_4 (6 torr) were irradiated with an unfocused, pulsed CO_2 TEA laser tuned to 1027.36 cm^{-1}. Pure **1** does not decompose under unfocused conditions, energy/pulse ranged from 0.11 to 0.27 J/pulse, 180 pulses.

It was decided that the surface-catalysis hypothesis could be tested by introducing bulky, thermally-inert groups into the tetralin nucleus where they would not interfere with the retro-Diels-Alder reaction (reaction 2) but would protect the molecule from collisions with

the surfaces that catalyze loss of hydrogen. Benzylic hydrogens, being the most thermally labile, need the most protection. In order that the protecting groups would not affect the retro-Diels-Alder reaction, they would have to be bound to the aromatic ring. Substitution in the aliphatic ring is known to infuence the thermal chemistry there.[1] The phenyl group was chosen as being fairly bulky and the least likely to react pyrolytically. Thus, the molecule chosen for pyrolysis was 5,8-diphenyltetralin (**9**). If the loss of ethylene in the pyrolysis of **9** is comparable to that in the FVP of tetralin (**1**) but the loss of hydrogen is diminished, then the surface-catalysis hypothesis will be supported.



9

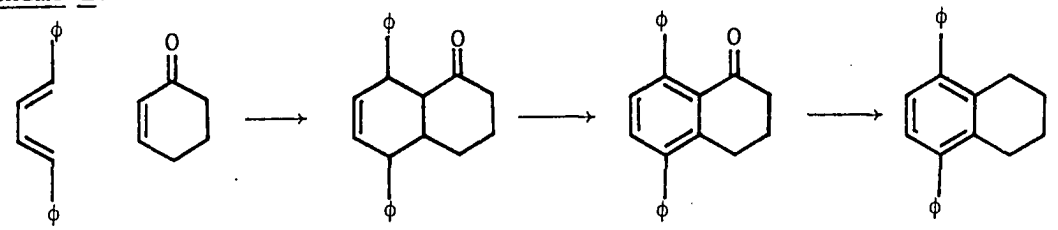
5,8-Diphenyltetralin has never been synthesized before, so the first task was to design a workable synthesis of **9**. The second task was to pyrolyze **9** and **1** under identical conditions in order that the results could be compared.

RESULTS

5,8-Diphenyltetralin (**9**) was prepared two different ways. The first method gave low yields but was useful as an independent synthesis to confirm the structure of **9**. Both methods began with a Diels-Alder reaction to form the central ring to ensure the correct substitution pattern.

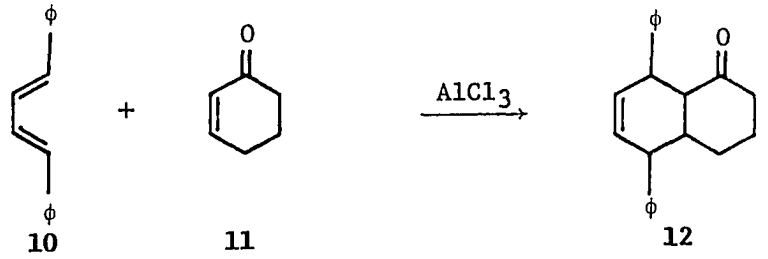
The first method is shown in Scheme 1. The first step in the synthesis was a Diels-Alder reaction between 1,4-diphenyl-1,3-butadiene (**10**) and cyclohexenone (**11**) to give **12**. This was followed by aromatization of **12** to give **13** and reduction of the carbonyl group of **13** to afford **9**.

Scheme 1:



10 **11** **12** **13** **9**

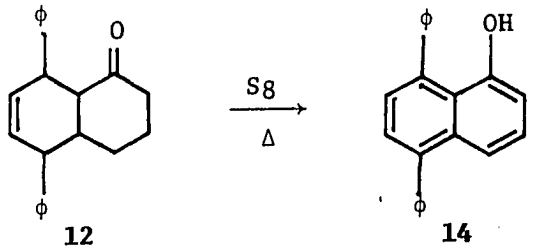
Cyclohexenone (**11**) is not a good dienophile and most Diels-Alder reactions with this compound are Lewis-acid catalyzed.[12] This was the method used here, but the yield of the adduct (**12**) was low (reaction 6). A substantial amount of high molecular weight hydrocarbons was obtained and when the reaction was followed by chromatography, the rapid disappearance of the diene (**10**) was observed while the enone (**11**) remained



10 11 12 6.

virtually unchanged. Varying the ratios of the reactants and running high-temperature, uncatalyzed reactions failed to improve the yield. Compound **12** was obtained as a mixture of two stereoisomers formed in about a 4:1 ratio. Each was characterized by a broad singlet in the olefinic region of the ^{1}H-NMR spectrum (Figure 1) and a shift of the carbonyl stretching frequency to higher wave numbers in the IR spectrum.

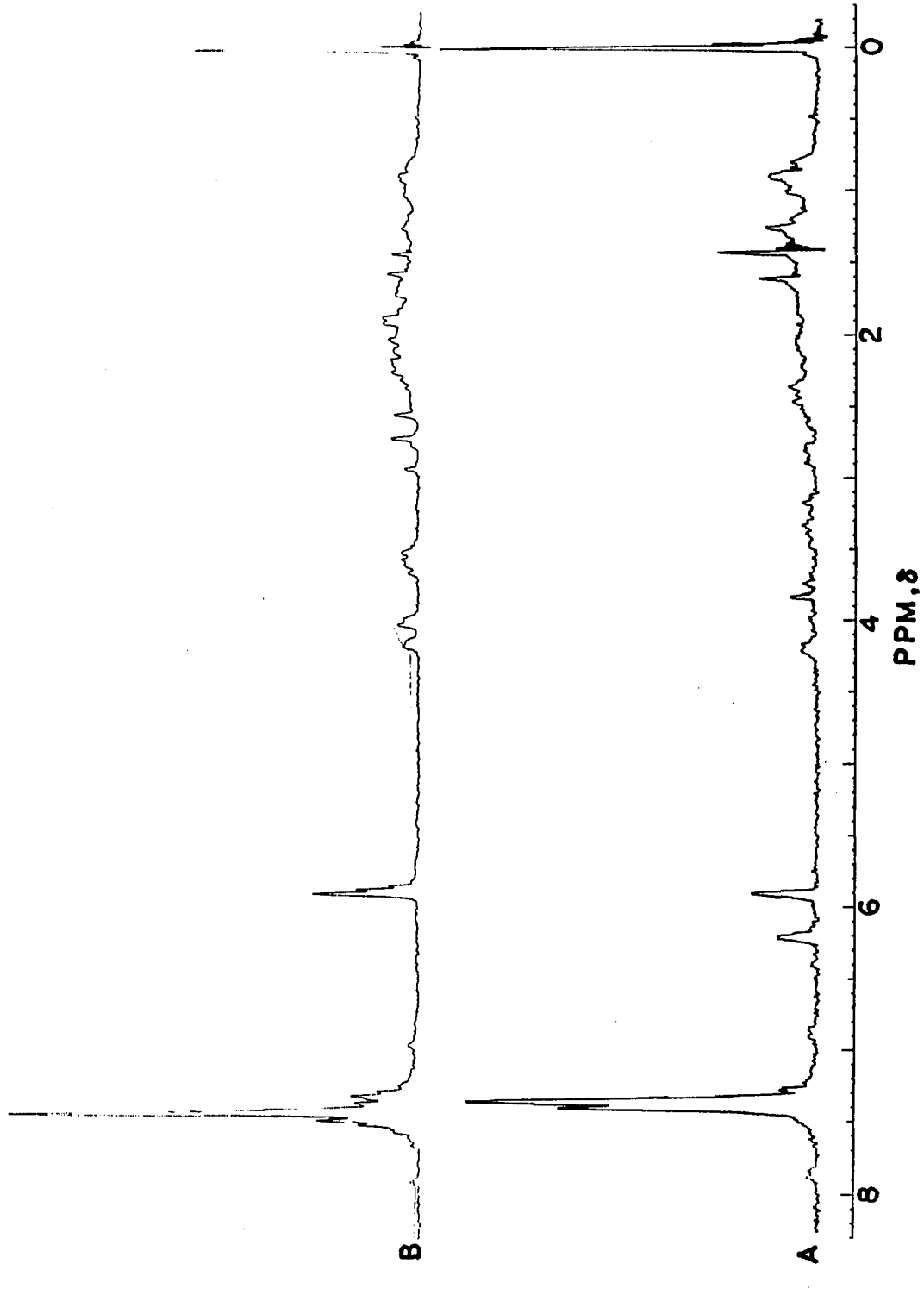
Surveying the literature on aromatization of Diels-Alder adducts suggested a convenient method might be by reaction with sulfur.[13] This resulted in complete aromatization to the α-naphthol (**14**) (reaction 7).



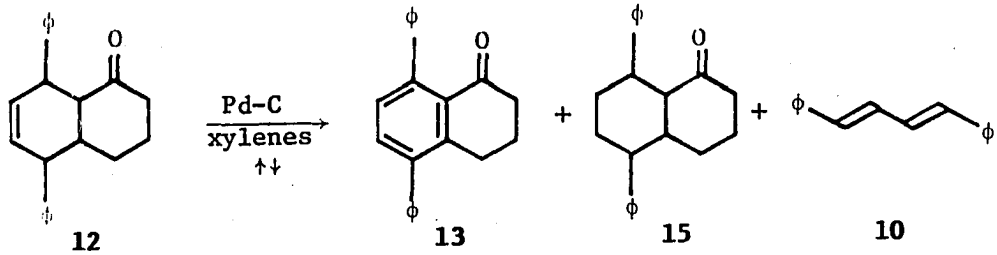
12 14 7.

Literature on the catalytic hydrogenation of α-naphthols indicated that high pressures were required and that the phenol ring might not be specifically hydrogenated[14] so another means of aromatizing **12** was sought. Dichlorodicyanoquinone, an excellent dehydrogenating agent for

Figure 1. Proton NMR spectra (60 MHz) of 5,8-diphenyl-1,2,3,4,4a,5,8,8a-octahydronaphthalen-1-one (**12**): (a) first isomer to elute from chromatography column, (b) second isomer to elute mixed with the first


B
A
8
6
4
2
0
PPM, δ

some systems,[13] only gave an intractable product mixture so palladium on carbon in refluxing xylenes[13] was tried with limited success. The desired product (**13**) was obtained, but only in low yield (reaction 8).

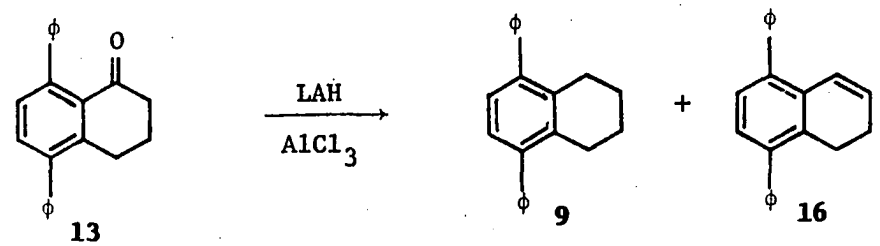


12 **13** **15** **10** 8.

Other products isolated were **10** and the hydrogenated product, **15**. Also, starting material (**12**) was recovered even after days of refluxing.

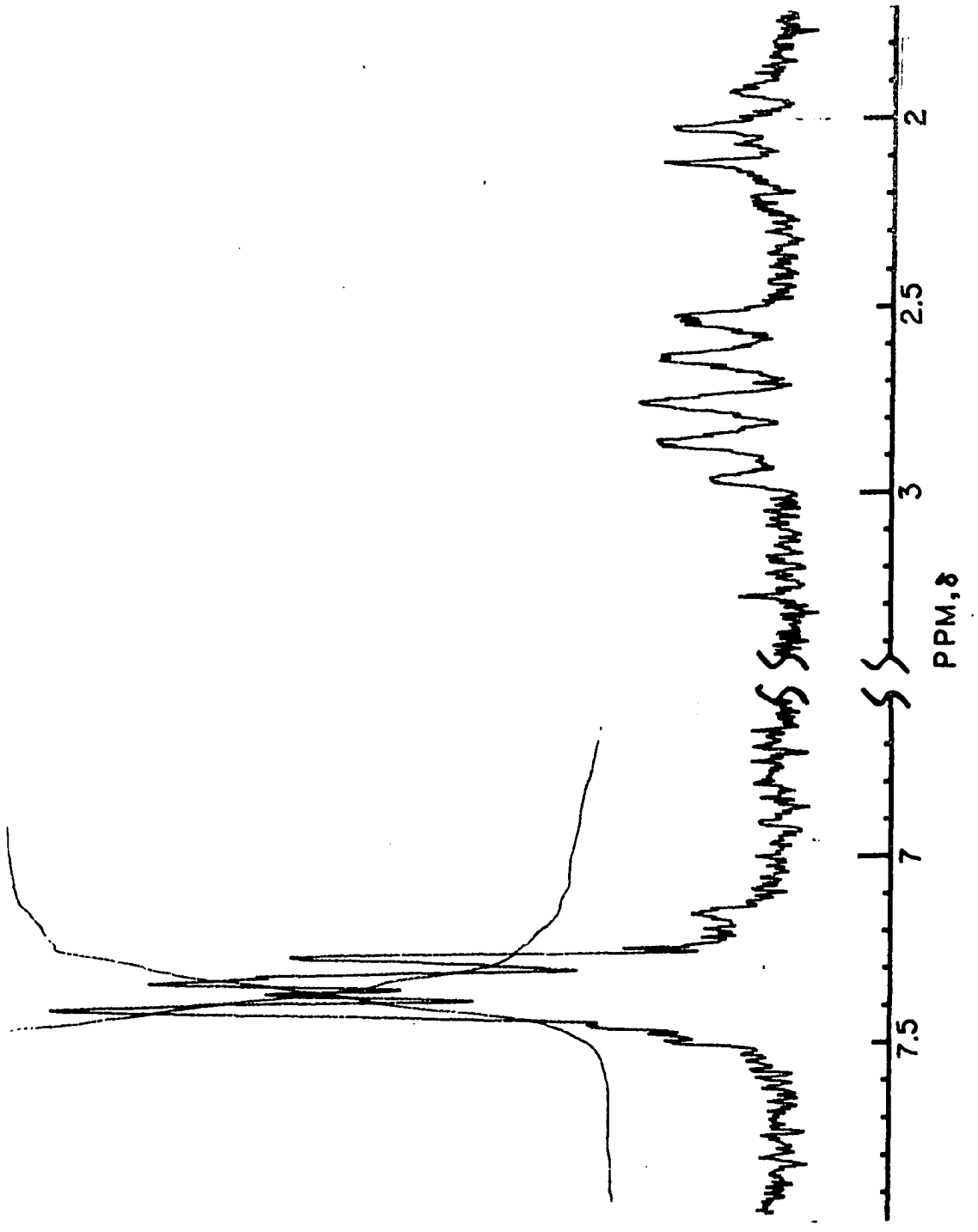
Compound **13** was identified by its IR, ^{1}H-NMR and ^{13}C-NMR spectra. The ^{13}C NMR contained three aliphatic signals, a carbonyl peak, and 14 different aromatic signals. The ^{1}H-NMR spectrum showed two triplets at δ 2.88 and 2.63 coupled to a multiplet at δ 2.08 (Figure 2).

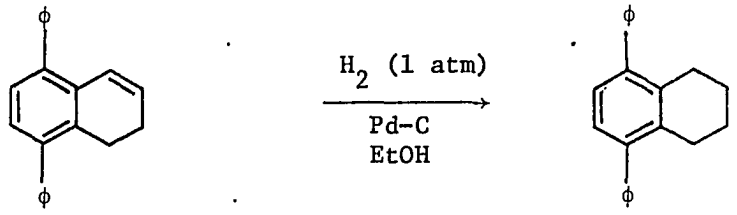
Compound **13** was easily converted to the target molecule (**9**) by treatment with lithium aluminum hydride (LAH) and aluminum chloride using the general procedure of Blackwell and Hickinbottom (reaction 9).[15] Some olefin (**16**) was formed, which was easily converted to **9** by catalytic hydrogenation (reaction 10).[14]



13 **9** **16** 9.

Figure 2. Proton NMR spectrum (60 MHz) of 5,8-diphenyl-1-tetralone (13)


7.5
7
3
2.5
2
PPM, δ



16 **9** 10.

Compound **9** was identified by its IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra. The mass spectra indicated the appropriate molecular weight and the IR showed the absence of a carbonyl stretching band. The ^{13}C-NMR spectrum showed two aliphatic signals and 7 aromatic signals which fit the molecule and showed the higher degree of symmetry over the tetralone (**13**). The ^{1}H-NMR spectrum (Figure 3) indicated the tetralin nucleus by two aliphatic multiplets which were indistinguishable from the spectrum of the parent compound (**1**).

Even though the target molecule (**9**) was finally obtained, there was only a small amount. Thus, since the yields of two of the reactions were so low, an alternate synthesis was sought. The naphthalene (**17**) is a known compound and, since the reduction of naphthalene (**6**) to tetralin (**1**) by catalytic hydrogenation (reaction 11) is convenient,[16] synthesis through **17** was chosen. It was felt that hydrogenation of 17 would give primarily 9 since the phenyl groups should protect the central ring to which they are bound.

There are a few published procedures for the synthesis of **17**.[17-19] One of the older ones[18] was chosen since it appeared convenient and high-yielding. The first step was a Diels-Alder reaction between a very hot

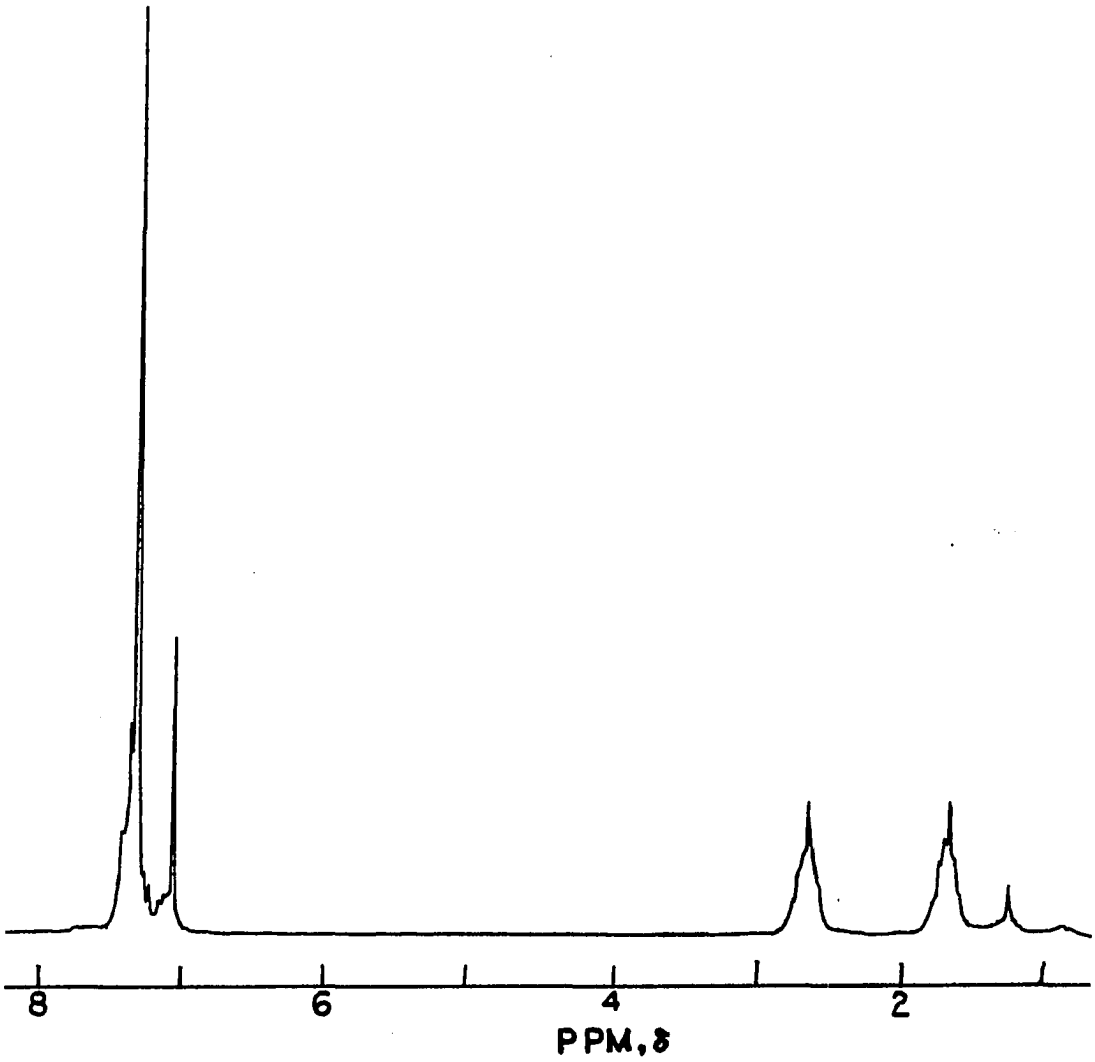
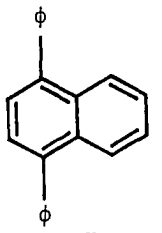
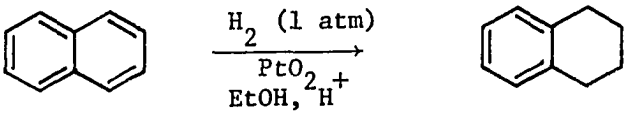


Figure 3. Proton NMR spectrum (90 MHz) of 5,8-diphenyltetralin (9)

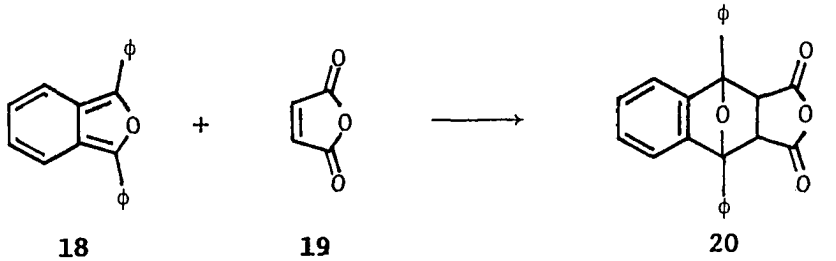


17

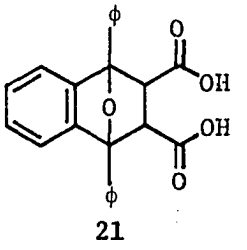


6 1 11.

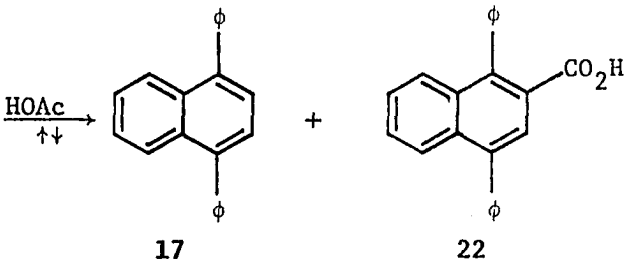
diene (18) and a hot dienophile (19). The adduct (20) was formed in excellent yield (reaction 12). The adduct (20) was hydrolyzed and acidified to give the diacid (21) (reaction 13), which was dehydrated and decarboxylated in refluxing acetic acid to give 17 and a β-naphthoic acid (22) (reaction 14). Compound 22 was decarboxylated to give more of the naphthalene (17) (reaction 15).[17]



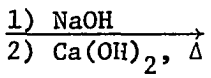
18 19 20 12.



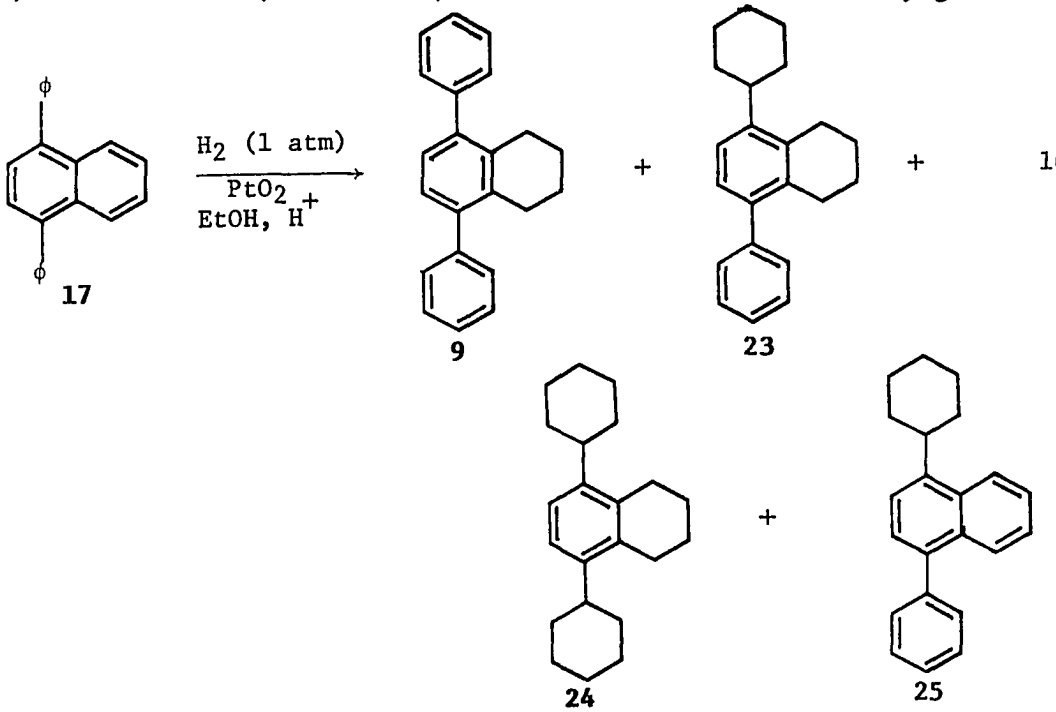
20 21 13.

21  14.

17 22

22  17 15.

Hydrogenation of **17** was accomplished using Adam's catalyst in acidic ethanol under conditions similar to those of Price, Enos and Kaplan for the reduction of naphthalene (6) (reaction 11).[16] The target molecule was indeed the major product, but three other products (23, 24, 25) were obtained (reaction 16). The reaction was followed by gc and



17 9 23 24 25 16.

stopped after the yield of **9** reached a maximum.

Compound **9** was identical in all respects to the product of the first synthesis. Compounds **23**, **24** and **25** were identified by their mass, ^{1}H-NMR and ^{13}C-NMR spectra. The mass spectra showed how much hydrogen was taken up to form each product. The ^{13}C-NMR spectra showed how many different aromatic and aliphatic carbons were in each compound which indicated the symmetry of the product. The ^{1}H-NMR spectra established the structures. Compound **23** was a tetralin like **9**; thus, it showed similar but different characteristics since one of the phenyl groups was hydrogenated. Because of this, compound **23** lacked the symmetry found in **9** so 18 signals appeared in the ^{13}C-NMR spectrum. The lack of symmetry was also reflected in the ^{1}H NMR. The aromatic protons of the tetralin nucleus in **9** appear as a singlet at δ 7.05 apart from the rest of the aromatic signals (Figure 3). In the spectrum of **23**, these are differentiated and coupled to each other (Figure 4). The signals of the two different sets of benzylic hydrogens of **23** are also differentiated and appear as multiplets of δ 2.9 and 2.7. The signal at δ 2.9 has a shoulder due to the new benzylic proton of the cyclohexyl ring. Other protons on this ring give rise to signals between 1 and 2 ppm which are not found in the spectrum of **9**. The other tetralin isolated (**24**) is the product of hydrogenation of both phenyl groups. This compound has all the symmetry of **9**. Thus, the aromatic protons of the tetralin nucleus appear as a singlet as in **9**, just upfield from the chloroform peak (Figure 5) and the benzylic protons of the tetralin nucleus have only one signal as well. In this spectrum, the signal for the benzylic methines

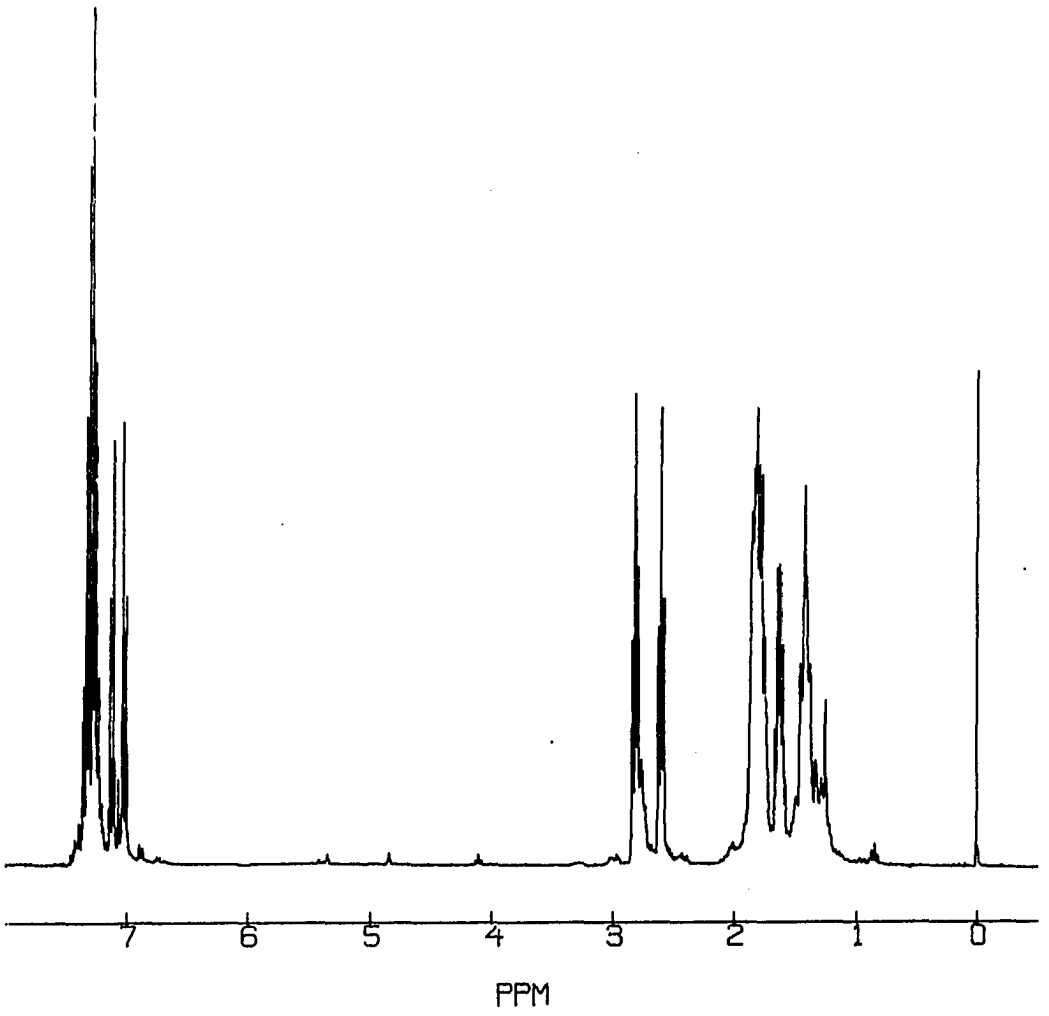


Figure 4. Proton NMR spectrum (300 MHz) of 5-cyclohexyl-8-phenyl-tetralin (23)

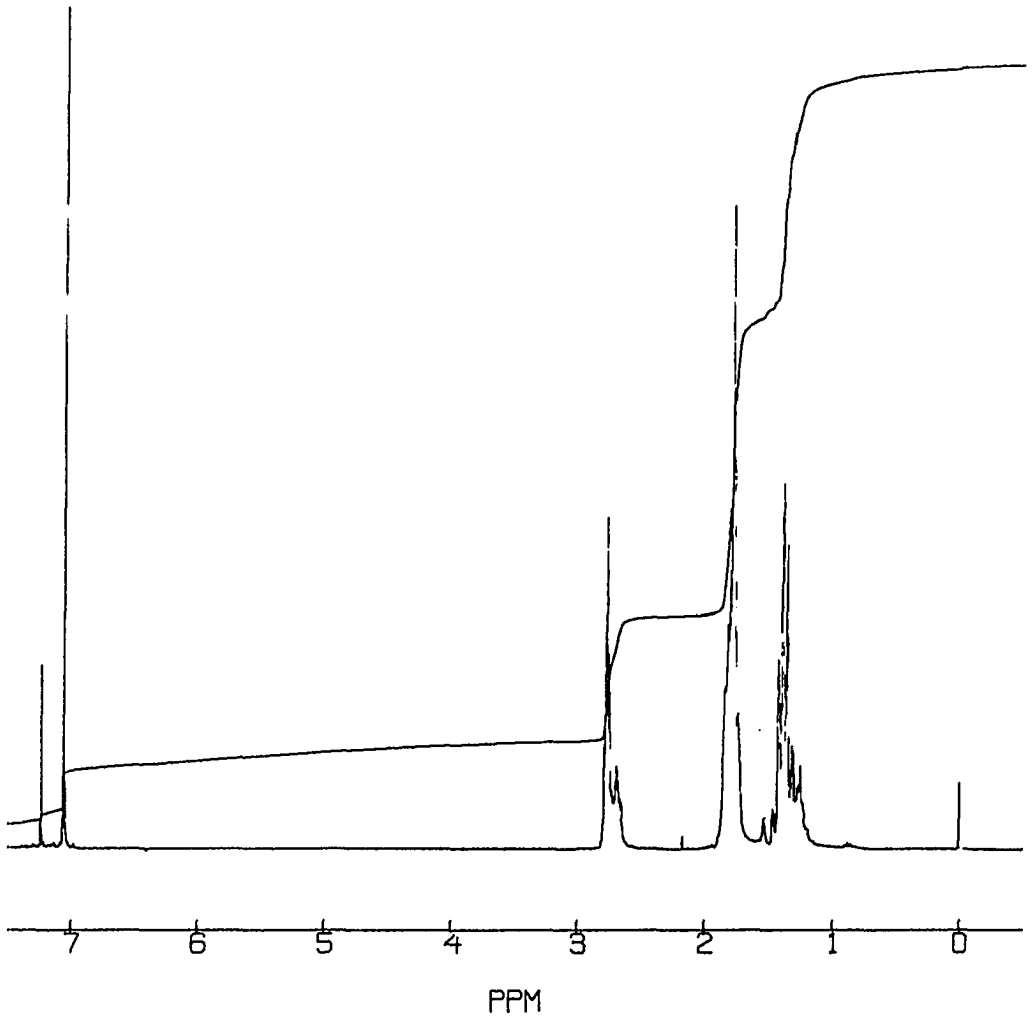


Figure 5. Proton NMR spectrum (300 MHz) of 5,8-dicyclohexyltetralin (24)

of the cyclohexyl rings is seen as a shoulder to the benzylic signal of the tetralin nucleus as in the spectrum of **23** (Figure 4). The other side product isolated was 1-cyclohexyl-4-phenylnaphthalene (**25**). Here again, the symmetry of the starting material was lost in the formation of this compound. This is reflected in the ^{13}C-NMR spectrum which contains 18 signals. The only benzylic proton of **25** is the methine proton of the cyclohexyl ring which appears as a multiplet at δ 3.4 (Figure 6). Also, the two doublets at δ 8.2 and 7.9 have approximately the same chemical shift as a multiplet at δ 8.0 in the spectrum of the starting material (**17**) (Figure 7) which is the best indication that the naphthalene nucleus is intact in **25**.[20]

Once a good supply of 5,8-diphenyltetralin (**9**) was at hand, pyrolysis studies were undertaken. Tetralin (**1**) was pyrolyzed under the standard conditions described by Trahanovsky and Swenson[1] in the same apparatus that they used to ensure that the technique used could reproduce their results. This was accomplished to a reasonable extent (Table 2). The same compounds were obtained (reaction 1) in roughly the same yields. The pyrolysis temperature in their study was slightly higher, resulting in a higher conversion and more secondary reactions. Also seen in Table 2 are the results of tetralin pyrolysis in the high-vacuum apparatus that was required for the pyrolysis of 5,8-diphenyltetralin (**9**). The expected shift due to pyrolysis at a lower pressure towards more benzocyclobutene (**2**) and styrene (**3**) relative to the dehydrogenation products (**4**, **5**, and **6**) was observed. Because of the lower pressure, a higher temperature was required to attain the same amount of conversion

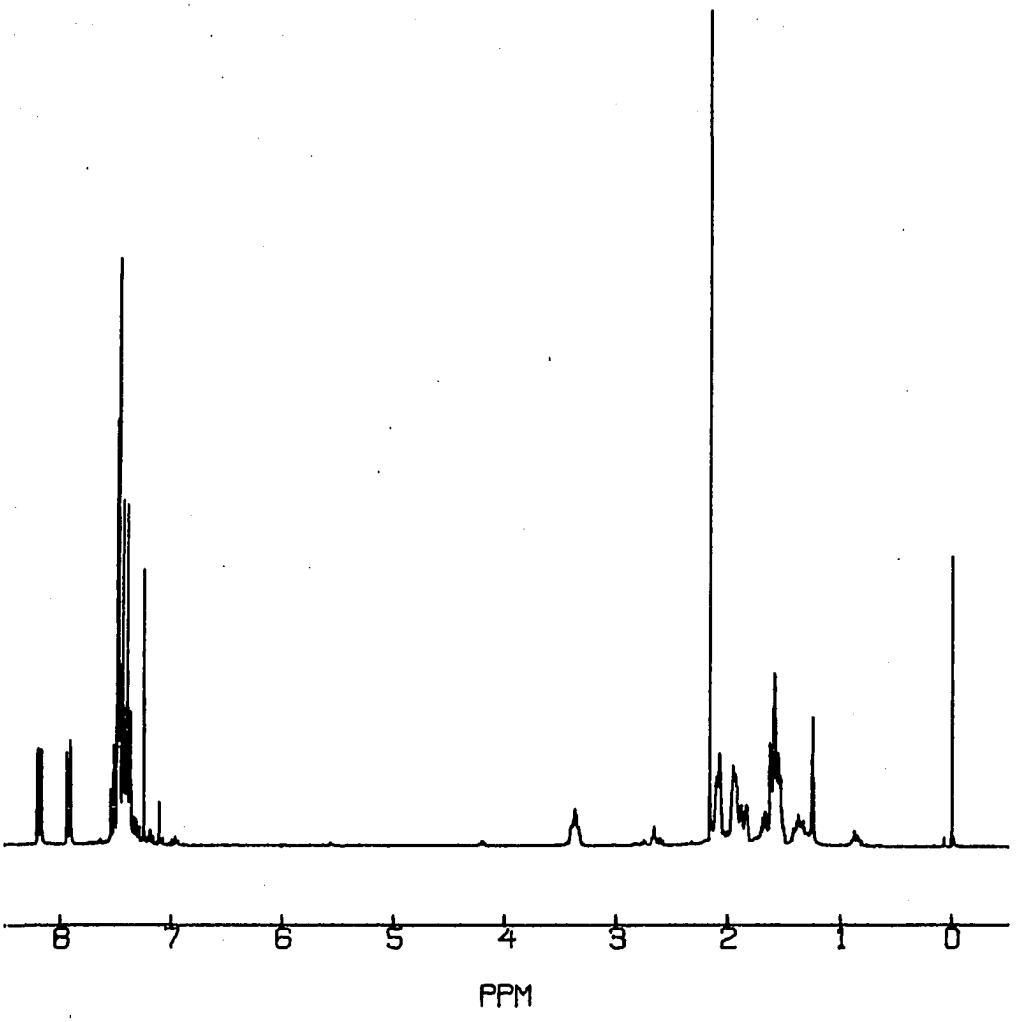


Figure 6. Proton NMR spectrum (300 MHz) of 5-cyclohexyl-8-phenyl-tetralin (25)

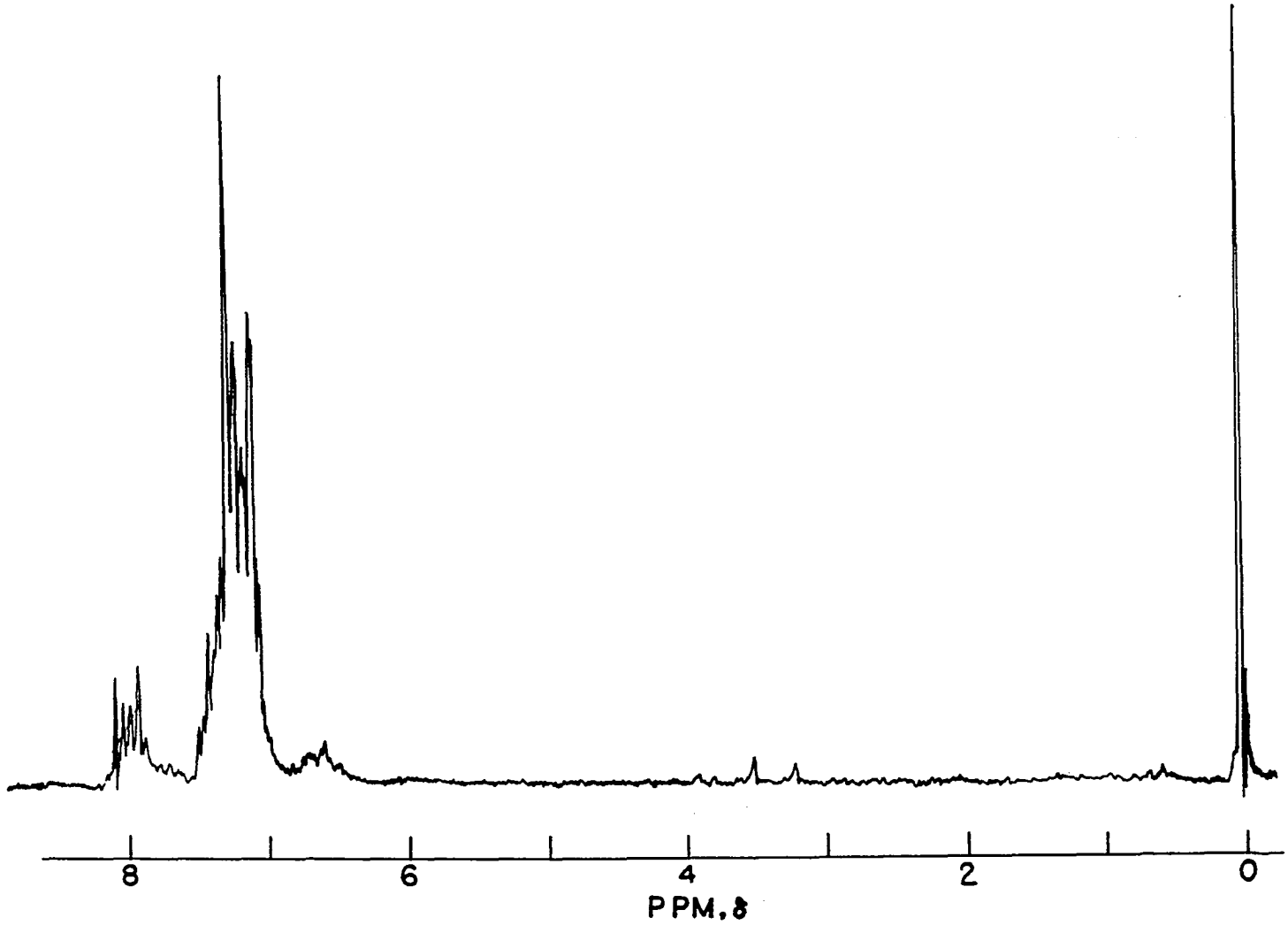


Figure 7. Proton NMR spectrum (60 MHz) of 1,4-diphenylnaphthalene (17)

observed at lower temperatures and lower vacuum.

Table 2. Product distribution for the FVP of tetralin (1)

Conditions	Products, %[a]						Conversion, %[c]	Recovery, %[b]
	2	3	4	5	6	Others		
1. 888°C, 0.1 torr[d]	6	23	15	5	31	20	89	76
2. 862°C, 0.3 torr	9	18	11	14	32	16	65	79
3. 1000-1030°C,[e] 4×10^{-4} torr	9.9	48.2	12.2	1.4	20.9	7.4	92.8	79

[a]Numbers are percent of total product found.

[b]Total absolute yield of all recovered material.

[c]Based on the amount of recovered **1**.

[d]Data are from reference 1.

[e]Average of two pyrolyses. The average deviation in the yields of products was ±0.5%.

When 5,8-diphenyltetralin (**9**) was pyrolyzed at 1000-1030"C and 4×10^{-5} torr, some thermal chemistry different from that of **1** was observed. None of the products were isolated and characterized but analysis of the product mixture by gas chromatography/mass spectrometry indicated that the major product (**28**) was due to the net loss of C_2H_6. This does not correspond to any product in the pyrolysis of **1** (Table 3). Also, the recovery of material was low. Even though the yields of the hydrogen-loss products were lower than in the parent system, the ethylene-loss products were also formed in diminished yields. The ^{1}H-NMR spectrum of the product mixture shows the aliphatic multiplets of the starting material and three aliphatic singlets at δ 3.93, 3.89 and 3.44 (Figure 8).

Table 3. Comparison of tetralin (**1**) to 5,8-diphenyltetralin (**9**) in the FVP at 1000-1030°C and high vacuum by the net fragment lost in formation of each product

FVP of **9**		Net fragment lost	FVP of **1**[a]	
Compound	Yield,%[b]		Compound	Yield,%
26[c]	6.0	C_3H_6	--	
27[c]	2.2	C_2H_6	--	
28[c]	12.1	C_2H_6	--	
29[c]	2.7	C_2H_6	--	
30[c]	0.7	C_2H_4	**2**[d]	7.1
31[c]	3.9	C_2H_4	**3**[d]	34.6
32[c]	2.6	CH_4	**4**[d]	8.8
17[e]	2.5	$2H_2$	**6**[d]	15.0
16[e]	0.7	H_2	**5**[d]	1.0
33[c]	0.7	Isomerization	--	--
9[e]	10.2	Starting material	**1**[d]	7.2
Others	3.0	Varies	Others	5.3
Recovery, total	47.3			79.0

[a]Same data as in entry 3 of Table 2 except yields are reported as absolute.

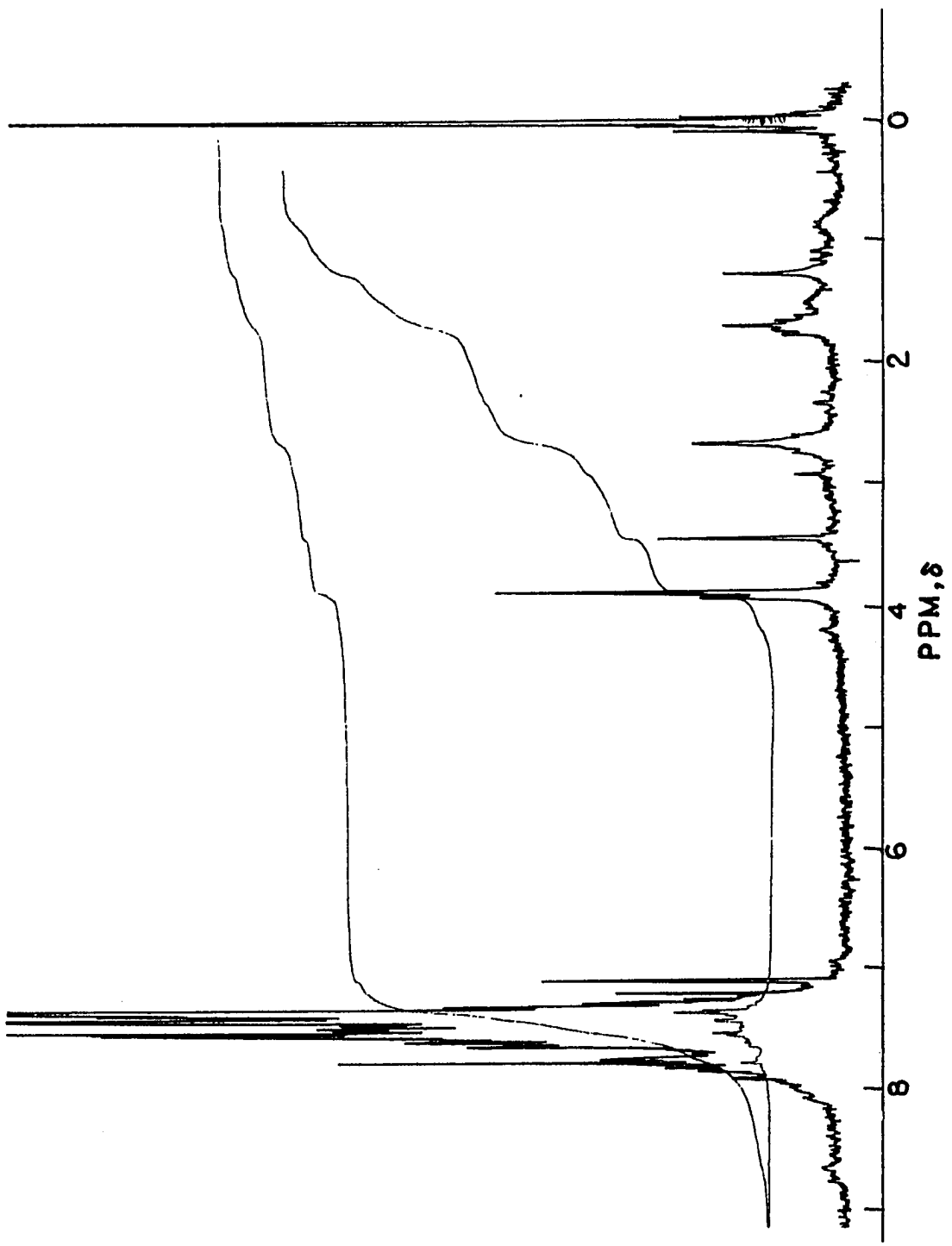
[b]Determined by gc by comparison to an internal standard. FID response factors were assumed to be 1.

[c]The identities of compounds **26-33** are unknown. Only their molecular weights are known from gc/ms analysis.

[d]The products of the pyrolysis of tetralin are benzocyclobutene (**2**), styrene (**3**), indene (**4**), 1,2-dihydronaphthalene (**5**), and naphthalene (**6**). They were identified by comparison of the gc data to those of Trahanovsky and Swenson[1].

[e]5,8-Diphenyl-1,2-dihydronaphthalene (**16**), 1,4-diphenylnaphthalene (**17**), and 5,8-diphenyltetralin (**9**) were identified by gc/ms and gc retention times.

Figure 8. Proton NMR spectrum (90 MHz) of the pyrolyzate from the pyrolysis of 5,8-diphenyltetralin (**9**) at 1000-1030°C and 4-6 x 10^{-5} torr


0
2
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DISCUSSION

In the first synthesis of 5,8-diphenyltetralin, the problems resulting in low yields were obvious. In the Diels-Alder reaction (reaction 6), the diene (**10**) was reacting with itself to give the high-molecular-weight-hydrocarbon mixture. The aromatization of the Diels-Alder adduct (**12**) (reaction 8) proceeded with difficulty, no doubt because the central ring was inaccessible to the catalyst. Thus, some of the starting material was recovered and the retro-Diels-Alder reaction was able to compete. Another problem was hydrogenation of the olefinic bond resulting in an unreactive cyclohexane ring (**15**). The hydrogenation of the naphthalene (**17**) showed how inaccessible the central ring is since this ring was not hydrogenated in any of the products isolated (reaction 16).

The comparison of pyrolyses of tetralin (**1**) found in Table 2 shows that the techniques used for this work were adequate to reproduce the results of Trahanovsky and Swenson.[1] Thus, there is good reason to be confident of the accuracy of these results. The slight differences in yields in entries 1 and 2 of Table 2 can be attributed to the difference of 26°C in the pyrolysis temperatures. Their temperature was higher, resulting in a higher conversion and more secondary reactions.

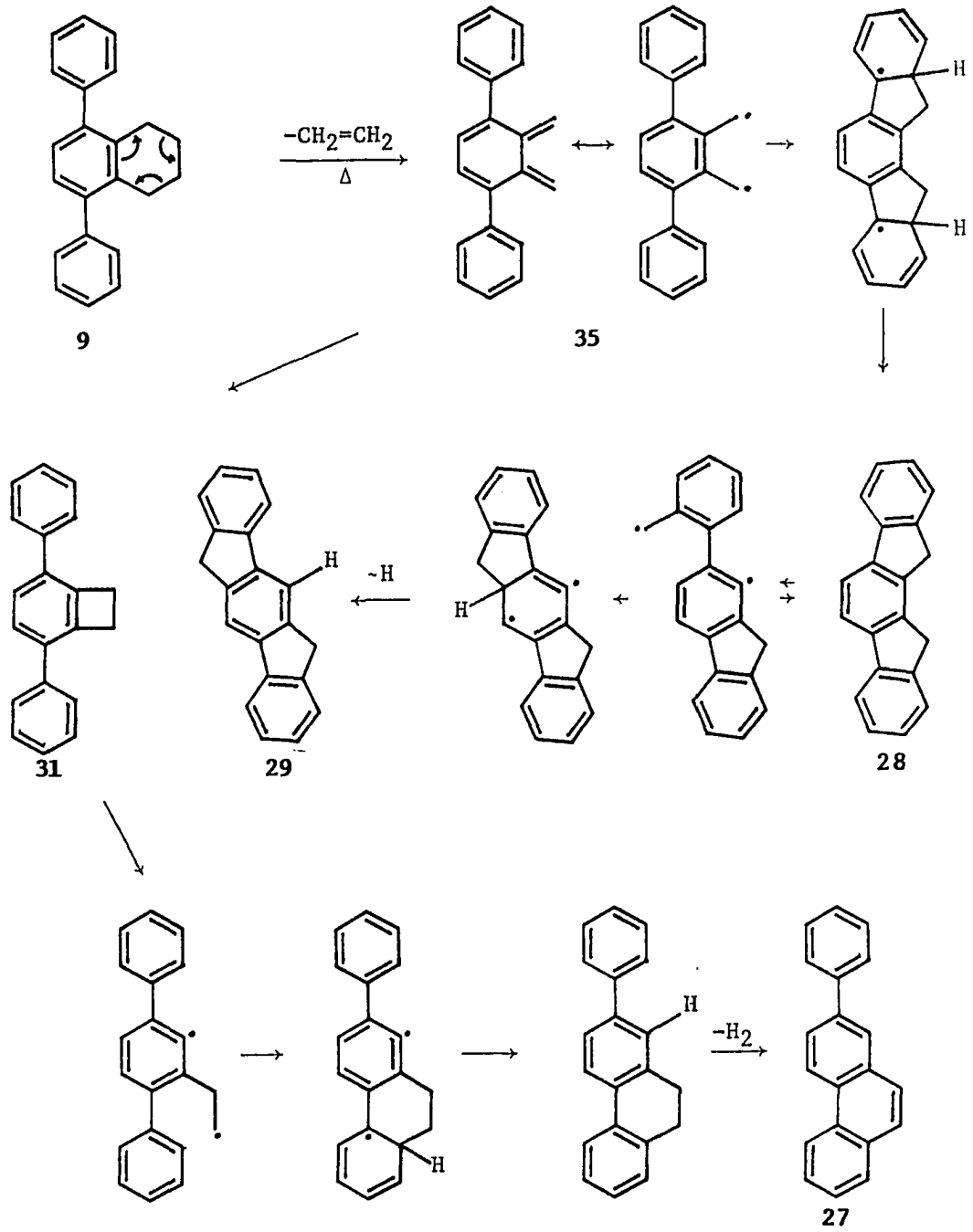
The results of the high-vacuum tetralin pyrolysis (entry 3, Table 2) followed the trend seen in Table 1. That is, at higher vacuum, the loss of ethylene (reaction 2) is competitive with loss of hydrogen (reaction 3). It was surprising that this held true even at a high conversion. The only effect that this seemed to have was to increase

the secondary reactions as evidenced by the high yield of styrene (3) and naphthalene (6).

The results of the 5,8-diphenyltetralin (9) pyrolysis are inconclusive since there are new reactions and a low recovery. If the products of C_2H_6-loss (27-29) were secondary products from the primary ethylene-loss product (34) (Scheme 2), then one could say that there was a substantial change in the ratio of ethylene-loss to hydrogen-loss. This would, of course, support the surface-catalysis theory. However, the mechanism of formation of the C_2H_6-loss products is uncertain. One cannot even look only at the ethylene-loss products (31, 32) vs. the hydrogen-loss products (17, 18, 33), since some of the ethylene-loss product might have been diverted to the C_2H_6-loss product.

Proposed structures for compounds 27, 28, 29 and 31 are seen in Scheme 2. Although their identity is unknown, support for these structures is found in the ^{1}H-NMR spectrum of the product mixture (Figure 8). The singlet at δ 3.44 is what one would expect for diphenylbenzocyclobutene (31) since the chemical shift for the parent is δ 3.17. The fluorene structures shown for 28 (the major product) and 29 fit the NMR of the product mixture (Figure 8) since the methylene signals of these compounds should appear just downfield from the benzocyclobutene signal,[21] which is where the largest singlet and a close neighbor appear (δ 3.89 and 3.93, respectively).

Scheme 2:



9 35 31 29 28 27

EXPERIMENTAL

General

The low-vacuum pyrolysis apparatus was the one used by Trahanovsky and Swenson.[1] The apparatus and its use have been described elsewhere.[22] The high-vacuum pyrolysis apparatus was the one described in part I of this thesis (pp. 39a-39b). Besides the oil-diffusion pumping system of the high vacuum apparatus, the only major difference in the two apparatus is the dimensions, the high-vacuum apparatus having the larger diameter. The pyrolysis temperature was measured with an Omega chromel-alumel potentiometer by placing the thermocouple wire on the outside of the tube at the center of the hot zone. Gas chromatography (gc) analysis was performed on a Hewlett-Packard 5840A gc equipped with a microprocessor and a flame-ionization detector (FID). Yields of pyrolysis products were determined by gc using biphenyl as an internal standard. For tetralin (1) pyrolysis, FID response factors for major products were those determined by Trahanovsky and Swenson.[23] For 5,8-diphenyltetralin (9) pyrolysis, all FID response factors were assumed to be 1. Melting points were determined with a Thomas-Hoover capillary-melting-poing apparatus and are uncorrected. Catalytic hydrogenations were carried out using a 1 atmosphere apparatus like the one described by Augustine.[24]

Infrared spectra were recorded on a Beckman Acculab II spectrophotometer. ^{1}H-NMR spectra were obtained on either a Varian EM360, A60, a JEOL FX90Q or a Bruker WM300. ^{13}C-NMR spectra were recorded on the

JEOL FX90Q. Chemical shifts are reported in δ units downfield from TMS internal standard. Commercially available compounds and their sources are listed in Table 4.

5,8-Diphenyl-1,2,3,4,4a,5,8,8a-octahydronaphthalen-1-one (**12**)

This compound was prepared according to the general procedure of Fringuelli et al.[12] Freshly-distilled cyclohexenone (**11**) (6.7 g, 68 mmole) was stirred for 40 min at 25°C under N_2 with $AlCl_3$ (8.0 g, 60 mmole) in toluene (250 mL) which had been dried by azeotropic distillation. 1,4-Diphenyl-1,3-butadiene (**10**) (31 g, 150 mmole) was added as a solid, turning the gray cyclohexenone - $AlCl_3$ mixture to yellow. The resulting mixture was stirred at 70°C under N_2 and analyzed periodically by gc by removing aliquots and working them up in a fashion similar to that described below for the main body. The gc analysis showed a dramatic drop in the amount of **10** within 24 h while the amount of **11** changed little. The reaction mixture was stirred for an additional 32 h, then quenched with H_2SO_4 (6N). The organic layer was washed with water and brine and dried over $MgSO_4$. Filtration and concentration yielded 43 g of residue which was chromatographed (silica gel, 5% ether in hexanes elution). The majority of product was a mixture of high-molecular-weight hydrocarbons as judged by gc and IR: several components eluted as a body in the gc with retention times much longer than the ketone adducts; analysis of the mixture by IR showed no carbonyl stretching bands. Fractions which contained the first ketone to elute (k #1) were concentrated to give 2.9 g of one isomer of **12** (14% yield): IR

Table 4. Commercially available chemicals

Compound	Source
Alumina (neutral, activity I)	J. T. Baker Chemical Co.
Aluminum chloride	Fisher Scientific Co.
Benzene	Fisher
Biphenyl	Eastman Kodak Co.
Calcium hydroxide	J. T. Baker
Chloroform	Fisher
Chloroform-d	Aldrich Chemical Co.
Cyclohexenone	Wittaker Corporation
Diethyl ether	Fisher
Dichloromethane	Fisher
Diphenylbutadiene	Aldrich
Ethanol	Worum Chemical Co.
Ethyl acetate	Fisher
Hexanes	Fisher
Isobenzofuran	Aldrich
Lithium tetrahydroaluminate (LAH)	Morton Thiokol, Inc.
Magnesium sulfate	J. T. Baker
Malaic anhydride	J. T. Baker
Methanol	Fisher
Nitrogen (g)	Quickway, Inc.
Nitrogen (ℓ)	Air Products and Chemicals, Inc.
Palladium on Carbon (5%)	The Matheson Co., Inc.
Pentane	Mallinckrodt, Inc.
Petroleum ether (bp 30-60°C)	Fisher
Platinum oxide (Adam's catalyst)	Aldrich
Potassium carbonate	J. T. Baker
Potassium hydroxide	J. T. Baker
Silica gel	E. Merck, Darmstadt, Germany
Sodium chloride	J. T. Baker
Sodium hydroxide	J. T. Baker
Sulfur	J. T. Baker
Sulfuric acid	Captree Chemical Corp.
Tetralin	Aldrich
Toluene	Fisher
Xylenes	Mallinckrodt

(neat) 1715, 1608, 1497, 1458, 765, 705 cm^{-1}; ^{1}H-NMR (60 MHz, $CDCl_3$) δ 7.47 (m, 10 H), 5.90 (m, 2 H), 4.10 (m, 1 H), 3.59 (m, 1 H), 2.94-0.90 (m, 8 H). Fractions which contained the second ketone to elute

(k #2) also contained k #1 (1:1 mole ration by ^{1}H NMR). These were concentrated to yield 1.7 g of **12** as a mixture of isomers: IR (neat) 1715 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.22 (m), other signals overlap with those of k #1, taken together, the peaks integrated the same as k #1: δ 7.4 (m, 20 H), 6.22 (m, 2 H), 5.90 (m, 2 H), 4.20-0.8 (m, 16 H).

5,8-Diphenyl-1-naphthol (14)

A general procedure of Fieser *et al.* was followed.[25] The diphenylenone (**12**) (168 mg, 0.56 mmole) and S_8 (54.8 mg, 1.71 mmole) were combined in a 5-mL flask and heated to 225°C under N_2 for 75 min. The heat was withdrawn after gas evolution had ceased. The product mixture was taken up in ether and washed with KOH (5%). The aqueous layer was acidified, causing a precipitate to form. Extraction with ether, drying over $MgSO_4$, filtration and evaporation of solvent gave 1.2 mg of **14**. The organic layer was dried over $MgSO_4$, filtered and concentrated to give 163 mg of residue which was chromatographed (silica gel, 30% CH_2Cl_2 in hexanes elution). Fractions containing the major component were combined and concentrated to give 20.7 mg of **14** (total yield 13.7%) which was recrystallized from ethanol-water: mp 132.5-134.5°C; IR ($CDCl_3$) 3530 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$)δ 7.57-7.14 (m, 14 H), 6.90 (d of d, J_1 = 7 Hz, J_2 = 2 Hz, 1 H), 5.46 (s, 1 H, disappears with D_2O exchange); ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 153.2, 141.5, 140.8, 135.7, 134.0, 130.1, 129.5, 129.0, 128.6, 128.2, 128.0, 127.3, 126.8, 126.1, 119.3, 111.9.

5,8-Diphenyl-1,2,3,4-tetrahydronaphthalen-1-one (**13**)

A general procedure of Mosettig and Duval was followed.[26] The diphenylenone (**12**) (36.g) as a mixture of isomers was dissolved in xylenes (250 mL) and stirred with 5% Pd on C (2.3 g) for 4 days with refluxing under N_2. The catalyst was filtered and the solvent was distilled to give a residue which was chromatographed (silica gel, 40% ether in hexanes elution). Fractions containing **13** were concentrated to give 1.5 g of a yellow oil. This was only 50% **13** by TLC, so it was chromatographed again. (TLC, silica gel, 20% ether in hexanes elution.) The band that contained **13** yielded 0.5 g of **13** after recrystallization from methanol: mp 178-179°C, IR 1695 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$)δ 7.50-7.16 (m, 12 H), 2.88 (t, J = 6 Hz, 2 H), 2.63 (t, J = 6 Hz, 2 H), 2.08 (m, J = 6 Hz, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 199.0, 143.1, 142.9, 140.9, 140.6, 132.9, 132.1, 129.7, 129.2, 128.3, 128.2, 127.8, 127.3, 126.8, 126.5, 40.1, 28.9, 22.9. Also isolated from the reaction mixture was 1,4-diphenyl-1,3-butadiene (**10**) identified by its IR and NMR spectra which were identical to literature spectra.[27,28] Another compound isolated was 5,8-diphenyl-1-decalone (**15**) contaminated with **13** (0.5 g): mp 169-175°C; IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$)δ 7.32 (br. s, 10 H), 3.1-1.2 (m, 14 H); ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 211.1 (s), 146.2 (s), 145.0 (s), 128.5 (d, J = 160 Hz), 128.1 (d, J = 160 Hz), 127.2 (d, J = 160 Hz, 2 C), 126.4 (d, J = 160 Hz), 125.8 (d, J = 160 Hz), 60.0 (d, J = 124 Hz), 51.3 (d, J = 124 Hz), 50.7 (d, J = 124 Hz), 42.9 (t, J = 128 Hz), 42.5 (d, J = 128 Hz), 35.2 (t, J = 128 Hz), 34.6 (t, J = 128 Hz), 31.0 (t, J = 135 Hz), 27.5

(t, J = 128 Hz).

5,8-Diphenyl-1,2,3,4-tetrahydronaphthalene (**9**), Method 1

This compound was prepared following a general procedure of Blackwell and Hickinbottom.[15] A suspension of LAH (41.3 mg, 1.09 mmole) in dry ether (1 mL) was stirred under N_2 while $AlCl_3$ (290 mg, 2.17 mmole) was added as an ether solution (2 mL). The tetralone (**13**) (185 mg, 0.62 mmole) was added to the freshly-prepared reagent as an ether solution (20 mL) and the mixture was stirred with refluxing for 2 h. The reaction was quenched with ethyl acetate (2 mL) and poured into cold H_2SO_4 (20%). The solid that resulted dissolved into the ether upon shaking. The layers were separated and the organic layer was dried over $MgSO_4$. After filtration and concentration, the product mixture was chromatographed (TLC, silica gel, CH_2Cl_2 elution). The band that contained **9** also contained 5,8-diphenyl-1,2-dihydronaphthalene (**16**) as evidenced by ^1H NMR: the olefinic protons appeared at δ 6.57 (d, J = 10 Hz, 1 H), 6.00 (d of t, J_d = 10 Hz, J_t = 5 Hz, 1 H). The mixture of **9** and **16** was dissolved in 95% ethanol (25 mL) and stirred with 5% Pd on C (70 mg) under one atmosphere of H_2 until no more H_2 was consumed (1 h). The catalyst was filtered and the solvent was distilled until 5 mL remained which was taken up in ether. The ether solution was washed with water and brine, dried over $MgSO_4$, filtered and concentrated. The residue was chromatographed (TLC, silica gel, CH_2Cl_2 elution) to give 120 mg of **9** (68% yield) which was recrystallized from methanol: mp 56-59°C, IR (KBr) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$)δ 7.39-7.35 (br. s, 10 H) 7.09 (s, 2 H), 2.66 (m, 4 H), 1.68 (m, 4 H); ^{13}C NMR (22.5 MHz, $CDCl_3$)

δ 142.2, 141.3, 135.2, 129.3, 128.0, 126.8, 126.7, 28.6, 23.0; MS (70 eV) 284 (100), 283 (34), 256 (77), 241 (57), 207 (35), 178 (38), 165 (51), 126 (32), 91 (30), 57 (34); $C_{22}H_{20}$, calculated 284.15650, measured 284.15573, error: -2.7 ppm.

1,4-Diphenyl-1,4-oxo-1,2,3,4-tetrahydronaphtho-2,3-dioic Acid Anhydride (**20**)

This compound was prepared following the procedure of Dufraisse and Priou.[18] Diphenylisobenzofuran (**18**) (1.35 g, 5.0 mmole) was mixed with maleic anhydride (**19**) (0.52 g, 5.3 mmole) in xylenes (25 mL). The greenish-yellow mixture was stirred at 115°C under N_2 for 1 h turning the greenish color to yellow. It was stirred at room temperature overnight affording a white slurry. The solid was filtered and washed with cold xylenes to give 1.77 g. Concentration of the supernatant solution under vacuum (bath 50°C) afforded an additional 0.1 g of **20** (99%+ yield): mp 271-277°C (lit.[18] mp 270-274°C).

1,4-Diphenyl-1,4-oxo-1,2,3,4-tetrahydronaphtho-2,3-dioic Acid (**21**)

The anhydride (**20**) was stirred with NaOH (4 M, 125 mL) for 4 days at room temperature, resulting in a clear aqueous solution and a more-dense salt which dissolved upon dilution. The solution was carefully neutralized with H_2SO_4 (6 N) causing a precipitate to form which was extracted with ether. The ether solution was dried over $MgSO_4$, filtered and concentrated to give 1.4 g of the diacid (**21**) (90% yield).

1,4-Diphenylnaphthalene (17) and 1,4-Diphenyl-2-naphthoic Acid (22)

The diacid (21) (1.4 g) was dissolved in glacial acetic acid (100 mL). The solution was heated to reflux under N_2 for 7 h following the procedure of Dufraisse and Priou.[18] Most of the solvent was distilled and the residue was partitioned between NaOH (1.75 M, 300 mL) and benzene. The organic phase was dried over $MgSO_4$ and filtered. Removal of the solvent gave 0.5 g of 17. Recrystallization from ethanol afforded 0.4 g of 17 (39% yield): mp 131-134°C (lit.[18] mp 135-136°C), ^{1}H NMR (60 MHz, $CDCl_3$)δ 7.98 (m, 2 H), 7.50-7.10 (m, 14 H). Acidification of the aqueous phase with H_2SO_4 (6 N) caused a precipitate to form which was extracted with ether. The ether solution was dried over $MgSO_4$, filtered and concentrated to give 0.42 g of 22 (36% yield): mp 220-223°C (lit.[18] mp 225-226°C), ^{1}H NMR (60 MHz, acetone-d_6)δ 7.85 (s, 1 H), 7.55-7.12 (m, 14 H), 4.97 (br. s, 1 H).

1,4-Diphenylnaphthalene (17) from 1,4-Diphenyl-2-naphthoic Acid (22)

Following the procedure of Weiss et al.[17] 22 (0.42 g) was dissolved in dilute NaOH (30 mL) and stirred while NaOH (conc.) was added, which caused a precipitate to form. After the solid settled, the supernatant liquid was decanted. The solid (0.4 g) was dried and mixed with $Ca(OH)_2$ (0.8 g). The mixture was heated with a bunsen burner in a distillation apparatus with a flow of N_2. The product that distilled was chromatographed (TLC, silica gel, hexanes elution) to afford 0.18 g of 17 (50% yield): mp 132-135°C (lit.[17] mp 135-137°C).

5,8-Diphenyltetralin (9), Method 2

Following a general procedure of Price et al.,[16] 1,4-diphenylnaphthalene (17) (0.5 g) was mixed with PtO_2 (150 mg) in absolute ethanol (100 mL). HCl (5 drops), which was prepared by bubbling HCl (g) through absolute ethanol for 5 min, was added and the mixture was stirred under one atmosphere of H_2. Aliquots (0.25 mL) were taken periodically, shaken with K_2CO_3, and analyzed by gc. After 102 h, the concentration of **9** stopped increasing and uptake of H_2 had slowed. The ethanol was removed by distillation and the residue was taken up in $CHCl_3$, shaken with K_2CO_3 and filtered. Evaporation of the solvent gave 0.45 g which was chromatographed (neutral alumina, activity grade I, pet. ether elution). Four products were isolated (**9**, **23**, **24**, and **25**). Compound **9** (0.21 g) was recrystallized from methanol: mp 56-59°C, when this product was mixed with crystals from the first preparation the melting point was not depressed; ^1H NMR (90 MHz, $CDCl_3$) and ^{13}C NMR (22.5 MHz, $CDCl_3$) were identical to the spectra of **9** from the first method of preparation. 5-Cyclohexyl-8-phenyltetralin (**23**) (0.12 g): ^1H NMR (300 MHz, $CDCl_3$)δ 7.36-7.23 (m, 5 H), 7.12 (d, J = 7.92 Hz, 1 H), 7.05 (d, J = 7.92 Hz, 1 H), 2.84-2.76 (m, 3 H), 2.62-2.58 (m, 2 H), 1.85-1.75 (m, 6 H), 1.67-1.60 (m, 2 H), 1.46-1.26 (m, 6 H); ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 144.9, 142.4, 139.6, 134.6, 134.2, 129.3, 128.7, 128.3, 127.8, 127.0, 126.3, 122.6, 39.2, 34.2, 33.8, 29.1, 27.2, 26.4, 26.2, 23.2, 22.8. 5,8-Dicyclohexyltetralin (**24**) (0.04 g): ^1H NMR (300 MHz, $CDCl_3$)δ 7.06 (s, 2 H), 2.79-2.64 (m, 6 H), 1.84-1.73 (m, 12 H), 1.58-1.20 (m, 12 H). ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 143.0, 134.1, 122.7, 39.1,

34.0, 27.4, 26.5 (br., 2 unresolved peaks), 23.1. 1-Cyclohexyl-4-phenylnaphthalene (**25**) (0.01 g): ^{1}H NMR (300 MHz, $CDCl_3$)δ 8.18 (d, J = 8.6 Hz, 1 H), 7.92 (d, J = 8.2 Hz), 7.55-7.34 (m, 9 H), 3.41-3.34 (m, 1 H), 2.15-2.03 (m, 2 H), 2.00-1.83, (m, 2 H), 1.75-1.51 (m, 4 H), 1.43-1.25 (m, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$)δ 143.4, 141.3, 138.3, 132.1, 131.6, 130.2, 129.4, 128.2, 127.1, 126.8, 125.5, 125.3, 123.4, 121.9, 39.4, 34.3, 27.4, 26.6.

FVP of Tetralin (**1**) in the Low-Vacuum Apparatus

Tetralin (1) (179.0 mg), which had been distilled prior to use, was pyrolyzed at 862°C and 0.3 torr. The sample was kept at 20°C by immersion in a Dewar flask filled with cold tap water. Transfer was complete in 3 h. After pyrolysis, the system was filled with N_2 and the product condenser was allowed to warm. Before it reached 0°C, the product mixture was taken up in pentane (8 mL) and added to the internal standard, biphenyl (17.4 mg). The mixture was analyzed by gc using a 3' x 1/8" column packed with 3% OV-225. Products were identified by their retention times and relative amounts by comparison to gc traces of Trahanovsky and Swenson who had identified the major components. The results are tabulated in Table 2.

FVP of Tetralin (**1**) in the High-Vacuum Apparatus

Tetralin (**1**) (133.3 mg), which had been distilled prior to use, was pyrolyzed at 1000-1030°C and 3.6 x 10^{-4} torr. Prior to evacuation, the system was filled with N_2, the sample was cooled to -34°C and the product condenser was cooled to -196°C. Transfer was complete in 4.5 h.

The product mixture was worked up and analyzed in a fashion identical to that for the low-vacuum pyrolysis. The amount of biphenyl used was 17.2 mg. The pyrolysis was repeated using 136.9 mg of 1 and 24.4 mg of biphenyl. Transfer of material took 6.5 h in this experiment. The results of the two pyrolyses were averaged and the average tabulated (Table 2).

FVP of 5,8-Diphenyltetralin (9) in the High-Vacuum Apparatus

Compound 9 (45.1 mg) was pyrolyzed at 1000-1030°C and 4-6 x 10^{-5} torr. The sample was warmed to 60°C by insulating the sample chamber such that the pressure of the system remained in the 4-6 x 10^{-5} torr range. Transfer was complete in 6.5 h. The quartz chips were carbonized and brown decomposition product was deposited just outside the oven. After pyrolysis, the system was filled with N_2 and the product condenser was allowed to warm to room temperature. The product mixture was taken up in benzene (8 mL) and analyzed by gc with a 30 m capillary column coated with SP-2100. Biphenyl (10.2 mg) was added and the solution was analyzed again by gc to determine the yields of products and by gc/ms to determine their molecular weights. The gc and ms data are given in Table 5. After gc analysis, the solvent was evaporated and the residue was analyzed by ^1H NMR (90 MHz, $CDCl_3$) (Figure 8).

Table 5. GC and MS data for products of FVP of 5,8-diphenyltetralin (**9**)

Compound	Ret. time, min	Yield, %	MS (70 eV), m/e (% of base peak)
26	26.56	6.0	242 (100), 165 (37), 120 (69)
33	26.95	0.7	284 (70), 256 (77), 241 (75), 120 (100)
9	27.36	10.2	284 (100), 241 (25), 165 (46), 120 (88)
31	27.66	3.9	256 (100), 239 (29), 126 (88), 120 (89)
30	28.65	0.7	256 (100), 239 (14), 126 (61), 120 (60)
17	28.82	2.5	280 (100), 202 (43), 138 (73), 126 (41)
27	30.55	2.2	254 (100), 207 (10), 127 (65), 113 (33)
32	31.14	2.6	268 (100), 252 (22), 133 (82), 126 (85)
28	31.39	12.1	254 (69), 126 (100), 113 (32), 101 (13)
29	31.56	2.7	254 (68), 126 (100), 113 (27), 101 (11)
16	32.06	0.7	282 (54), 207 (71), 126 (91), 73 (100)

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GENERAL SUMMARY

Flash vacuum pyrolysis (FVP) has been used successfully to discover some novel thermal reactions. These provide new insights into some fundamental chemistry.

In part I, benzocyclobutene (**9**) and its [4+4] dimer, 1,5-dibenzocyclooctadiene (**14**) were found to give anthracene (**7**) as a major product. The similarity of the product mixtures is taken as evidence that essentially the same mechanism is operating in both cases. By labeling studies, the [4+2] spirodimer (**14'**) appears to be an intermediate. The fragmentation by which **14'** is thought to give **7** is new and analogous to the retroene reaction. The proposed mechanism lends new insight into the mechanism of the pyrolytic formation of benzene and higher aromatics.

In part II, vinylketene (**66**), prepared by FVP, was characterized by low-temperature ^{1}H- and ^{13}C-NMR spectroscopy. It was found to dimerize by a novel [4+2] cyclo-addition reaction. The resulting δ-lactone (**90**) was isomerized to a mixture of sibirinone (**91**) and 6-allyl-α-pyrone (**92**). Acid-catalyzed isomerization gave primarily **91** (9:1 mole ratio). When vinylketene was mixed with cyclopentadiene, the [2+2] cycloadduct (**72**) was formed with high regio- and stereospecificity. Compound **72** was isomerized to bicyclo[4.2.1]nona-3,7-dien-2-one (**97**).

Part III described an attempt to determine the effect of surface catalysis in FVP. The synthesis of 5,8-diphenyltetralin (**9**) was described. Comparison of the pyrolysis of **9** to that of the parent compound, tetralin (**1**) was not possible since the thermal chemistry of **9**

was found to be too different from that of **1**. The major product of the pyrolysis of **9** at 1000°C and 10^{-5} torr was due to the loss of C_2H_6 while **1** gave styrene as the major product by the loss of C_2H_4 under similar conditions.

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