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Formation of benzene by the pyrolysis of 4-vinylcyclohexene Regiospecific formation of anthracenes in the pyrolysis of dibenzosuberones and related systems

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FORMATION OF BENZENE BY THE PYROLYSIS OF 4-VINYLCYCLOHEXENE
REGIOSPECIFIC FORMATION OF ANTHRACENES IN THE PYROLYSIS OF
DIBENZOSUBERONES AND RELATED SYSTEMS

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Formation of benzene by the pyrolysis of 4-vinylcyclohexene

Regiospecific formation of anthracenes in the pyrolysis of

dibenzosuberones and related systems

by

Jay Leslie Tunkel

A Dissertation Submitted to the

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TABLE OF CONTENTS

LIST OF TABLES

ix

LIST OF FIGURES

Page

DEDICATION

In memory of Dr. Leon Saul Tunkel

INTRODUCTION

Benzocyclobutene (BCB) (1) is known to be in equilibrium with its valence isomer ortho-quinodimethane (2)[1]. ortho-Quinodimethane (2) is of interest as it is a simple, yet highly reactive hydrocarbon. The

1   **2**
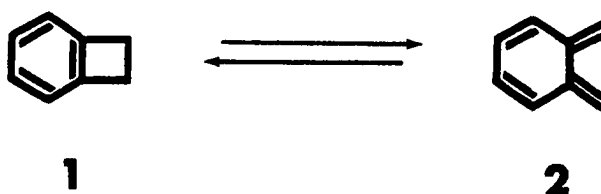
reactivity of 2 can be accounted for by the gain in energy produced upon aromatization of the benzene nucleus. The energetics of the interconversion of 1 and 2 have recently been determined.[1] Compound 2 is 13 kcal/mole less stable than 1, and a substantial barrier (26 kcal/mole) to its isomerization exists. The high reactivity of 2 coupled with the observation that it is not prone to isomerize immediately to 1 allows the opportunity for some unique chemistry to be examined. Experiments performed in this laboratory on the thermal chemistry of 1 and 2 have led to the research to be described herein.

Our interest in 1 was initiated from mechanistic studies on what is today still the easiest method of its generation, the flash vacuum pyrolysis (FVP) of o-methylbenzyl chloride (3).[2,3] The FVP of 3 can

produce 1 in a high yield reaction. Although this transformation
involves the net δ-elimination of HCl, it was conceivable that the

3   **1**   1.
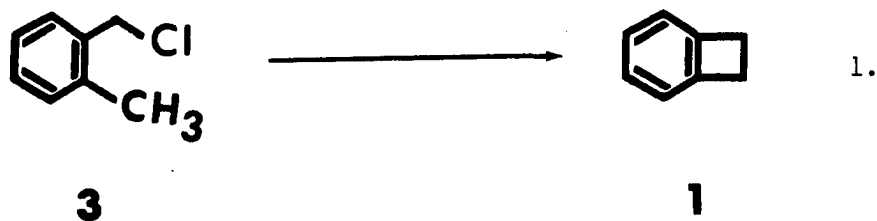
reaction proceeded by initial α-elimination to produce carbene 4 which
is known to close to BCB (1).[4,5,6] Accordingly, the FVP of o-methyl-

4
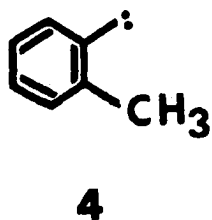
benzyl chloride-α,α-d$_2$ (5) was studied.[7] If carbene 4 was involved,
the BCB produced would contain only 1 deuterium atom. The FVP of 5
produced the BCB 6 (Scheme 1), whose formation can be accounted for by

the two pathways shown[7]. Regardless of which pathway is occurring,

the involvement of the dideuterio-<u>ortho</u>-quinodimethane 8, an intermediate

common to both pathways, is implied.

<u>Scheme 1</u>
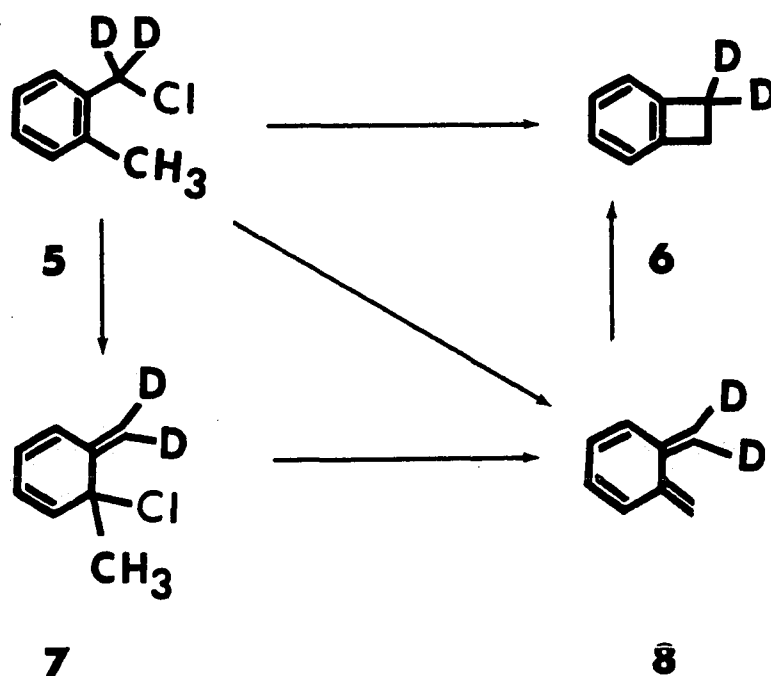
It is pertinent to note at this point that the chemistry of

<u>ortho</u>-quinodimethane and related systems is not limited solely to

mechanistic investigation. Indeed, there is a great potential for

efficient organic synthesis which stems from the fact that 2 is a

potent eneophile. This work has received much attention in the recent

literature, and one of the most powerful applications has been the

development of intramolecular [4+2] cycloadditions which can quickly

build up ring systems while taking advantage of the well known stereo-

specificity of the cycloaddition.[8,9,10,11,12] A generalized sequence

is shown.

9   **10**
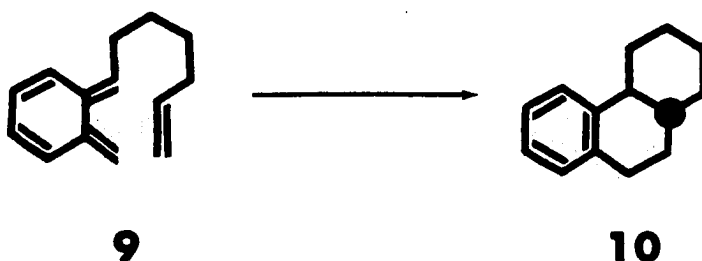
Our interest in the chemistry of BCB and related systems was

heightened with experiments on the pyrolysis of tetralin (11).[13] The

FVP of 11 gave, among other products, 1 and styrene (12) which was

shown to be produced from 1 in a secondary reaction.[13,14,15] Follow

up experiments suggested that the loss of ethylene from 11 occurred

in a concerted manner, generating 2 by a retro [4+2] reaction followed

by isomerization to 1.[13]
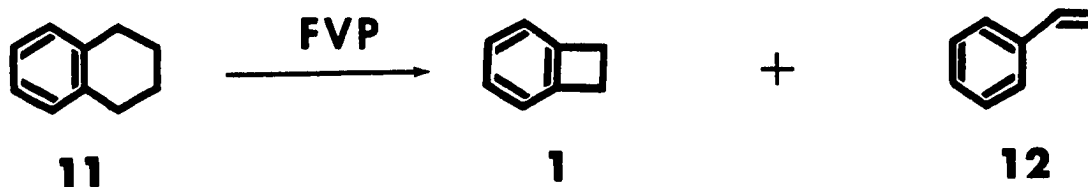
The mechanism of the conversion of 1 to 12, which at first glance appears trivial, was studied using appropriately labeled deuterated substrates in our laboratories[16] and by carbon-13 labeling studies of Chapman and Tsou.[17] The mechanism favored by these investigations is shown in Scheme 2. Clearly, a complicated series of steps takes place in this transformation.

During the course of the investigations discussed previously, there was a constant need for benzocyclobutene (1) and related derivatives. Often, the pyrolysis route outlined in equation 1 was utilized. It was noted that a ring of colorless material was deposited on the pyrolysis tube just outside of the hot zone during the FVP of o-methylbenzyl chloride (3). The production of this assumedly high molecular weight material seemed to depend on the rate at which the starting material entered the hot zone. It was recently determined

Scheme 2
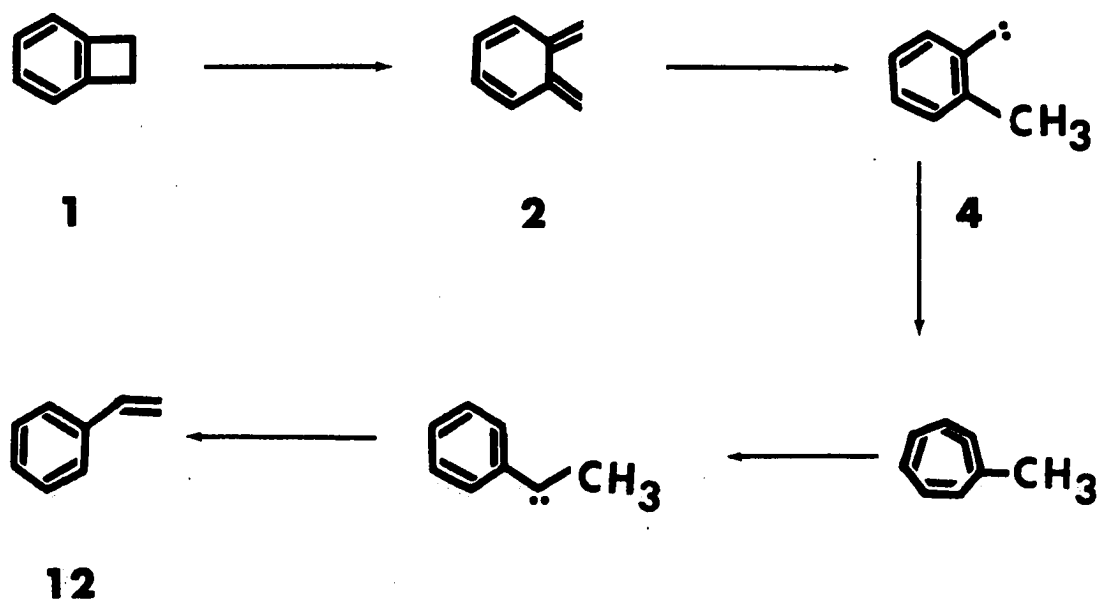
that the major component of this high molecular weight material deposited outside of the hot zone in the FVP of 3 is anthracene (13).[18,19]
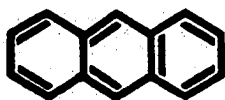
The FVP of 1,2-bis(phenylselenomethyl)benzene (14) gives, as a
mixture with other selenium containing compounds, BCB (1), anthracene
(13), and 9,10-dihydroanthracene (15) as the hydrocarbon products.[20]
These results imply that 1 might be involved in the production of 13

14   **1**   **13**   **15**
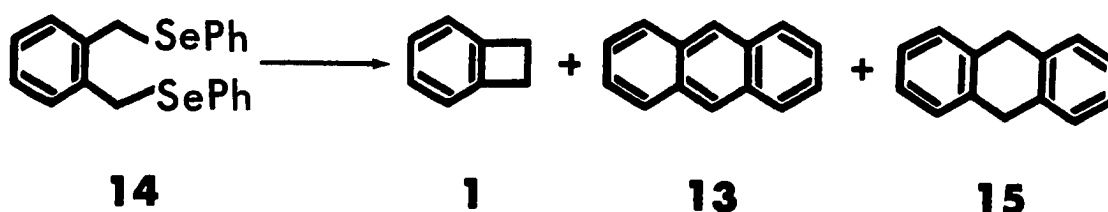
under FVP conditions. It is known that 15 can readily lose hydrogen
in a [1,4] sense giving 13.[21,22] Thus, 15 may also be involved in the
conversion of 14, or more importantly 1, to 13.

Anthracene (13) (molecular weight (mw) = 198) is two carbons and
six hydrogens short of being a formal dimer of either 1 or 2 (mw = 104).
The major product in the condensed phase thermolysis of 1 at 200°C
is the [4+4] dimer of 2, compound 16 (Scheme 3).[23,24] Production of
16 arises either from [4+2] cycloaddition between two molecules of 2
to give 17, which then rearranges to the thermodynamically more stable
16, or by direct biradical dimerization of 2.[19,25] When the static
phase pyrolysis of o-methylbenzyl chloride (3) was conducted at 430°C,
anthracene (13) was reported as a product during the terminal stages
of the reaction.[26]

Scheme 3
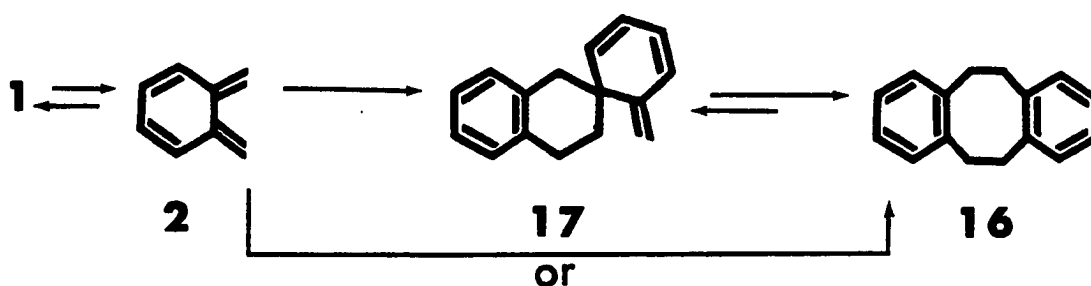
As 17 would probably thermally rearrange to 16 in the sample introduction chamber under FVP conditions,[8,23,27,28,29] the FVP of 16 was undertaken to see how it fit into the puzzle. At 920°C, anthracene (13) was seen to be the major product.[18,19] Also present in the pyrolyzate were seven $C_{16}H_{16}$ isomers (mw = 208) and two compounds with a mw of 192. Importantly absent was BCB (1), or any other material which could be considered as being produced by a unimolecular, secondary reaction of 1 (such as styrene (12)). These results are consistent with the results observed in the FVP of o-methylbenzyl chloride (3), as a

high rate of sample introduction would produce a high flux of ortho-

quinodimethane (2) in the hot zone, conditions consistent with dimer

formation.

In experiments that were designed to extend the generality of this

conversion, the corresponding naphthalene [4+4] dimers 18 and 19 were

subjected to FVP.[18,19] A 1:1 molar ratio of 18:19 produced a 1:1

mixture of 20:21.

18   **+**   **FVP**   **19**

20   **+**   **21**
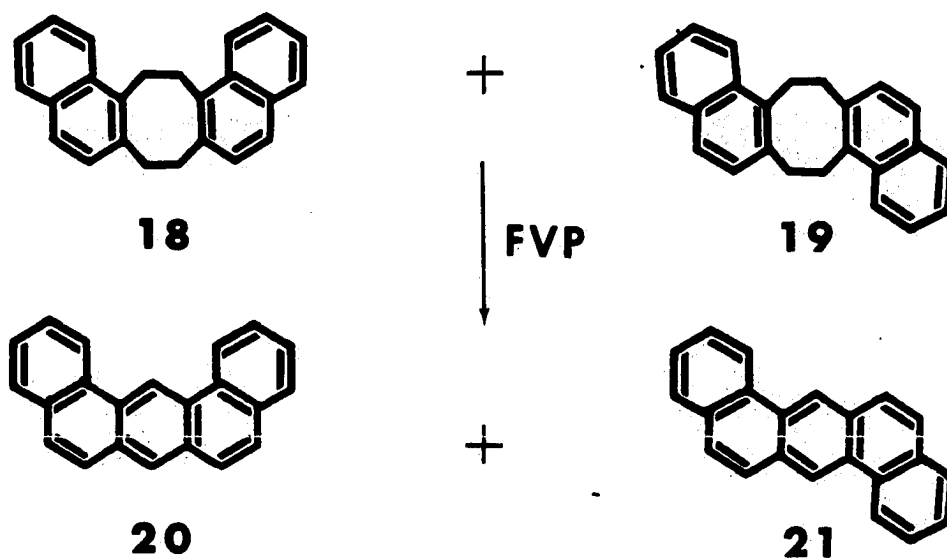
Subsequent experiments in this laboratory showed that the

transformation of a [4+4] dimer to its corresponding anthracene was

regiospecific. The appropriately labeled dimethyl derivatives 22 and

23 upon FVP at 920°C gave regiospecifically the dimethylanthracenes
24 and 25, respectively.[18,19] Thus, the regiochemistry shows that a
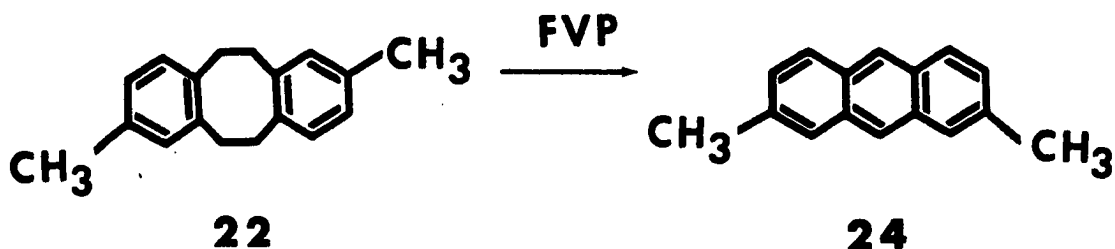
180° ring flip of the benzene rings relative to one another is occurring;
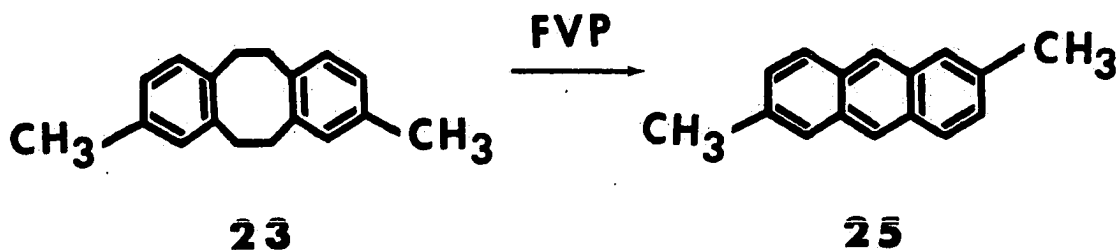
the "transoid" [4+4] dimer (22) gives the "cisoid" anthracene (24) and

the "cisoid" [4+4] dimer (23) gives the "transoid" anthracene (25).

The high regiospecificity of the transformation also rules out the

possibility that the [4+4] dimers are reverting back to the respective

ortho-quinodimethane prior to anthracene formation.

A mechanism which explains the experimental results was proposed,[18,19] and is shown in Scheme 4 utilizing the transformation of 23 as an example. In going from 26 to 27, one half of the 180° ring flip is accounted for. Compound 27, the [4+2] dimer corresponding

Scheme 4
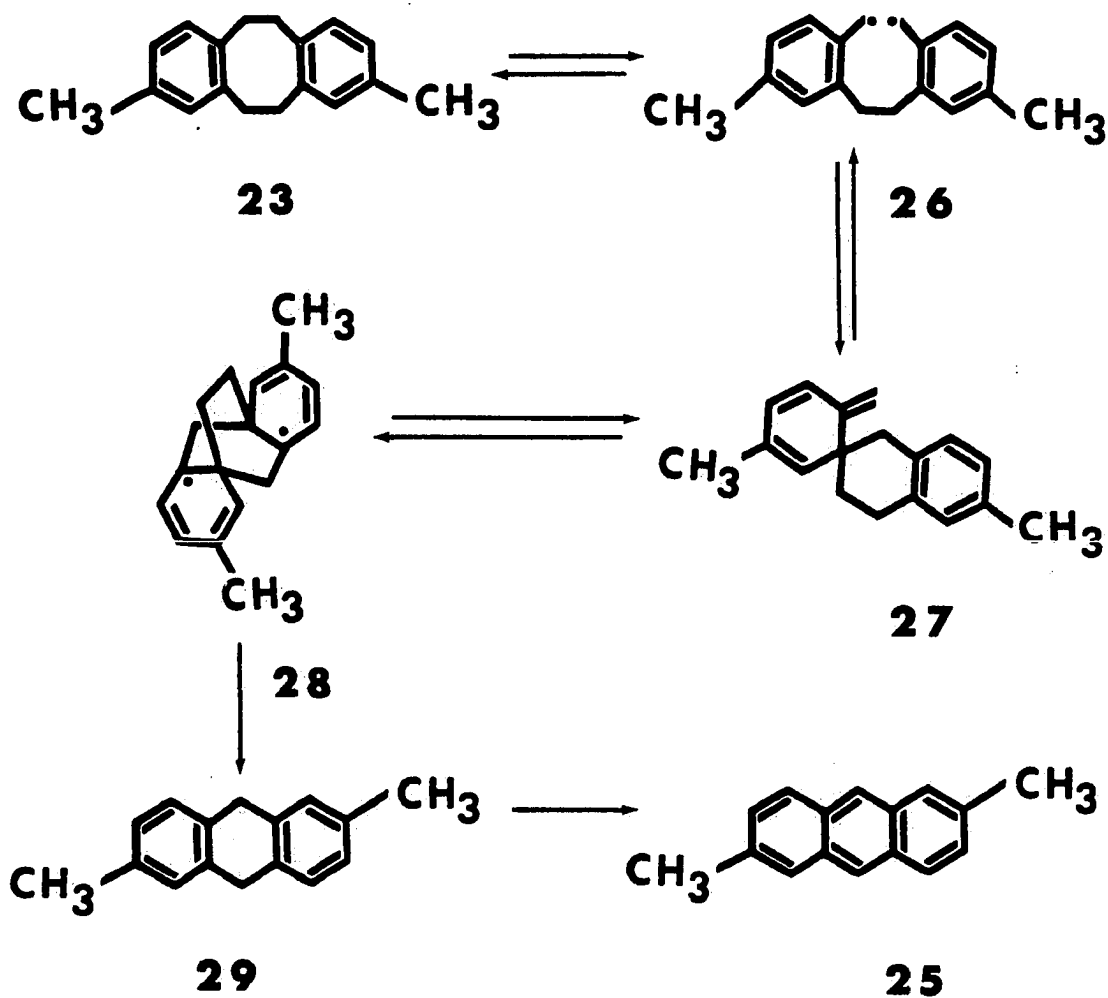
to 23, can rearrange to 28, thus completing the ring flip. Compound 28 is an attractive intermediate since both radicals are highly delocalized and the intermediate has no highly strained bonds. The orbitals involved in the extrusion of ethylene are all properly oriented, and this extrusion would be energetically favorable as two aromatic rings and two closed shell molecules would be generated. The conversion of 29 to 25 has already been described as a facile process.[21,22] Although biradical intermediates are invoked in Scheme 4, the corresponding concerted reactions cannot be ruled out.

The experiments to be described in this dissertation serve both to extend the mechanistic insight of the transformation described above and to extend the generality of the reaction. There is no need to dwell on the importance of hydrocarbons and their thermal chemistry in the modern world. Indeed, the production of an aromatic system such as anthracene (13) in such an unexpected manner may have far reaching implications. One can derive from this production of anthracene the possibility of other aromatic systems arising via a related process. The application of this hypothesis to the production of the simplest aromatic hydrocarbon, benzene (30) is thus the genesis of the research described herein.

An early theory on the production of benzene (30) by the pyrolysis of feedstock suggested the involvement of small molecules which are produced by the thermal breakdown of the feedstock. The so called

30

diene-synthesis theory proposes that aromatic molecules are formed

by Diels-Alder reactions and subsequent dehydrogenation.[30,31]

Accordingly, benzene (30) was thought to arise from the cycloaddition

of ethylene (31) and butadiene (32) followed by the loss of two moles

of hydrogen. This theory, first proposed by Hague and Wheeler,[30]
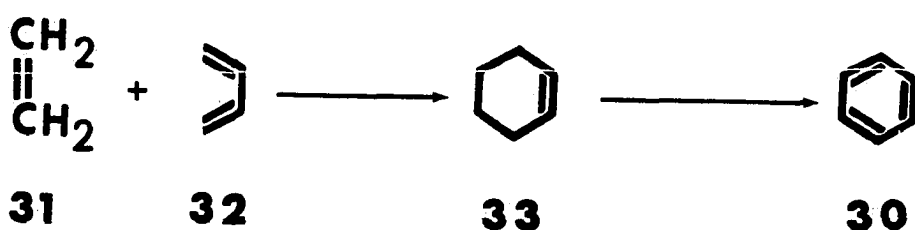
enjoyed early acceptance,[32,33,34,35] but has come under growing

scrutiny.[36-42] The direct dehydrogenation of 33 to 30 under thermal

conditions has not been established.[37,43,44,45]

The thermal reactions of pure butadiene (32) under pyrolysis conditions which can not be considered as purely unimolecular has been studied. In the nitrogen flow pyrolysis of 32, the major product is its dimer, 4-vinylcyclohexene (VCH) (34).[46] Gil-Av, in a thorough study on the pyrolysis of butadiene (32) found VCH (34) to be the major

32   **34**   **30**
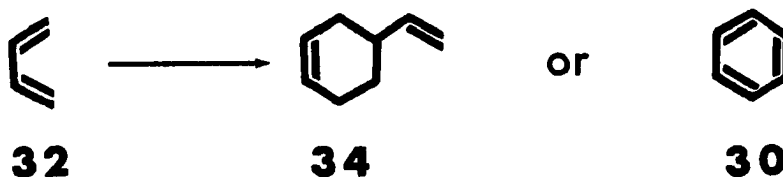
product at 550°C, however, at 700°C no 34 was observed and benzene (30) was the major liquid product.[39] Interestingly, the amount of ethylene (31) produced in the pyrolysis of 32 under a variety of conditions was always equal to the amount of benzene (30) produced.

If one strips away some of the carbons from 17, VCH (34) appears as a sub unit. Therefore, a study was undertaken to examine benzene (30) formation in the FVP of VCH (34), rationalized by an extension of the mechanism outlined in Scheme 4 and presented in Scheme 5. The experiments were accomplished by the FVP of a deuterated analog of 34. The results of these experiments led to a reinvestigation of the FVP

17 ⟹ **34**
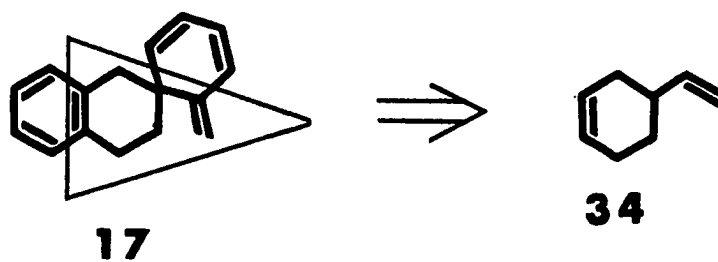
of the [4+4] dimer (16) in an attempt to correlate the findings for both systems.

Scheme 5

34 ⟶ **35**

$-CH_2CH_2$

30 ⟵ $-H_2$ **36**
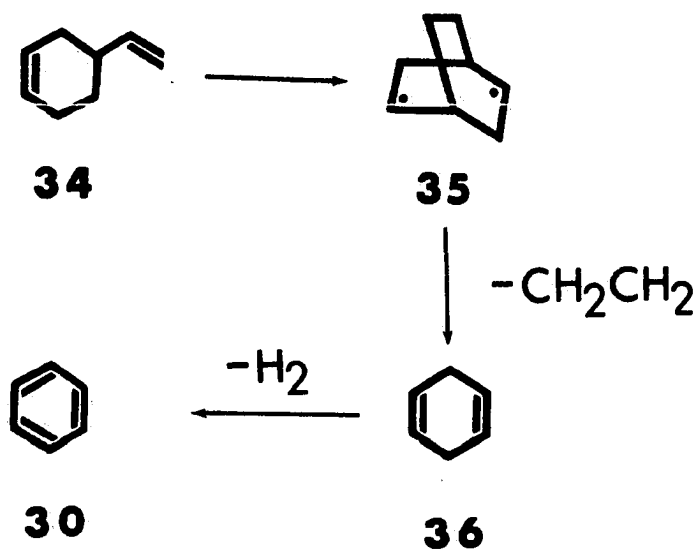
It has been reported that the FVP of the dibenzosuberone 37 gives a high yield of anthracene (13).[47] As the rationale for the conversion of 37 to 13 was not totally consistent with the experimental results

37   **13**
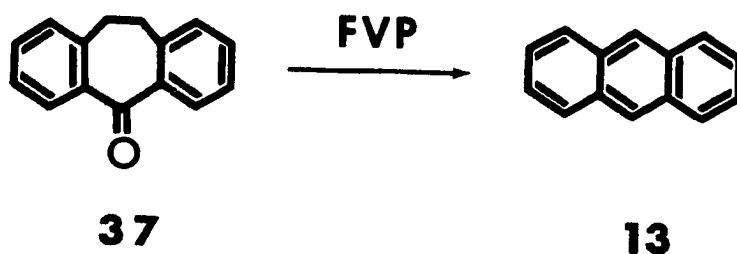
(see discussion section), the FVP of 38 was undertaken to see if this transformation fit into our general mechanistic scheme. The methyl

38   **25**
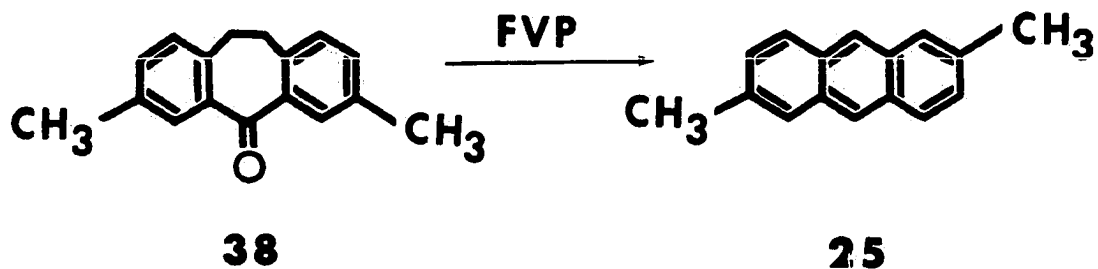
groups were attached to the dibenzosuberone nucleus to serve as regio-chemical markers in order to gain evidence for the 180° ring flip of

the original aromatic rings, which is a signature of our mechanistic

proposals. The FVP of 38 gave regiospecifically, and in high yield,

2,6-dimethylanthracene (25).

In an effort to extend the generality of this transformation and

to derive synthetic utility for it, the FVP of the functionalized

dibenzosuberones 39 and 40 was undertaken. These compounds, upon

flash vacuum pyrolysis, produce, regiospecifically, the corresponding
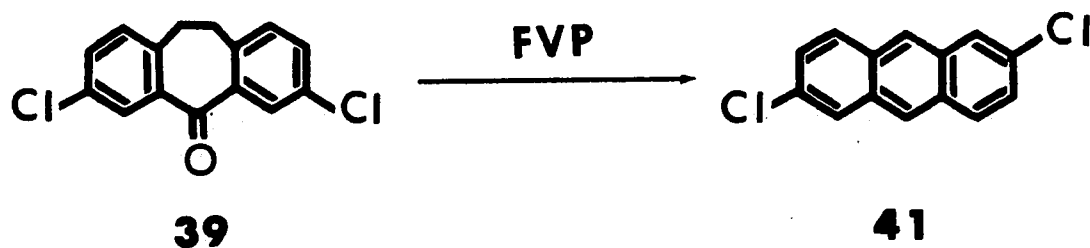
difunctionalized anthracenes 41 and 42, respectively.
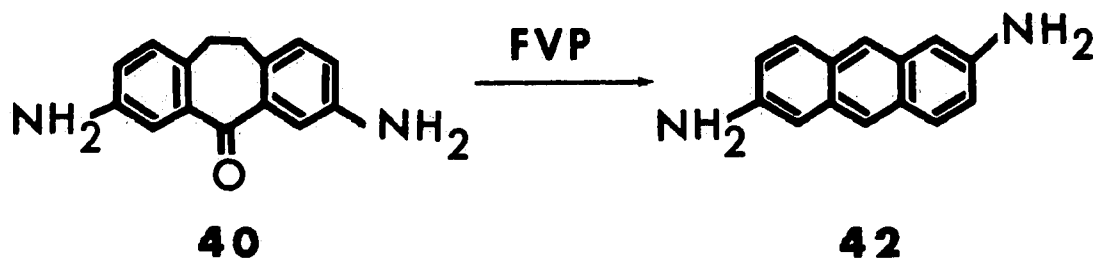
RESULTS

Experiments on the 4-Vinylcyclohexene System

Butadiene (32) was readily obtained by thermolysis of sulfone 43 at 130°C.[48,49] The reaction stream was bubbled through 10% NaOH to

$$\text{43} \quad \text{SO}_2 \longrightarrow \text{32} \quad + \quad \text{SO}_2$$

43   **32**
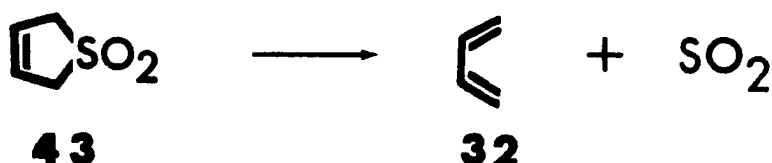
trap the sulfur dioxide produced and then the butadiene (32) was condensed at -150°C to give an analytically pure sample. The ^{1}H NMR and ^{13}C NMR of 32 are shown in Figures 1 and 2, respectively.[50,51]

The butadiene (32), which was a solid at the cold trap temperatures, was transferred directly to a prepared sealed tube via a bulb to bulb distillation apparatus. After three freeze-thaw cycles, the tube was sealed and placed in an autoclave with pentane. After the autoclave was sealed, the sample was heated to 136°C for twelve hours.[52,53] The autoclave technique was necessary because a large percentage of the sealed tubes would burst when heated directly.

Figure 1. Proton NMR spectra (300 MHz) of (a) butadiene (32) and (b) butadiene-1,1,4,4-$\underline{d}_4$ (32-$\underline{d}_4$)

CHCl₃

b

a

8   6   4   2   0   PPM.
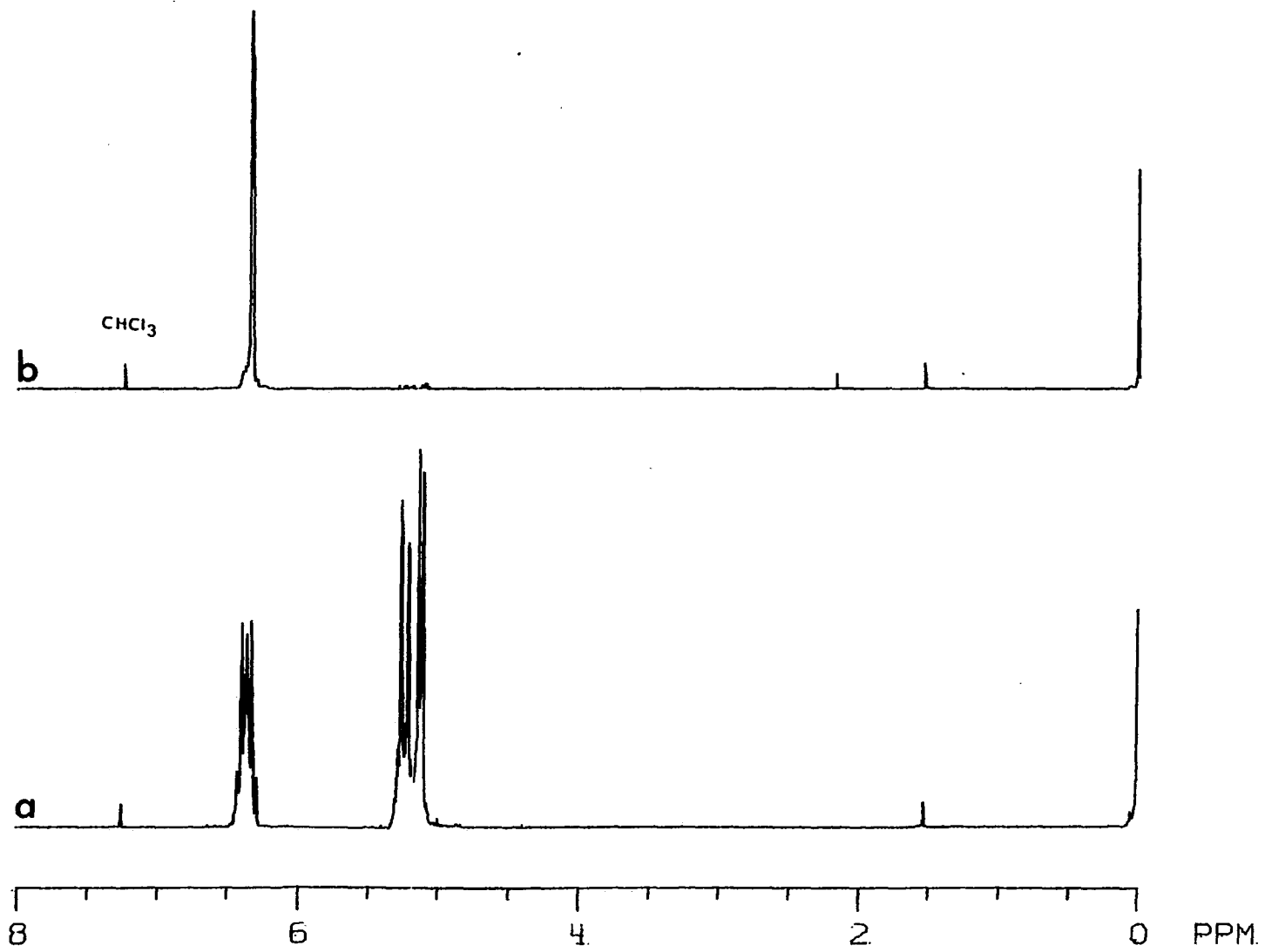
Figure 2. Carbon-13 NMR spectra (74 MHz) of (a) butadiene (32) and (b) butadiene-1,1,4,4-$\underline{d}_4$ (32-$\underline{d}_4$)
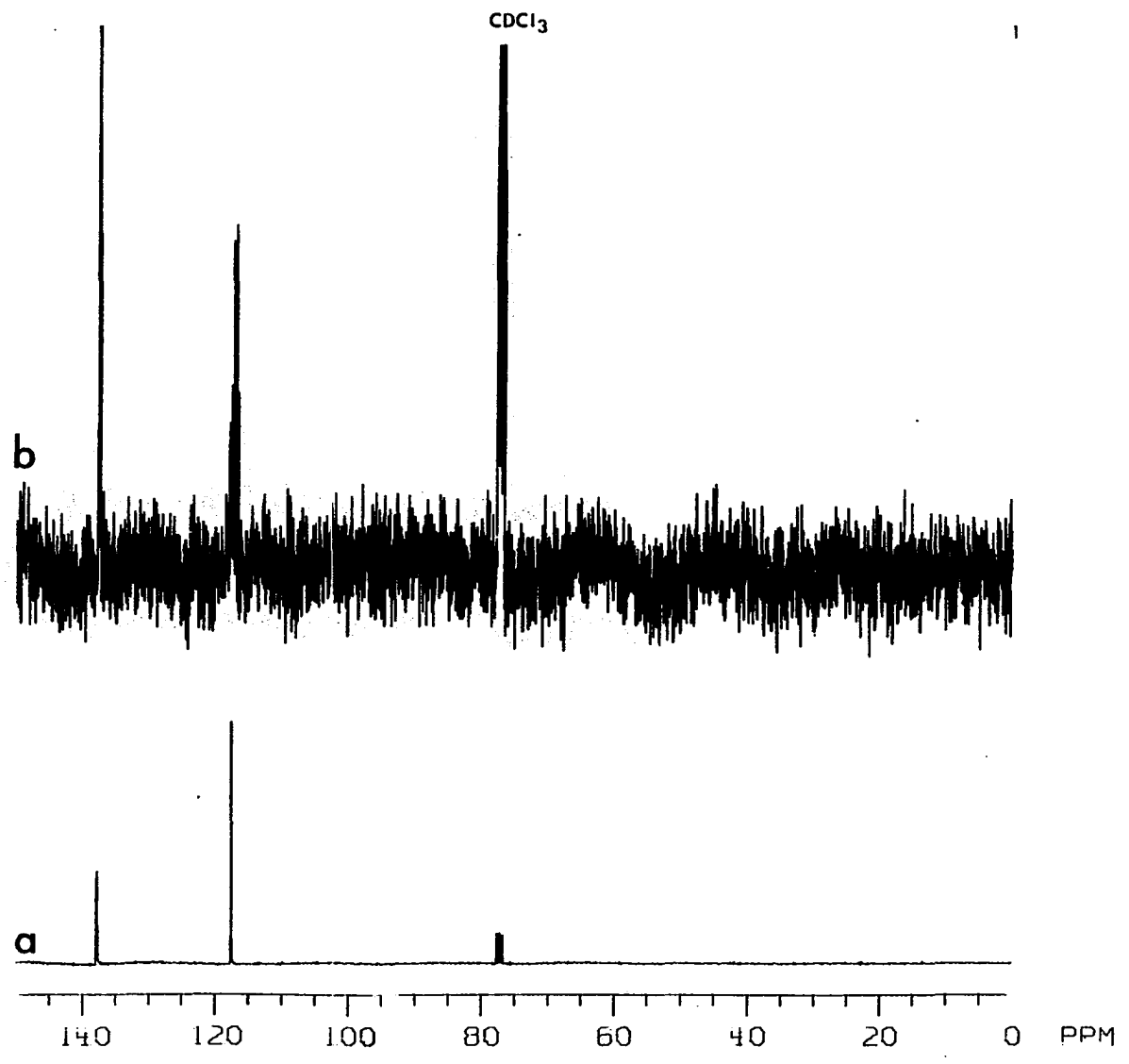
The static thermolysis of butadiene (32) gave as the major product

4-vinylcyclohexene (VCH) (34), which arises from a Diels-Alder reaction

(Figure 3).[52,53,54] Combined gas chromatography (gc) and mass spectra

(ms) analysis showed the product to be 94% pure, contaminated by 5%

44 and 0.3% 45, which arise from secondary rearrangements of 34.
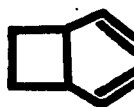
44   **45**

The relative amount of the impurities is dependent on the reaction

time, as 44 and 45 are ultimately converted to 34, the thermodynamic

product (vide infra).

Sulfolene (43) could be readily deuterated by modification of

literature procedures (Scheme 4).[49,55,56] Deuterium incorporation was

determined by ^{1}H NMR through integration of the C-2 (3) protons vs. the

residual of the C-1 (4) protons, and was found to be equal to 98% -d_4.

In Figure 4, one can see that the position of deuteration is unambiguous,

as the only aliphatic absorption of 43 disappears after the completion

of this transformation. In Figure 5, one can see the development of

carbon-deuterium coupling for the C-1 (4) positions.[57] Throughout

Figure 3. Proton NMR spectra (300 MHz) of (a) 4-vinylcyclohexene (34) and (b) 4-vinylcyclohexene-3,3,5,5,6,6,8,8-$\underline{d}_8$ (34-$\underline{d}_8$)
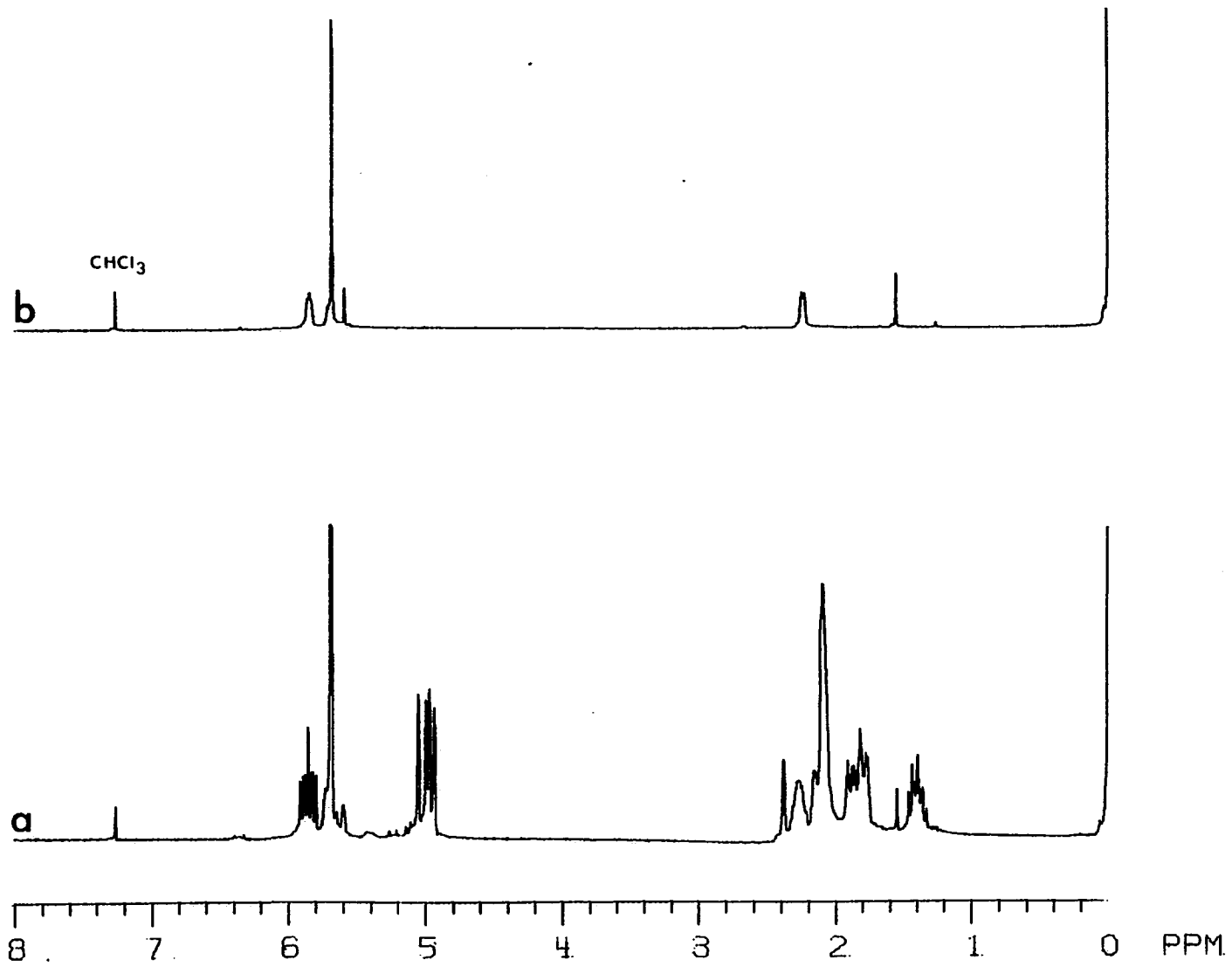
Figure 4. Proton NMR spectra (300 MHz) of (a) sulfolene ($\underset{\sim\sim}{43}$) and (b) sulfolene-2,2,5,5-$\underline{d}_4$ ($\underset{\sim\sim}{43}$-$\underline{d}_4$)
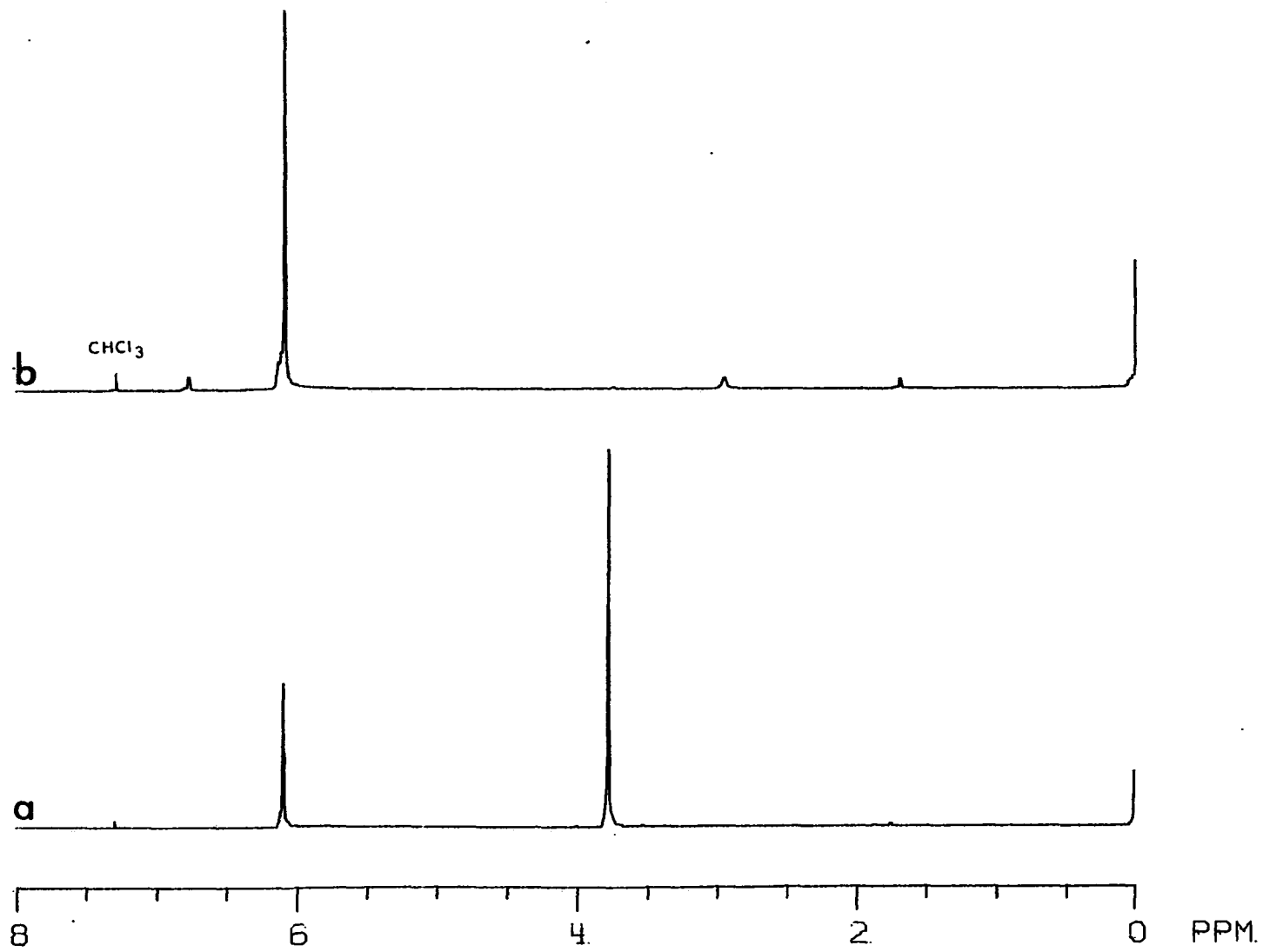
Figure 5. Carbon-13 NMR spectra (74 MHz) of (a) sulfolene (43) and (b) sulfolene-2,2,5,5-$\underline{d}_4$ (43-$\underline{d}_4$)
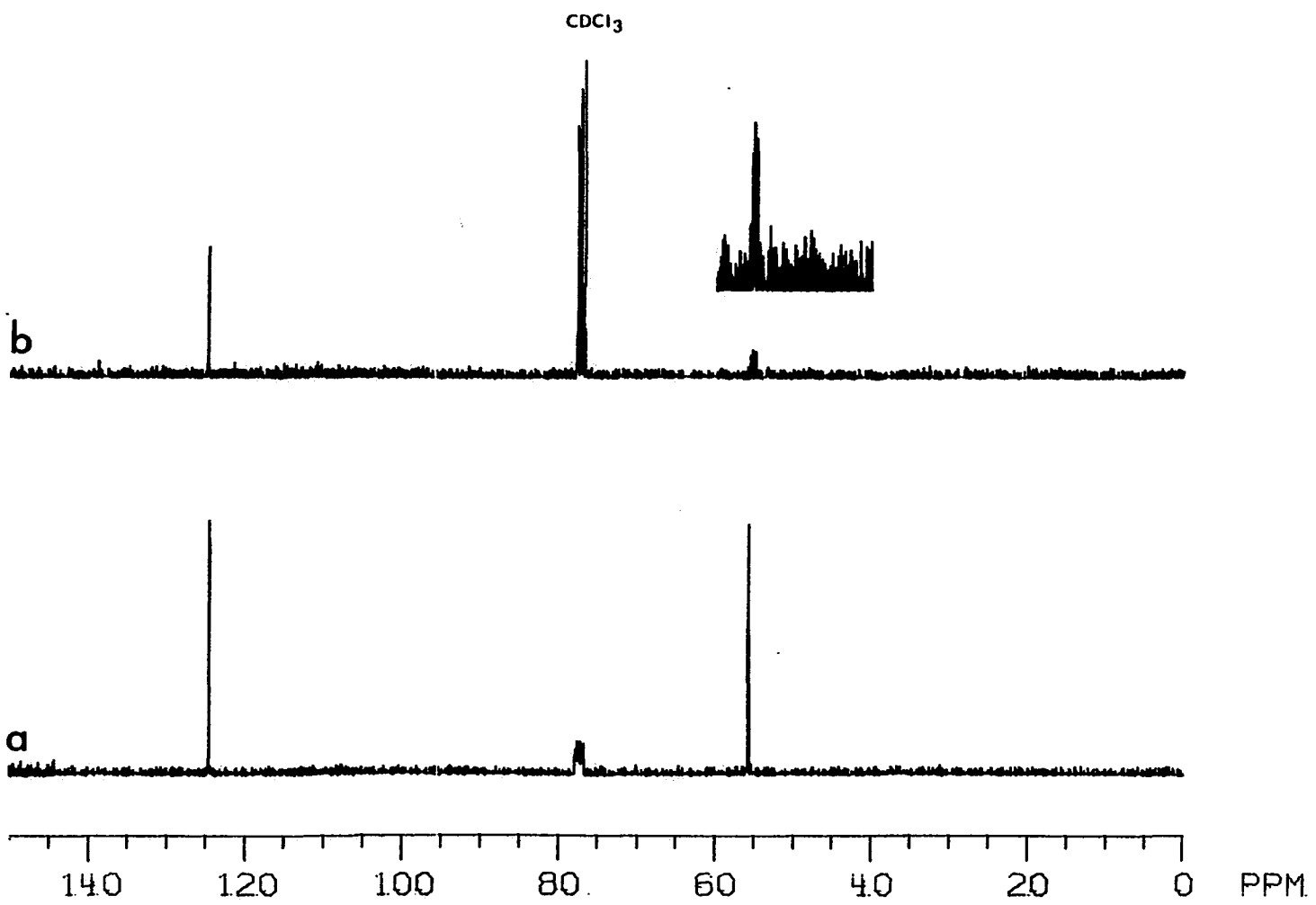
this dissertation, the corresponding deuterium containing compound

will be referred to simply by placing a "-d_x" after the number of the

parent compound. The subscript indicates the number of deuterium

atoms which have been incorporated. A "-d" placed after the number

of the parent compound will signify that the compound is of mixed

deuterium content. Thus, deuteration of sulfone 43 produced 43-d_4

(Scheme 6).

Scheme 6
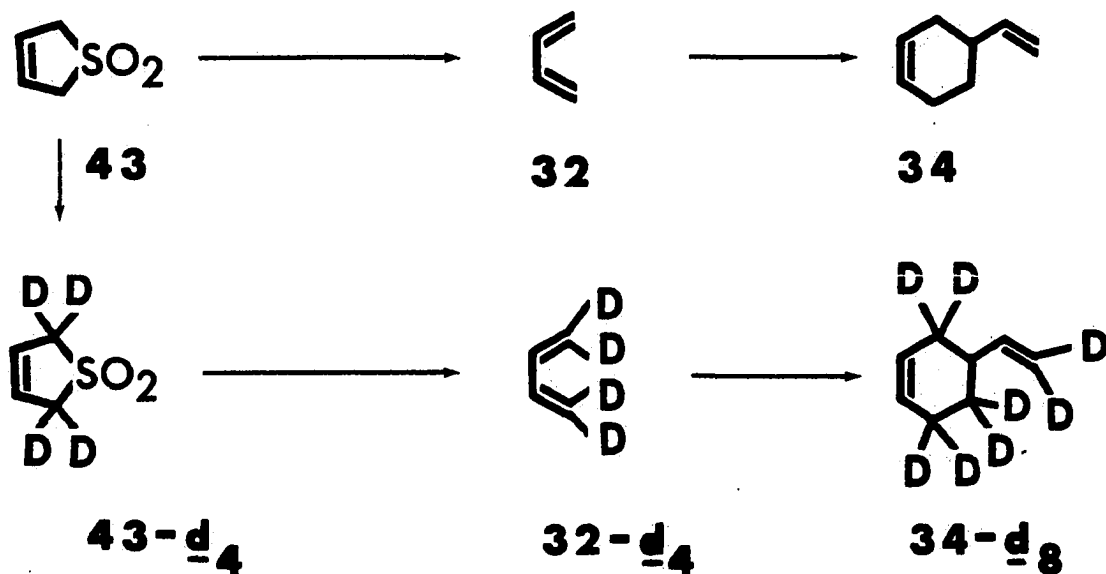
Thermolysis of $\underline{43}$-$\underline{d}_4$ was accomplished by the same procedure which was used for the light system. NMR analysis (^{1}H) of the butadiene ($\underline{32}$-$\underline{d}_4$) produced showed the deuterium content to be equal to 98% -$\underline{d}_4$. The ^{1}H NMR spectrum (Figure 1) establishes the position of the deuterium. The absorption corresponding to the C-1 (4) positions (internal and external) has disappeared, and a singlet results for the C-2 (3) protons. The ^{13}C NMR spectrum confirms this analysis, as coupling is now observed for the absorption at 117 ppm, while the absorption at 138 ppm remains as a singlet (Figure 2).[57] From ms analysis (Table 1), the following is calculated; 0.1% $\underline{d}_0$, 0.1% $\underline{d}_1$, 0.6% $\underline{d}_2$, 3.0% $\underline{d}_3$, 95.2% $\underline{d}_4$ and 1.0% $\underline{d}_5$.[58]

The static thermolysis of $\underline{32}$-$\underline{d}_4$ produced the octadeuterio-4-vinyl-cyclohexene $\underline{34}$-$\underline{d}_8$, 98% -$\underline{d}_8$ by ^{1}H NMR (Figure 3). The deuterium position was as expected for this [4+2] cycloaddition as can be seen from the remaining absorptions which correspond to the protons on carbons 1, 2, 3, and 7 (δ 5.65, 5.68, 2.26 and 5.82 respectively). From ms analysis (Table 2), the following is calculated: 0.84% $\underline{d}_6$, 5.15% $\underline{d}_7$, 85.7% $\underline{d}_8$, 7.84% $\underline{d}_9$.[58]

Flash vacuum pyrolysis (FVP) of VCH ($\underline{34}$) at 688°C (pressure = 0.007 mm Hg) produced butadiene ($\underline{32}$) as the sole product. Formation of $\underline{32}$ arises from a retro [4+2] reaction. Analysis by gc showed that the minor impurities, 1,5-cyclooctadiene ($\underline{44}$) and divinylcyclobutane

Table 1. Mass spectra data of butadiene (32) and of butadiene-1,1,4,4-$\underline{d}_4$ (32-$\underline{d}_4$)

M/e	Relative peak intensity of 32[a]	Relative peak intensity of 32-$\underline{d}_4$[a]	Calculated peak intensity					
			$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$	$\underline{d}_5$
52	31	82						
53	654	86						
54(P)	35999	118	118					
55	1642	129	6	123				
56	48	647		6	641			
57	.	3465			29	3436		
58		108263			1	157	108105	
59		6073				5	4931	1137
60		192						

[a] Ionization voltage was 18 e/V.

(45) were completely converted to 34 at this temperature. Pyrolysis at higher temperatures, 800-830°C, also gave 32 as the major product (76%) (Figure 6), but in addition two new products were obtained.

Table 2. Mass spectra data of 4-vinylcyclohexene ($\underset{\sim\sim}{34}$) and of 4-vinyl-cyclohexene-3,3,5,5,6,6,8,8-$\underline{d}_8$ ($\underset{\sim\sim}{34}$-$\underline{d}_8$)

M/e	Relative peak intensity of $\underset{\sim\sim}{34}$[a]	Relative peak intensity of $\underset{\sim\sim}{34}$-$\underline{d}_8$[a]	Calculated peak intensity			
			$\underline{d}_6$	$\underline{d}_7$	$\underline{d}_8$	$\underline{d}_9$
106	109					
107	231					
108(P)	7672					
109	447	23				
110	16					
111						
112		65				
113		31				
114		215	215			
115		1318	13	1305		
116		21952		76	21876	
117		3416		3	1275	2139
118						

[a]Ionization voltage was 18 eV.
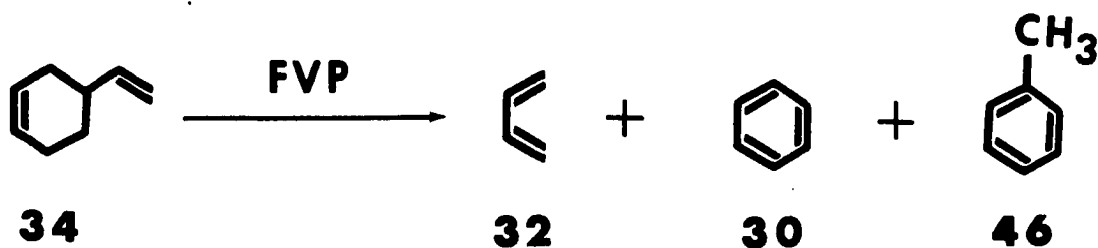
Benzene (30) and toluene (46) were produced in a 1:1.2 molar

ratio (average of 6 runs) (Table 3). These products were identified

by the following methods: 1) coinjection techniques using authentic

samples; 2) gc/ms analysis utilizing a computer assisted library search;

3) isolation by preparative gas liquid chromatography and subsequent

^{1}H NMR analysis.

The FVP of 34-d_8 at 800°C gave products that correlated with the

pyrolysis of the light system by gc analysis and by NMR (Figure 6).

For the benzene (30) produced, the deuterium content was determined

as 2% d_0, 0.5% d_1, 12% d_2, 35% d_3, 34% d_4, 14% d_5, and 2% d_6 (Table 4),[58]

experimentally a 1:3:3:1 ratio of d_2:d_3:d_4:d_5 species. An accurate

quantification of the deuterium content for the toluene-d (46-d) was

not possible due to the large contribution of the M-1 peak in the ms

Table 3. Relative yields of starting material, benzene (30), and
toluene (46) produced in the FVP of 4-vinylcyclohexene (34)
at 800°C

| Conditions | | | Relative yields, % | | | Analysis | Ratio |
T,°C	Sample head T,°C	P, mm Hg	34	30	46	method	46/30
688	0	0.007	100			gc	
800	-15	0.015	54.3	22.3	23.4	gc[a]	1.05
800	-15	0.004	39.6	26.7	33.7	gc[a]	1.26
800	-15	0.005	38.7	27.5	33.8	gc[a]	1.23
			27.4	31.4	41.2	NMR[b]	1.31
825	-15	0.010	3.1	40.0	56.9	gc[a]	1.42
830	-15	0.006	10.0	43.5	46.3	gc[a]	1.06
810[c]	-15	0.007	8.8	42.4	48.8	gc	1.15

[a]Uncorrected for response factor.

[b]Determined by integration of the aromatic protons of 30 and 46 and also the olefinic protons of 34.

[c]Data given are for the FVP of 34-d_8.

Figure 6. Proton NMR spectra (300 MHz) of (a) the pyrolyzate of the FVP of 4-vinylcyclohexene ($\underset{\sim}{34}$) at 800°C and (b) the pyrolyzate of the FVP of 4-vinylcyclohexene-3,3,5,5,6,6,8,8-$\underline{d}_8$ ($\underset{\sim}{34}$-$\underline{d}_8$) at 800°C
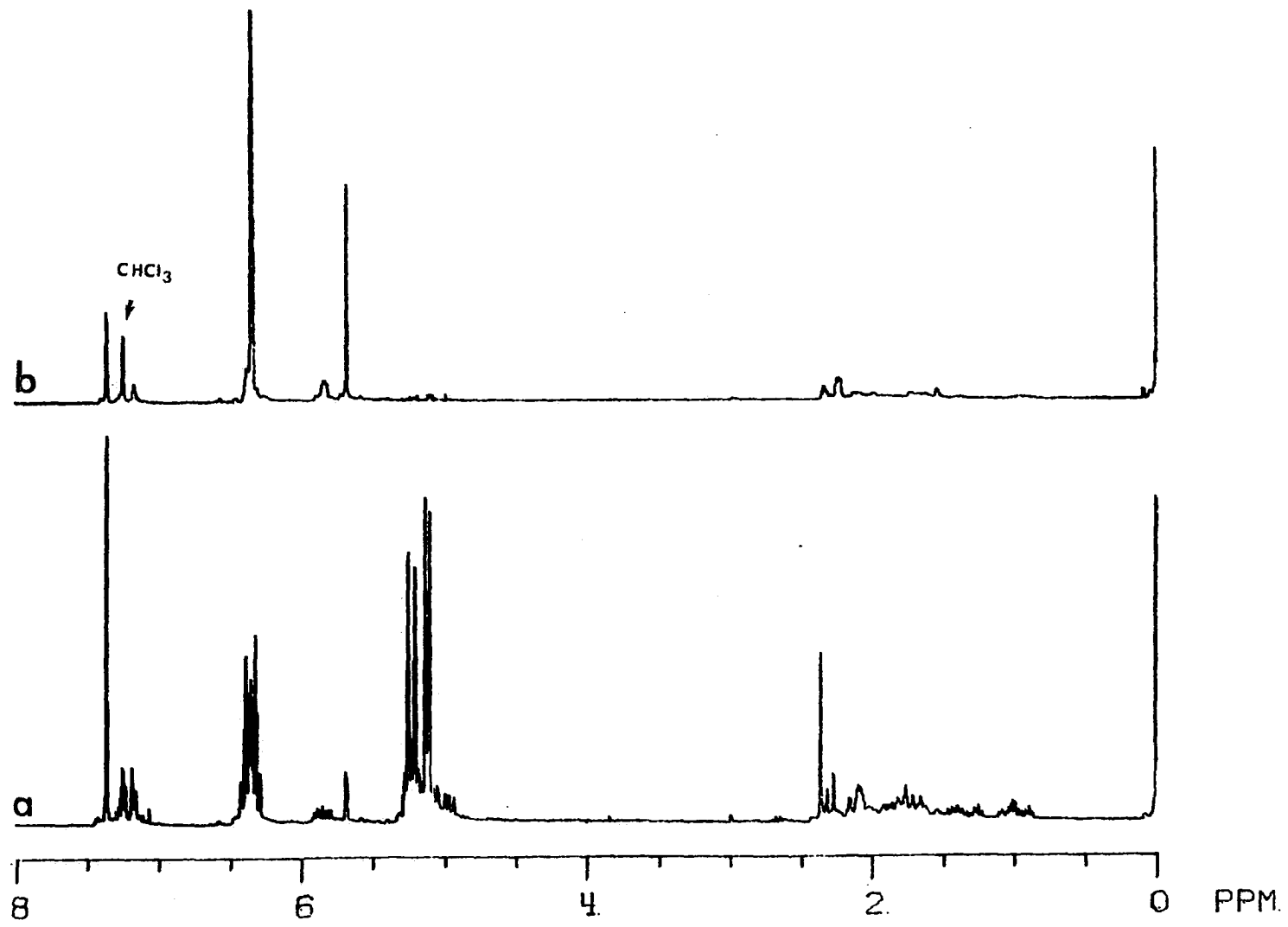
Table 4. Mass spectra data of benzene ($\underset{\sim\sim}{30}$) and of benzene-$\underline{d}$ ($\underset{\sim\sim}{30}$-$\underline{d}$) produced in the FVP of 4-vinylcyclohexene-3,3,5,5,6,6,8,8-$\underline{d}_8$ ($\underset{\sim\sim}{34}$-$\underline{d}_8$) at 800°C

M/e	Relative peak intensity of $\underset{\sim\sim}{30}$ [a]	Relative peak intensity of $\underset{\sim\sim}{30}$-$\underline{d}$ [a]	Calculated peak intensity						
			$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$	$\underline{d}_5$	$\underline{d}_6$
76	845								
77	4619	83							
78(P)	447504	5945	5945						
79	28166	1482	375	1107					
80	2099	28429	28	70	28331				
81		85198		5	1785	83408			
82		87417			133	5255	82029		
83		39426				392	5168	33686	
84		7066					385	2122	455
85		838							
86		160							

[a] Ionization voltage was 20 eV.

of $\underset{\sim\sim}{46}$.[58] By inspection of the ^{1}H NMR of the pyrolyzate (Figure 7) and by inspection of the ms data on $\underset{\sim\sim}{46}$-$\underline{d}$ (Table 5), one can be convinced that the deuterium content is, as is the case for $\underset{\sim\sim}{30}$-$\underline{d}$, scrambled.

Figure 7. Proton NMR spectra (300 MHz) of (a) the toluene (46) produced in the FVP of 4-vinylcyclohexene (34) and (b) the pyrolyzate of the FVP of 4-vinylcyclohexene-3,3,5,5-6,6,8,8-d_8 (34-d_8) (with butadiene-1,1,4,4-d_4 (32-d_4) removed)
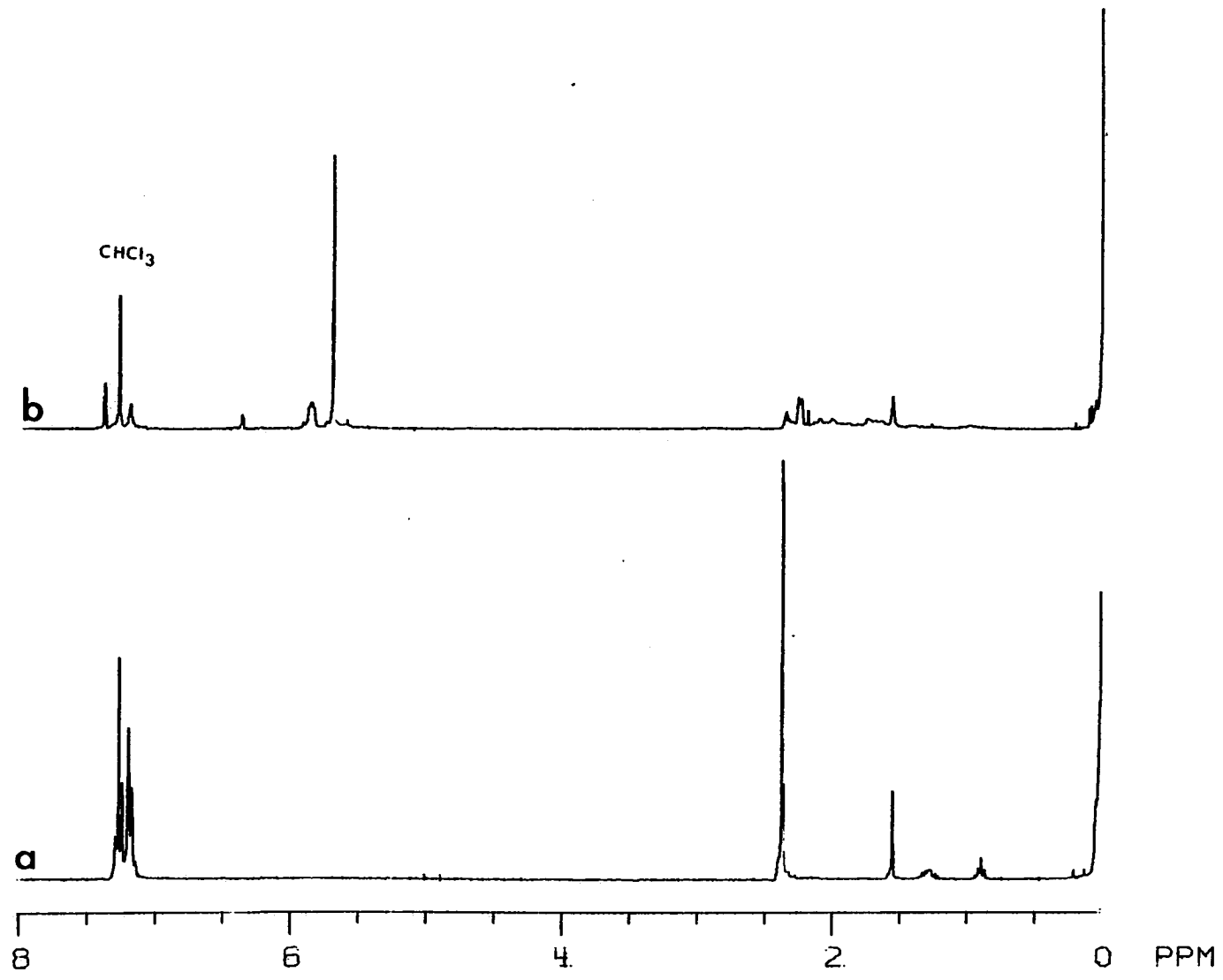
Table 5. Mass spectra data of toluene ($\underset{\sim\sim}{46}$) and of toluene-$\underline{d}$ ($\underset{\sim\sim}{46}$-$\underline{d}$) produced in the FVP of 4-vinylcyclohexene-3,3,5,5,6,6,8,8-$\underline{d}_8$ ($\underset{\sim\sim}{34}$-$\underline{d}_8$) at 800°C

M/e	Relative peak intensity of $\underset{\sim\sim}{46}$[a]	Relative peak intensity of $\underset{\sim\sim}{46}$-$\underline{d}$[a]
90	521	38
91	201182	7441
92(P)	745449	28508
93	56534	2174
94		2630
95		18237
96		54989
97		131362
98		104077
99		14177
100		3091
101		1610
102		383

[a]Ionization voltage was 18 eV.

Analysis of the recovered starting material in the above pyrolysis

is informative. By ^{1}H NMR, the spectrum (Figures 6 and 8) of the

unchanged starting material was identical to the spectrum of original

VCH-d_8 (34-d_8) introduced (Figure 3). By ms analysis, the deuterium

content was also identical, within experimental error (Tables 6 and 7).

The same observation holds for the butadiene-d_4 (32-d_4) produced via

the retro [4+2] reaction, the deuterium has not undergone any scrambling,

as can be seen by identical NMR spectra (Figures 1 and 9) and by ms

analysis (Tables 8 and 9).

The FVP of bicyclo[2.2.2]octene (47) was studied briefly. The

47

FVP of 47 from 625-825°C gave benzene (30) and 1,3-cyclohexadiene (48)

as the major products. No evidence for any significant amount of

1,4-cyclohexadiene (36) was obtained. The results of the pyrolysis

experiments are summarized in Table 10. The conditions for these

experiments (Table 10) were not designed to mimic those of the pyrolysis

Figure 8. Proton NMR spectra (300 MHz) of (a) 4-vinylcyclohexene (34) and (b) the pyrolyzate of the FVP of 4-vinylcyclohexene-3,3,5,5,6,6,8,8-$\underline{d}_8$ ($\underline{34}$-$\underline{d}_8$) (with butadiene-1,1,4,4-$\underline{d}_4$ ($\underline{32}$-$\underline{d}_4$) removed)

44
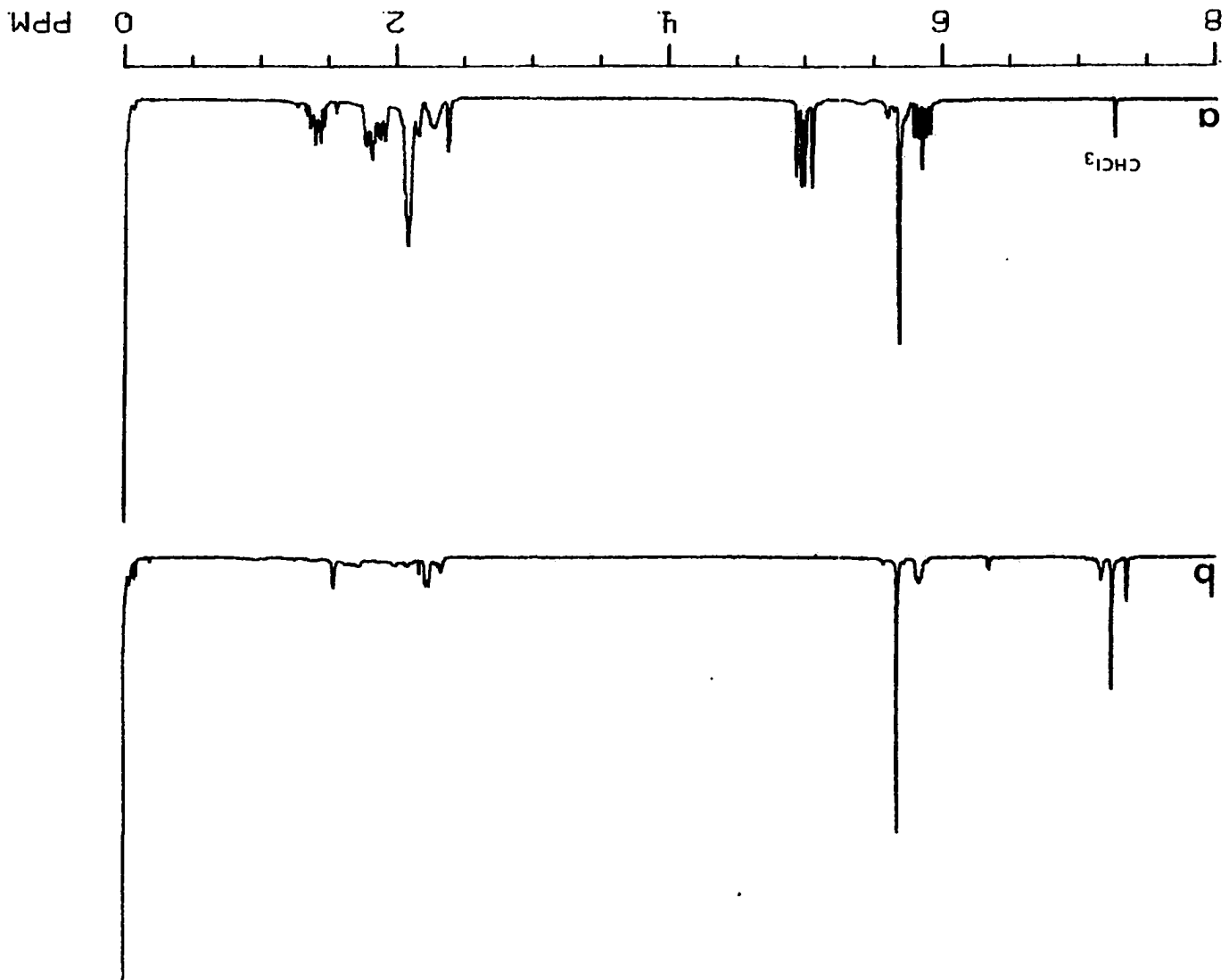
Table 6. Mass spectra data of 4-vinylcyclohexene (34) and of the
recovered starting material in the FVP of 4-vinylcyclohexene-
3,3,5,5,6,6,8,8-d_8 (34-d_8) at 800°C

M/e	Relative peak intensity of 34[a]	Relative peak intensity of recovered 34-d_8[a]	Calculated peak intensity			
			d_6	d_7	d_8	d_9
106	109					
107	231					
108(P)	165032	6				
109	10315	16				
110	39608	18				
111		18				
112		9				
113		26				
114		83	83			
115		301	5	296		
116		5621		17	5604	
117		673		1	325	347
118		27				

[a]Ionization voltage was 18 eV.

Table 7. Comparison of the deuterium content of 4-vinylcyclohexene-3,3,5,5,6,6,8,8-d_8 (34-d_8) and of the recovered starting material in the FVP of 34-d_8 at 800°C

Deuterium species	Deuterium content,%[a]		
		Recovered	
	34-d_8[b]	34-d_8[c]	Difference[d]
d_6	0.8	1.3	0.5
d_7	5.1	4.7	0.4
d_8	85.7	88.5	2.8
d_9	8.4	5.5	2.9

[a]Based on ms analysis.

[b]Data given in Table 2.

[c]Data given in Table 6.

[d]Absolute value.

4 8

3 6

Figure 9. Proton NMR spectra (300 MHz) of (a) butadiene-1,1,4,4-$\underline{d}_4$ ($\underset{\sim\sim}{32}$-$\underline{d}_4$) and (b) the pyrolyzate of the FVP of 4-vinylcyclohexene-3,3,5,5,6,6,8,8-$\underline{d}_8$ ($\underset{\sim\sim}{34}$-$\underline{d}_8$)

b

a

CHCl₃

8.   6   4.   2.   0   PPM
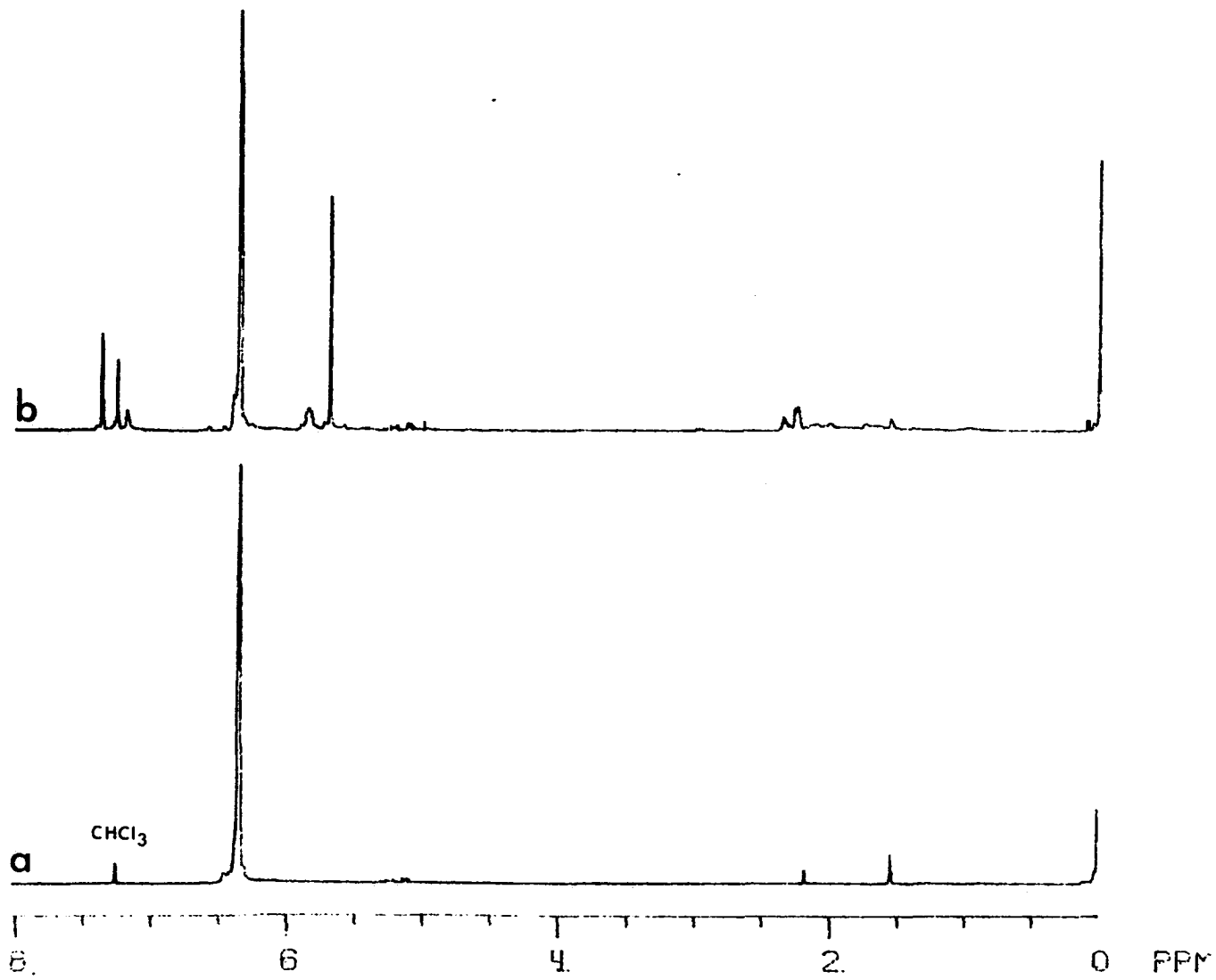
Table 8. Mass spectra data of butadiene ($\underset{\sim}{32}$) and of butadiene-1,1,-4,4-$\underline{d}_4$ ($\underset{\sim}{32}$-$\underline{d}_4$) produced in the FVP of 4-vinylcyclohexene-3,3,5,5,6,6,8,8-$\underline{d}_8$ ($\underset{\sim}{34}$-$\underline{d}_8$) at 800°C

M/e	Relative peak intensity of $\underset{\sim}{32}$[a]	Relative peak intensity of $\underset{\sim}{32}$-$\underline{d}_4$[a]	Calculated peak intensity					
			$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$	$\underline{d}_5$
52	31	8						
53	654	7						
54(P)	35999	22	22					
55	1642	52	1	51				
56	48	236		2	234			
57		2090			11	2079		
58		31387				95	31292	
59		2104				3	1427	674
60		75						
61		21						

[a]Ionization voltage was 18 eV.

of 4-vinylcyclohexene ($\underset{\sim}{34}$), they were only performed to establish that benzene ($\underset{\sim}{30}$) could be produced from $\underset{\sim}{47}$ under FVP conditions.

Table 9. Deuterium content of butadiene-1,1,4,4-d_4 (32-d_4) and of
32-d_4 produced in the FVP of 4-vinylcyclohexene-3,3,5,5-
6,6,8,8-d_8 (34-d_8) at 800°C

Deuterium species	Deuterium content, %		
	32-d_4 [a]	Recovered 32-d_4 [b]	Difference[c]
d_0	0.1	0.06	0.0
d_1	0.1	0.15	0.05
d_2	0.6	0.68	0.08
d_3	3.0	6.0	3.0
d_4	95.2	91.1	4.1
d_5	1.0	2.0	1.0

[a]Data given in Table 1.

[b]Data given in Table 8.

[c]Absolute value.

Table 10. Relative yields of unchanged starting material, benzene (30),
1,3-cyclohexadiene (48), and 1,4-cyclohexadiene (36) in the
FVP of bicyclo[2.2.2]octene (47)

Conditions			Relative Yield, %[a]			
T, °C	Sample head T, °C	p, mm Hg	47	30	48	36
560	25	0.02	94.0		6.0	
625	25	0.02	73.2	0.5	26.3	
725	25	0.02	2.4	19.3	78.3	trace
825	25	0.02	1.9	29.4	68.7	

[a]Determined by averaging the results from the NMR integration and
the results of gc analysis uncorrected for response factor.

Experiments on Allylic Esters

The pyrolysis of allylic esters was undertaken in order to establish

the generality of the transformation described herein. Compound 49

was synthesized by the reaction of benzoyl chloride (50) with allyl
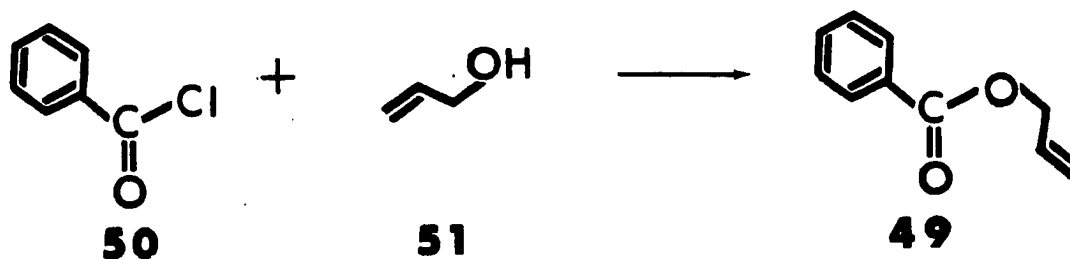
alcohol (51).[59,60] The allylic esters 52 and 53 were produced in a
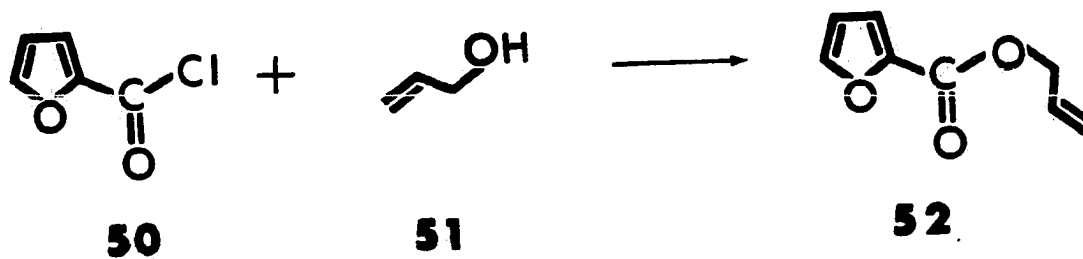
similar manner.[59]
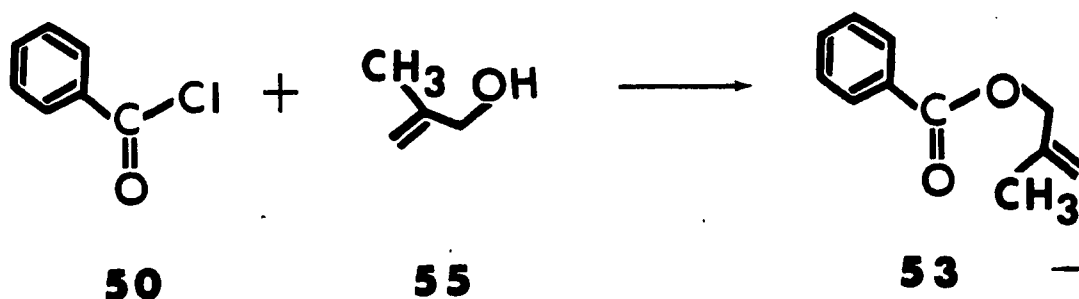
The FVP of these esters gave the results shown in Table 11. The products of the FVP of 49 were identified by gc analysis by coinjection of authentic samples and by ^{1}H NMR analysis. The products of the FVP of 52 and 53 were determined by NMR analysis by comparison to the results obtained in the FVP of 49. Yields of the reactions of these three esters were determined by NMR analysis after the addition of an internal standard.[61]

Experiments on the Dibenzocyclooctene System

In an effort to correlate the results obtained in the FVP of VCH (34) and 34-d_8 to the [4+4] dimer 16, the synthesis of 16-d_4 was undertaken. The key intermediate in this synthesis was the sulfone 56. Our experience has shown that sulfones can be readily deuterated,

Table 11. Summary of the product yields in the FVP of allyl benzoate
(49), allyl furoate (52) and 2-methylpropenyl-1 benzoate
(53) at 800°C

Allylic ester $ArCOOCH_2CRCH_2$			Product yield, $\%^{a,b}$			
Ar	R	Cmpd. #	$ArCH_2CRCH_2$	ArCOOH	ArH	Recovered starting material
Ph	H	49	6.4	11	57	17
2-furyl	H	52	1.2	12	20	13
Ph	CH_3	53	4.0	10	15	14

[a]Yields determined by ^1H NMR after the addition of CH_3NO_2 as an internal standard.

[b]Average of two determinations.

16-$\underline{d}_4$

56
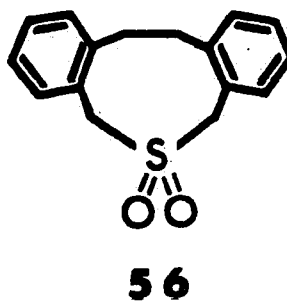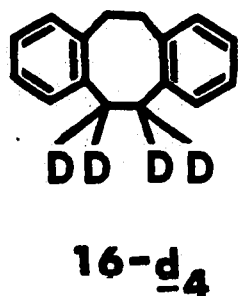
and it is well-known that SO_2 can be readily extruded at relatively low pyrolysis temperatures.[62] The synthetic strategy, which followed literature procedures, is shown in Scheme 7.[63-68] The deuteration of 56 could not be accomplished simply with D_2O and K_2CO_3 alone, as the sulfone was insoluble under these conditions, even at reflux. Addition of 1 part of THF per 5 parts of D_2O made the sulfone partially soluble only at the elevated temperature and deuteration could then proceed. The deuterium position was clearly established by ^1H NMR (Figure 10), and is as expected, adjacent to the SO_2 functionality.[68] The deuterium incorporation for 56-d_4, as calculated from ms data (Table 12), is given in Table 13.

Both sulfones 56 and 56-d_4 could be cleanly converted to their corresponding dibenzocyclooctenes 16 and 16-d_4 by FVP at 550°C (Figure 11). The deuterium content for both 56-d_4 and 16-d_4 was calculated to be 96% -d_4 by ^1H NMR. The ms data for 16-d_4 are presented in Table 14 and summarized in Table 13.

Earlier work on the FVP of the [4+4] dimer 16 in these laboratories showed that the major product was anthracene (13).[18,19] Also identified in the pyrolyzate mixture were unchanged 16, seven $C_{16}H_{16}$ compounds (mw = 208), and two compounds with a mw of 192. The results reported herein are consistent with this analysis, and the comparison will be displayed further on in this section (Table 15).

Scheme 7

57 → 58 → 59

60 → 61

62

56

56-d₄ → 16-d₄

63 → 64 → 65
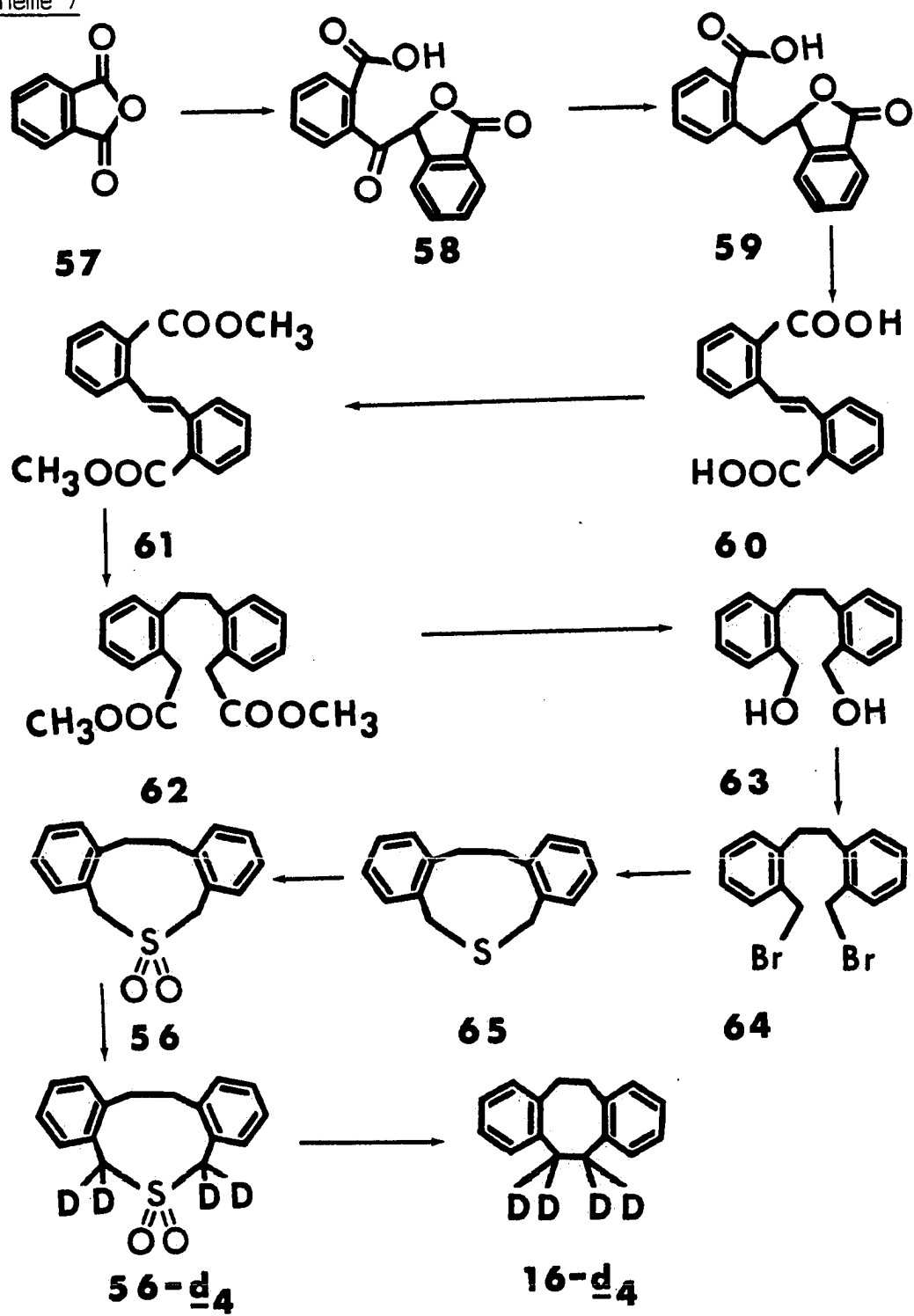
Figure 10. Proton NMR spectra (300 MHz) of (a) dibenzo[c,g]thiapinedioxide (56) and (b) dibenzo-
[c,g]thiapinedioxide-5,5,7,7-d₄ (56-d₄)
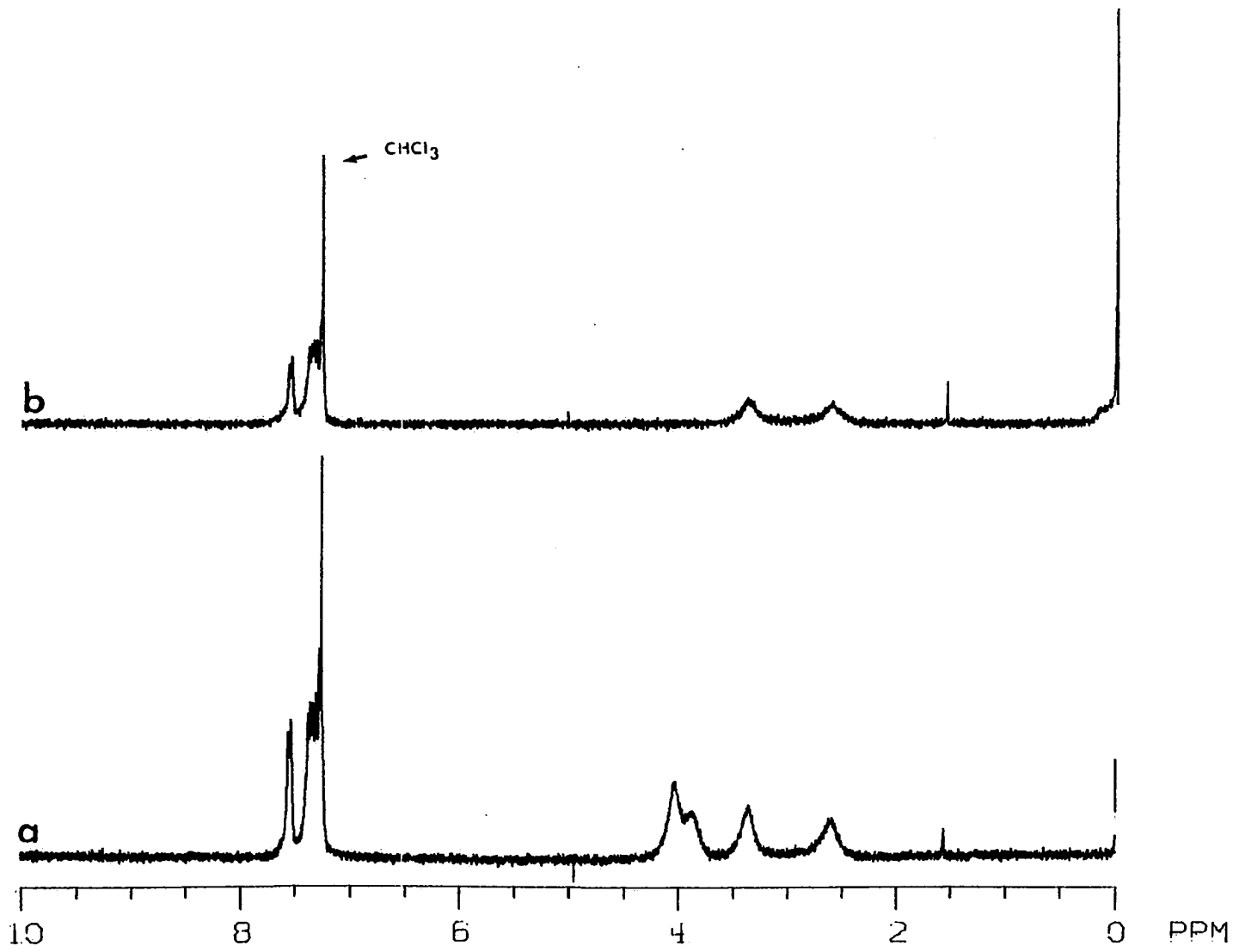
Table 12. Mass spectra data of dibenzo[c,g]thiapinedioxide (56) and of dibenzo[c,g]thiapinedioxide-5,5,7,7-$\underline{d}_4$ (56-$\underline{d}_4$)

M/e	Relative peak intensity of 56 [a,b]	Relative peak intensity of 56-$\underline{d}_4$ [a,b]	Calculated peak intensity					
			$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$	$\underline{d}_5$
270	230	15						
271	457	24						
272(P)	54608	213	213					
273	8359	55	33	22				
274	2126	242		3	239			
275	127	1067		1	37	1028		
276		93604			9	158	93437	
277		15524				40	14303	1181
278		4559						
279		343						

[a]Ionization voltage was 16 eV.

[b]Determined on a solid sample.

It is appropriate, at this point, to mention the expected results from the pyrolysis of 16-$\underline{d}_4$. In what was expected to be a straight-forward experiment, the FVP of 16-$\underline{d}_4$ was designed to prove unambiguously

Table 13. Summary of the deuterium content for dibenzo[c,g]thiapine-
dioxide-5,5,7,7-$\underline{d}_4$ ($\underset{\sim\sim}{56}$-$\underline{d}_4$) and for 5,6,11,12-tetrahydro-
dibenzo[a,e]cyclooctene-5,5,6,6-$\underline{d}$ ($\underset{\sim\sim}{16}$-$\underline{d}_4$)

Deuterium species	Deuterium content, %	
	$\underset{\sim\sim}{56}$-$\underline{d}_4$ [a]	$\underset{\sim\sim}{16}$-$\underline{d}_4$ [b]
$\underline{d}_0$	0.22	
$\underline{d}_1$	0.02	
$\underline{d}_2$	0.25	0.40
$\underline{d}_3$	1.1	2.3
$\underline{d}_4$	96.2	97.3
$\underline{d}_5$	1.2	

[a]Data given in Table 12.

[b]Data given in Table 14.

which carbons were being lost in the transformation from [4+4] dimer

to anthracene. Thus, anthracene ($\underset{\sim\sim}{13}$) and anthracene-9,10-$\underline{d}_2$ ($\underset{\sim\sim}{13}$-$\underline{d}_2$)

were expected in roughly an equal ratio (Scheme 8).

The FVP of $\underset{\sim\sim}{16}$-$\underline{d}_4$ gave a pyrolyzate which had identical retention

times and product distributions to that observed for the light system.

However, ms analysis of the anthracene ($\underset{\sim\sim}{13}$) produced did not show a

1:1 ratio of $\underline{d}_0$:$\underline{d}_2$, but rather a 1:2:1 ratio of $\underline{d}_0$:$\underline{d}_1$:$\underline{d}_2$; an unexpected,

statistical ratio. The FVP of $\underset{\sim\sim}{56}$-$\underline{d}_4$ gave results which were identical

to those obtained from the FVP of $\underset{\sim\sim}{16}$-$\underline{d}_4$ (Table 15, Figure 12). Mass

Figure 11. Proton NMR spectra (300 MHz) of (a) 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (16) and 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene-5,5,6,6-d$_4$ (16-d$_4$)

Table 14. Mass spectra data of 5,6,11,12-tetrahydrodibenzo[a,e]cyclo-
octene (16) and of 5,6,11,12-tetrahydrodibenzo[a,e]cyclo-
octene-5,5,6,6-$\underline{d}_4$ (16-$\underline{d}_4$)

M/e	Relative peak intensity of 16[a]	Relative peak intensity of 16-$\underline{d}_4$[a]	Calculated peak intensity		
			$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$
207	10714				
208(P)	463484				
209	76905				
210	6673	321	321		
211	326	1943	54	1889	
212		79299	5	320	78974
213		13095			
214		1046			

[a]Ionization voltage was 20 eV.

spectra analysis (Tables 16-22) showed that the seven $C_{16}H_{16}$ isomers, which must be constitutional isomers of the [4+4] dimer, retained all four of their deuterium atoms (Table 23).

A ^{2}D NMR of the pyrolyzate showed that the deuterium incorporation in the anthracene-$\underline{d}$ (13-$\underline{d}$) produced was only in the equivalent 9,10 positions, where it was originally expected (Figure 13). Indeed, the

Table 15. Comparison of the product distribution in the FVP of 5,6,11,-12-tetrahydrodibenzo[a,e]cyclooctene (16) performed in earlier work to the FVP of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene-5,5,6,6-$\underline{d}_4$ (16-$\underline{d}_4$), dibenzo[c,g]thiapinedioxide (56), and dibenzo[c,g]thiapinedioxide-5,5,7,7-$\underline{d}_4$ (56-$\underline{d}_4$) performed in this work

Compound[a]	Yield, %[b]				
	Earlier work from 16[c]		Present work, 860°C		
	805°C	800°C	From 16-$\underline{d}_4$[d]	From 56	From 56-$\underline{d}_4$[d]
66	1.1	4.4	3.3	2.8	2.8
67	1.5	2.6	3.0	3.1	3.1
68	3.7	1.6	2.8	2.7	2.8
75	1.6	3.2	3.5	3.8	3.8
16	58.8	9.5	29.5	22.7	22.7
13	4.9	25.1	19.0	23.0	23.0
69	0.5	4.8	3.5	4.2	4.2
70	5.7	6.6	14.4	12.2	12.2
71	4.3	9.0	12.4	13.7	13.7
76	1.1	8.1	5.9	7.8	7.8
77		1.0	1.3	2.3	2.3

[a]See pages 78 and 83 for compound structures.

[b]Uncorrected for response factor.

[c]Reference 19.

[d]Percentages refer to products, not deuterium content or position.

Figure 12. Proton NMR spectra (300 MHz) of (a) the pyrolyzate of the FVP of dibenzo[c,g]thia-
pinedioxide-5,5,7,7-$\underline{d}_4$ ($\underline{56}$-$\underline{d}_4$) and (b) the pyrolyzate of the FVP of 5,6,11,12-tetra-
hydrodibenzo[a,e]cyclooctene-5,5,6,6-$\underline{d}_4$ ($\underline{16}$-$\underline{d}_4$)

PPM 2 3 4 5 6 7 8 9

a

b

CH₂Cl₂

Scheme 8

13   **16-d₄**   **13-d₂**
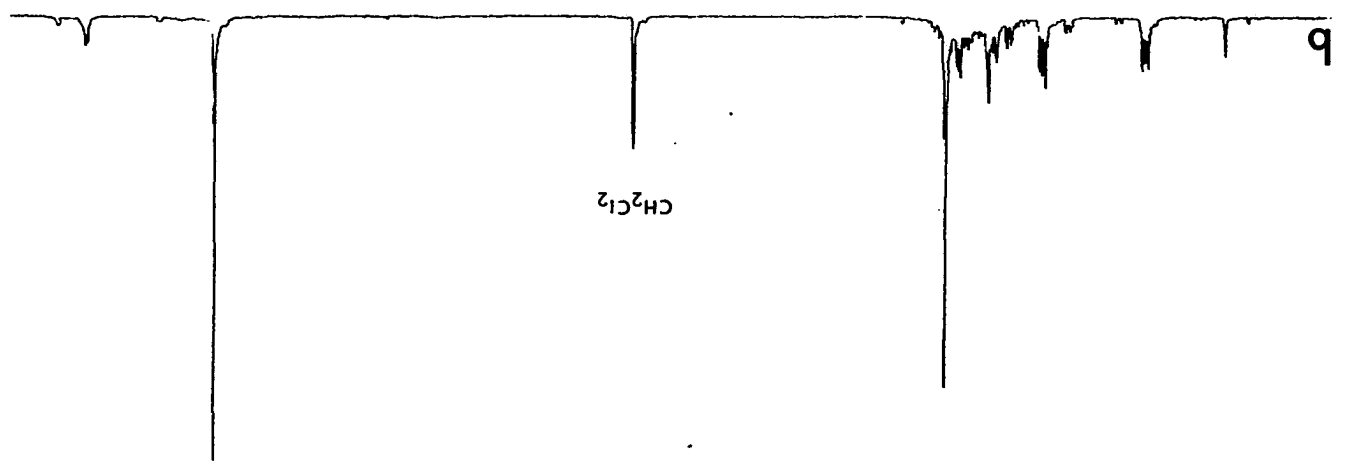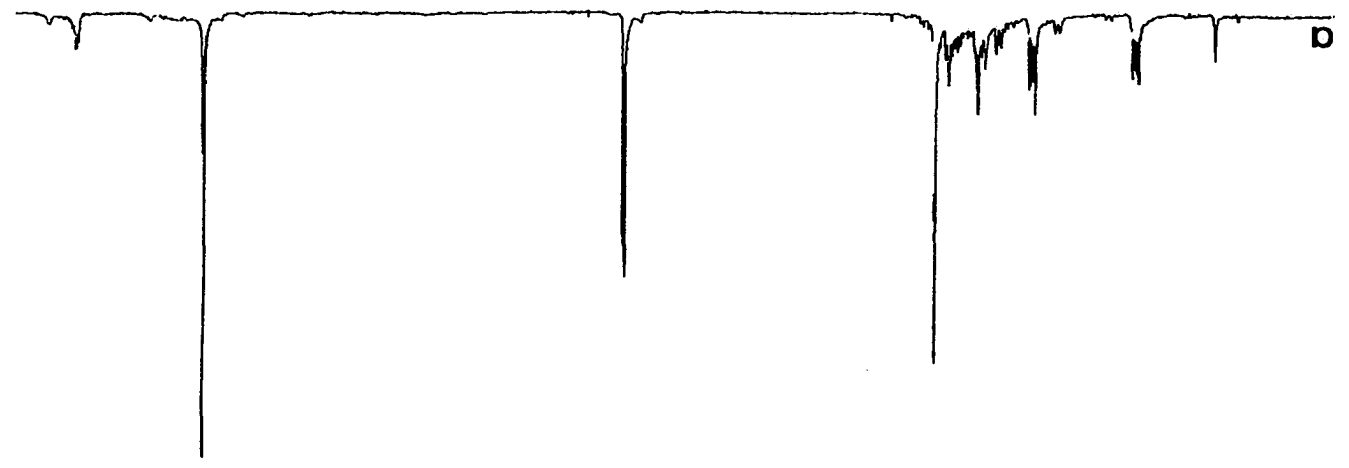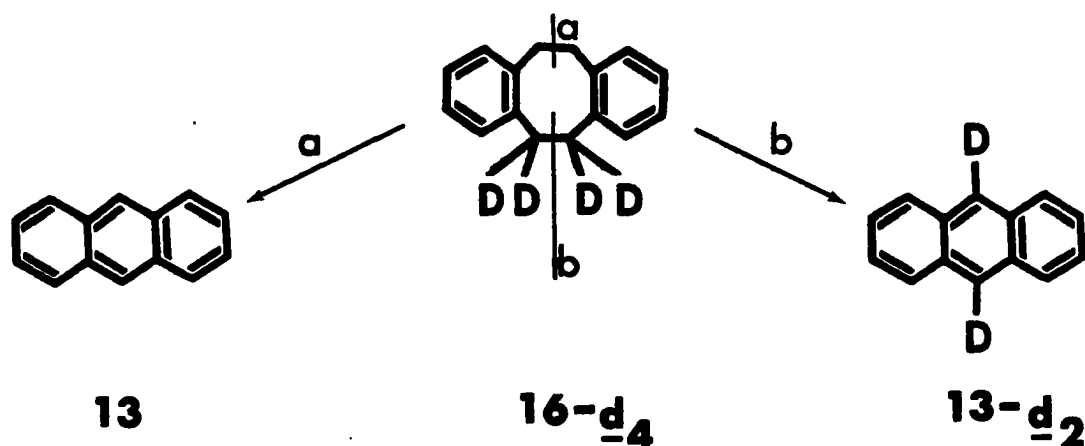
only absorptions in the aromatic region were from anthracene-$\underline{d}$ ($\underline{13}$-$\underline{d}$),

and from the compounds of mw 192 (vide infra). Thus, not only did

recovered $\underline{16}$-$\underline{d}_4$ and the seven $C_{16}H_{16}$ isomers retain all of their

deuterium, none of the deuterium was scrambled into an original aromatic

nucleus.

This is an important result in itself. Since deuterium was not

transferred from one molecule to another, the above results demonstrate

the unimolecularity of these low pressure pyrolysis reactions. It

was thought, at this point, that the deuterium scrambling might be due

to the equilibration of the seven $C_{16}H_{16}$ isomers before transformation

to anthracene ($\underline{13}$). Thus, if these isomers could be identified, then

Table 16. Mass spectra data of 1-($\underline{m}$-toly)indan ($\underline{66}$) and of 1-($\underline{m}$-tolyl)indan-$\underline{d}_4$ $\underline{66}$-$\underline{d}_4$ produced in the FVP of dibenzocyclooctene-5,5,6,6-$\underline{d}_4$ ($\underline{16}$-$\underline{d}_4$) and dibenzo[c,g]thiapinedioxide-5,5,7,7-$\underline{d}_4$ ($\underline{56}$-$\underline{d}_4$) at 860°C

| M/e | Relative peak intensity of $\underline{66}$[a] | From $\underline{16}$-$\underline{d}_4$ | | | | | From $\underline{56}$-$\underline{d}_4$ | | | |
| | | Relative peak intensity of $\underline{66}$-$\underline{d}_4$[a] | Calculated peak intensity | | | | Relative peak intensity of $\underline{66}$-$\underline{d}_4$[a] | Calculated peak intensity | | |
			$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$	$\underline{d}_5$		$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$
206	26									
207	385									
208(P)	17684									
209	3036									
210	270	18	18				34	34		
211		161	3	158			152	6	146	
212		6432		27	6405		6577		25	6552
213		1162		2	1100	60	1066			
214		109					76			

[a]Ionization voltage was 20 eV.

Table 17. Mass spectra data of 1-(o-tolyl)indan (67) and of 1-(o-tolyl)indan-d_4 (67-d_4) produced in the FVP of dibenzocyclooctene-5,5,6,6-d_4 (16-d_4) and dibenzo[c,g]thiapinedioxide-5,5,7,7-d_4 (56-d_4) at 860°C

M/e	Relative peak intensity of 67[a]	From 16-d_4				From 56-d_4			
		Relative peak intensity of 67-d_4[a]	Calculated peak intensity			Relative peak intensity of 67-d_4[a]	Calculated peak intensity		
			d_2	d_3	d_4		d_2	d_3	d_4
206	101								
207	360								
208(P)	14326								
209	2410								
210	227	18	18			29	29		
211		118	6	112		121	5	116	
212		3736	1	40	3695	4137	1	19	4118
213		690				664			
214		66				44			

[a]Ionization voltage was 20 eV.

Table 18. Mass spectra data of cis-2,2'-dimethylstilbene (68) and of cis-2,2'-dimethylstilbene-d_4 (68-d_4) produced in the FVP of dibenzocyclooctene-5,5,6,6-d_4 (16-d_4) and dibenzo-[c,g]thiapinedioxide-5,5,7,7-d_4 (56-d_4) at 860°C

M/e	Relative peak intensity of 68[a]	From 16-d_4					From 56-d_4			
		Relative peak intensity of 68-d_4[a]	Calculated peak intensity				Relative peak intensity of 68-d_4[a]	Calculated peak intensity		
			d_2	d_3	d_4	d_5		d_2	d_3	d_4
206	14									
207	254									
208(P)	5865									
209	1001									
210	90	18	18				16	16		
211		124	3	121			66	3	63	
212		3148		21	3127		1995		11	1984
213		556		2	534	20	274			
214		50					17			

[a]Ionization voltage was 20 eV.

Table 19. Mass spectra data of 2-(m-tolyl)indan ($\underline{75}$) and of 2-(m-tolyl)indan-$\underline{d}_4$ ($\underline{75}$-$\underline{d}_4$) produced in the FVP of dibenzocyclooctene-5,5,6,6-$\underline{d}_4$ ($\underline{16}$-$\underline{d}_4$) and dibenzo[c,g]thiapinedioxide-5,5,7,7-$\underline{d}_4$ ($\underline{56}$-$\underline{d}_4$) at 860°C

| M/e | Relative peak intensity of $\underline{75}$[a] | From $\underline{16}$-$\underline{d}_4$ | | | | | From $\underline{56}$-$\underline{d}_4$ | | | |
| | | Relative peak intensity of $\underline{75}$-$\underline{d}_4$[a] | Calculated peak intensity | | | | Relative peak intensity of $\underline{75}$-$\underline{d}_4$[a] | Calculated peak intensity | | |
			$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$	$\underline{d}_5$		$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$
206	220									
207	1133									
208(P)	18513									
209	3168									
210	312	42	42				46	46		
211		348	7	341			302	8	294	
212		6296	1	58	5717		5297		52	5245
213		1126		6	977	143	881			
214		104					61			
215		3								

[a]Ionization voltage was 20 eV.

Table 20. Mass spectra data of 2-(o-tolyl)indan (69) and of 2-(o-tolyl)indan-d_4 (69-d_4) produced in the FVP of dibenzocyclooctene-5,5,6,6-d_4 (16-d_4) and dibenzo[c,g]thiopinedioxide-5,5,7,7-d_4 (56-d_4) at 860°C

M/e	Relative peak intensity of 69[a]	From 16-d_4 Relative peak intensity of 69-d_4[a]	Calculated peak intensity d_2	d_3	d_4	d_5	From 56-d_4 Relative peak intensity of 69-d_4[a]	Calculated peak intensity d_2	d_3	d_4
206	315									
207	383									
208(P)	18881									
209	3260									
210	304	26	26				44	44		
211		68	4	64			103	8	95	
212		3708		11	3697		5992	1	16	5975
213		670		1	638	31	929			
214		66					56			
215		2								

[a]Ionization voltage was 20 eV.
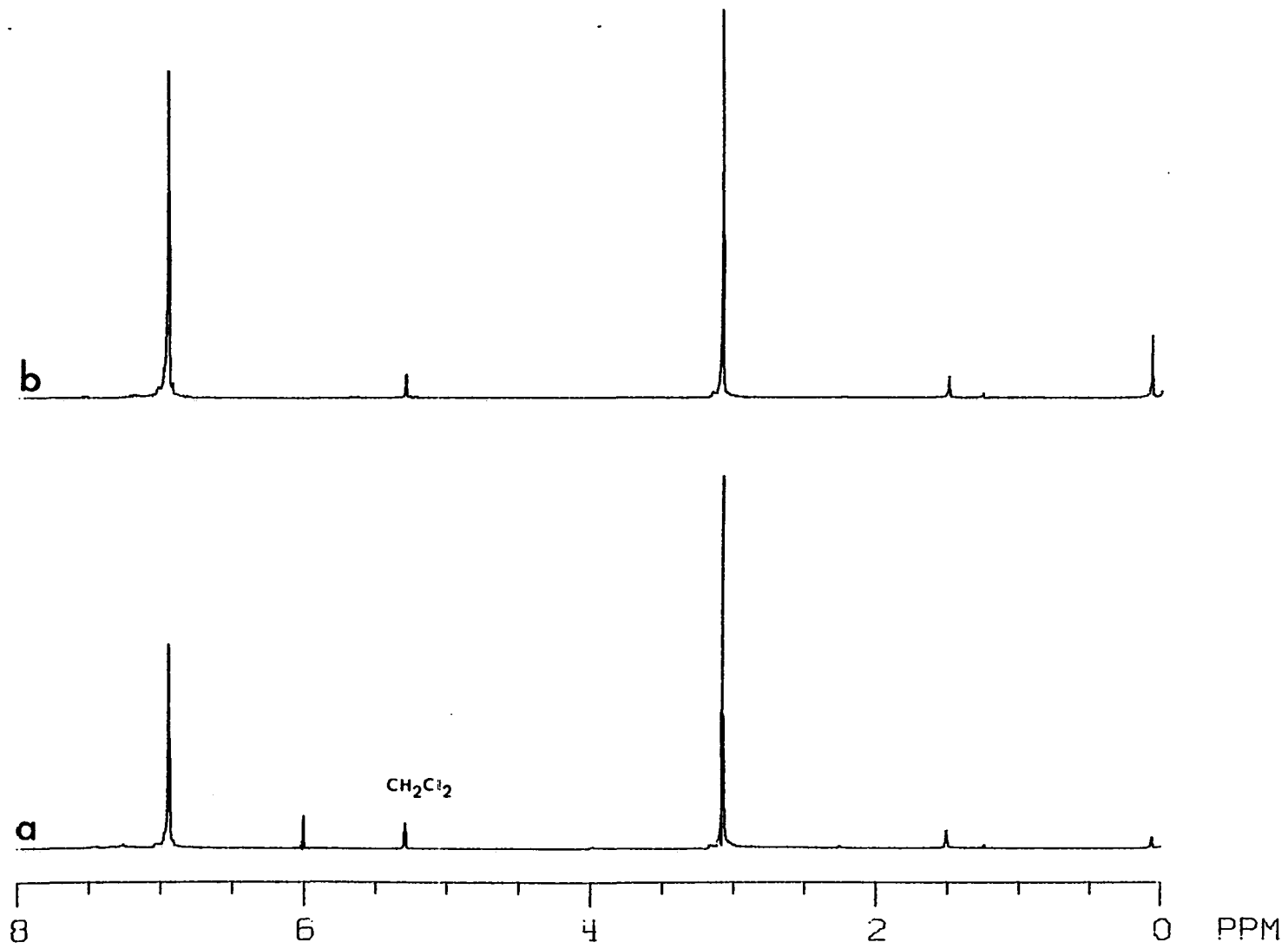
Table 21. Mass spectra data of 5,6,7,12-tetrahydrodibenzo[a,d]cycloctene (70) and of 5,6,7,12-tetrahydrodibenzo[a,d]cyclooctene-$\underline{d}_4$ (70-$\underline{d}_4$) produced in the FVP of dibenzocyclooctene-5,5,6,6-$\underline{d}_4$ (16-$\underline{d}_4$) and dibenzo[c,g]thiapinedioxide-5,5,7,7-$\underline{d}_4$ (56-$\underline{d}_4$) at 860°C

M/e	Relative peak intensity of 70[a]	From 16-$\underline{d}_4$				From 56-$\underline{d}_4$			
		Relative peak intensity of 70-$\underline{d}_4$[a]	Calculated peak intensity			Relative peak intensity of 70-$\underline{d}_4$[a]	Calculated peak intensity		
			$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$		$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$
206	171								
207	2008								
208(P)	54469								
209	9273								
210	810	798	798			133	133		
211		5965	136	5829		849	23	826	
212		152347	12	992	151343	22562	2	141	22419
213		26368				3776			
214		2371				299			

[a]Ionization voltage was 20 eV.

Table 22. Mass spectra data of trans-2,2'-dimethylstilbene ($\underline{71}$) and of trans-2,2'-dimethyl-stilbene-d_4 ($\underline{71}$-d_4) produced in the FVP of dibenzocyclooctene-5,5,6,6-d_4 ($\underline{16}$-d_4) and dibenzo[c,g]thiapinedioxide-5,5,7,7-d_4 ($\underline{56}$-d_4) at 860°C

M/e	Relative peak intensity of $\underline{71}$[a]	From 16-d_4				From 56-d_4			
		Relative peak intensity of $\underline{71}$-d_4[a]	Calculated peak intensity			Relative peak intensity of $\underline{71}$-d_4[a]	Calculated peak intensity		
			d_2	d_3	d_4		d_2	d_2	d_3
206	245								
207	1670								
208(P)	73581								
209	12742								
210	1142	765	765			143	143		
211		4429	132	4297		643	25	618	
212		155595	12	744	154839	22782	2	107	22673
213		27223				3843			
214		2484				303			

[a]Ionization voltage was 20 eV.

Table 23. Summary of the deuterium content of the seven $C_{16}H_{16}$ isomers produced in the FVP of dibenzocyclooctene-5,5,6,6-d_4 (16-d_4) and dibenzo[c,g]thiapinedioxide-5,5,7,7-d_4 (56-d_4) at 860°C

Compound[a]	Deuterium content, %[b]						
	From 16-d_4				From 56-d_4		
	d_2	d_3	d_4	d_5	d_2	d_3	d_4
66	0.27	2.38	96.4	0.91	0.51	2.17	97.3
67	0.47	2.89	95.6		0.68	2.72	96.6
68	0.55	3.68	95.2	0.62	0.78	3.07	96.2
75	0.67	5.46	91.6	2.3	0.82	5.30	93.9
69	0.68	1.66	96.8		0.72	1.56	97.7
70	0.51	3.69	95.8		0.51	3.53	95.9
71	0.48	2.69	96.8		0.61	2.64	96.8

[a]See page 78 for compound structures.

[b]Mass spectra data given in Tables 16-22.

the energy surface in the conversion of dibenzocyclooctene 16 to anthracene (13) might be discernable. To meet this end, a large scale pyrolysis of 16 was performed so that a sufficient quantity of these isomers would be produced for subsequent identification.

A sufficient quantity of 16 was obtained by literature procedures. BCB (1) was produced in the FVP of o-methylbenzyl chloride (3) (equation 1).[2,3,69] Condensed phase thermolysis of BCB (1) gave 16.[24] In the

Figure 13. Deuterium NMR spectrum (34 MHz) of the pyrolyzate of the FVP of dibenzo[c,g]thia-pinedioxide-5,5,7,7-$\underline{d}_4$ ($\underset{\sim\sim}{\underline{56}}$-$\underline{d}_4$)

CD₂Cl₂
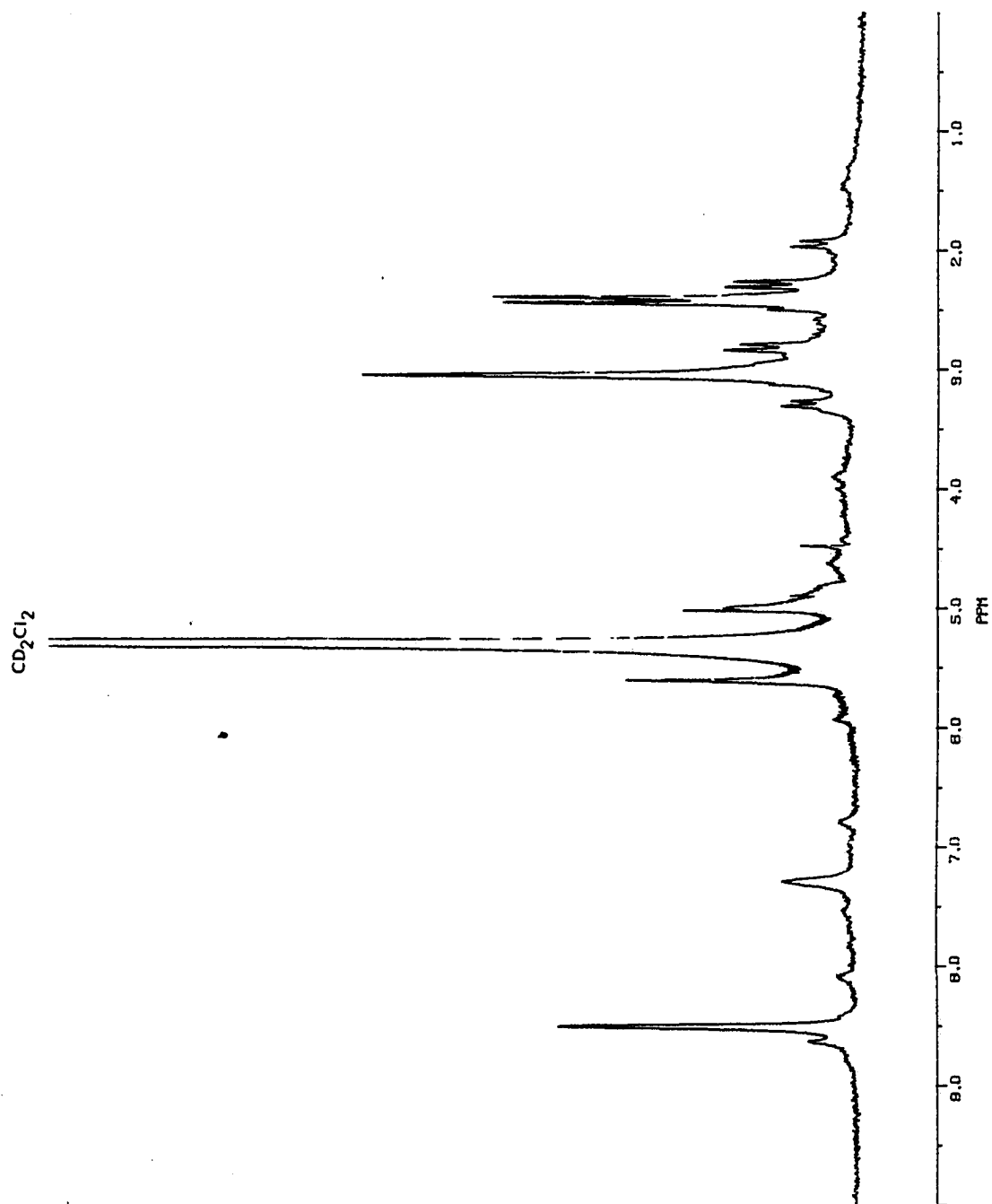
large scale FVP of 16, gc analysis showed the product mixture to be identical to that of the small scale experiments.

1   **16**
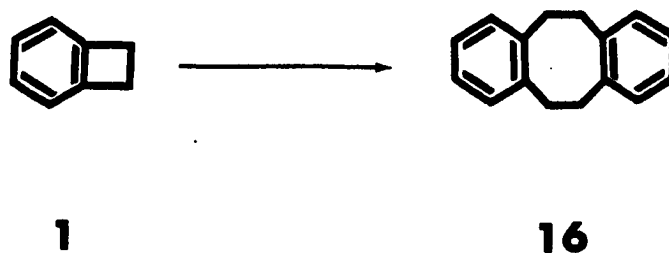
Ultimately, six out of the seven $C_{16}H_{16}$ isomers were isolated (compounds 66-71). The rationale for their assignments is described below.

Compounds 70[70,71] and 71[72] are known, and exist as solids. The melting points obtained agree with reported values, and the corresponding ^1H and ^{13}C NMR spectra are consistent with their structure. The ^1H NMR of 68 is clearly that of a symmetrical compound. The absorption for the olefinic proton is upfield for that observed in the NMR of 71, consistent with what has been observed for stilbene systems.[73] The ortho substitution of 68 is made based on its IR spectrum, which contains a strong band at 730 cm^{-1}. This is consistent with the out of plane (OOP) stretch of 4 adjacent hydrogens on an aromatic ring.[74,75] The corresponding band appears at 720 cm^{-1} for 71.
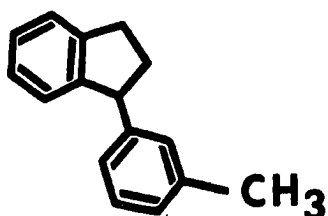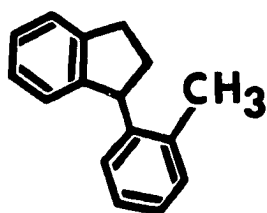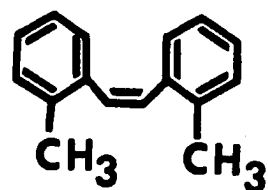
66   **67**   **68**
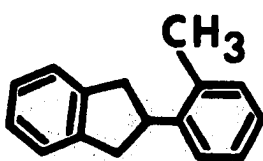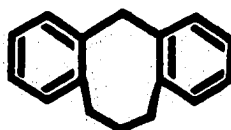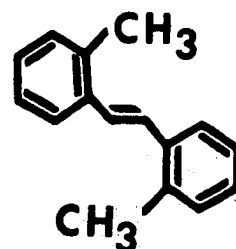
69   **70**   **71**

Compound 66 gives a complicated ^{1}H NMR spectrum. From two dimensional NMR (COSY),[76] the coupling of the eight aliphatic protons (integration = 1:1:1:1:1:3) was found to consist of an ABB' pattern, two AA'BB' patterns, two AA'BB'C patterns and a singlet (Figure 14). The position of the methyl group was determined by IR spectroscopy; the spectrum contained a strong band at 785 cm^{-1} (indan ring, 4 adjacent hydrogens) and a strong band at 695 cm^{-1} which corresponds to the OOP stretch of 1 isolated and 3 adjacent hydrogens on an aromatic ring.[74,75]

Figure 14. Closeup of the aliphatic region of (a) the 300 MHz NMR
spectrum (^{1}H) of 1-(m-tolyl)indan (66) and (b) the two
dimensional NMR spectrum (COSY) of 1-(m-tolyl)indan (66)
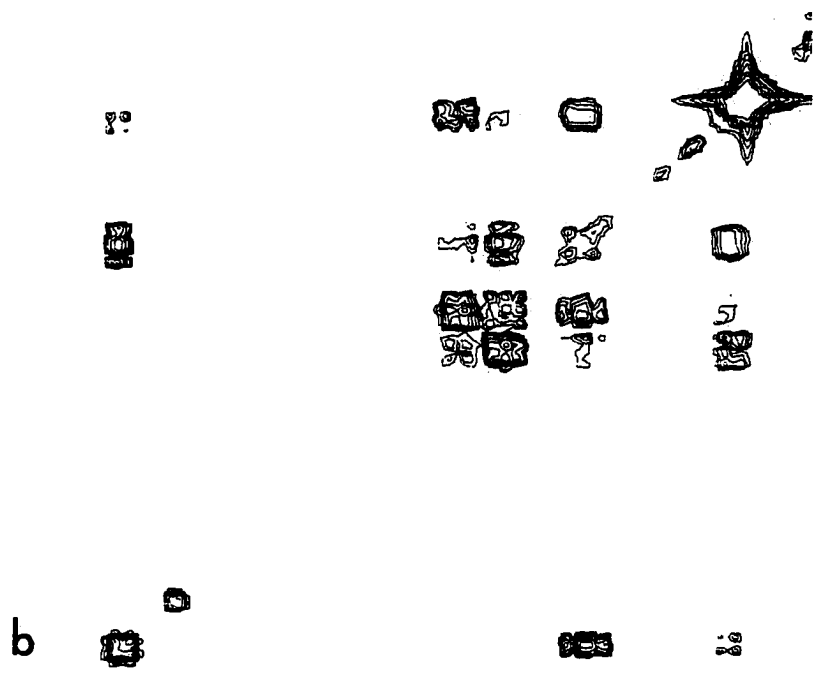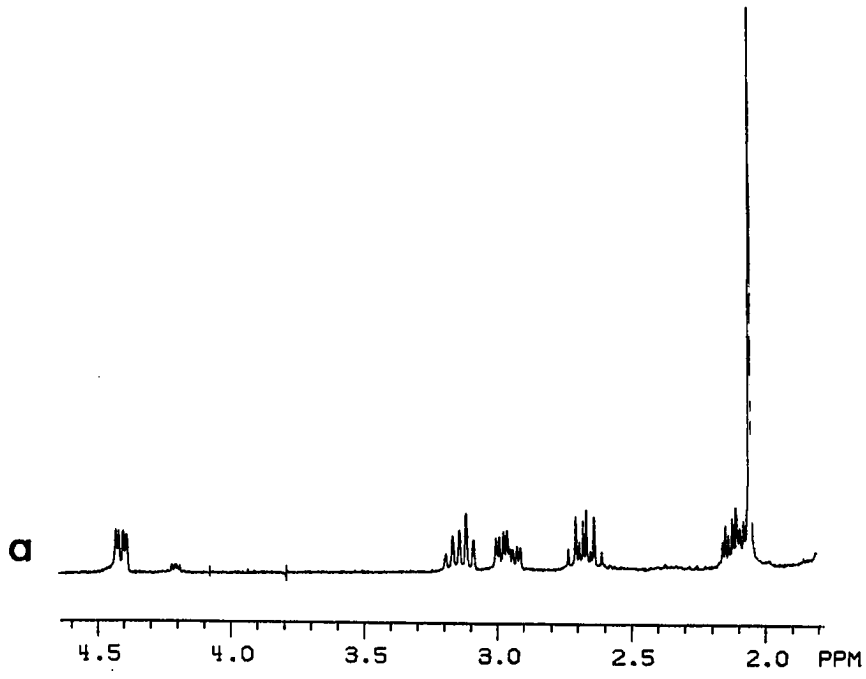
Bothersome at first was the position of the absorption of the C-1 proton of 66, centered far downfield at 4.40 ppm. As a model, 1-phenylindan (72) shows the C-1 absorption at 3.65 ppm, not quite far enough downfield for confidence in our structural assignment.[77] Compound 73 has its C-1 proton absorbing at 4.2 ppm.[78] For compound 74, the

72   **73**   **74**
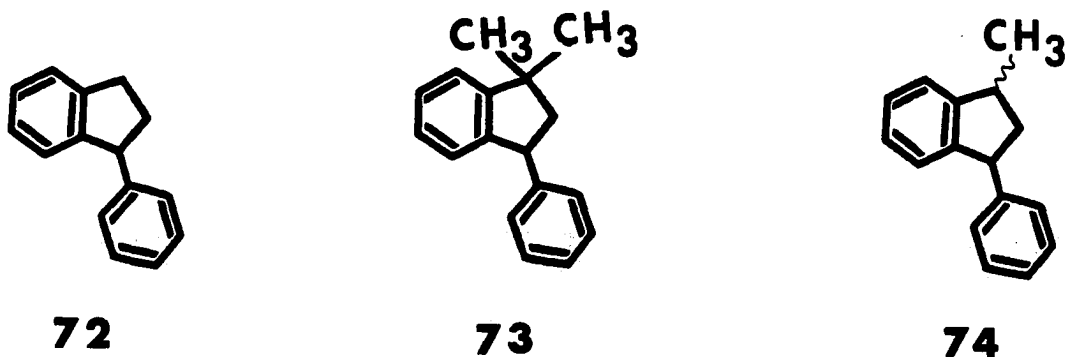
two isomers (cis and trans) absorb at 5.2 and 4.1 ppm.[78] Thus, it appears that conformational factors play an important role in the resonance position of the C-1 proton of 1-arylindans, which renders our assignment for 66 as consistent with the reported spectral data.

The ^{1}H NMR of 67 was quite similar to that of 66 in the aliphatic region and only a change in chemical shifts was seen. Based on the arguments on conformational differences given above, it was also assigned as a 1-tolylindan. Ortho substitution of the benzene ring was indicated by strong bands at 735 and 750 cm^{-1} in the IR spectrum.[74,75]
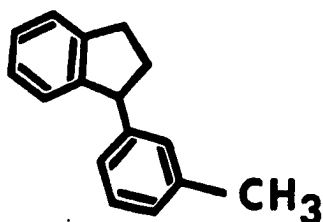
66
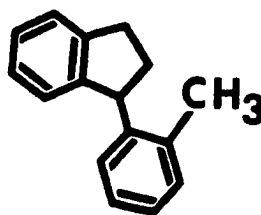
67

The assignment for 69 was made based on its 12 line ^{13}C NMR

spectrum, and by the crisp coupling in the aliphatic region of the
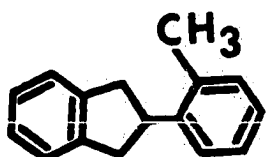
69
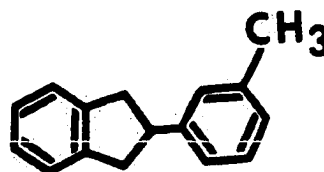
75

^{1}H NMR spectrum.[79] The ortho substituted phenyl ring was determined

by IR spectroscopy. The seventh $C_{16}H_{16}$ isomer, although never isolated,

can be tentatively assigned as 75 based on its ms spectrum. The other

positional pairs described above have quite similar spectra, the same

being true for 69 and 75.

In addition to the $C_{16}H_{16}$ isomers, the two compounds of mw = 192 were identified; however, they were isolated as a mixture with anthracene (13). As they clearly cannot be phenanthrenes, which have characteristic absorptions at ca. 8.6 ppm,[73] they were assigned as 1-methylanthracene (76) and 9-methylanthracene (77) on the basis of their methyl group absorption. The literature values are 2.71, 2.42
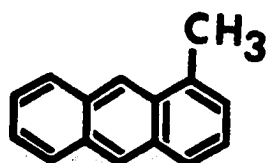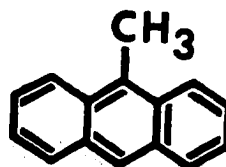
76   **77**

and 3.0 ppm for 1,2, and 9-methyl anthracene, respectively.[61,80] The observed values are 2.77 and 3.04 ppm.

As was mentioned, the [4+4] dimer 16 had been pyrolyzed in earlier work.[18,19] Shown in Table 15 is the comparison between that work and the present work. Included are the results for the FVP of the deuterated systems 16-d_4 and 56-d_4 in terms of the product distribution, not deuterium content or position. The analogy between the two works was made on the basis of gc elution order and checked by the comparison of their respective ms spectra (for the light systems).

As mentioned earlier, the seven $C_{16}H_{16}$ isomers produced in the FVP of 16-d_4 and 56-d_4 retained all of their deuterium atoms. A summary of the percent incorporation is presented in Table 23, and the pertinent ms data appears in Tables 16-22. The deuterium content of the three anthracenes (13, 79, and 80) also appears (Tables 24-26, 27).

Experiments on the Dibenzosuberone System

Synthesis of the unknown 2,9-dimethyldibenzosuberone (38) was accomplished by a two step route (Scheme 9). Coupling of p-methyl-benzyl chloride (79),[81] followed by the addition of the carbonyl group

Scheme 9
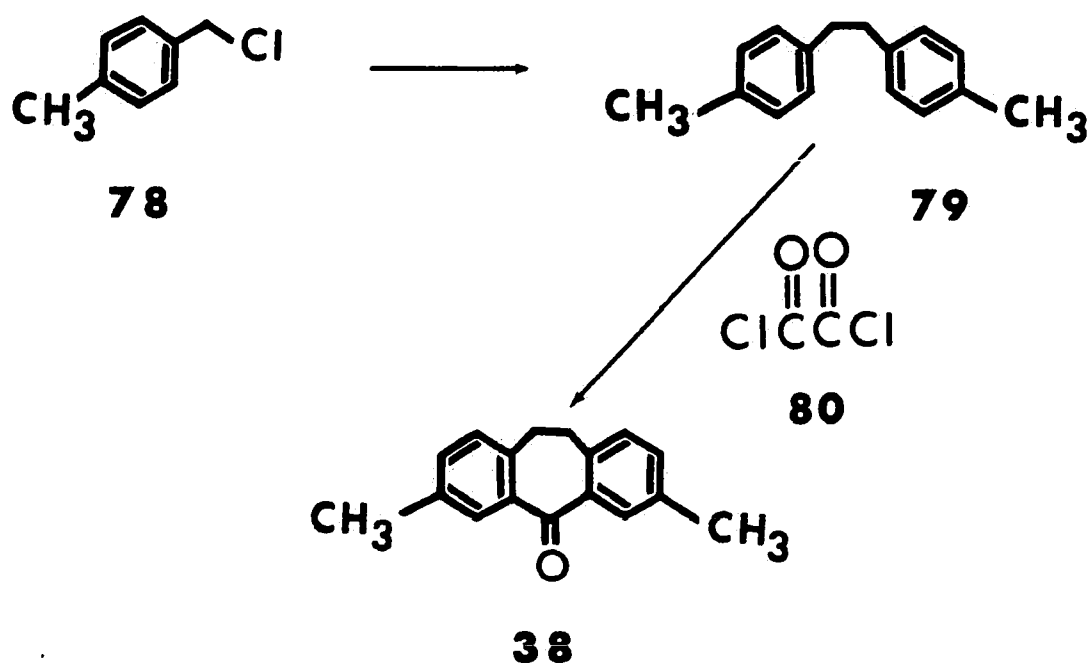
Table 24. Mass spectra data of anthracene (13) and of anthracene-$\underline{d}$ (13-$\underline{d}$) produced in the FVP of dibenzocyclooctene-5,5,6,6-$\underline{d}_4$ (16-$\underline{d}_4$) and dibenzo[c,g]thiapinedioxide-5,5,7,7-$\underline{d}_4$ (56-$\underline{d}_4$) at 860°C

M/e	Rel. peak inten. of 13[a]	From 16-$\underline{d}_4$ Rel. peak inten. of 13-$\underline{d}$[a]	Calculated peak intensity $\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$	From 56-$\underline{d}_4$ Rel. peak inten. of 13-$\underline{d}$[a]	Calculated peak intensity $\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$
176	12496	6045						2450					
177	5558	10780						4117					
178(P)	231258	100906	100906					17383	17383				
179	35805	228000	15632	212368				36590	2691	33899			
180	3348	132232	1462	32880	97890			20646	252	5248	15146		
181		22241		3074	15156	4011		3330		491	2345	494	
182		2969			1417	621	931	410			219	76	115

[a]Ionization voltage was 20 eV.

Table 25. Mass spectra data of 1-methylanthracene (76) and of 1-methylanthracene-d (76-d) produced in the FVP of dibenzocyclooctene-5,5,6,6-d_4 (16-d_4) and dibenzo[c,g]thiapine-dioxide-5,5,7,7-d_4 (56-d_4) at 860°C

M/e	Rel. peak inten. of 76[a]	Rel. peak inten. of 76-d[a]	From 16-d_4 Calculated peak intensity d_0	d_1	d_2	d_3	d_4	Rel. peak inten. of 76-d[a]	From 56-d_4 Calculated peak intensity d_0	d_1	d_2	d_3	d_4
190	3185	3745						1086					
191	6202	6220						1573					
192(P)	50738	6244	6244					1495	1495				
193	10701	9046	1317	7729				1684	315	1369			
194	1246	48923	154	1630	47139			7933	37	289	7607		
195		54160		190	9941	44029		8484		34	1604	6848	
196		14556			1159	9286	4111	2456			187	1443	826
197		2576						400					
198		283											

[a]Ionization voltage was 20 eV.

Table 26. Mass spectra data of 9-methylanthracene ($\underset{\sim\sim}{77}$) and of 9-methyl-anthracene-$\underline{d}$ ($\underset{\sim\sim}{77}$-$\underline{d}$) produced in the FVP of dibenzocyclo-octene-5,5,6,6-$\underline{d}_4$ ($\underset{\sim\sim}{16}$-$\underline{d}_4$) and dibenzo[c,g]thiapinedioxide-5,5,7,7-$\underline{d}_4$ ($\underset{\sim\sim}{56}$-$\underline{d}_4$) at 860°C

M/e	Relative peak intensity of 77[a]	Relative peak intensity of 77-d[a]	Calculated peak intensity				
			$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$
190	362	1202					
191	714	1592					
192(P)	4142	1747	1747				
193	1273	3501	537	2964			
194	220	8557	93	911	7553		
195		7295		157	2321	4817	
196		3168			401	1480	1287
197		580					

[a]Ionization voltage was 20 eV.

through a bis-acylation utilizing oxalyl chloride ($\underset{\sim\sim}{80}$) at high dilution

produced $\underset{\sim\sim}{38}$. All spectral data and elemental analysis are consistent

with its formation. The position of the methyl groups is as expected,

as the aromatic region shows an AM, AMX, MX pattern (Figures 15 and

16). The ^{13}C NMR shows a 9 line pattern (Figure 17).

Table 27. Summary of the deuterium content of anthracene-$\underline{d}$ ($\underline{\underline{13}}$-$\underline{d}$),
1-methylanthracene-$\underline{d}$ ($\underline{\underline{76}}$-$\underline{d}$), and 9-methylanthracene-$\underline{d}$ ($\underline{\underline{77}}$-$\underline{d}$)
produced in the FVP of dibenzocyclooctene-5,5,6,6-$\underline{d}_4$ ($\underline{\underline{16}}$-$\underline{d}_4$)
and dibenzo[c,g]thiapinedioxide-5,5,7,7-$\underline{d}_4$ ($\underline{\underline{56}}$-$\underline{d}_4$) at 860°C

Compound	Deuterium content, %[a]									
	From $\underline{\underline{16}}$-$\underline{d}_4$					From $\underline{\underline{56}}$-$\underline{d}_4$				
	$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$	$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$
$\underline{\underline{13}}$-$\underline{d}$	24.2	51.0	25.5	1.0	0.2	25.9	50.6	22.6	0.7	0.2
$\underline{\underline{76}}$-$\underline{d}$	5.7	7.1	43.1	40.3	3.8	8.2	7.5	41.9	37.7	4.6
$\underline{\underline{77}}$-$\underline{d}$	9.5	16.1	41.2	26.2	7.0					

[a]Data based on calculations shown in Tables 24, 25 and 26.

The FVP of $\underline{\underline{38}}$ gave 2,6-dimethylanthracene $\underline{\underline{25}}$ as the sole product
(Figures 18, 19 and 20). Under the best conditions for this reaction,
92% of $\underline{\underline{25}}$ was produced and 7% unchanged $\underline{\underline{38}}$ was recovered. Higher

38   **25**
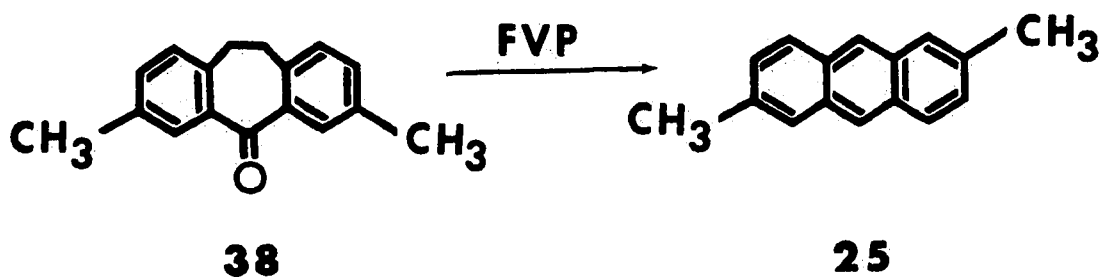
Figure 15. Proton NMR spectrum (300 MHz) of 2,9-dimethyldibenzosuberone (38)
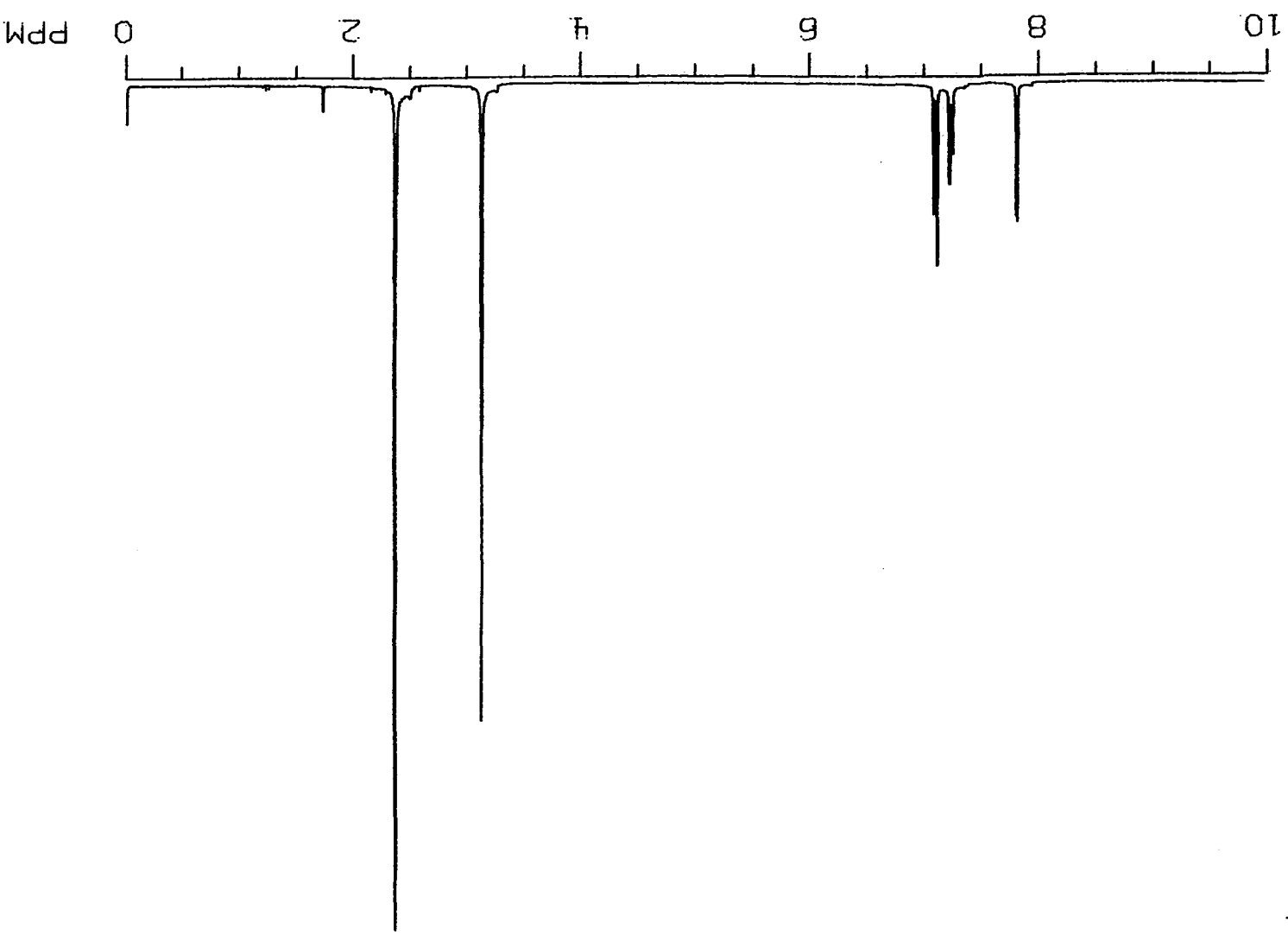
Figure 16. Proton NMR spectrum (300 MHz) showing a closeup of the aromatic region of 2,9-dimethyldibenzosuberone (38)

CHCl₃
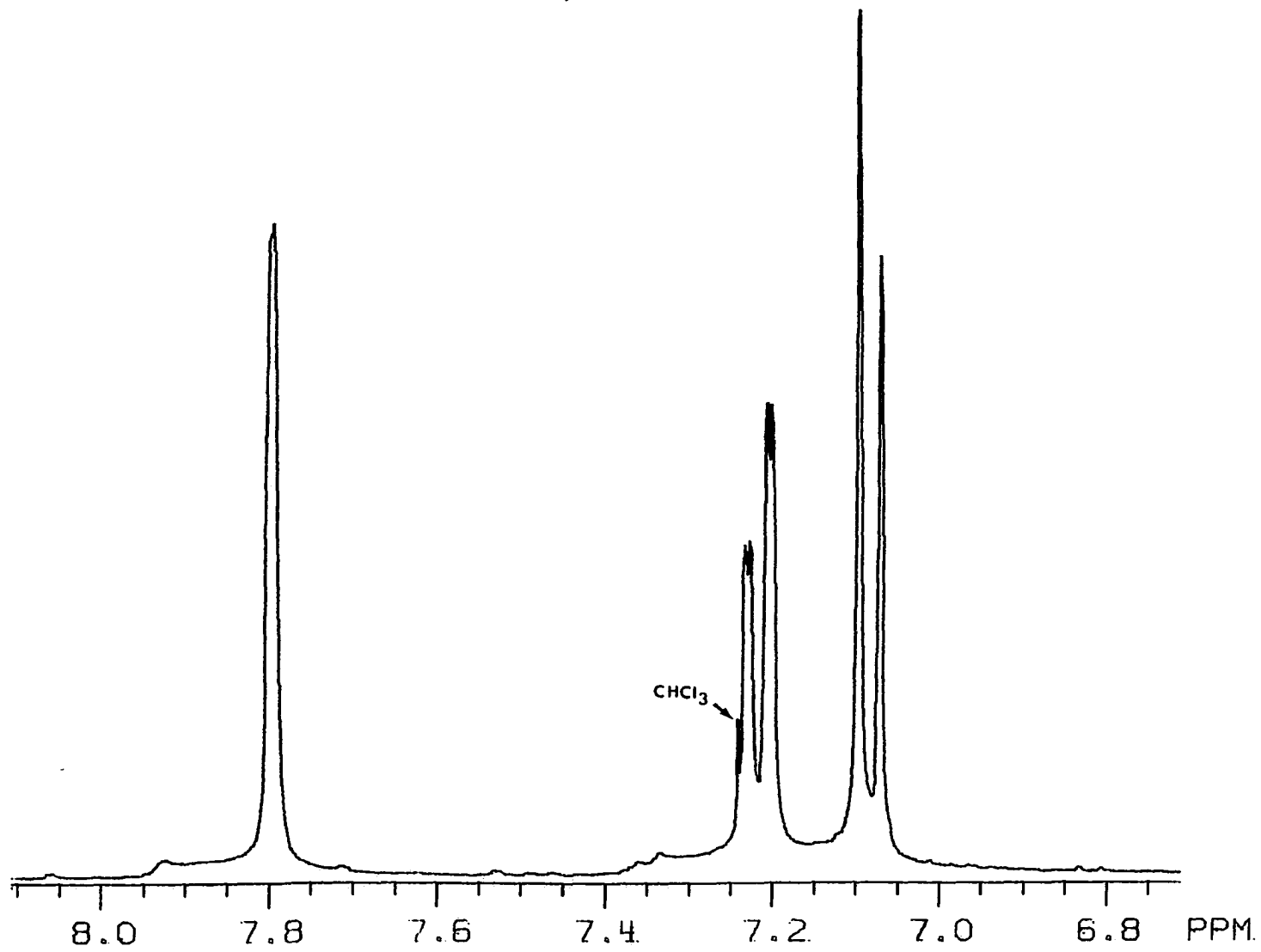
Figure 17. Carbon-13 NMR spectrum (74 MHz) of 2,9-dimethyldibenzosuberone (38)

CDCl$_3$

200   150   100   50   0   PPM
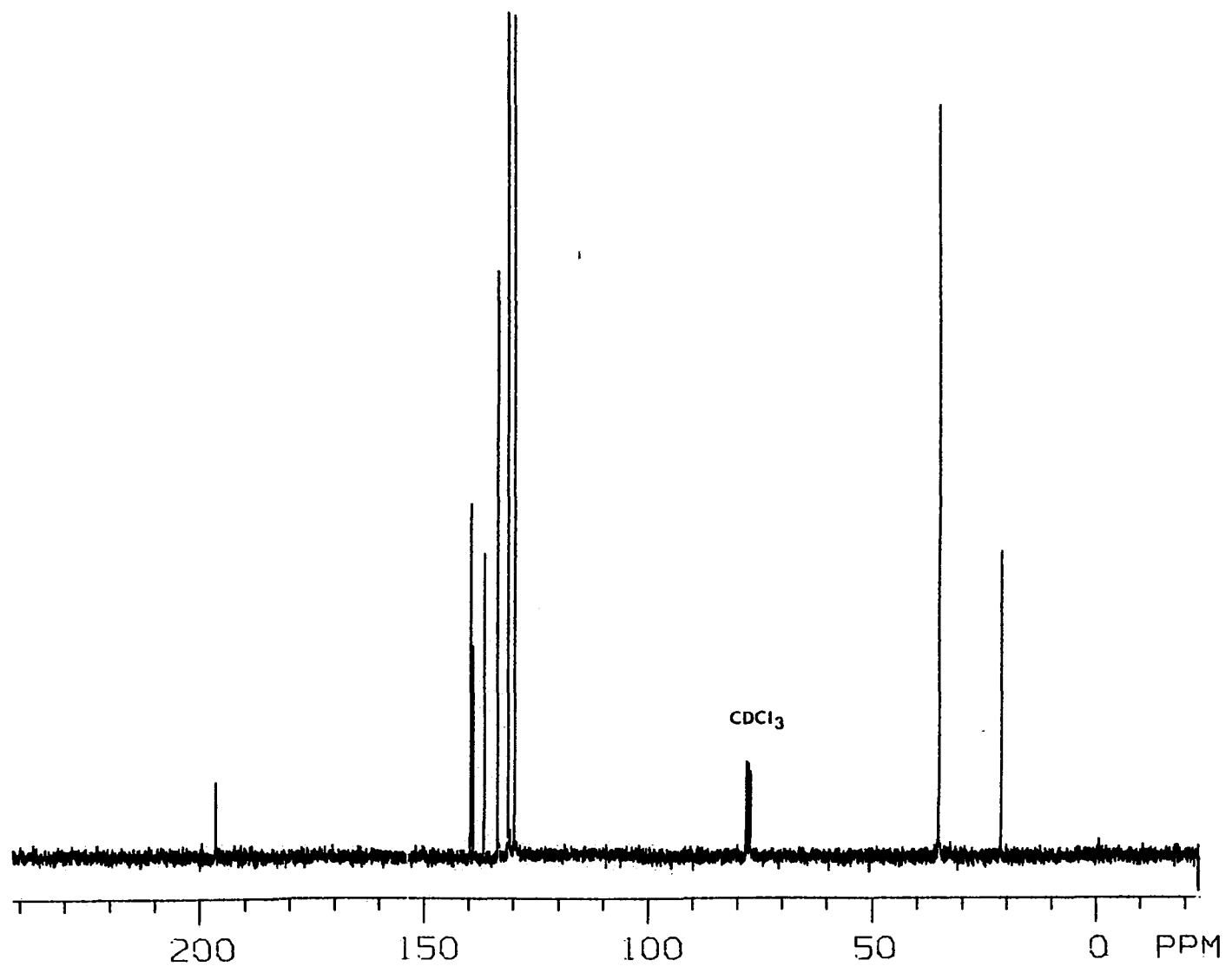
Figure 18. Proton NMR spectrum (300 MHz) of 2,6-dimethylanthracene (25) produced in the FVP of
2,9-dimethyldibenzosuberone (38) at 950°C

CH$_2$Cl$_2$

9 8 7 6 5 4 3 2 PPM
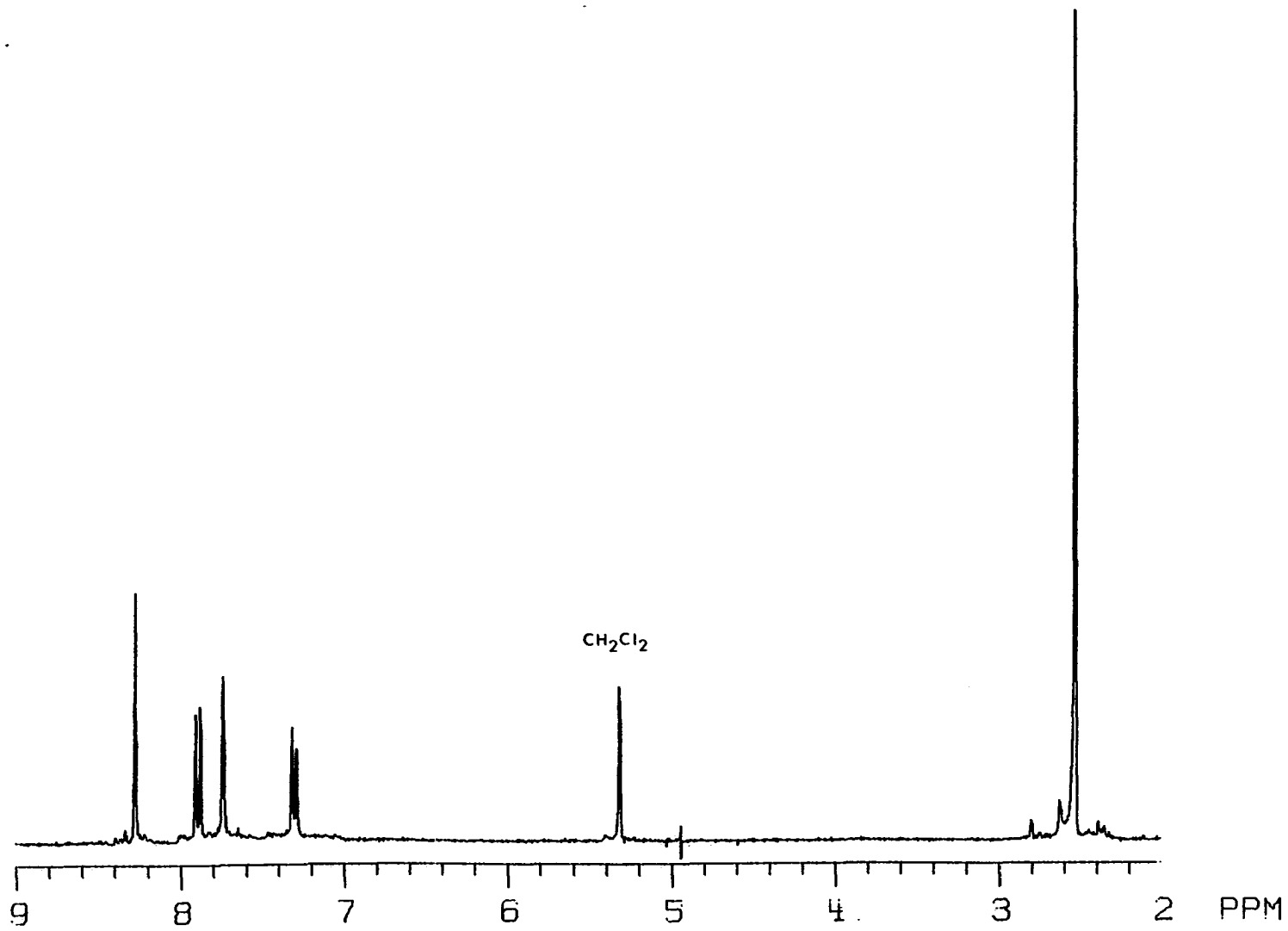
Figure 19. Proton NMR spectra (300 MHz) showing a closeup of the aromatic region for (a) 2,6-di-methylanthracene (25) and (b) an authentic sample of 2,7-dimethylanthracene (24)
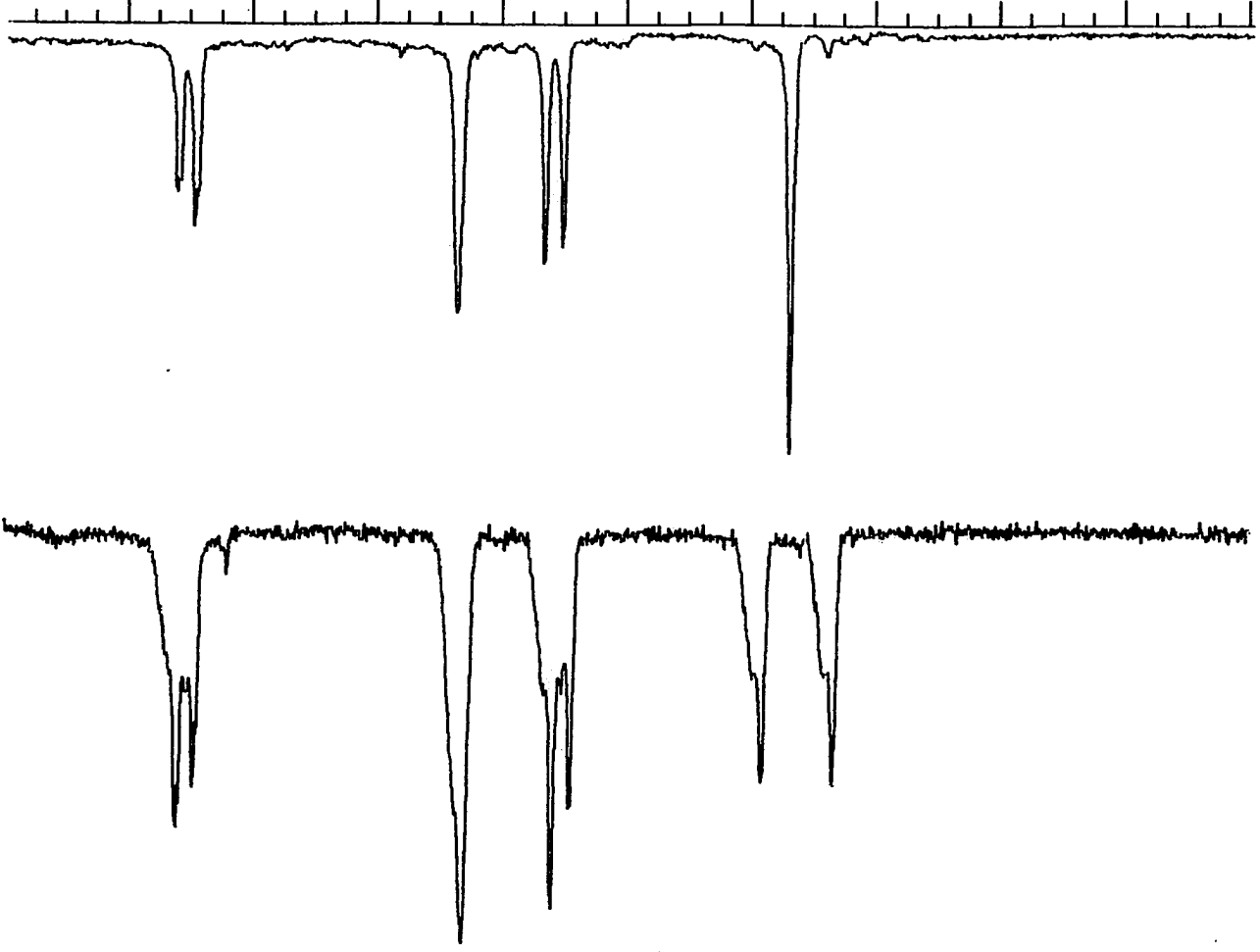
Figure 20.   Carbon-13 NMR spectrum (74 MHz) of 2,6-dimethylanthracene (25) produced in the FVP of 2,9-dimethyldibenzosuberone (38) at 950°C
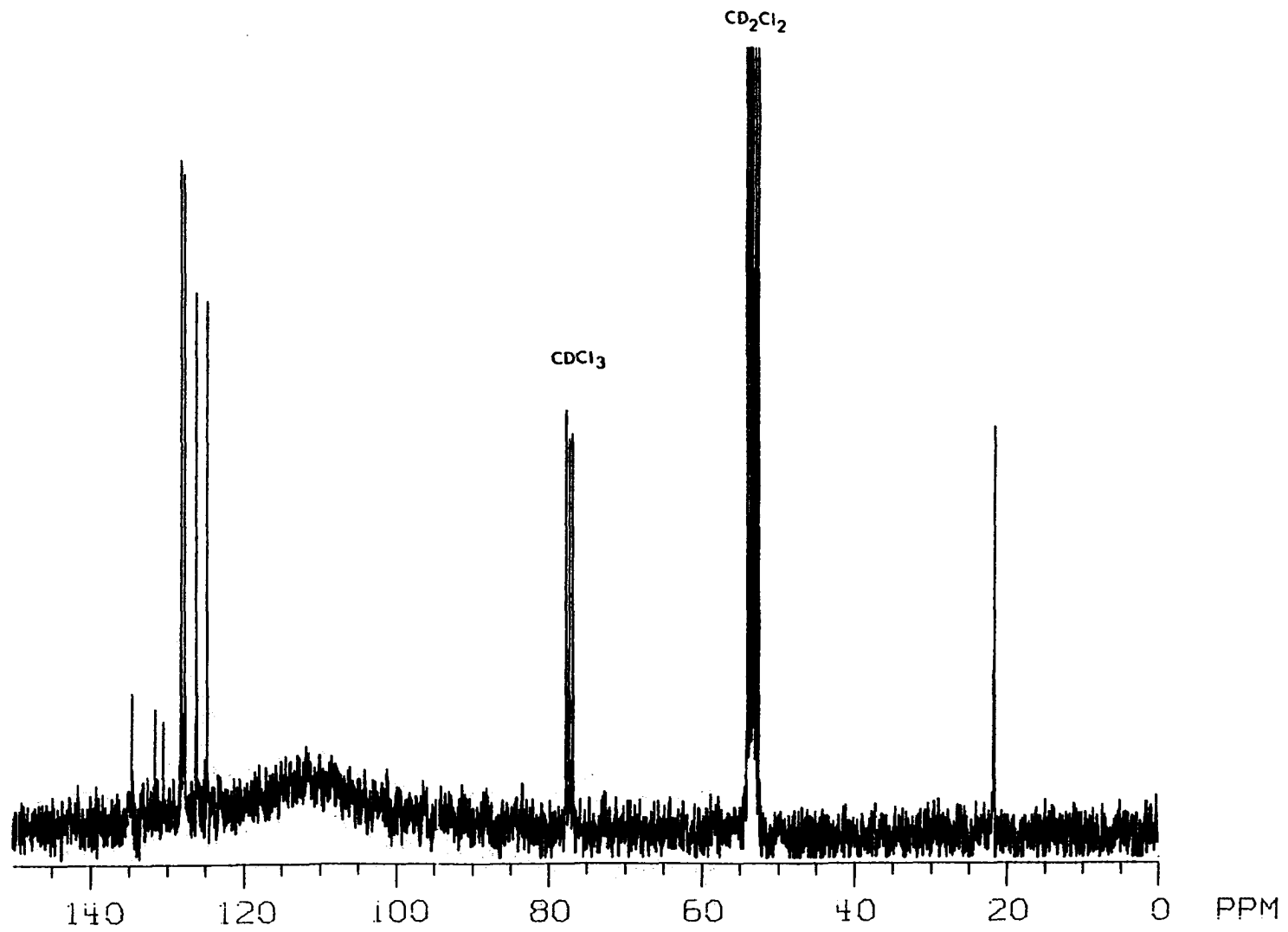
temperatures, used to try to drive the reaction to completion, led

only to the formation of decomposition products. The effect of pyrolysis

temperature is shown in Table 28. The yields for this reaction were

determined by ^{1}H NMR analysis using an internal standard.

Table 28. The effect of temperature on the yields of unchanged starting
material and 2,6-dimethylanthracene in the FVP of 2,9-di-
methyldibenzosuberone (38)

Pyrolysis temperature, $^\circ C$ [b]	Yield, % [a]	
	38 (recovered)	25
900 [c]	31.3	66.5
950 [d]	6.8	91.6
1000 [c]	5.0	76.0

[a]Determined by ^{1}H NMR after the addition of $CHCl_2CHCl_2$ as an
internal standard.

[b]Pressure was 0.002 mm Hg.

[c]Average of two trials.

[d]Average of five trials.

As 25 is a known compound, identification was made by comparison

to reported values.[82,83,84] Satisfactory agreement was obtained in

all cases. Figure 19 shows a comparison between 25 and an authentic

sample of the only other dimethylanthracene which would have an AM, AMX, MX coupline pattern, 24. The equivelency of the C-9, 10 protons for 25 can be seen (Figures 19, 20), which is not the case for 24.
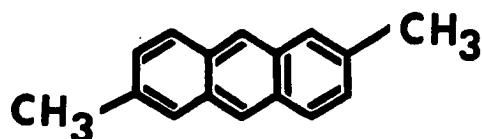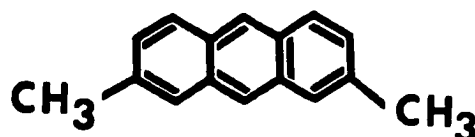
25   **24**

Because of the differences in the absorption of the C-9, 10 protons of 24 (at 8.34 and 8.20 ppm) and those of 25 (at 8.26 ppm), the overall regiospecificity of the transformation from 38 to 25 can be determined by integration on a 300 MHz instrument and was found to be $\geqslant$ 98.6%. Compounds 24 and 25 could not be separated by capillary gc.

In the interest of determining the scope and establishing synthetic utility for this transformation, the synthesis of functionalized, regiochemically pure pyrolysis precursors was undertaken (Scheme 10). By analogy to fluorenone (81) chemistry,[85] commercially available dibenzosuberone (37) was nitrated with fuming nitric acid to give 82.[83] Reduction of the nitro groups with $SnCl_2$ gave the unknown diaminodi-benzosuberone 40.[85,86,87,88] Compound 40 could be readily tetrazotized,

81

Scheme 10

37

82

39
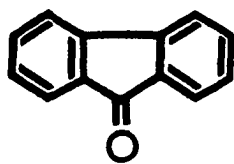
40
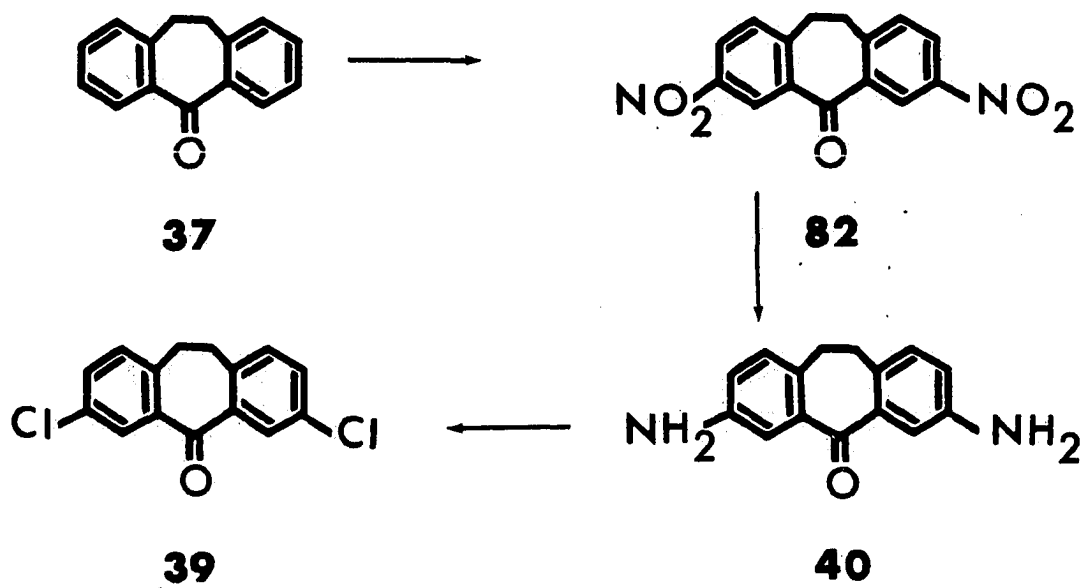
and underwent the Sandmeyer reaction with CuCl to give the dichloride
39.[89,90] The position of the introduced functionality is as shown.

The coupling patterns for 39 (Figures 21 and 22) and for 40 (Figures 23

and 24) are analogous to those seen for 2,6-dimethyldibenzosuberone

(38). All three compounds have an AM, AMX, MX pattern.

The FVP of 39 at 950°C (pressure = 0.002 mm Hg) gave 96% 41 and 3%

unchanged starting material (average of three runs).[91] The formation

of 41 is confirmed by noting the equivalence of the 9, 10 positions

39 → **FVP** → **41**
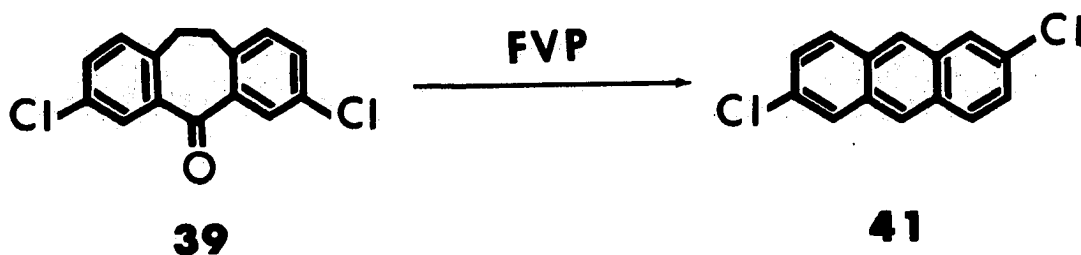
in its ^{1}H NMR spectrum (Figures 25 and 26) and ^{13}C NMR spectrum. The

regiospecificity of this conversion was also high.

Diaminodibenzosuberone 40 was subjected to FVP conditions. In the

pyrolysis trap could be seen a brilliant yellow solid. Attempts to

remove the product by the usual "rinsing out" of the pyrolysis trap

failed as the product was only slightly soluble, and what little was

Figure 21. Proton NMR spectrum (300 MHz) of 2,9-dichlorodibenzosuberone (39)
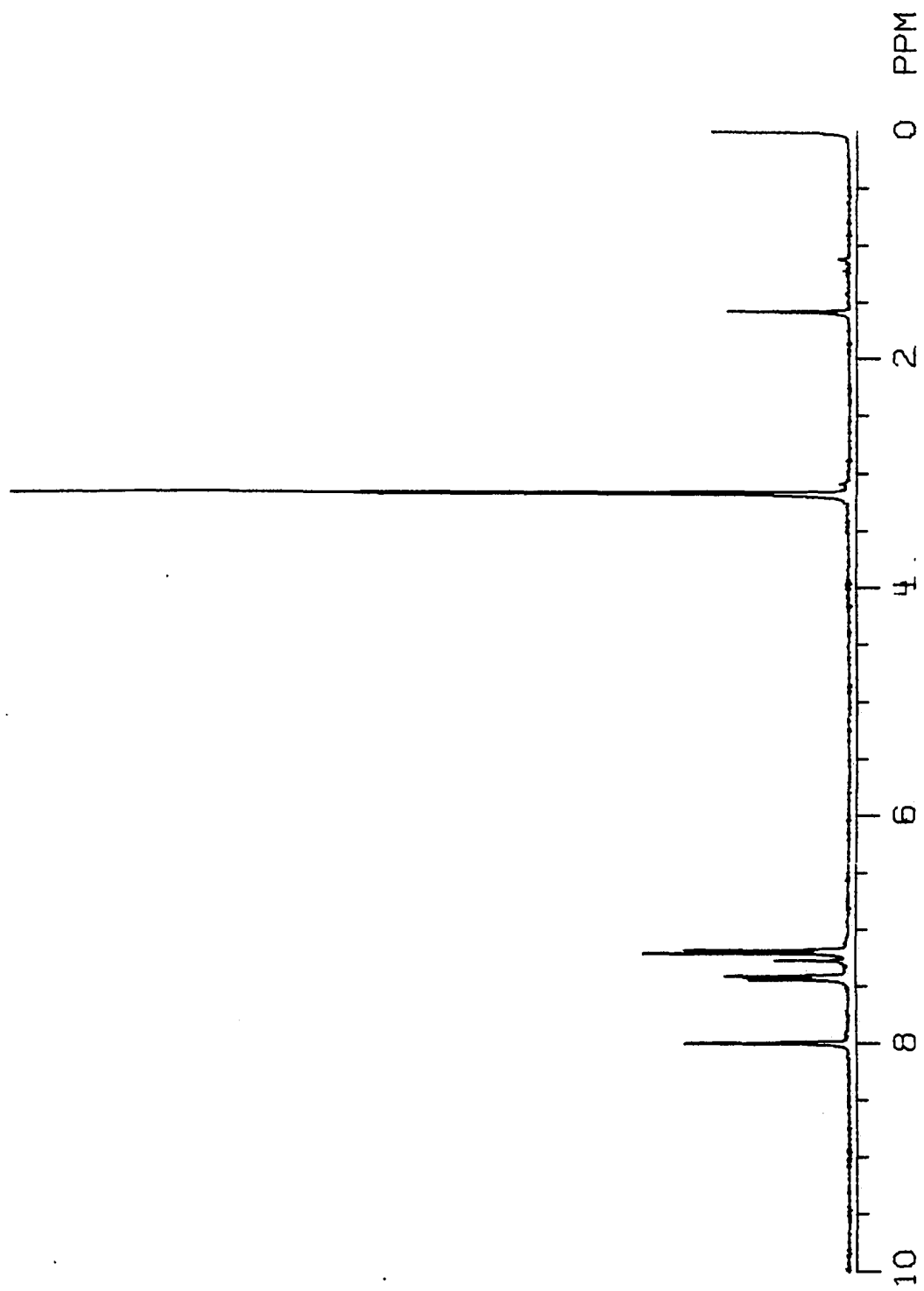
Figure 22. Proton NMR spectrum (300 MHz) showing a closeup of the aromatic region of 2,9-dichloro-dibenzosuberone (39)

CHCl$_3$

8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 PPM
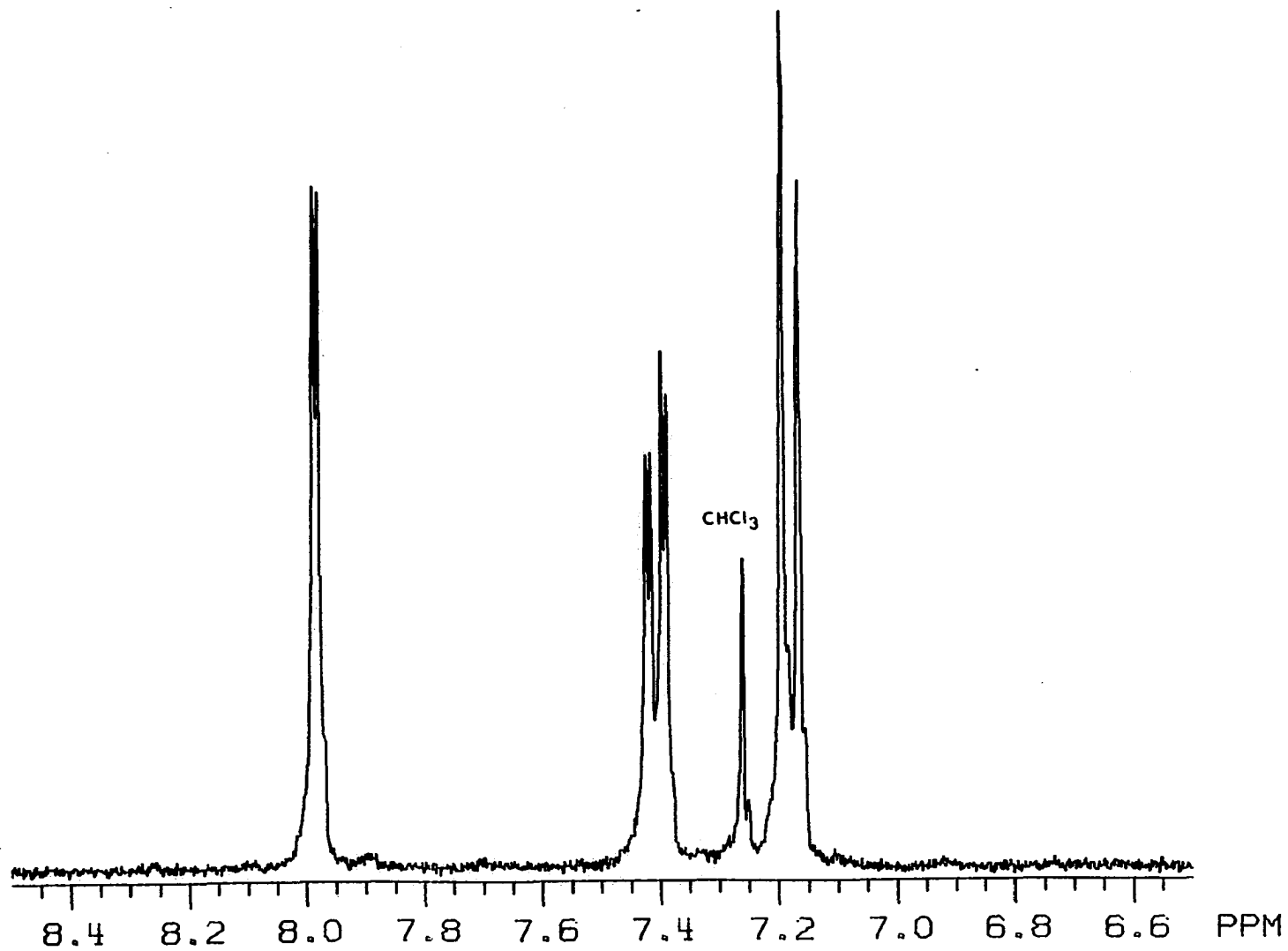
Figure 23. Proton NMR spectrum (300 MHz) of 2,6-dichloroanthracene (41) produced in the FVP of 2,9-dichlorodibenzosuberone (39) at 950ºC
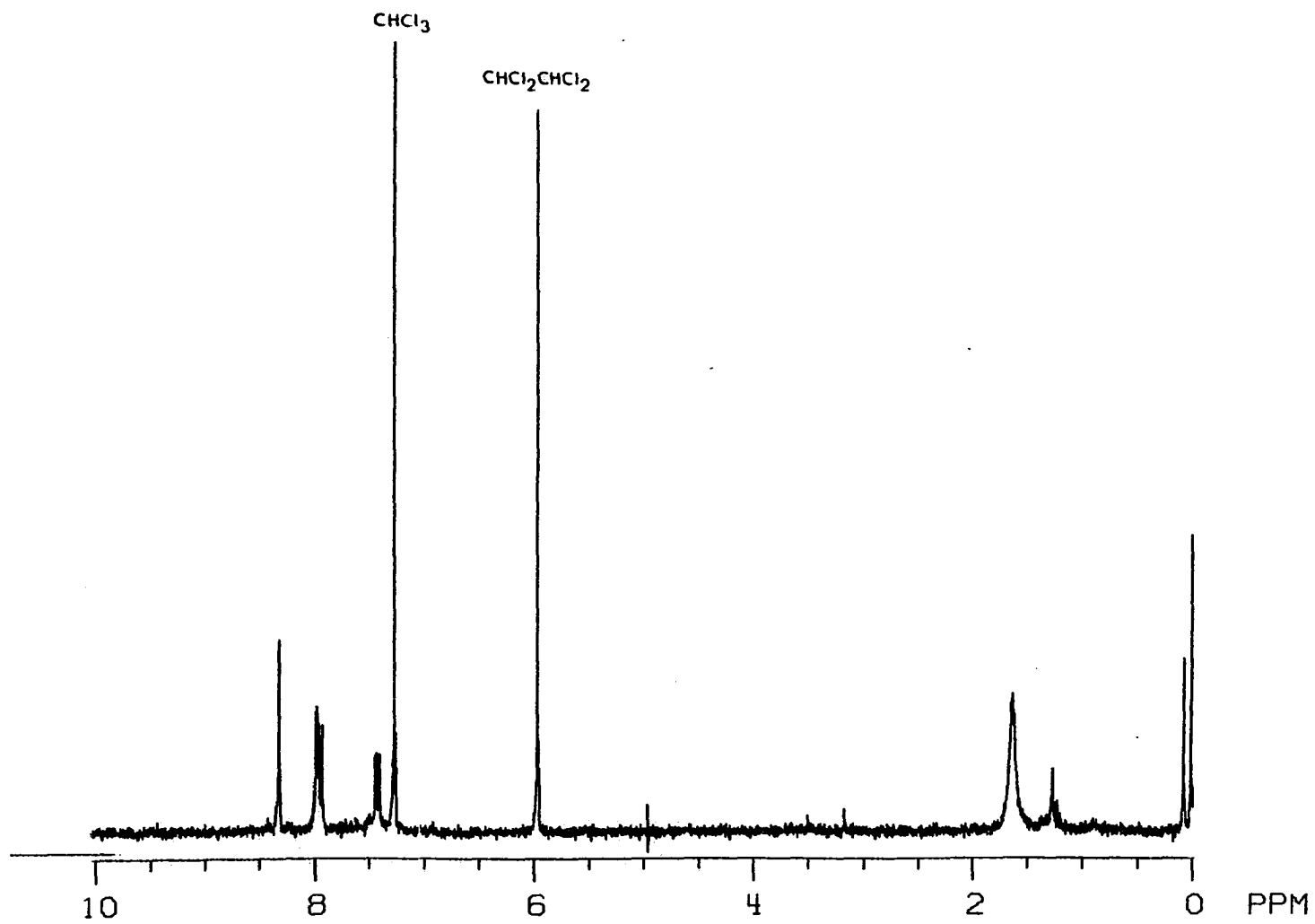
Figure 24. Proton NMR spectrum (300 MHz) showing a closeup of the aromatic region of 2,6-dichloro-anthracene (41)
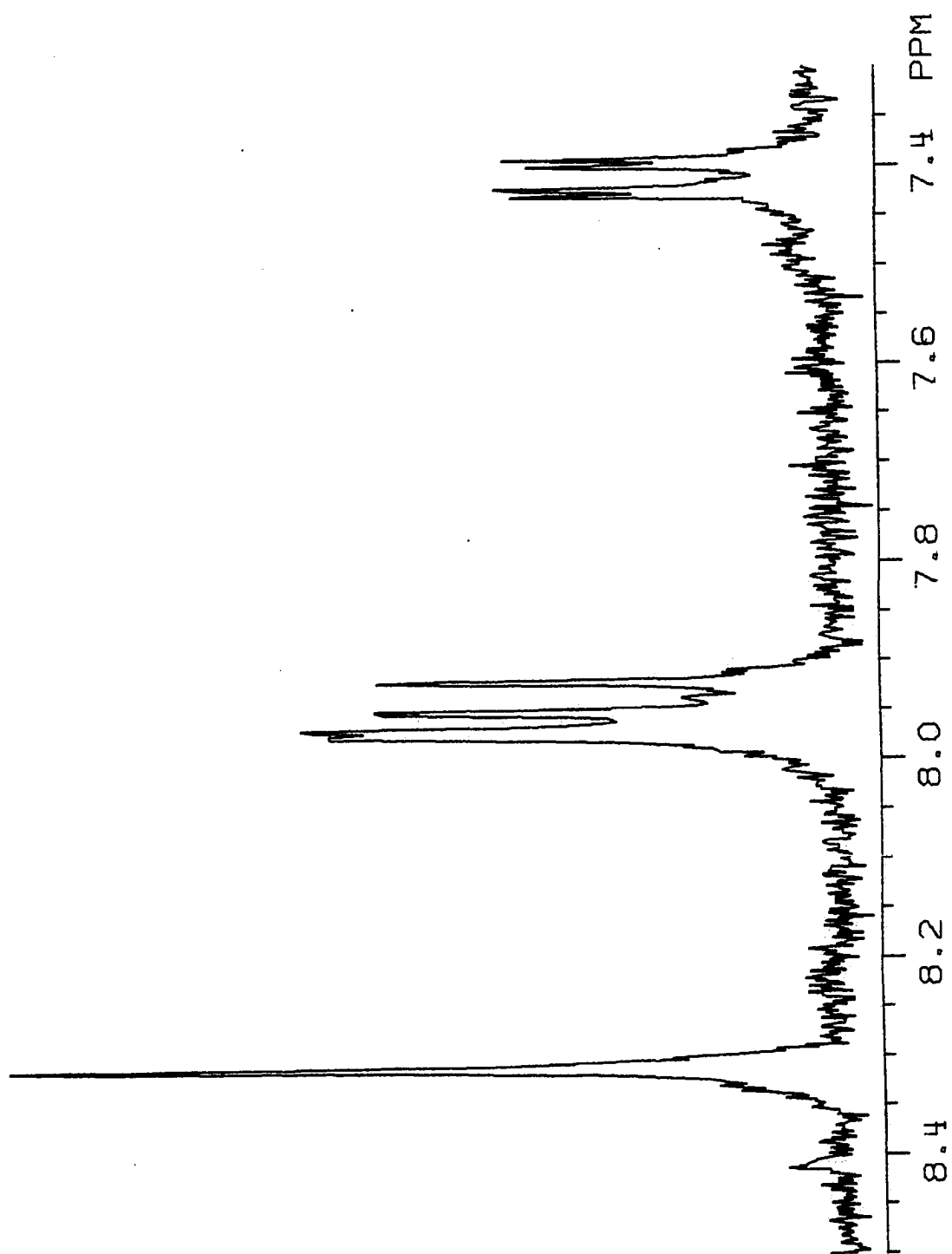
Figure 25. Proton NMR spectrum (300 MHz) of 2,9-diaminodibenzosuberone (40)

CH$_2$Cl$_2$

10   8   6   4   2   0   PPM.
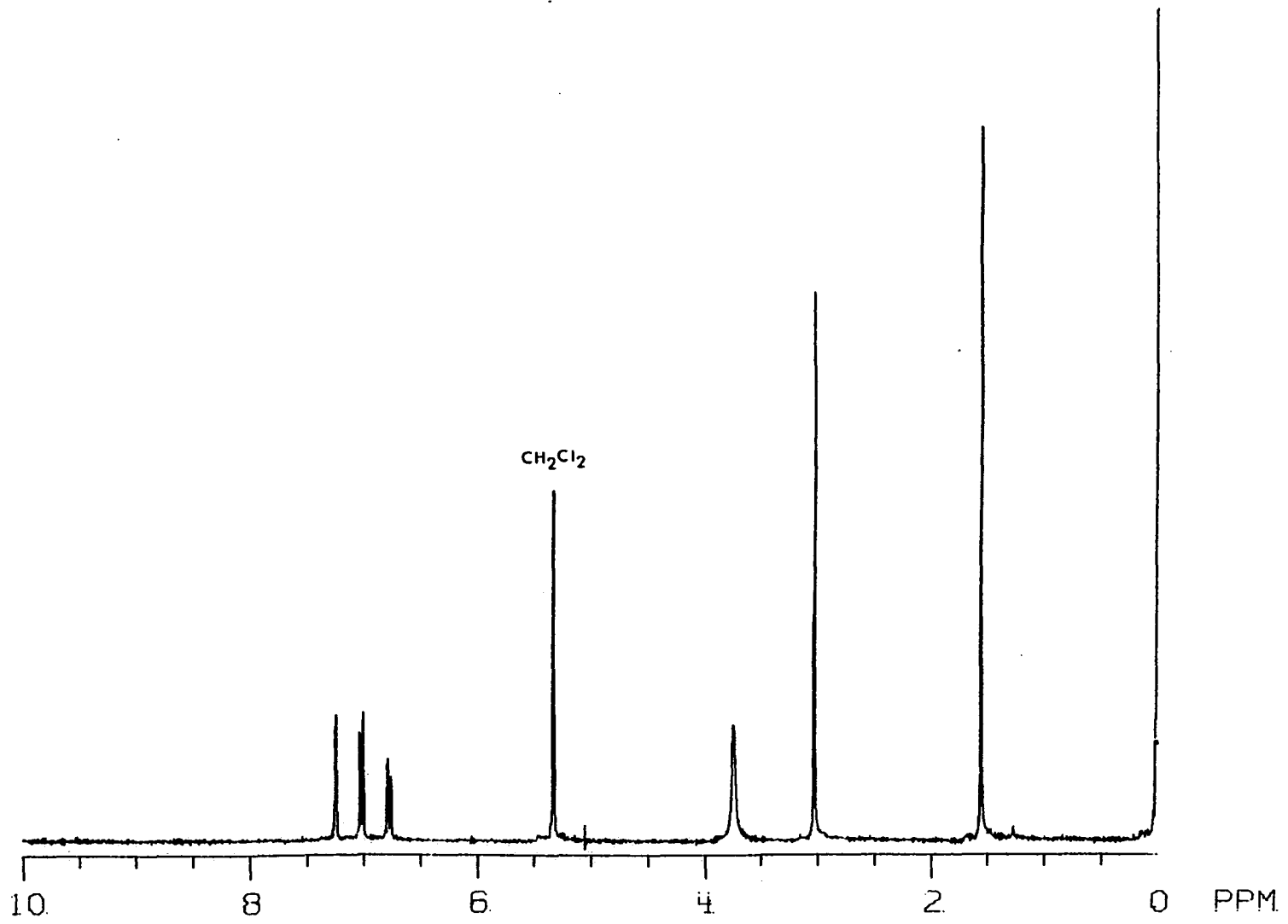
Figure 26. Proton NMR spectrum (300 MHz) showing a closeup of the aromatic region of 2,9-diamino-dibenzosuberone (40)
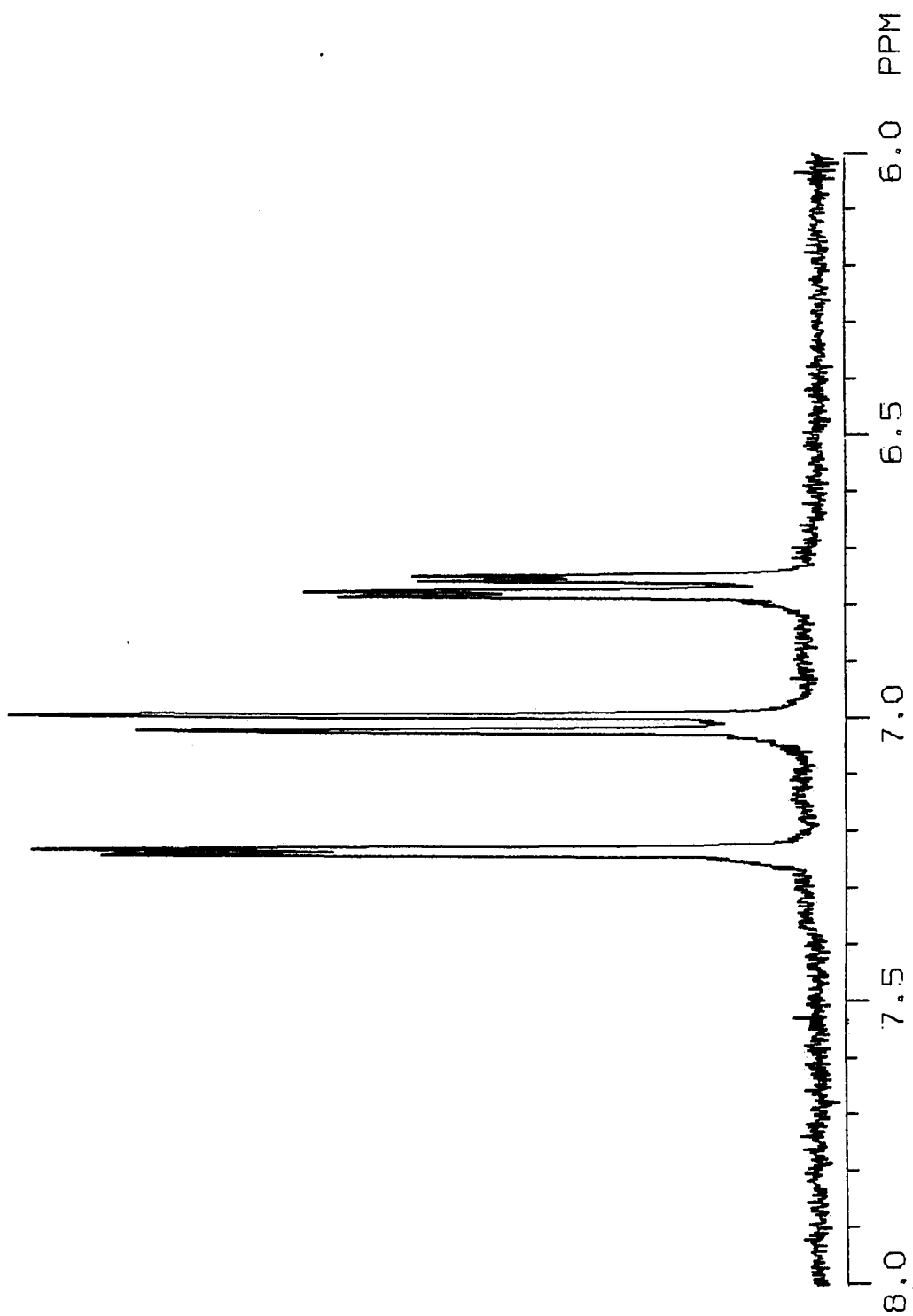
obtained could be seen to decompose. The product could not even be

rinsed out with dilute acid. The product was recovered simply by

scraping it out of the cold trap, by no means a quantitative process.

A portion of the product was taken up in an acetone-d_6/DMSO-d_6 solution,

and a ^{1}H NMR was quickly obtained (Figures 27 and 28). The ^{1}H NMR

clearly shows the equivalence of the 9 and 10 positions, and an AM,

AMX, MX coupline pattern, indicating that a ring flip had occurred.

The high resolution ms spectrum is consistent with a $C_{14}H_{12}N_2$ species.

Thus, the FVP of 2,9-diaminodibenzosuberone (40) gives 2,6-diamino-

anthracene (42). Compound 42 decomposes rapidly in solution, but
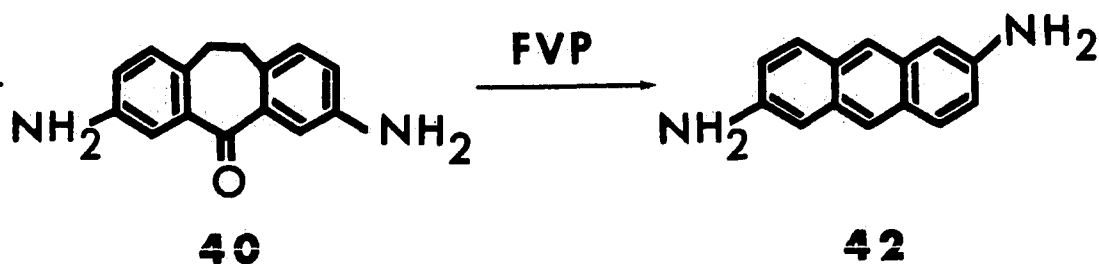
appears to be stable for long periods of time if stored under nitrogen

in its crystaline state. A 60% yield of diaminoanthracene (42) could

be obtained by this process.

Figure 27. Proton NMR spectrum (300 MHz) of 2,6-diaminoanthracene (42) produced in the FVP of 2,9-diaminodibenzosuberone (40) at 950°C

CH₃SOCH₃   CH₃COCH₃

10   8   6   4   2   0   PPM
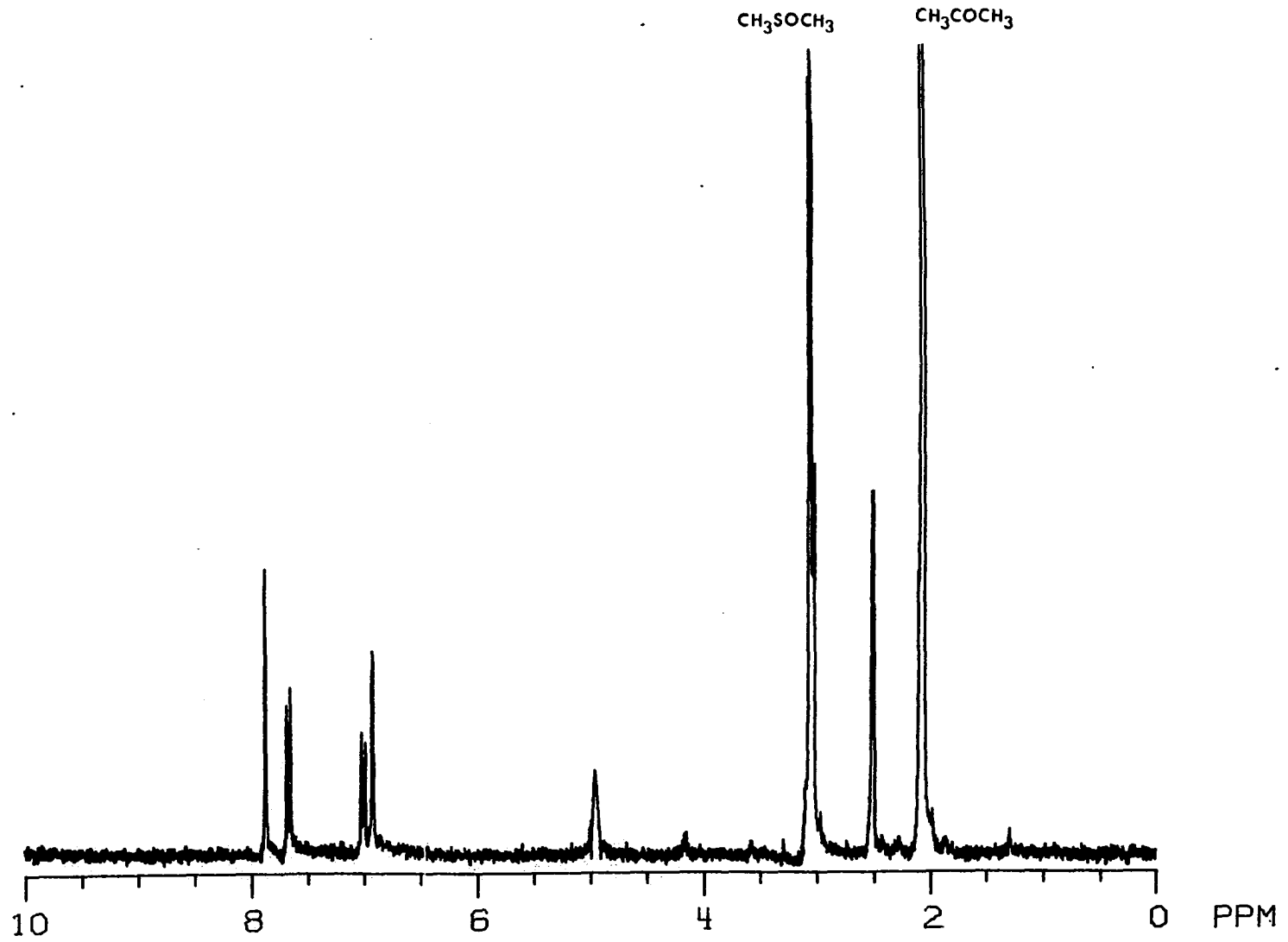
Figure 28.   Proton NMR spectrum (300 MHz) showing a closeup of the aromatic region of 2,6-diamino-
            anthracene (42)
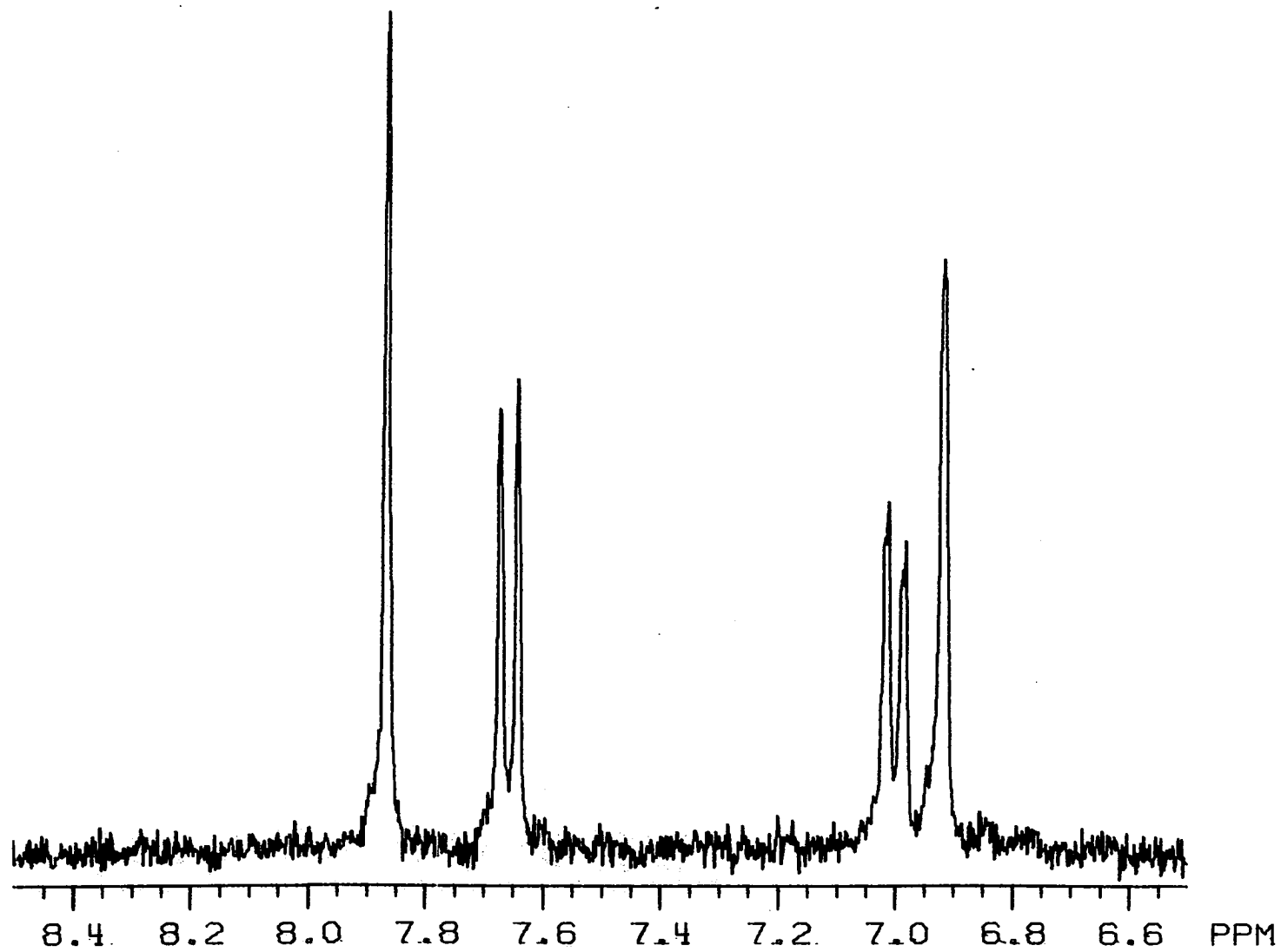
DISCUSSION

The Production of Benzene by the Pyrolysis of 4-Vinylcyclohexene

It has been proposed that the thermal rearrangement of dibenzo-
[a,d]cyclooctene (16) to anthracene (13) involves a biradical

intermediate.[18,19] By analogy, the production of benzene (30) by the

16   **121**   **13**
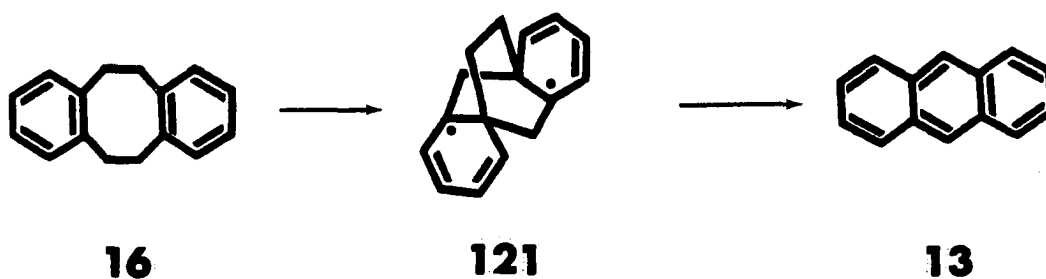
pyrolysis of 4-vinylcyclohexene (34) could occur by a pathway which

involves the same type of biradical, 35. Thus, the flash vacuum

34   **35**   **30**
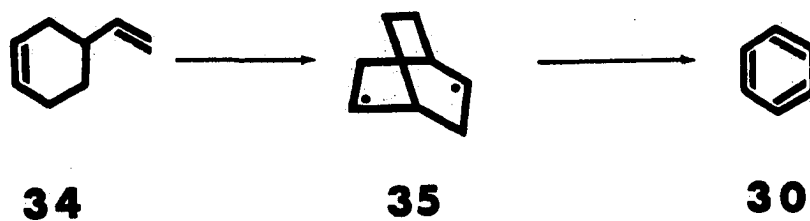
pyrolysis (FVP) of 34-d_8 was undertaken to test this hypothesis.
If the transformation shown in Scheme 11 is correct, the expected
product from this pyrolysis is benzene-1,4-d_2 (30-1,4-d_2).

Scheme 11
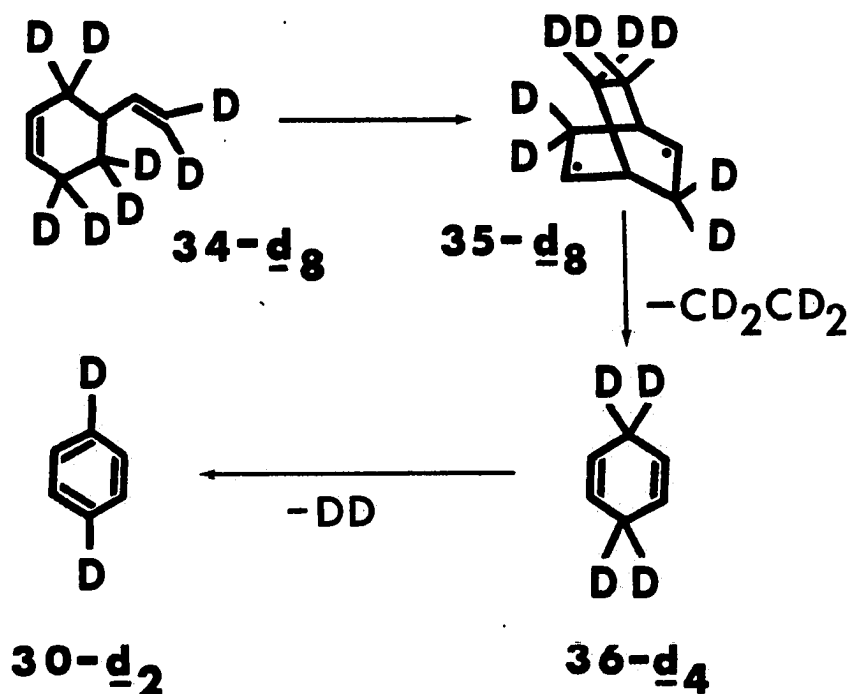
The results of the FVP of 34-d_8 showed that the benzene-d (30-d)
which was produced had a deuterium content which had resulted from a
scrambling of the deuterium and hydrogen atoms. The deuterium content
of the benzene-d (30-d) produced was as follows: 2% d_0, 0.5% d_1,

12% $\underline{d}_3$, 35% $\underline{d}_3$, 34% $\underline{d}_4$, 14% $\underline{d}_5$, and 12% $\underline{d}_6$. Clearly, these results are

not consistent with our initial postulates, as benzene-1,4-$\underline{d}_2$ ($\underset{\sim\sim}{30}$-$\underline{d}_2$)

was not the sole product. The scrambling which was observed does,

however, give insight into the formation of benzene ($\underset{\sim\sim}{30}$) from 4-vinyl-

cyclohexene (VCH) ($\underset{\sim\sim}{34}$).

First and foremost, the results described herein on the FVP of

$\underset{\sim\sim}{34}$-$\underline{d}_8$ are inconsistent with every mechanism that has been published

to date explaining the production of benzene ($\underset{\sim\sim}{30}$) by the initial

Diels-Alder reaction of butadiene ($\underset{\sim\sim}{32}$).[39,46,92-98] Central to these

theories is the initial loss of the ethylene fragment, either

homolytically or in concert with a hydrogen loss (Scheme 12). Since

Scheme 12
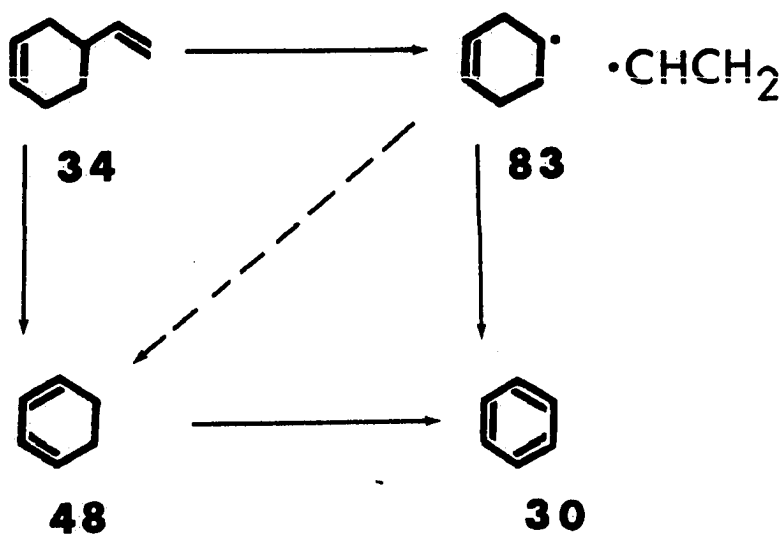
neither the butadiene-$\underline{d}_4$ ($\underline{32}$-$\underline{d}_4$) produced in the FVP of $\underline{34}$-$\underline{d}_8$ nor

the recovered starting material had undergone any deuterium scrambling,

the deuterium scrambling in the benzene-$\underline{d}$ ($\underline{30}$-$\underline{d}$) produced must have

occurred at some point along a necessarily irreversible pathway.

The initial loss of the vinyl portion of $\underline{34}$-$\underline{d}_8$ leaves only three

hydrogens attached to the six-membered-ring ($\underline{83}$-$\underline{d}_6$) destined to become

benzene. The experimental results show that 12% benzene-$\underline{d}_2$ ($\underline{84}$) is
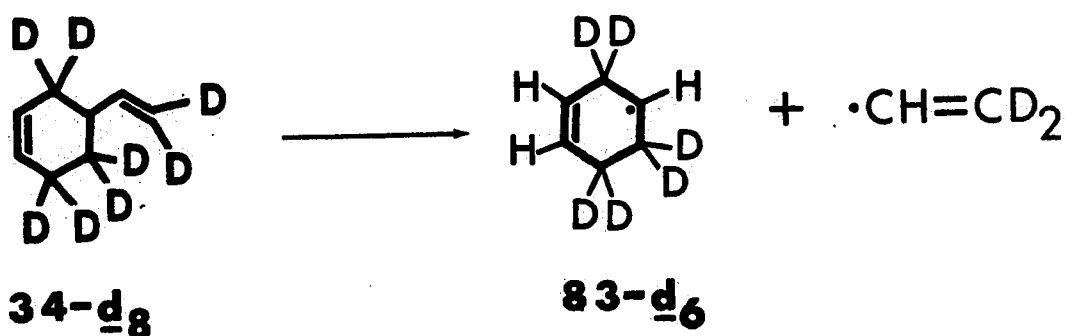
produced. Since benzene-$\underline{d}_2$ ($\underline{84}$) must have four hydrogens, mechanisms

that have been published to date on the production of benzene ($\underline{30}$) from

VCH ($\underline{34}$) fail to account for this one hydrogen discrepancy. This

cannot be rationalized by invoking intermolecular transfer of hydrogen

(deuterium) under the reaction conditions, as the FVP of tetradeuterio-

dibenzocyclooctene $\underline{16}$-$\underline{d}_4$ clearly demonstrates the unimolecularity of

these low pressure thermal rearrangements.

The interconversion of 34 to its valence isomers 1,5-cyclooctadiene (44) and divinylcyclobutane (45) has received much attention in the literature although the actual pathway is still open to debate.[52,54,99,100,101] Whichever pathway is operating, it is sufficient for our purposes to illustrate that both pathways fail to scramble the deuterium of 34-d_8 (Scheme 13).

Scheme 13

85   45-d_8
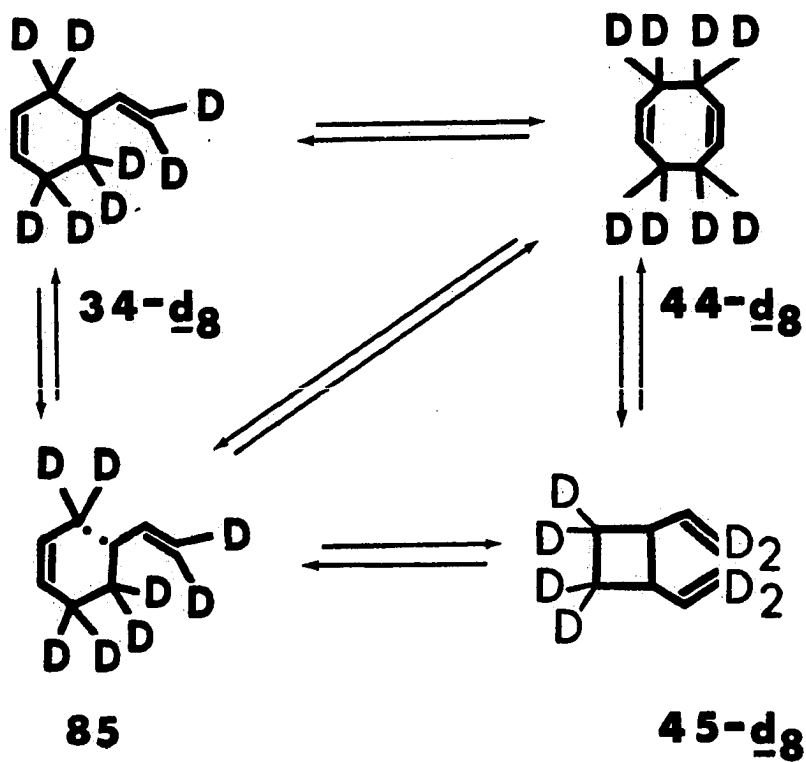
It is possible for VCH (34) to undergo a Cope rearrangement.
Interestingly, one extreme for the transition state of this reaction
is the diyl 35. If a Cope rearrangement did occur in this system

34   **35**   **34**
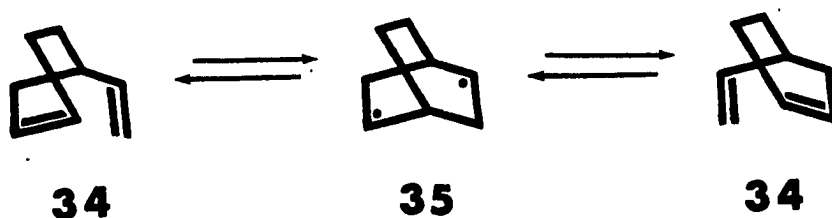
it would be degenerate for both 34 and 34-d$_8$, and thus unobservable
as no new compound would be generated.

Intermediate 35 can revert back to starting material. Proceeding
in the forward direction would also produce starting material, as the
rearrangement is degenerate. Another possibility is the direct loss
of ethylene (32) to produce 1,4-cyclohexadiene (36), followed by the
loss of hydrogen and concomitant benzene (30) formation (Scheme 11).
The latter is inconsistent with the experimental results, as it cannot
account for the formation of benzene-d$_5$ (86). A third possibility
is for a hydrogen shift to occur, which would produce bicyclo[2.2.2]-
octene (47) (Scheme 14). Compound 47 is known to readily lose ethylene
(32) under low pressure conditions and produces 1,3-cyclohexadiene
(48).[102] Compound 48 is known to produce benzene (30) with a unimolecular

Scheme 14

35   **47**   **48**   **30**

rate constant only under low pressure conditions.[103,104] Study of 47

was undertaken and our results show that benzene (30) is indeed

produced.

The mechanism for the formation of 30 from 48 has received some

attention in the literature.[22,103,104] It has been proposed that

direct loss of hydrogen in a [1,2] sense does not occur, but rather

that 48 rearranges first to 36 and then direct [1,4] hydrogen loss

occurs with a rate that is much faster than the interconversion of 48

and 36 (Scheme 15).[22,103,104] The interconversion of 48 and 36 is not

intuitively obvious, but it has been carefully postulated that the

intermediacy of 87 is responsible,[103,104] as the low pressure thermolysis

of 87 produces both 36 and 48.[103] Nevertheless, our results on the FVP

of 47 show that as the pyrolysis temperature is decreased the relative

amount of 48 increases, yet 36 cannot be observed. This is consistent

with the published results.

Scheme 15

48   **87**   **36**   **30**

The interconversion of VCH-d_8 (34-d_8) to benzene-d (30-d) can be rationalized as shown in Scheme 16 based on the arguements given. The biradical intermediate which might be involved in the FVP of 34-d_8, 35-d_8, could undergo a deuterium shift. The bicyclo[2.2.2]octene-d_8 (47-d_8) thus produced could then lose either ethylene bridge, which in this case are different. Loss of ethylene by pathway (a) would result in the loss, at this point, of four deuterium atoms. Loss of ethylene by pathway (b) would result in the loss of three deuterium atoms. Compounds 88 and 89 would be produced by each of these transformations, respectively. These 1,3-cyclohexadienes can then undergo [1,5] hydrogen (deuterium) shifts, which would result in the complete scrambling of the labels and the concomitant formation of 90 and 91.

It can be assumed that 88 and 89 would be produced with an equal frequency, since the phenomenon known as the secondary deuterium isotope effect decreases with increasing temperature.[105,106] Further,

Scheme 16
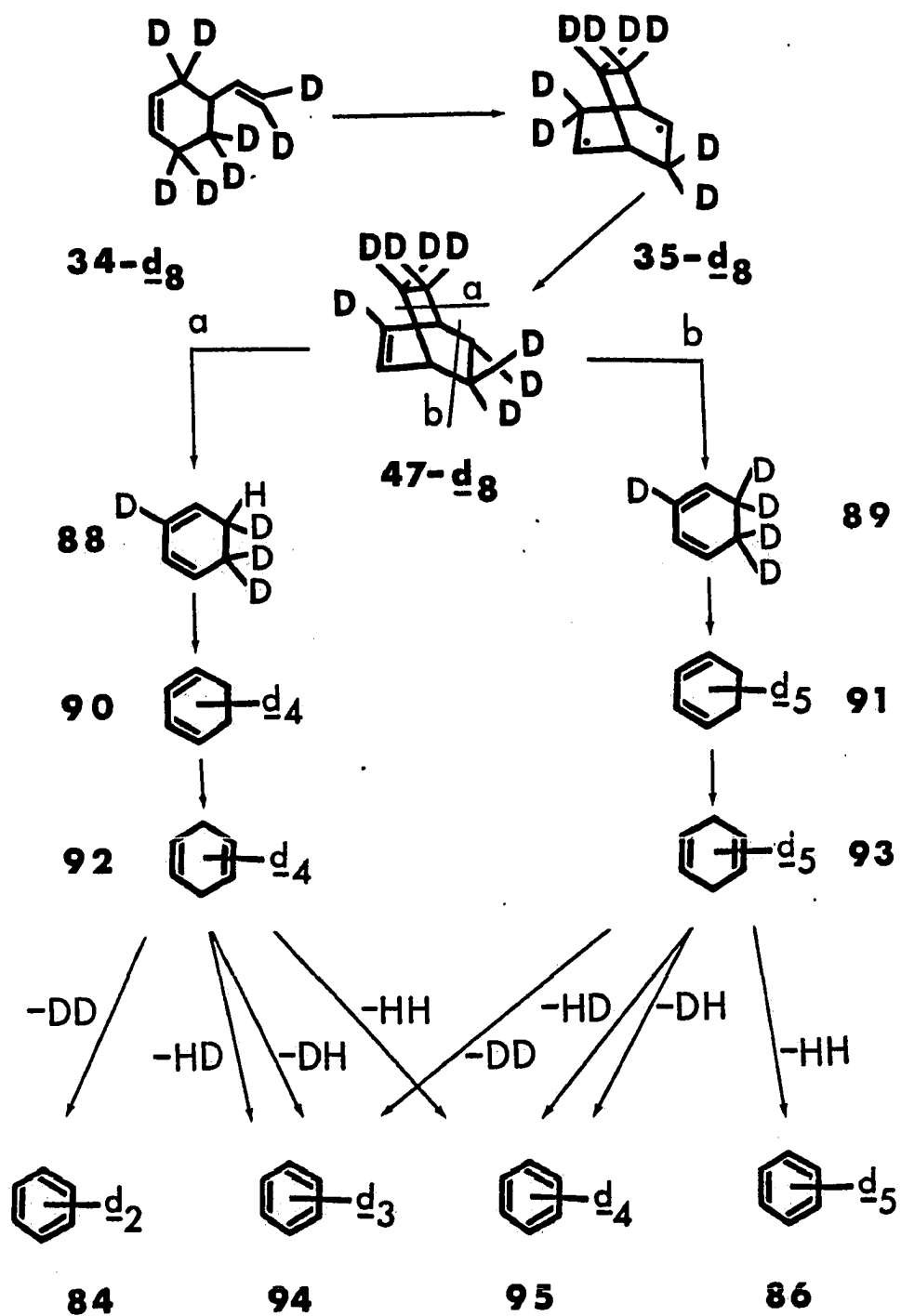
for a retro Diels-Alder reaction, secondary isotope effects are near a value of unity at moderate temperatures,[107,108] even if the reaction is not synchronous.[109] For example, the loss of ethylene ($\underset{\sim\sim}{31}$) from dibenzobicyclo[2.2.2]octene ($\underset{\sim\sim}{96}$) has been studied as a function of increasing deuterium content.[108] The change in rate of anthracene ($\underset{\sim}{13}$)

96   **13**
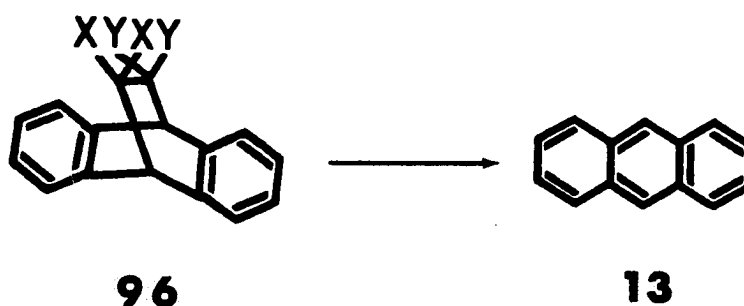
a X = Y = H $\underline{k}_H$

b X = H, Y = D $\underline{k}_H/\underline{k}_{D_2}$ = 1.08

c X = Y = D $\underline{k}_H/\underline{k}_{D_4}$ = 1.17

formation on going from a $\underline{d}_0$ species ($\underset{\sim\sim}{96a}$), to a $\underline{d}_2$ species ($\underset{\sim\sim}{96b}$), on to a $\underline{d}_4$ species ($\underset{\sim\sim}{96c}$) is less than 10% for each two-deuterium-atom jump. Thus, for the bicyclo[2.2.2]octene system ($\underset{\sim\sim}{47}$-$\underline{d}_8$) under present scrutiny, the difference in the rate of loss of ethylene-$\underline{d}_3$ ($\underset{\sim\sim}{32}$-$\underline{d}_3$)

relative to ethylene-d_4 (32-d_4), a one-deuterium-atom jump, should be negligible at the temperatures employed for this reaction.[105,106]

The randomly labeled 1,3-cyclohexadienes 90 and 91 should produce, upon rearrangement, the randomized 1,4-cyclohexadienes 92 and 93, respectively (Scheme 16).[22,103,104] There are four pathways which 92 can then follow for aromatization (Scheme 16). A purely statistical loss of hydrogen and deuterium atoms, which would result if there are no kinetic isotope effects, produces a 1:2:1 ratio of benzene-d_2 (84):benzene-d_3 (94):benzene-d_4 (95).

Theory predicts that the maximum primary deuterium isotope effect decreases with increasing temperature and approaches a value of 1.4 at high temperatures.[110,111,112] The β-elimination reaction of the sulfoxide 97 shows this type of temperature dependence, the k_H/k_D ratio can be seen to decrease with increasing temperatures.[112,113,114] This effect is not attributable to the involvement of a heteroatom.[115]

This author is not aware of any detailed study on the primary deuterium isotope effect involving the direct [1,4] loss of hydrogen. Fleming and Wildsmith have noted a lower isotope effect with increasing

97 → 98   98-d₁
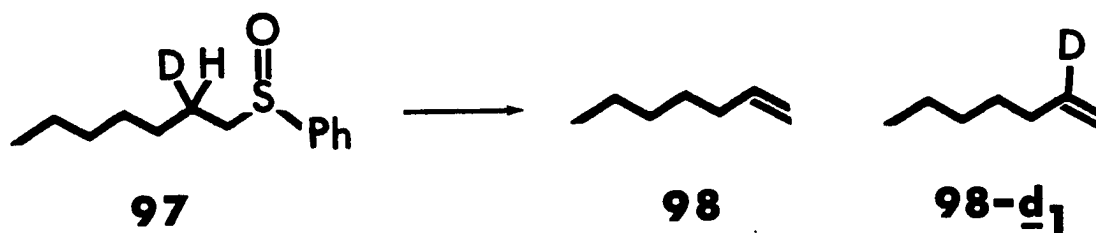
T, °C	k_H/k_D
130	3.17
190	2.63
230	2.38

"effective temperature" in a study on the aromatization of 99.[116]

The primary isotope effect in the retro Diels-Alder reaction of 100

99
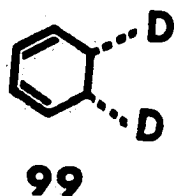
has been reported.[117] The bridge oxygen isotope effect was $\underline{k}_{16}/\underline{k}_{18}$ = 1.014 and the bridgehead carbon isotope effect was $\underline{k}_{12}/\underline{k}_{13}$ = 1.013 at 130°C.

100   **101**
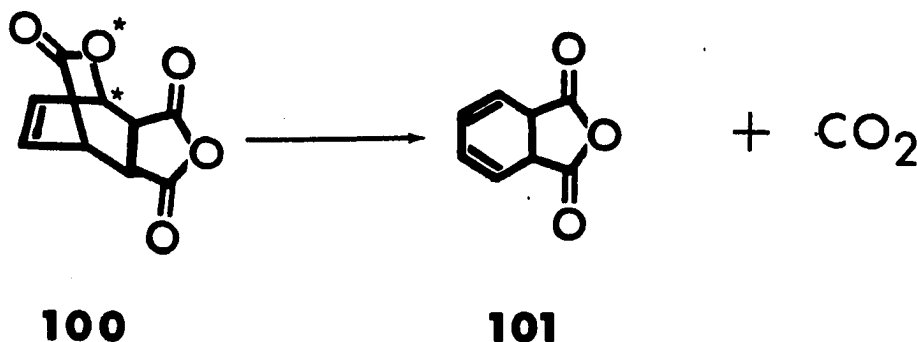
The transition state for the Diels-Alder reaction is thought to occur via a boat-like transition state.[118] By microscopic reversibility, then, the retro Diels-Alder reaction should also proceed through a boat-like transition state. It has also been postulated that the transition state in retro Diels-Alder reactions largely resembles the starting material and that it is reached at an early point along the energy surface.[119] Isotope effects have their smallest values when transition states are reached early (or late).[105,106] The concerted, cis [1,4] loss of hydrogen from 1,4-cyclohexadiene (36)[116,120,121,122,123] should, by geometric constraints, occur through a boat-like transition state. Thus, the assumption that hydrogen (deuterium) loss from the randomly scrambled 1,4-cyclohexadiene-$\underline{d}_4$ (92) at 800°C would be statistical is not unreasonable.

36
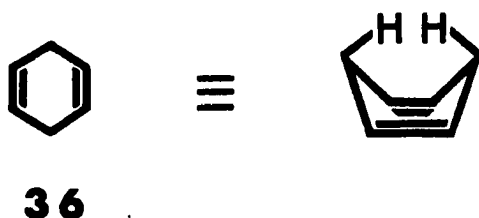
The pathways available to the 1,4-cyclohexadiene-d_5 (93) are
the same as those open to 92 (Scheme 16), although not at the same
frequency as there is not an equivalent number of hydrogen and deuterium
atoms in 93. Thus, approximately a 1:2:1 ratio of benzene-d_3
(94):benzene-d_4 (95):benzene-d_5 (86) would be expected. The amount
of d_4 and d_5 species would be somewhat greater than 1 and 2, respectively,
and the amount of d_3 species would be somewhat less than 1 in the 30-d
produced from 93.

Adding together the expected deuterium species upon aromatization
of 92 and 93 (Scheme 16), one obtains approximately a 1:3:3:1 ratio of
benzene-d_2 (84):benzene-d_3 (94):benzene-d_4 (95):benzene-d_5 (86).
Thus, the mechanism proposed (Scheme 16) for the production of benzene
(30) from 4-vinylcyclohexene (34) is in accordance with the experimental
results.

Kopinke and coworkers have recently published the results of the pyrolysis of butadiene-1-^{14}C (102) under conditions allowing bimolecular reactions to occur in the hot zone.[42] Under these conditions,

102

butadiene-^{14}C (102) is capable of dimerizing to VCH 104 directly in the hot zone (Scheme 17). Then, subsequent rearrangement to benzene can ensue. Their results are tabulated in a manner which assumes that the butadiene contains two labels at the equivalent, experimentally indistinguishable 1 and 4 positions. By this type of analysis, the benzene produced in the pyrolysis of 102 contained 2.2 labels. No mechanistic rationale was set forth to explain these results.

The mechanism presented in Scheme 16 can account for these results (Scheme 17). Dimerization of the labeled butadiene (102) and subsequent rearrangement would produce the bicyclo[2.2.2]octene 106 (Scheme 17). Loss of ethylene could occur by the loss of either bridge, and the result would be the production of a 1:1 ratio of

Scheme 17
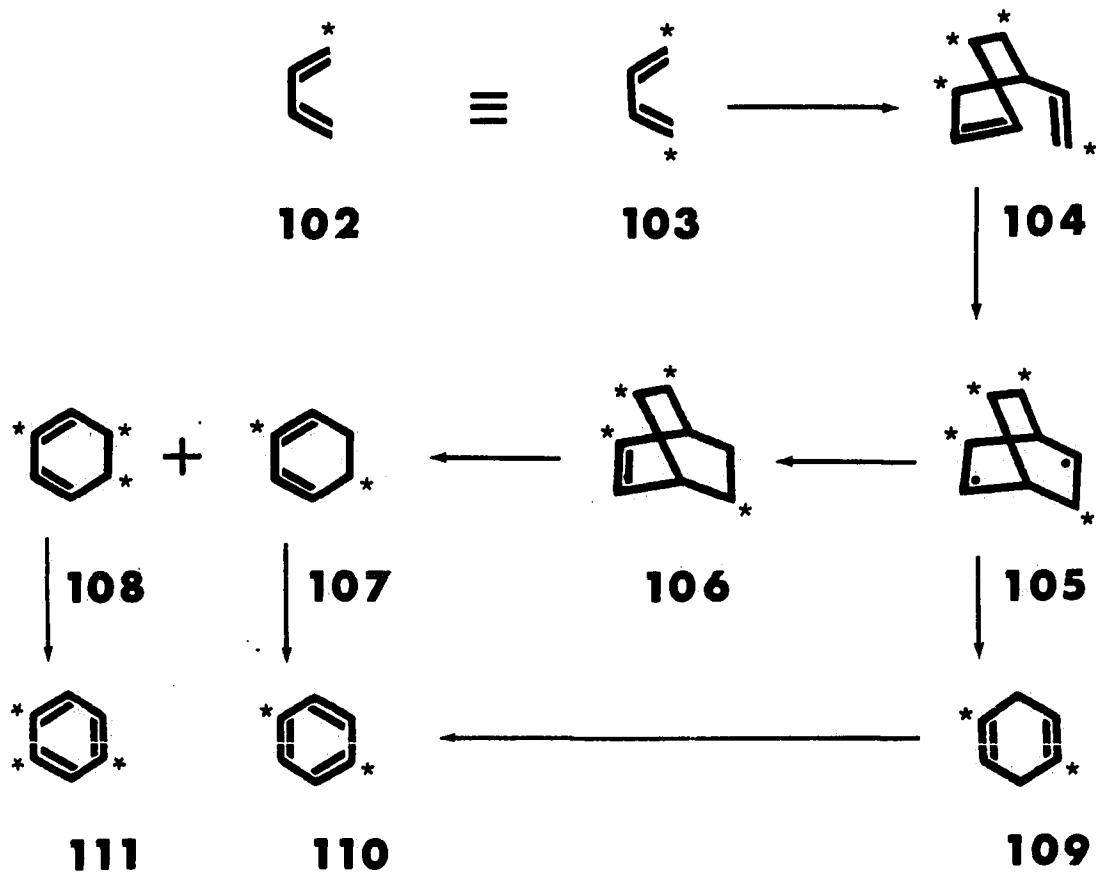
benzene with 2 (110) or 3 (111) labels. The relative label content

for the benzene produced via the mechanism proposed herein would be 2.5.

The actual conditions for the pyrolysis described by Kopinke and coworkers have to be different than those of FVP.[42] This can readily be seen by the production of toluene in the respective experiments. We observed a toluene/benzene ratio of 1.2; Kopinke and coworkers observed a ratio of 0.21. It is possible that under their conditions, the direct loss of ethylene from 105 is occurring, at least to a small extent (Scheme 17). Thus, the relative label content of the benzene produced would be in effect lowered from the predicted value of 2.5.

Kopinke and coworkers also observed that the toluene (46) produced in the pyrolysis of 102 contained three labeled carbon atoms.[42] This result gives some insight into the mechanism for the production of toluene (46) in the FVP of VCH (34). The route diagrammed in Scheme 18 is proposed.

The biradical intermediate 112 can be produced in an analogous manner to that of 35. Loss of methylene from the biradical intermediate would generate a new closed shell molecule, 113, which could readily lose hydrogen to produce cycloheptatriene (114). The rearrangement of 114 to toluene (46) is well-established in the literature.[124] The assumed deuterium scrambling of the toluene-d (46-d) in the FVP of 34-d_8 can be rationalized by rapid [1,5] hydrogen (deuterium) shifts of 114.[124] The uninterpreted results of Kopinke and coworkers also fits this analysis (Scheme 19).[42]

Scheme 18

34 → **112**

|||

113 ←$-CH_2:$—

$-H_2$

114 → **115** → **46** (CH_3)

Scheme 19

104　　　　**116**　　　　**117**　　　　**118**
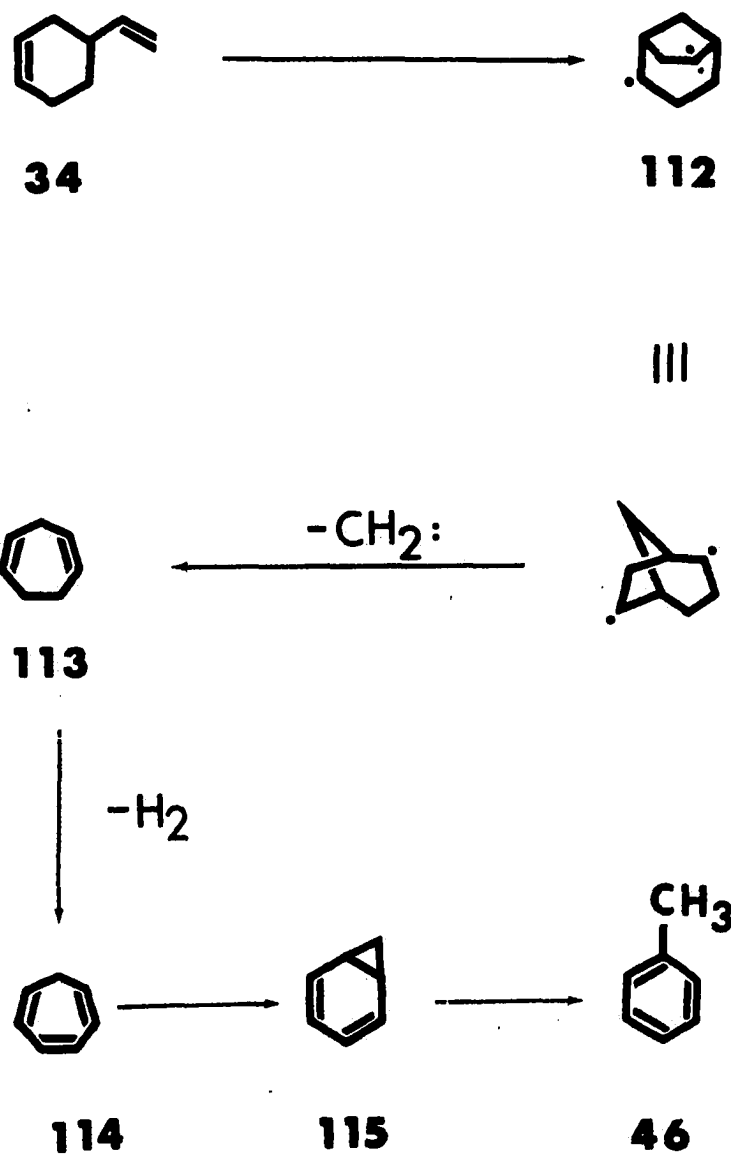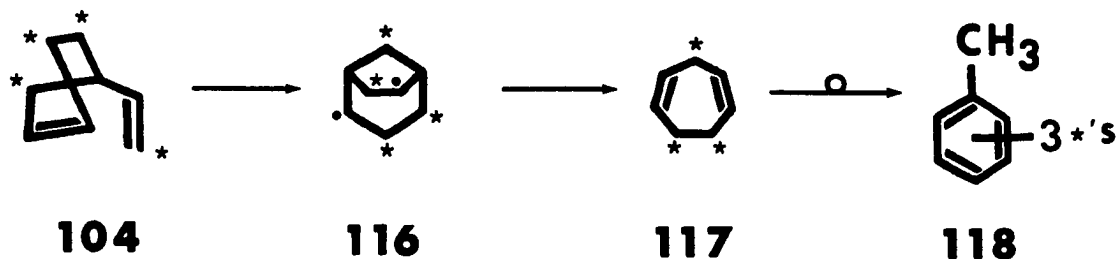
Comparison of the FVP of 4-Vinylcyclohexene to

the FVP of Dibenzocyclooctene

It is interesting to compare the 4-vinylcyclohexene (34) system to

that of the [4+4] dimer of ortho-quinodimethane (16). The lowest

energy species of the eight carbon system is 34.[100] The lowest energy

species of the sixteen carbon system is 16 (Scheme 20).[23] Why 16 is more

stable than 17 follows from the additional stability gained on producing

the second aromatic ring. The stability of 34 over 44 is not as concrete,

yet calculations using the group equivalent constants of Benson and

coworkers[125] show VCH (34) to be 7.1 kcal/mole more stable than 1,5-cyclo-

octadiene (44).[100]

Scheme 20

34   **44**

17   **16**
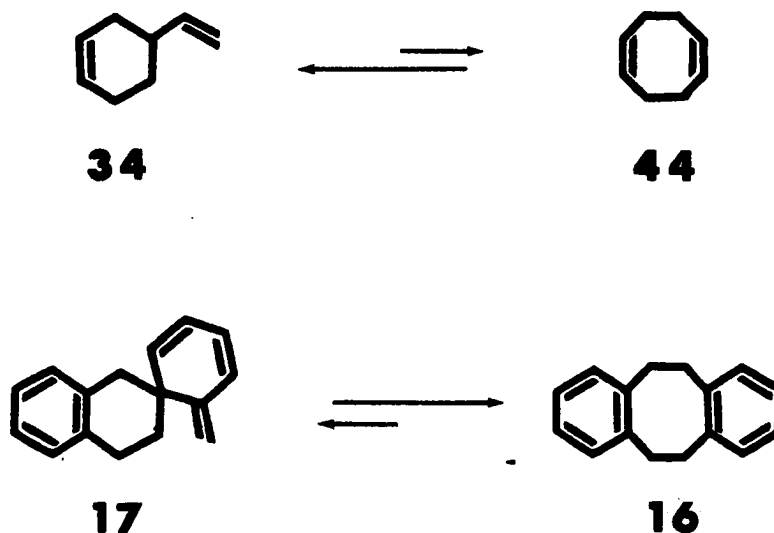
As shown in Scheme 13, the rearrangement of 34 to 44 is thought to occur either in a concerted fashion or via a biradical intermediate.[52,54,99,100] Since for this eight carbon system, either pathway can be rationalized from the experimental results, then for the sixteen carbon system a biradical intermediate can be readily invoked due to the stabilization of the radical centers by delocalization into the aromatic rings (Scheme 21). For the FVP of 16, a most reasonable first step is, then, homolytic cleavage to 120. Rearrangement of 120 to 121 serves as a starting point for the variations in the transformations of 16 as compared to 34 (Scheme 22).

Scheme 21

17   119

16   120
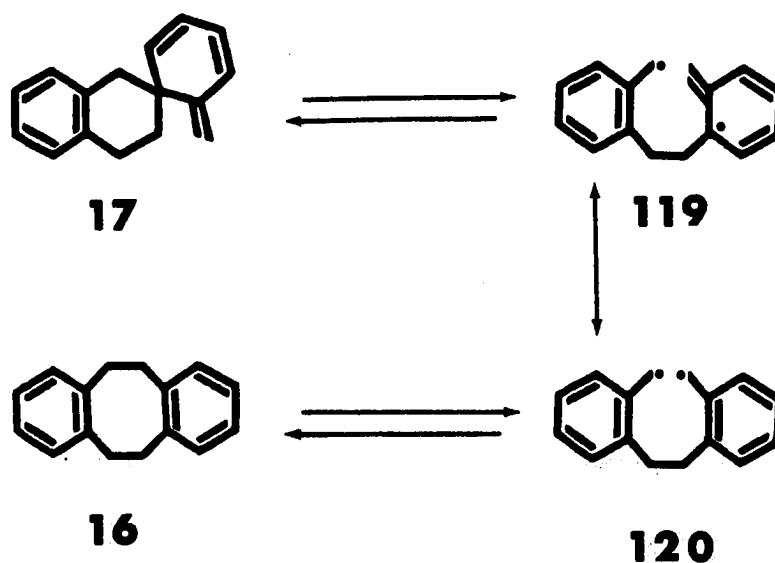
It is unlikely that intermediate 121 would undergo a hydrogen

shift producing 122, which is analogous to 35 going to bicyclo[2.2.2]-

octene (47) (Scheme 14). In this case, significant ring strain is

introduced and no aromaticity is regenerated. Direct loss of ethylene

regenerates two aromatic rings and should be a more facile process.

The mode of deuterium scrambling for 16-d_4 and 34-d_8 must also

occur at different points along the energy surface leading to products,

as the experimental results show that no deuterium is incorporated into

the original aromatic rings of 16-d_4. Once dideuteriodihydroanthracene

Scheme 22

15   **121**   **122**
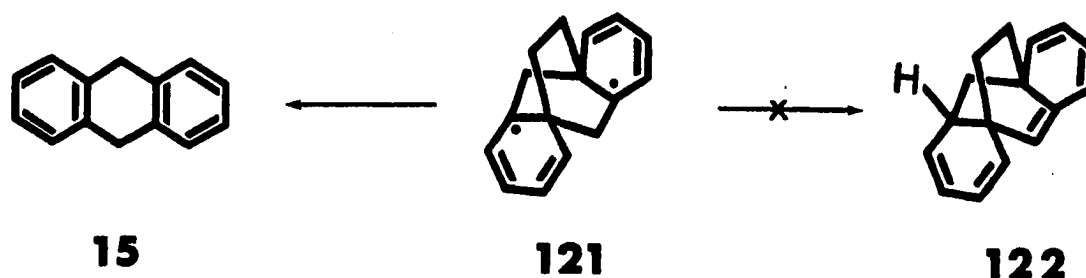
($\underset{\sim\sim}{15}$-9,10-$\underline{d}_2$) is produced, the lowest energy pathway is direct loss of

hydrogen (deuterium) (Scheme 23).[21,22] The analogy between the rearrange-

ment of $\underset{\sim}{34}$ (Scheme 13) and $\underset{\sim}{16}$ to their isomers provides an opportunity

to rationalize the deuterium scrambling in the FVP of $\underset{\sim\sim}{16}$-$\underline{d}_4$. Initial

homolytic cleavage of $\underset{\sim\sim}{16}$-$\underline{d}_4$ gives $\underset{\sim\sim\sim}{123}$, which can be followed by a

series of intramolecular hydrogen abstractions to produce the tetra-

deuterio species $\underset{\sim\sim}{130}$. Although only one of the ethylene bridges is

being shown to cleave in Scheme 23, cleavage of the other ethylene

bridge would produce the equivalent result. Compound $\underset{\sim\sim\sim}{129}$ can then

Scheme 23

123

124

125

127

126

129

130
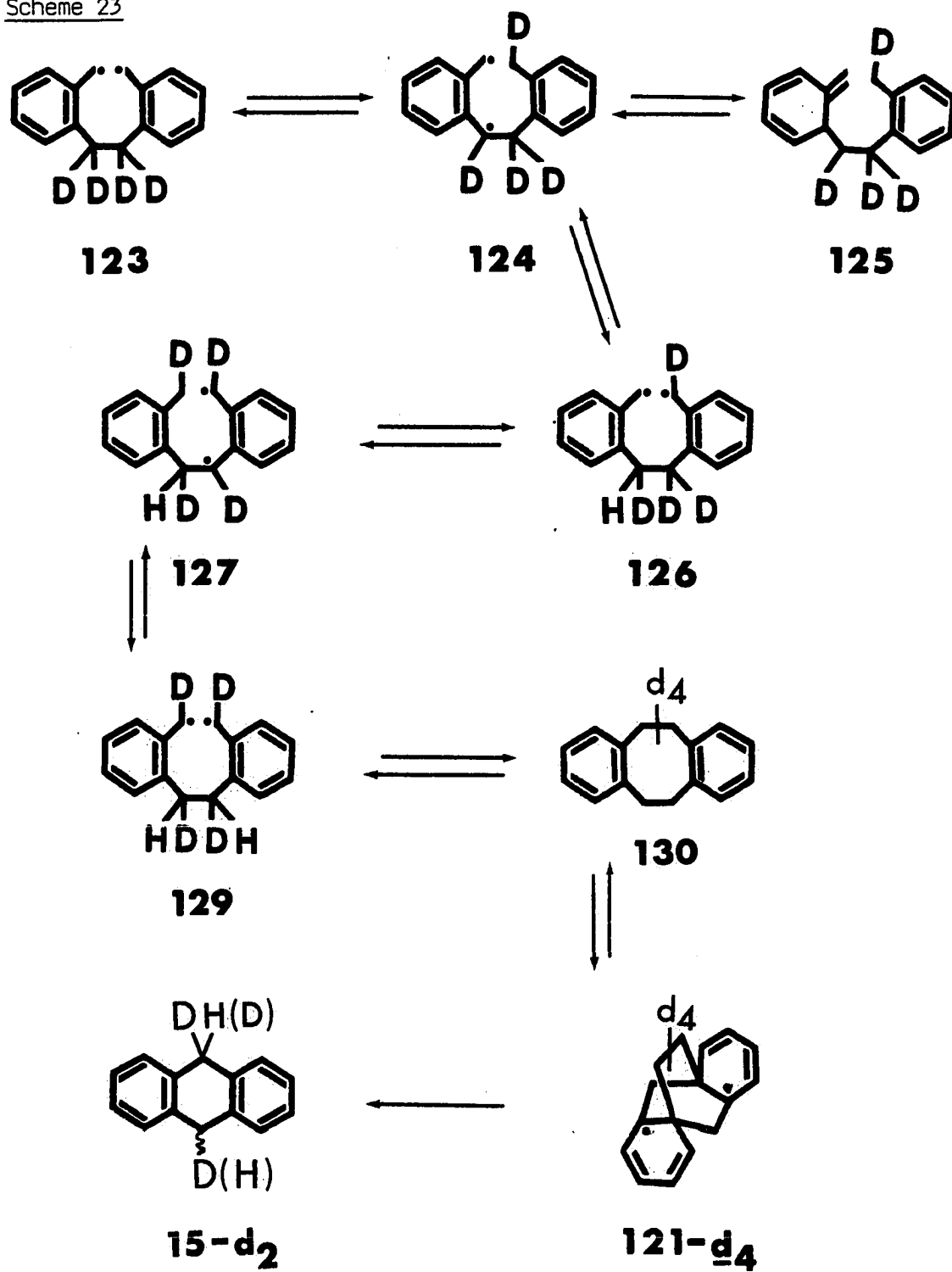
15-d$_2$

121-d$_4$

produce $\underset{\sim\sim}{15}$-$\underline{d}_2$ through the intermediacy of $\underset{\sim\sim\sim}{121}$-$\underline{d}_4$. Loss of ethylene-$\underline{d}_2$

($\underset{\sim\sim}{32}$-$\underline{d}_2$) from $\underset{\sim\sim\sim}{121}$-$\underline{d}_4$ would produce $\underset{\sim\sim}{15}$-9,10-$\underline{d}_2$, which would possess random

stereochemistry with regard to the hydrogen and deuterium atoms at the

9 and 10 positions. At this point, cis [1,4] hydrogen (deuterium)

loss would occur by the pathways shown in Scheme 24. With no kinetic

isotope effect, loss of HH, DD, HD or DH would give a 1:2:1 ratio of

Scheme 24
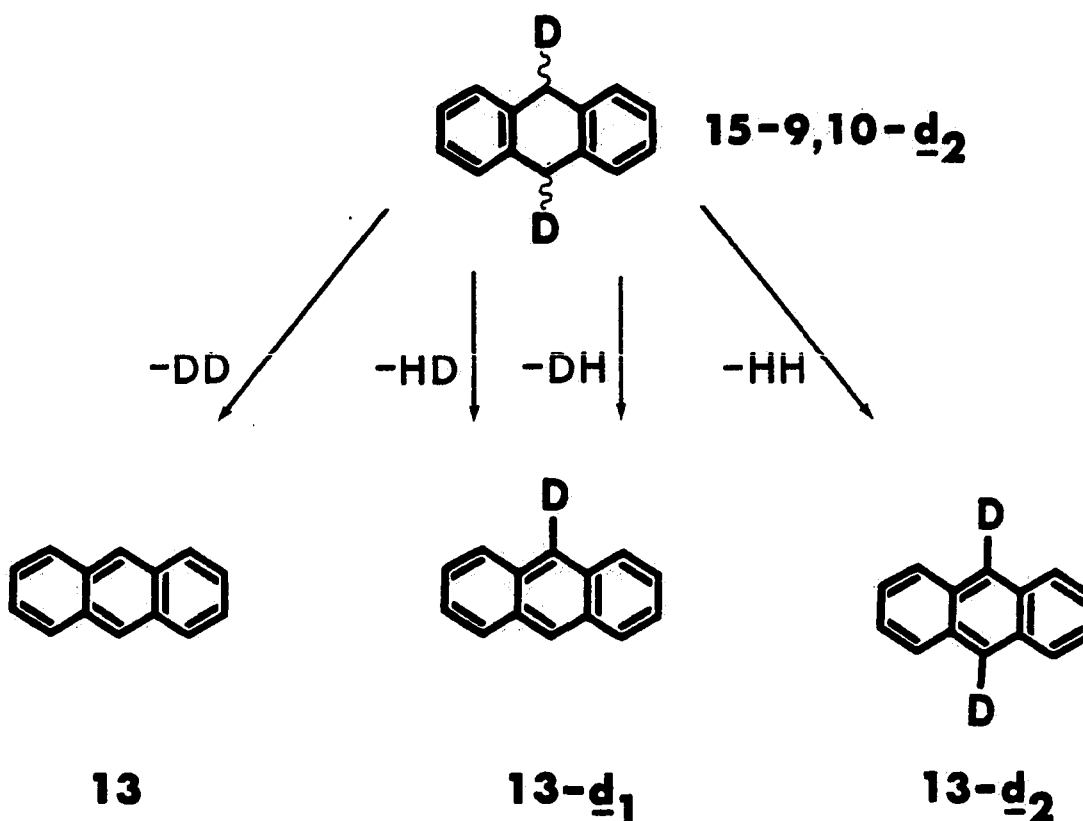
$\underline{d}_0:\underline{d}_1:\underline{d}_2$ species for the anthracene (13-$\underline{d}$) produced. This example

is in accordance with the experimental results.

The other products obtained in the FVP of 16 can be rationalized

by deviations of the mechanistic scheme shown for the deuterium

scrambling. In Scheme 25 are possible routes to some of the $C_{16}H_{16}$

isomers which were produced (relative yields are given in Table 12

and Schemes 25, 26 and 27). It should be noted that the steps shown

in Scheme 25 can circuitously return to 16, and thus can also be

invoked as an alternative explanation of the deuterium scrambling.

In Scheme 26 is shown the rationale for the formation of 9-methyl-

anthracene (77) by analogy to the rearrangement of VCH (34) to toluene

(46). The formation of 66, 67, 75 and 76 (Scheme 27) is not

intuitively obvious and is not well-understood at this time. The

fact that 76 is produced at the expense of 75 suggests a common inter-

mediate between these two compounds. Speculative routes to 66, 67 and

76 are shown in Scheme 27. No acceptable route to 75 could be derived

(Scheme 27).

<div align="center">Attempted Extension of our General Mechanistic

Proposals; the FVP of Allylic Esters</div>

The transformation from 34 to 35 involves the combination of

two olefinic moieties with concomitant formation of a biradical species.

This is a unique organic sequence and experiments were performed to

establish its generality.

Scheme 25

16   **120**   **17**

133   **130**   **70**(13%)

CH₃   CH₃

68(3%)   **131**   **132**

CH₃

CH₃

71(14%)   **134**   **69**(4%)

Scheme 26

17

135

137

136

CH₃

77 (3%)

Scheme 27

133 → **134** → **138**

139 → **140**   **141**

142   **67** (3%)   **66** (3%)

76 (8%)   **16** —?→ **75** (4%)

34   **35**
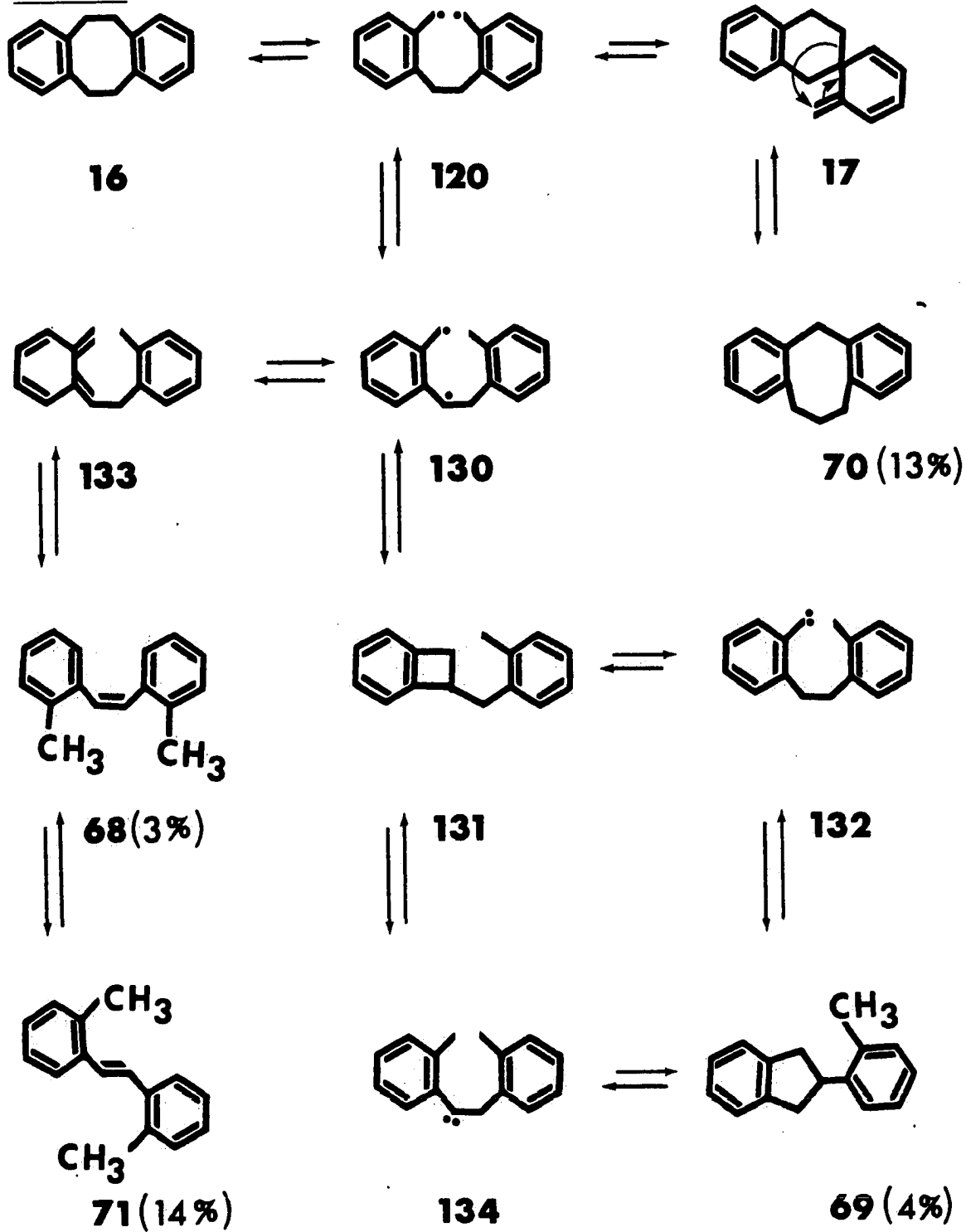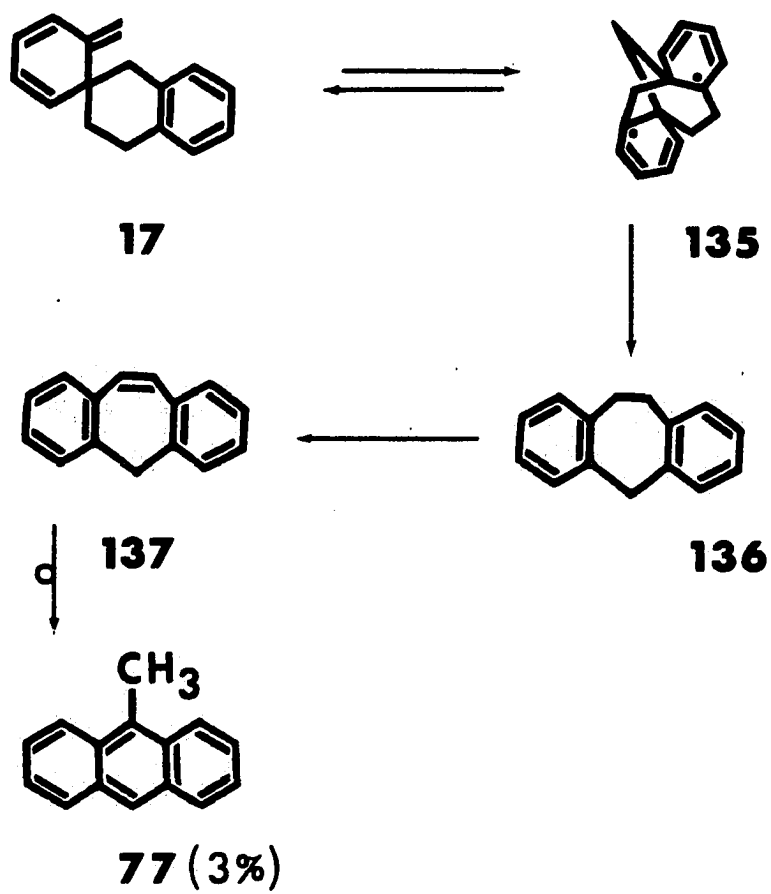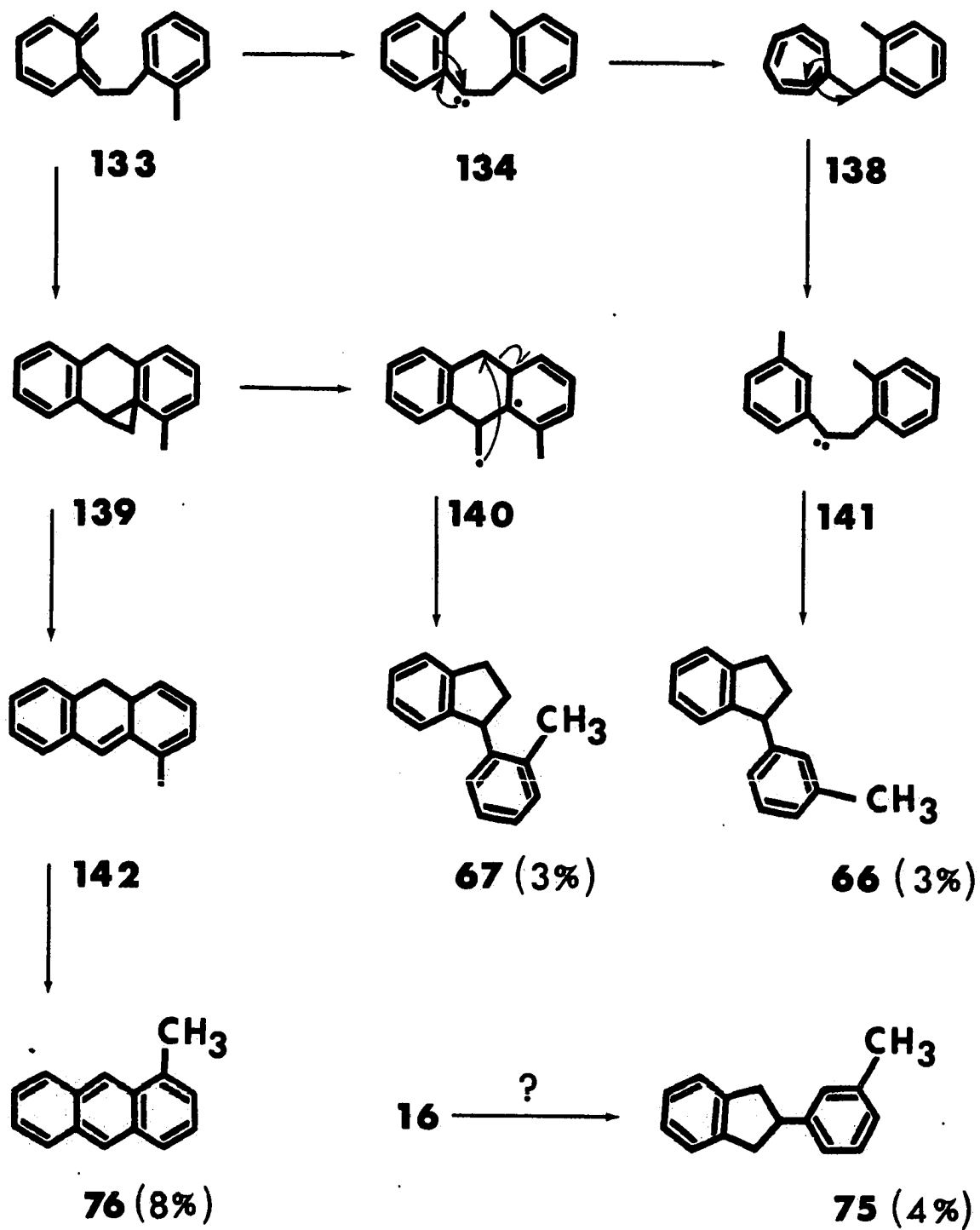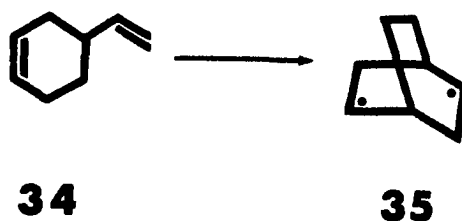
The pyrolysis of the allylic ester 49 has been reported.[126,127] A major product in these studies was allyl benzene (143) (Scheme 28). The formation of 14 was best ascribed to a chain mechanism where it ultimately arises from induced decomposition. It was thought that by studying this reaction under purely unimolecular conditions, one might obtain 143 arising by this new type of transformation (Scheme 29).

The results of the FVP of 49 showed that only 5% 143 was produced. The products observed in this pyrolysis suggest that the lowest energy pathway for 49 is homolytic cleavage to form the allyl radical (145) and the benzoyloxy radical (144). In an effort to stabilize the biradical intermediate postulated for this transformation, a furan system (52) was studied since there would be a smaller loss of energy on the break up of the furan nucleus over that of the benzene nucleus.[128]

Scheme 28

Scheme 29

52   **148**
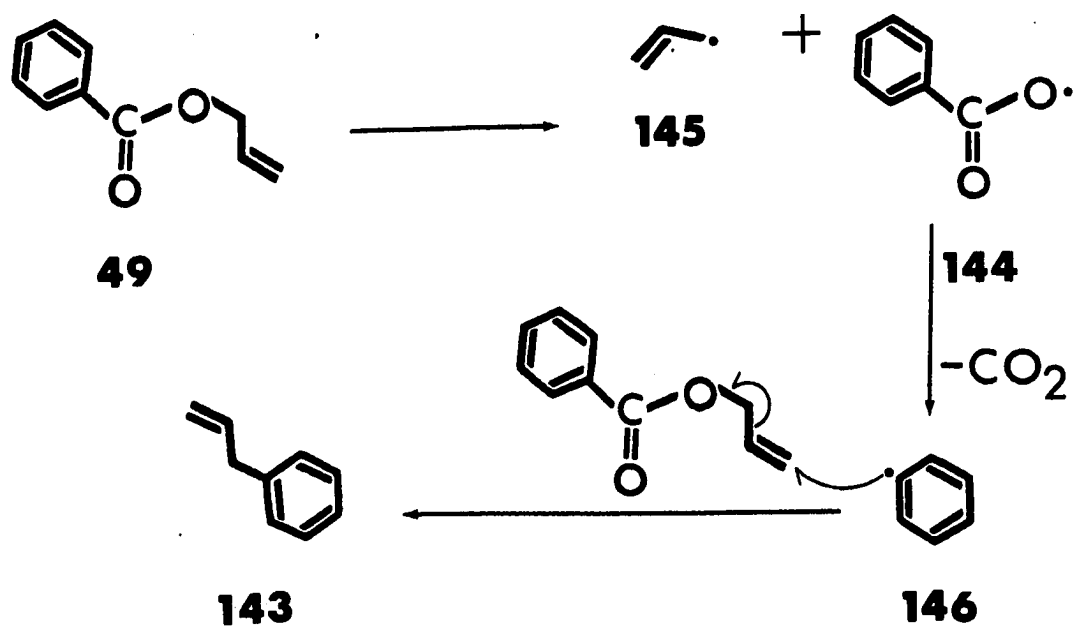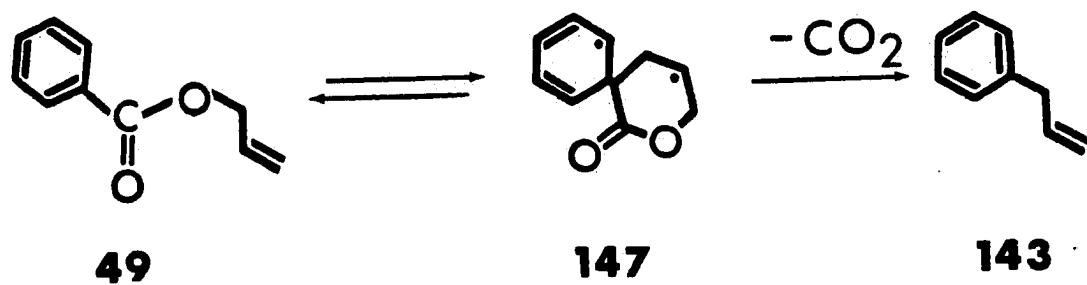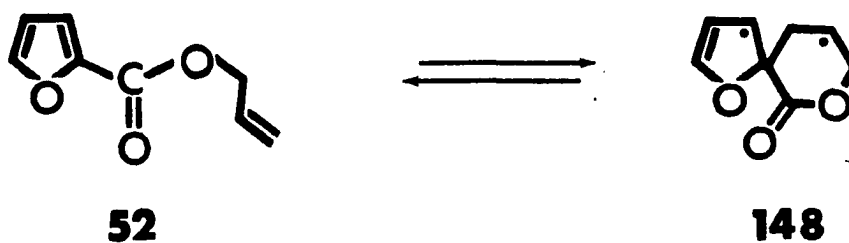
Additionally, a methyl substituent was added to the allyl portion of
the substrate (53) in hopes of stabilizing the biradical at that point.

53   **149**
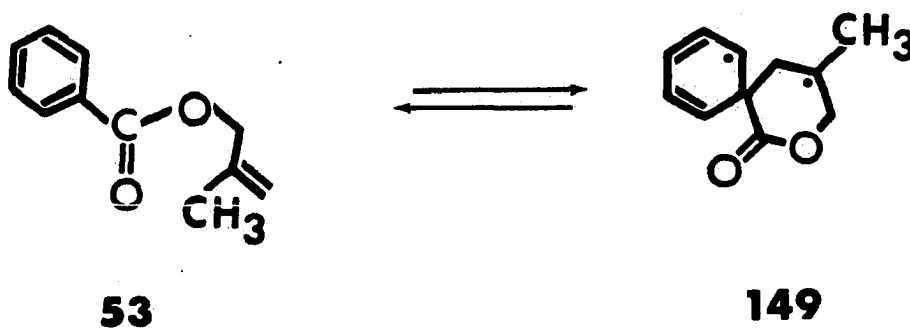
The results of the FVP of 52 and 53 were similar to the results
obtained in the FVP of 49. The only conclusion that can be made from
these series of experiments is that in the choice of the allylic esters,

we had underestimated the amount of initial homolytic cleavage. These experiments fail to support the mechanism shown in Scheme 29, yet they also fail to put the idea to rest.

The FVP of Dibenzosuberones; Regiospecific
Formation of Anthracenes

In another test of our general mechanistic scheme, the FVP of 38 was undertaken. Wiersum has published that the FVP of 37 gave an
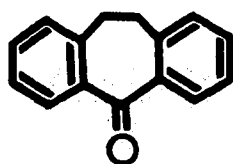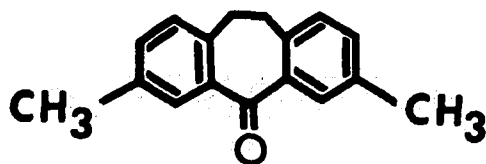
37   **38**

essentially quantitative yield of anthracene (13), yet the mechanistic rationale, which is presented below, is not without question.[47]

Intermediate 155 of the proposed intramolecular mechanism is the key to this discussion.[47] Wiersum suggested that homolytic cleavage of 155 to produce 156 is necessary for anthracene (13) production (pathway (a)). Indeed it is. However, if pathway (b) was followed instead, the biradical 157 would be formed. As 157 has both radical

Scheme 30

37   152   153

−CO

156   155   154

15   157   158

13   150   151
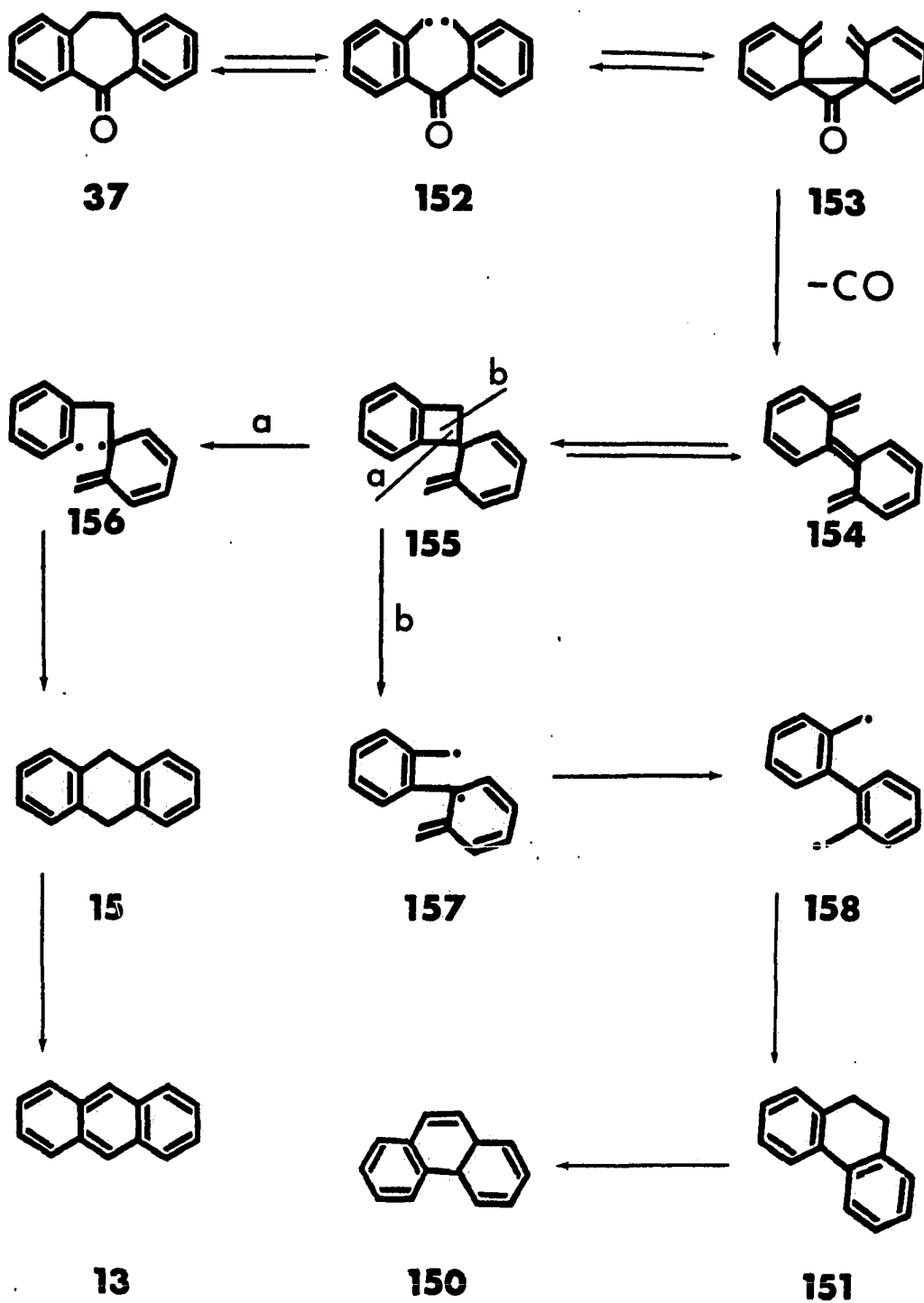
centers delocalized and 156 does not, one might expect the formation

of 157 to be more facile. From intermediate 157 comes 9,10-dihydro-

phenanthrene (151), and possibly, phenanthrene (150) (Scheme 30).

Since neither of these compounds can be observed in the pyrolyzate,

this intramolecular proposal of Wiersum (pathway (a)) is then

questionable.

Another possible route for this transformation was suggested by

Wiersum.[47] Intermediate 152 can lose CO directly (Scheme 31) to

produce either 159 or 160. Intermediate 159 can dimerize to 157,

which has already been discussed as a questionable intermediate for

the production of 13. Intermediate 160 can dimerize to 15, which is

known to go on rapidly to 13.[21,22] In reactions where 159 or 160

are generated directly, fullvenallene (161) and ethynylcyclopentadiene

(162) are often observed as products.[129] Yet in the FVP of 163,

161   **162**

Scheme 31

152   **159**   **160**

154   **13**   **15**
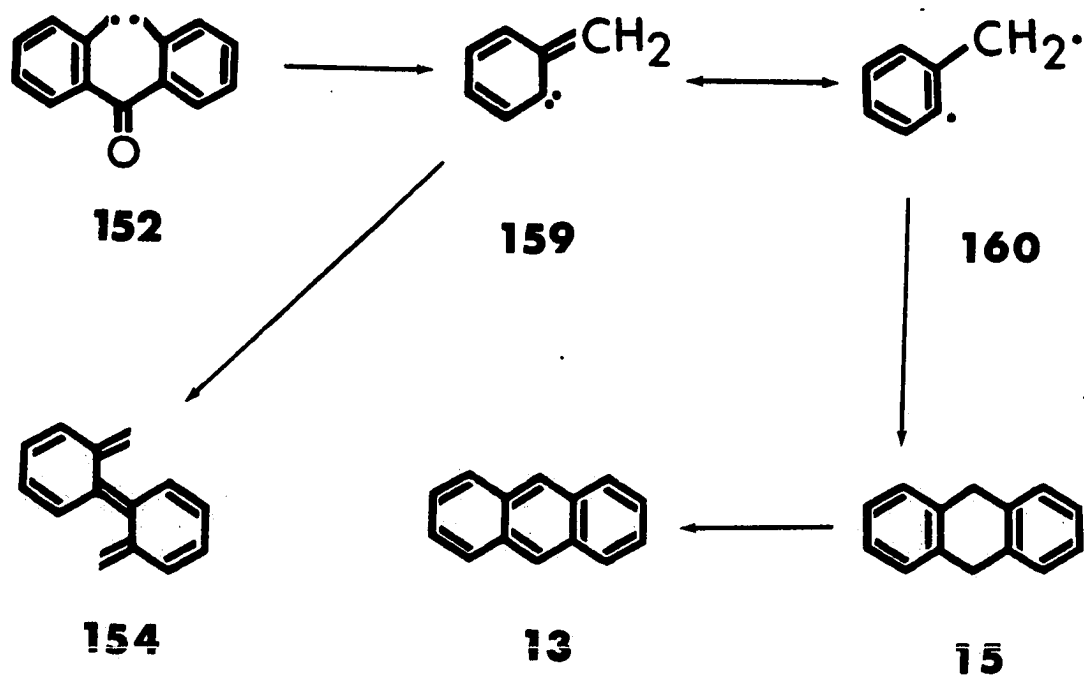
anthracene (13) is produced, and thus, Wiersum suggests that the

intermediacy of 160 cannot be ruled out in the FVP of 37.[47,130]

163   **160**   **13**
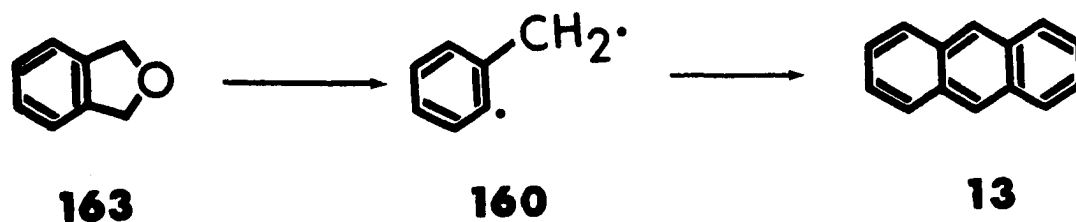
Our results from the FVP of tetradeuteriodibenzocyclooctene (16-$\underset{\sim\sim}{d}_4$) show that intermolecular reactions do not occur to any significant extent under FVP conditions. Therefore, our results are inconsistent with the intermolecular mechanism proposed by Wiersum (Scheme 31). It should be noted that a strong argument can also be made against the intramolecular mechanism of Scheme 30 (pathway (a)) without performing any experiments. In an attempt to establish if the FVP of 37 fits into the general mechanistic scheme described herein, the FVP of dimethyldibenzosuberone (38) was undertaken in order to gain evidence for the 180° ring flip.

The FVP of dimethyldibenzosuberone (38) produced 2,6-dimethyl-anthracene (125) as the sole product. Even though the mechanism presented in Scheme 30 would account for the observed regiochemistry, we feel that the rearrangement can better be accounted for by the

$$\text{38} \xrightarrow{\text{FVP}} \text{25}$$

38   **25**
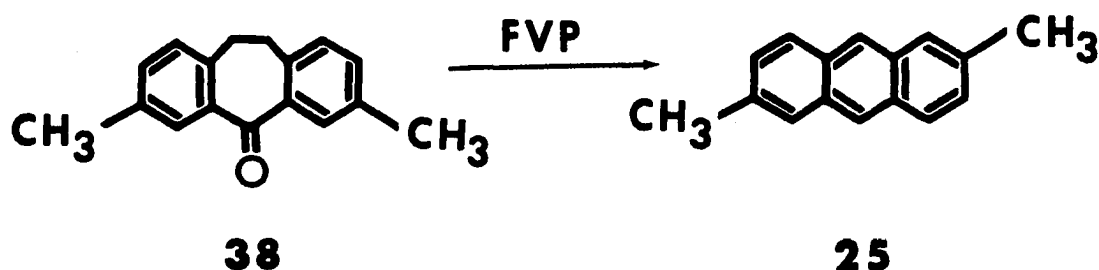
proposals described herein. Shown in Scheme 32 is our rationale for

the thermal, unimolecular rearrangement of 38 to 25.

Bibenzyl systems are known to undergo homolytic cleavage while

benzophenone systems are not.[131,132,133,134] Thus, the first step

of the transformation, formation of 164, is most reasonable. By

analogy to the sixteen carbon system, radical insertion into the

adjacent aromatic ring produces the spiro compound 166. The novel

combination step gives the biradical intermediate 166. This type of

intermediate has been discussed. It contains no highly strained bonds,

and it accounts for half of the 180° ring flip. The orbitals are all

properly oriented for the irreversible extrusion of carbon dioxide,

which should be a facile process. The actual extrusion produces two

closed shell molecules and regenerates two aromatic rings. The loss of

hydrogen from 29 then completes the transformation.[21,22]

Scheme 32
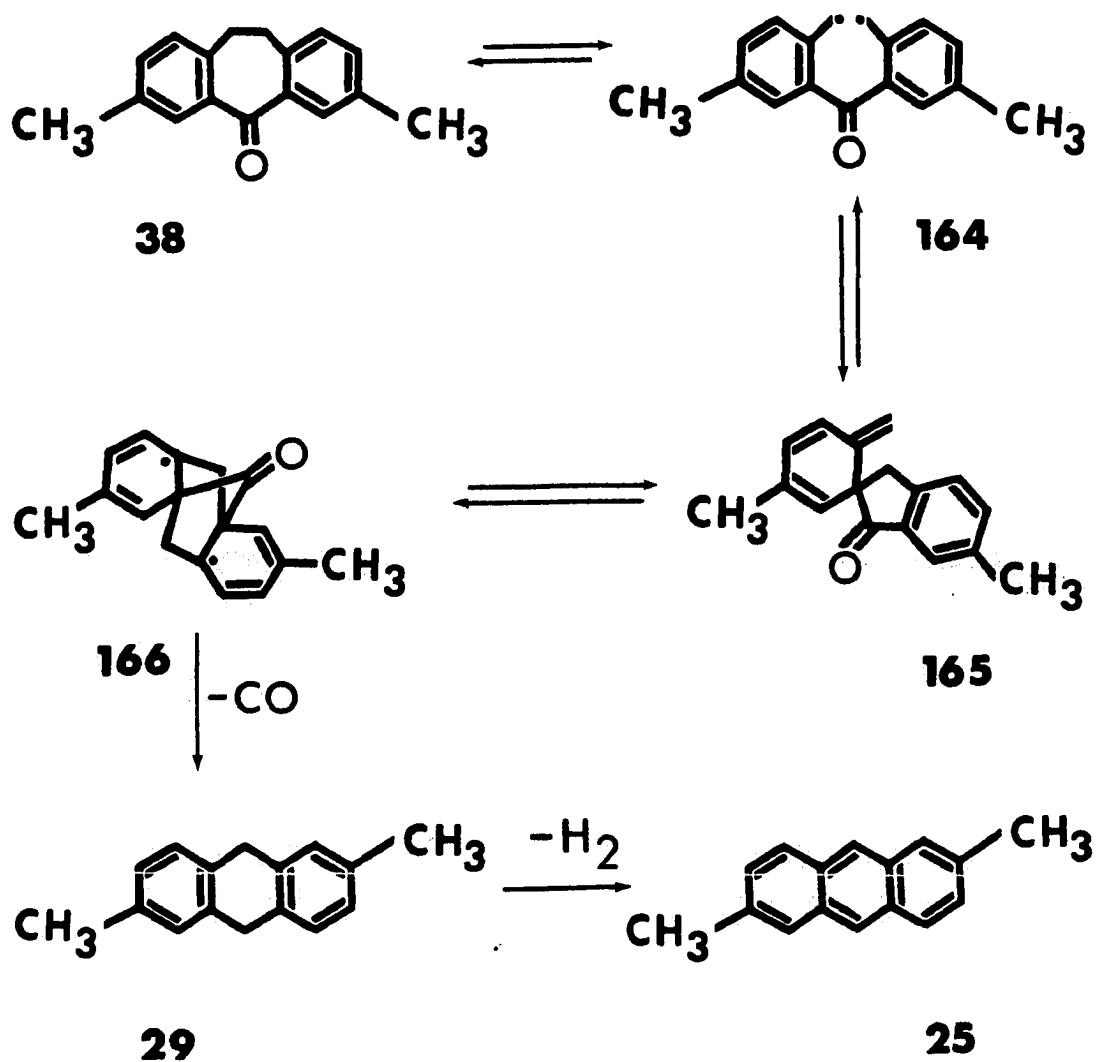
The derivitization of the parent dibenzosuberone was undertaken to extend the generality of the transformation just described. We set out to prove the usefulness of this reaction by investigating its

potential as a high yield, regiospecific reaction for the synthesis of disubstituted anthracenes. The synthetic route to the pyrolysis precursors necessary for this type of study was based on well-established chemical transformations. To test the overall regiochemistry of the thermal rearrangement, we first had to synthesize precursors of known regiochemistry.

By analogy to fluorenone (81) chemistry, nitration of commercially available dibenzosuberone (37) proceeded smoothly (Scheme 34)[86]. The two aromatic rings can be regarded as non-interacting, in terms of this reaction. The position of attack for each ring was determined by the directing effects of the carbonyl group and the steric influence of the ethylene bridge. Once nitration ensued, that particular aromatic ring was deactivated, and the overall process was repeated on the other side of the molecule. The desired compound was easily separated from by-products, as it was the only reaction product which was insoluble in EtOH. If desired, the by-products, mono and tri-nitrated compounds, could be further purified.[135] Large quantities of 82 could be obtained with relative ease.

The nitro groups could be readily reduced in the presence of the carbonyl functionality,[85,86,87] floculent yellow needles of the diamine 40 were obtained. The Sandmeyer reaction produced acceptable yields of the dichlorosuberone 39 in an unexpectedly vigorous reaction.[89] It was hoped that suitable oxygen containing functional groups could

Scheme 34

$$R = H, CH_3, \overset{\overset{\displaystyle O}{\parallel}}{C}CH_3$$
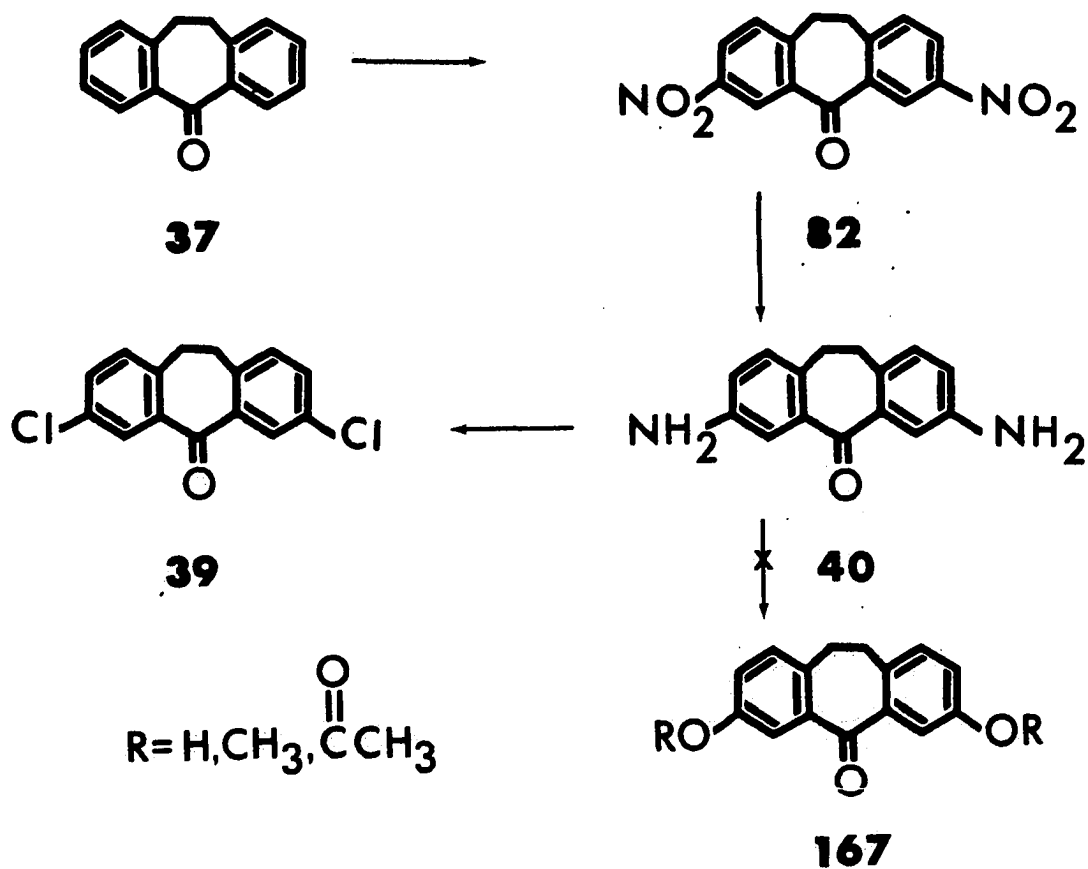
be attached at the tetrazonium stage, but all attempts at their
introduction failed miserably. It is probably the high reactivity of
the tetrazonium salt which prevented this reaction from occurring.

The FVP of 39 gave excellent yields of the dichloroanthracene 41 in a clean pyrolysis. The pyrolysis of 40 gave good yields of the
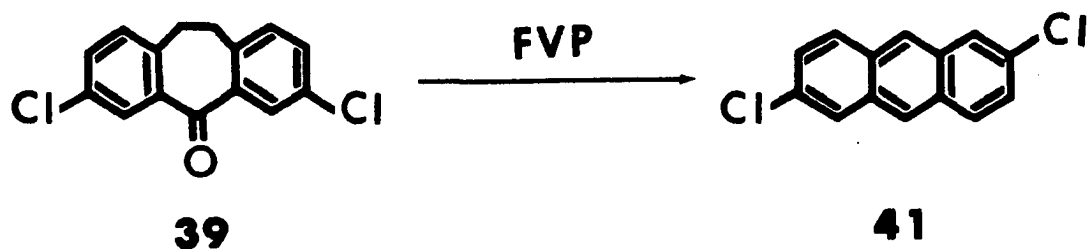
diaminoanthracene 42. To our knowledge, this is the first report of
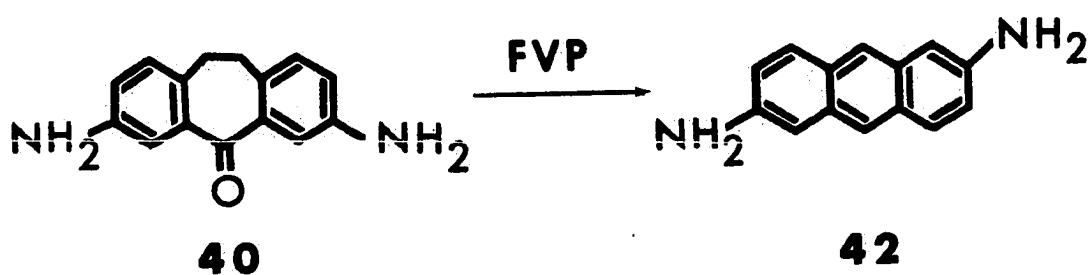
the synthesis of 42. Compound 42 was quite insoluble in common organic solvents, and what little went into solution could be seen to decompose rapidly. The diamine was, however, fairly stable in its crystalline

state when stored under nitrogen. Once again, flash vacuum pyrolysis
has proved itself as an excellent method for preparing reactive compounds
free of the possible interferences of solvent.

The thermal transformation of dibenzosuberones to anthracenes
appears to be a general, high yield, regiospecific reaction. The
reaction can tolerate both electron withdrawing and electron donating
functional groups and should be amenable to an everyday synthetic
route to anthracenes.

SUMMARY

The thermal rearrangement of the dimer of butadiene (32),
4-vinylcyclohexene (34), was investigated by flash vacuum pyrolysis
(FVP). The FVP of 4-vinylcyclohexene (34) gave benzene (30) and
toluene (46) as the major products. From the results of the FVP of
4-vinylcyclohexene-3,3,5,5,6,6,8,8-d_8 at 800°C, a new mechanism for
the formation of benzene (30) from 4-vinylcyclohexene (34), and thus
from butadiene (32), is proposed.

Also described is a study on dibenzocycloctene-5,5,6,6-d_4 (16-d_4)
and the isolation and characterization of the minor products produced
along with anthracene (13) in the FVP of 16. The FVP of the vinyl-
cyclohexene system is compared and contrasted to the FVP of the dibenzo-
cyclooctene system.

The FVP of 2,9-dimethyldibenzosuberone (38) gives, as the sole
product, 2,6-dimethylanthracene (25). The regiospecific transformation
arises from a 180° ring flip of the 2 original aromatic nuclei relative
to one another. The FVP of 2,9-dichlorodibenzosuberone (39) and
2,9-diaminodibenzosuberone (41) were investigated. These compounds
give, upon FVP, the corresponding 2,6-dichloro and 2,6-diamino
anthracenes, respectively. It appears that the FVP of functionalized
dibenzosuberones is a general, regiospecific route to difunctionalized
anthracenes.

EXPERIMENTAL

General

The flash vacuum pyrolysis (FVP) apparatus has been previously described[19] and the glassware is now sold commercially by Kontes Scientific Glassware. Gas chromatographic analysis was performed on a Hewlett Packard Model 5840-A gas chromatograph (gc) with a fused silica column coated with methyl silicone fluid (J&W Scientific DB-1) and a flame ionization detector. Combined gas chromatographic/mass spectra (gc/ms) analysis was performed on a Finnigan 4000 gc/ms with Incos data system and Finnigan 9610 gc. High resolution ms was performed at the University of Nebraska, Lincoln.

Proton and carbon NMR spectra were recorded on a Nicolet NT 300 and deuterium NMR was recorded on a Bruker WM 300. Chemical shift values are reported in δ values downfield from TMS as an internal standard.

Infrared spectra were recorded on either a Beckman Acculab II or an IBM FTIR model 98. Melting points were determined on a Hoover-Thomas melting point apparatus and are uncorrected.

The commercially available chemicals used are shown in Table 29. Anhydrous solvents were obtained by distillation from an appropriate drying agent and were stored under nitrogen over activated molecular sieves.

Table 29. Commercially available compounds

Compound	Source
Acetic acid	Fisher Scientific Company
Acetone	Fisher Scientific Company
Acetone-d_6	Stohler Isotope Chemicals
Allyl alcohol	Aldrich Chemical Company
Alumina (neutral powder)	J. T. Baker Chemical Company
Alumina (neutral powder)	Woelm
Aluminum trichloride	Fisher Scientific Company
Benzene	Fisher Scientific Company
Benzoyl chloride	Fisher Scientific Company
Calcium chloride	Fisher Scientific Company
Carbon dioxide(s)	Heller Carbonics
Carbon disulfide	J. T. Baker Chemical Company
Carbon tetrachloride	Fisher Scientific Company
Celite	J. T. Baker Chemical Company
Chloroform	Fisher Scientific Company
Chloroform-d	Aldrich Chemical Company
Copper(I)chloride	Mallinckrodt Chemical Works
Deuterium oxide	Aldrich Chemical Company
Dibenzosuberone	Aldrich Chemical Company
Diethyl ether	Fisher Scientific Company
Dimethylsulphoxide-d_6	Stohler Isotope Chemicals
Drierite	W. A. Hammond Company
Ethanol(absolute)	Hydrite Chemical Company
Ethanol (95%)	Hydrite Chemical Company
Ethyl acetate	Fisher Chemical Company
2-Furoic acid	Aldrich Chemical Company
Hexanes	Fisher Chemical Company
Hydrochloric acid	Fisher Chemical Company
Hydrogen	Cooks Inc.
Hydrogen peroxide (30%)	Fisher Chemical Company
Lithium aluminum hydride	Alfa Products
Magnesium sulfate	Fisher Chemical Company
Methanol	Fisher Chemical Company
o-Methylbenzyl chloride	Aldrich Chemical Company
Methylene chloride	Fisher Chemical Company
Methylene chloride-d_2	Stohler Isotope Chemicals
2-Methyl-2-propene-1-ol	Aldrich Chemical Company
Molecular sieves	Fisher Chemical Company
Nitric Acid	Fisher Chemical Company
Nitrogen (g)	Cooks Inc.
Nitrogen (l)	Air Products
Nitromethane	Eastman Kodak Company

Table 29. Continued

Compound	Source
Oxalyl chloride	Aldrich Chemical Company
Palladium (10% on carbon)	Matheson, Coleman and Bell
Pentanes	Eastman Kodak Company
Phosphorous tribromide	Aldrich Chemical Company
Phthalic anhydride	Eastman Kodak Company
Potassium carbonate	Fisher Chemical Company
Potassium hydroxide	Fisher Chemical Company
Pyridine	Fisher Chemical Company
Silica gel (60-200 mesh)	Davison Chemical
Silica gel (flash, 230-400 mesh)	E. M. Reagents
Silica TLC plates	Eastman Kodak Company
Sodium bicarbonate	Fisher Chemical Company
Sodium hydroxide	Fisher Chemical Company
Sodium nitrite	Matheson, Coleman and Bell
Sodium sulfide (nonahydrate)	Fisher Chemical Company
Sulfolene	Phillips Petroleum Company
Sulfuric acid	Captree Chemical Company
s-Tetrachloethane	Fisher Chemical Company
Tetrahydrofuran	Fisher Chemical Company
Tetramethylsilane	Stohler Isotope Chemicals
Thionyl chloride	Fisher Chemical Company
Tin(II)chloride (dihydrate)	Fisher Chemical Company
Zinc (dust)	Mallinckrodt Chemical Works

4-Vinylcyclohexene (34)

1,3-Butadiene (32) was prepared by modification of literature methods.[49] Sulfolene (43) (5.4 g, 46 mmoles) was placed into a 25-mL RB flask fitted with a gas inlet. After a stir bar was added, a vigreux column was attached. Leading from the top of the column was teflon tubing which was connected in such a manner as to allow the reaction stream to bubble through two flasks of 10% NaOH and then a tube of

Drierite, successively. The tubing then led into a receiver flask
which was cooled to -150°C (pentane/N$_2$(l)) and vented by an oil bubbler.
Nitrogen was slowly passed through the entire system, entering at the
reaction flask. After 5 min, the reaction was slowly heated to 120-
145°C. Stirring was initiated after the sulfolene had melted. After
no more starting material could be seen in the reaction flask, the
nitrogen flow rate was increased to flush all the butadiene. For an
analytical sample, CDCl$_3$ was added directly to the cold trap. Otherwise,
the sample was taken on directly. For butadiene (32): ^{1}H NMR (CDCl$_3$) δ
6.42-6.28 (m, 2H), 5.28-5.15 (m, 4H) (Figure 1); ^{13}C NMR (CDCl$_3$)
137.72, 117.20 (Figure 2) (lit.[51] (CDCl$_3$) δ 136.90, 116.30).

The collection flask was attached while cold to a bulb to bulb
distillation apparatus packed with drierite. The receiver, a constricted
sealed tube, was cooled in a liquid nitrogen bath and the system was
evacuated while the butadiene was still frozen. After the system was
closed off, the butadiene was allowed to warm to room temperature.
The collection tube was run through three freeze-thaw cycles and then
sealed. After the tube was placed in an autoclave with pentane, the
autoclave was sealed. The reaction was heated to 136°C by a hot air
bath for 14 h. Upon cooling, 2.1 g (20 mmol, 85%) of 4-vinylcyclo-
hexene (34) was obtained: ^{1}H NMR (CDCl$_3$) δ 5.96-5.78 (m, 1H), 5.68
(s, 2H), 5.00 (dd, J = 10.6, 17.4 Hz, 2H), 2.33-2.19 (m, 1H), 1.94-1.70
(m, 4H), 1.49-1.29 (m, 1H) (Figure 3); ^{13}C NMR (CDCl$_3$) δ 143.81,

126.92, 126.08, 112.28, 37.58, 31.09, 28.48, 24.88 (Figure 4) (lit.[51] ($CDCl_3$) δ 143.7, 126.8, 126.0, 112.3, 37.7, 31.1, 28.5, 24.9); ms (18 eV) 108(18), 93(11), 80(36), 79(49), 78(26), 66(100).

Butadienesulfone-2,2,5,5-d_4 (43-d_4)

This compound was prepared by modification of known routes.[49,55,56] To sulfolene (43) (2.7 g, 23 mmoles) in a 25-mL RB flask was added ca. 100 mg K_2CO_3 and a reflux condensor was attached. The system was flushed with nitrogen and 10 mL of D_2O was added by syringe. The solution was allowed to stir at 55°C for 14 h under N_2. The content of the reaction flask was poured into a separatory funnel and the organic layer was removed. The aqueous layer was washed twice with CH_2Cl_2. After the combined extract was dried ($MgSO_4$) the solvent was removed. This process was repeated an additional six times to give a quantitative yield of 43-d_4, 98.1% -d_4 by ^{1}H NMR: ^{1}H NMR ($CDCl_3$) δ 6.08 (s) (Figure 4); ^{13}C NMR ($CDCl_3$) 124.56 (s), 55.03 (m) (Figure 5).

4-Vinylcyclohexene-3,3,5,5,6,6,8,8-d_8 (34-d_8)

This compound was prepared by the procedure described above for the light system (34). The time for the condensed phase thermolysis was increased to 24 h. For butadiene-1,1,4,4-d_4, (32-d_4): ^{1}H NMR ($CDCl_3$) δ 6.34 (s) (Figure 1); ^{13}C NMR ($CDCl_3$) δ 137.40 (s), 116.94 (p, J = 24.1 Hz) (Figure 2). For 34-d_8: ^{1}H NMR ($CDCl_3$) δ 5.98-5.77 (m, 1H), 5.67 (s, 2H), 2.67-2.34 (d, J = 6.3 Hz, 1H) (Figure 3).

FVP of 4-Vinylcyclohexene ($\underset{\sim\sim}{34}$) and 4-Vinylcyclo-

hexene-3,3,5,5,6,6,8,8-$\underline{d}_8$ ($\underset{\sim\sim}{34}$-$\underline{d}_8$);

General Pyrolysis Procedure

A sample of 4-vinylcyclohexene (ca. 70 mg) in a small vial was

placed into the sample compartment. The pyrolysis apparatus was then

purged with nitrogen. The sample compartment was cooled to -196°C

(N_2 (l)) and the apparatus was evacuated to ca. 10^{-3} Torr. The sample

chamber was allowed to warm slowly to -15°C, and was kept at that

temperature by a cold bath (ethylene glycol/CO_2 (s)). At the end of

the pyrolysis, solvent was deposited on the liquid-nitrogen-cooled

trap through a side arm and nitrogen was introduced into the system.

The trap was allowed to warm slowly to room temperature. The pyrolyzate

solution was then analyzed directly or was subjected to further

manipulation as follows.

The conditions which gave optimum results for the pyrolysis of

$\underset{\sim\sim}{34}$ are given in Table 3. When the pyrolyzate was analyzed by gc or by

^{1}H NMR, $CDCl_3$ was the solvent which was introduced into the product

trap. Analysis was then made directly. Butadiene ($\underset{\sim\sim}{32}$) could be

removed from the pyrolyzate mixture by rotary evaporation while keeping

the flask which contained the product mixture at -24°C (CCl_4/CO_2 (s)).

The products of the pyrolysis, benzene ($\underset{\sim\sim}{30}$) and toluene ($\underset{\sim\sim}{46}$),

could be isolated as follows. Pentane was the solvent which was

introduced into the product trap. Preparative GLC on a 10' X ¼"

stainless steel column with 10% SE-30 as the stationary phase and the

oven at ambient temperature cleanly separated $\underset{\sim\sim}{30}$ and $\underset{\sim\sim}{46}$.

The FVP of 34-d$_8$ was performed in the same manner as described above. The solvent which was introduced into the product trap was CHCl$_3$. Analysis of the product mixture was then made directly by combined gc/ms spectroscopy.

For benzene (30): ^{1}H NMR (CDCl$_3$) δ 7.36 (s); ms (70 eV) 78(100), 77(22), 52(18), 51(19), 50(17); co-injection of an authentic sample of benzene produced no new peak in the gc trace.

For toluene (46): ^{1}H NMR (CDCl$_3$) δ 7.40-7.02 (m, 5H), 2.36 (s, 3H) (Figure 7); ms (70 eV) 92(62), 91(100), 65(15), 63(10), 51(11); co-injection of an authentic sample of toluene (36) produced no new peak in the gc trace, co-injection of cycloheptatriene (114) produced a new signal.

Allyl Benzoate (49)

Compound 49 was prepared from benzoyl chloride (50) and allyl alcohol (51) by literature procedures.[49,126] To 51 (4.92 g, 84.8 mmol) in 200 mL of dry hexane at 0°C was added 6.9 mL (1 eq.) of dry pyridine. To the stirred solution was added a solution of benzoyl chloride (50) (9.8 mL, 1 eq.) in 40 mL of dry benzene, dropwise, over 30 min. The reaction was placed in the refrigerator overnight. The crystals were filtered and rinsed with hexane. The filtrate was washed three times with dilute aqueous NaHCO$_3$ solution and one time with water. The organic solution was dried (MgSO$_4$) and the solvent was removed. Column chromatography (silica gel, Et$_2$O-hexane 1:20) gave 3.8 g (23 mmol,

28%) of a colorless liquid: ^{1}H NMR (CDCl$_3$) δ 8.20-7.93 (m, 2H),

7.65-7.3 (m, 3H), 6.20-5.90 (m, 1H), 5.40 (dt, J = 1.25, 17.24 Hz,

1H), 5.27 (dt, J = 1.25, 11.64 Hz, 1H), 4.81 (dt, J = 1.25, 5.54 Hz,

1H).

Allyl Furoate (52)[136]

This compound was prepared as described above. The acid chloride

(54) was prepared by refluxing 2-furoic acid with 4 eqs. of thionyl

chloride for 2 h. From 2.0 g (18 mmol) 54 was obtained 1.4 g (9.5

mmol, 53%) of 52: ^{1}H NMR (CDCl$_3$) δ 7.58 (d, J = 0.83 Hz, 1H), 7.21

(dd, J = 0.83, 3.16 Hz, 1H), 6.52 (m, 1H), 6.05 (m, 2H), 5.35 (m,

2H), 4.82 (m, 1H).

2-Methylpropenyl-1 Benzoate (53)

Compound 53 was prepared as above by substituting 2-methyl-2-

propene-1-ol (55) for allyl alcohol (51). Thus, 1.2 g (16.6 mmoles)

of 55 and 1.2 eqs. of benzoyl chloride (50) yielded 2.15 g (13.1 mmol,

79%) of 53: ^{1}H NMR (CDCl$_3$) δ 8.25-7.98 (m, 2H), 7.70-7.35 (m, 3H),

5.08 (s, 1H), 4.98 (s, 1H), 4.74 (s, 1H), 1.85 (s, 3H).

α-(o-Carboxybenzoyl)phthalide (58)[66]

To a vigorously stirred solution of Zn dust (30 g) suspended in

a solution of CaCl$_2$ (75 g) in 300 mL of 95% EtOH and 420 mL water at

room temperature was added 100 g (0.68 mol) phthalic anhydride (57)

over the course of 1 h. After an additional h, the reaction mixture

was allowed to settle. After the reaction mixture was suction filtered

through a coarse sintered glass funnel, the filtrate was acidified

with 10% HCl. The product was collected on a buchner funnel and rinsed

well with water. The product was dissolved in 10% NaOH and the solution

was filtered through paper. After the filtrate was acidified, the

product was collected on a buchner funnel. The product was rinsed

with water and dried ($MgSO_4$) under vacuum to give 16.1 g (56.7 mmol,

16%) of 58: mp 325°C (dec); ^{1}H NMR (acetone-d_6) δ 7.95-7.55 (m, 8H),

6.1 (s, 1H).

<div align="center">α-(o-Carboxybenzyl)phthalide (59)</div>

Compound 58 (55 g, 0.15 mmol) was dissolved in 1100 ml 6% NaOH.

After 89 g of Zn dust was added, the solution was heated to 110°C under

a nitrogen atmosphere for 8 h. After cooling, the solution was suction

filtered through Celite. The filtrate was immediately acidified with

10% HCl. The product was collected on a buchner funnel, dried ($MgSO_4$),

and then recrystallized from EtOH (95%) to give 37.2 g (0.14 mol, 92%)

of 59: mp 193-196°C (lit.[66] 198.5°C); ^{1}H NMR (acetone-d_6) δ 8.10

(d, J = 3.4 Hz, 2H), 7.90-7.70 (m, 2H), 7.65-7.50 (m, 3H), 7.45 (d,

J = 3.4 Hz, 2H), 5.82 (dd, J = 3.20, 13.56 Hz, 1H), 3.26 (dd, J =

8.74, 13.56 Hz, 1H).

<div align="center">trans-Stilbene-2,2'-dicarboxylic Acid (60)</div>

To 23.6 g (88.0 mmol) of 59 in a 250 mL RB flask was added a

solution which was made by dissolving 14.8 g KOH in 30 mL H_2O. The

solution was purged of oxygen by bubbling N_2 through it for 5 min.

An oil bath preheated to 240°C was then raised up to the flask and the reaction was heated while a constant stream of N_2 was flowing over the top of the flask. After the H_2O had boiled off, heating was continued for 3 h. After cooling, 100 mL of H_2O was added. The content of the flask was allowed to dissolve. After the solution was acidified with 10% HCl, the product was collected on a buchner funnel and rinsed well with water. Recrystallization from acetic acid gave 19.3 g (72.1 mmol, 82%) of 60: mp 275-280°C (lit.[66] 263-265°C); ^{1}H NMR (acetone-d_6) δ 8.01 (s, 2H), 8.00 (d, J = 7.64 Hz, 2H), 7.83 (d, J = 7.64 Hz, 2H), 7.62 (t, J = 7.52 Hz, 2H), 7.42 (t, J = 7.52 Hz, 2H).

Dimethyl trans-Stilbene-2,2'-dicarboxylate (61)

A quantity of 2.07 g (7.7 mmol) of the acid 60 was dissolved in 40 mL of MeOH and to this solution 3 mL of conc H_2SO_4 was added carefully. This solution was heated to reflux for 4 h and after cooling to 0°C, 10 mL of water was added. The product was collected on a buchner funnel and it was recrystallized from MeOH to give 2.08 g (7.03 mmol, 92%) of 61: mp 91-96°C (lit.[66] 101-102°C); ^{1}H NMR (CDCl$_3$) δ 7.93 (dd, J = 1.19, 7.86 Hz, 2H), 7.87 (s, 2H), 7.80 (dd, J = 0.98, 7.86 Hz, 2H), 7.53 (dt, J = 1.19, 7.60 Hz), 7.32 (dt, J = 0.98, 7.60 Hz, 2H).

Dimethyl Bibenzyl-2,2'-dicarboxylate (62)

A quantity of 61 (1.94 g, 6.55 mmoles) was dissolved in 40 mL of

ethyl acetate and to this solution a catalytic amount of 10% Pd/C

was added. After a balloon of hydrogen was attached to the reaction

flask, the solution was stirred for 3 h. After the reaction mixture

was filtered through Celite, the filter cake was washed well with

ethyl acetate. The solvent was removed from the filtrate to give 1.87

g (6.2 mmol, 95%) of 62: mp 102.5-103°C (lit.[66] 103°C); ^{1}H NMR ($CDCl_3$)

δ 7.88 (dd, J = 0.88, 7.57 Hz, 2H), 7.30 (dd, J = 1.20, 8.04 Hz, 2H),

7.24 (dd, J = 0.88, 8.04 Hz, 2H), 3.96 (s, 6H), 3.25 (s, 4H).

2,2'-Bis-(hydroxymethyl)bibenzyl (63)

A quantity of 62 (10.12 g, 33.96 mmol) was placed into an extraction

thimble. $LiAlH_4$ (1.93 g) was suspended in 500 mL Et_2O and a soxlet

extractor was assembled. The reaction was heated to reflux under a

nitrogen atmosphere until the addition of 66 was complete. The reaction

was carefully quenched with 10% H_2SO_4. The reaction solution was

transferred to a larger flask, and to the solution 100 mL of 10% H_2SO_4

and 200 mL of MeOH were added. The resulting mixture was stirred

overnight. The reaction solution was then filtered through paper and

the filter cake was washed well with MeOH. The filtrate was diluted

with water until precipitation was complete. The product was collected

on a buchner funnel and washed well with water. The product was dried

under vacuum and recrystallized from MeOH to give 6.88 g (28.4 mmol,

84%) 63 mp 150.5-152°C (lit.[66] 151°C); ^{1}H NMR (acetone-d_6) δ 7.41-7.38

(m, 1H), 7.26-7.17 (m, 3H), 4.69 (s, 2H), 2.95 (s, 2H).

<div align="center">2,2'-Bis-(bromomethyl)bibenzyl (64)</div>

As 0.65 mL of PBr$_3$ was added dropwise to 0.52 g (2.1 mmol) of 63

in 10 mL of dry benzene at room temperature, the crystals of 63 slowly

dissolved. Upon completion of the addition, the reaction mixture was

warmed to 60°C for 2 h. The solution was cooled and poured into water

and the organic layer was washed successively with saturated NaHCO$_3$

(aq) and water. The organic layer was dried (MgSO$_4$) and the solvent

was removed. The crude product was recrystallized from benzene to

give 0.62 g (1.7 mmol, 81%) of 64 as colorless crystals: mp 134-135°C

(lit.[68] 137-138°C); R$_f$ (silica gel, benzene-hexane 1:1) = 0.67; ^{1}H NMR

(CDCl$_3$) δ 7.26 (s, 8H), 4.56 (s, 4H), 3.11 (s, 4H) (lit.[68] (CDCl$_3$)

7.50-7.0 (m, 8H), 4.46 (s, 4H), 3.08 (s, 4H).

<div align="center">Dibenzo[c,g]thiapine (65)</div>

A quantity of 64 (0.59 g, 1.6 mmol) was dissolved in 250 mL of

MeOH. While this solution was being vigorously stirred, 0.42 g of

Na$_2$S·9H$_2$O (1.7 mmol) was added to it in one portion. The mixture was

then stirred overnight. The mixture was concentrated under vacuum in

successive portions and the residue was dissolved in hot EtOH (absolute)

and the mixture was gravity filtered through paper. A quantity of 0.22 g

(0.92 mmol, 58%) crystalized from the filtrate: mp 106-110°C (lit.[68]

100-111°C); R_f (silica gel, benzene-hexane 1:1) = 0.64; ^{1}H NMR (CDCl$_3$)

δ 7.47-7.38 (m, 2H), 7.6-7.3 (m, 1H), 3.34 (s, 2H), 2.90 (br s, 2H)

(lit.[68] (CDCl$_3$) δ 3.26 (s), 2.85 (s)).

Dibenzo[c,g]thiapinedioxide (56)

To a rapidly stirred solution of 65 (1.37 g, 5.5 mmol) in 50 mL of

glacial acetic acid at room temperature was added dropwise over 10 min,

25 mL of 30% H$_2$O$_2$. The solution was then heated slowly to 80°C for 1 h.

Upon cooling, the reaction mixture was diluted with 25 mL of water. The

product was collected on a buchner funnel, washed well with water,

and dried (MgSO$_4$) to give 1.28 g (4.7 mmol, 87%) of 56: mp 215-216°C

(lit.[68] 220-221°C); ^{1}H NMR (CDCl$_3$) δ 7.8-7.1 (m, 8H), 3.92 (br s, 4H),

3.0 (br s, 4H) (Figure 10) (lit.[68] (CDCl$_3$) δ 4.0 (br s), 3.55 (br s)); .

IR (CDCl$_3$) 3040, 3020, 2960, 2945, 1317, 1242, 1115 cm^{-1}; ms (21 eV)

272(3), 208(53), 194(16), 193(100), 180(11), 116(27), 164(11).

Dibenzo[c,g]thiapinedioxide-5,5,7,7-d$_4$ (56-d$_4$)

To 1.20 g (4.40 mmoles) of 56 was added 12 mL of a 5:1 D$_2$O:THF

solution. A catalytic amount of dry K$_2$CO$_3$ was added and the mixture

was heated to reflux under a N$_2$ atmosphere where it was kept for 8 h.

After the reaction was cooled to room temperature the solvent was

removed using a Horak transfer loop plugged with cotton. This

deuteration process was repeated 5 times.

178

At the end of this sequence, the product was collected on a buchner funnel and washed carefully with small portions of D_2O. The product was dried under vacuum and then was taken up in hot $CDCl_3$. The hot solution was filtered through celite, and the product was allowed to crystallize. A quantitative yield of 56-d_4 was obtained, 96.2% -d_4 by ^1H NMR: ^1H NMR ($CDCl_3$) δ 7.8-7.1 (m, 8H), 3.0 (br d, 4H) (Figure 10).

5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene (16)

A quantity of 56 (9.9 mg, 3.6×10^{-5} mol) was flash vacuum pyrolyzed at an oven temperature of 550°C and a pressure of 0.001 mm Hg. The sample head was heated to 120-140°C to drive the starting material over. The trap was rinsed repeatedly with CH_2Cl_2. The rinses were combined and the solvent was removed leaving colorless crystals. The product was then dissolved in CD_2Cl_2 and s-$C_2CH_2Cl_4$ was added as an internal standard. NMR analysis showed that 16 was the sole product (3.46×10^{-5} moles, 95%). For preparative scale reactions, the product was recrystallized from hexane mp 108-109 (lit.[24] 108.4-109°C); ^1H NMR (CD_2Cl_2) δ 6.96 (s, 8H), 3.09 (s, 8H) (Figure 11) (lit.[137] (CCl_4) δ 6.88 (s, 8H), 3.02 (s, 8H).)

5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene-5,5,6,6-d_4 (16-d_4)

This compound was prepared by FVP of 56-d_4 in a manner which was identical to that used for the light compound (56). ^1H NMR analysis showed the product to be 96% -d_4. For preparative scale reactions, the product was recrystallized from hexane: mp 108-109°C. ^1H NMR ($CDCl_3$) δ 6.96 (s, 4H), 3.08 (s, 4H) (Figure 11).

Isolation and Characterization of Pyrolysis Products in the

FVP of Dibenzo[a,e]cyclooctene (16)

Compound 16 was prepared on a large scale by the method of Jenson

by the condensed phase thermolysis of BCB (1).[24,69] The experimental

procedure has been described.[19]

A quantity of 16 (1.1 g, 5.3 mmol) was pyrolyzed at 860°C over the

course of 4 h. The product was dissolved in CH_2Cl_2 and the resulting

solution was concentrated. By GLC and ms analysis, the product mixture

was identical to the small scale experiments. The residue was adsorbed

onto 5 g of activated alumina (Woelm) which had been dried at 200°C.

The product was chromatographed on a 3 x 60 cm column utilizing hexane

as the elutent. A very slow drip rate gave the desired hydrocarbon

products after 3 weeks. Further purification as necessary, and spectral

data for each component are described below. The polyaromatic products

were removed from the column by slowly increasing the polarity of the

elutent to 10% ether-hexane. By gc/ms analysis of each component,

no rearrangement of products had occurred during chromatography. The

tolylindans, 66, 67, 69 and 75 are new compounds. Since they are

hydrocarbons of mw = 208, their composition was assumed to be the same

as the starting material, 16.

1-(m-Tolyl)indan (66)

Compound 66 was obtained sufficiently pure directly off the column

(99% by gc): ^{1}H NMR (CD_2Cl_2) (the coupling patterns were determined

by 2-dimensional NMR (Figure 14); however, not all J values could be

adequately measured), δ 7.34-6.83 (m, 8H), 4.40 (dd, J = 3.48, 8.80 Hz, 1H), 3.07 (d, J = 3.42 Hz, 1H), 2.88 (ddd, J = 3.37 Hz, 1H), 2.56 (dddd, J = 3.42 Hz, 1H), 1.98 (dddd, J = 3.37 Hz, 1H), 2.56 (dddd, J = 3.42 Hz, 1H), 1.98 (dddd, J = 3.37, 3.48 Hz, 1H), 1.93 (s, 3H) (Figure 14); ^{13}C NMR (CD$_2$Cl$_2$) δ 146.33, 144.95, 135.20, 128.83, 128.20, 127.89, 127.56, 126.31, 122.32, 50.84, 36.33, 32.45, 20.0. IR (NaCl, neat) 1600, 1595, 1552, 1017, 768, 758, 695 (s) cm^{-1}; ms (70 eV) 208(100), 194(14), 193(88), 192(19), 191(17), 179(22), 178(90), 165(13), 117(10), 116(50), 102(12), 102(11), 91(27), 71(10), 57(27), 56(11), 55(10).

1-(o-Tolyl)indan (67)

Recombination of column fractions in which 67 was the major component and flash chromatography[138] with hexanes as the elutent gave pure 67: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.31-6.84 (m, 8H), 4.60 (m, 1H), 2.98 (m, 2H), 2.58 (m, 1H), 2.42 (s, 3H), 1.94 (m, 1H); ^{13}C NMR (CD$_2$Cl$_2$) δ 129.81, 126.87, 126.06, 125.92, 125.72, 125.63, 124.47, 124.02, 47.18, 34.79, 31.29, 19.30. IR (NaCl, neat) 1605, 1490, 1475, 1455, 1020, 750 (s), 735, 720 cm^{-1}; ms (70 eV) 208(53), 194(17), 193(100), 178(35), 131(29), 130(26), 129(16), 116(15), 115(58), 91(27), 57(19).

cis-2,2'-Dimethylstilbene (68)[72]

Recombination of column fractions of which 68 was a major component and then flash chromatography[138] with hexanes as the elutent gave 68: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.16-7.02 (m, 4H), 6.90-6.86 (m, 4H), 6.73 (s, 2H), 2.27 (s, 6H); ^{13}C NMR (CD$_2$Cl$_2$) 137.04, 136.65, 130.26, 129.92, 129.38,

127.35, 125.60, 20.00. IR (NaCl, neat) 1750, 1460, 1380, 1018, 800,

730 cm^{-1}; ms (70 eV) 208(25), 194(16), 193(100), 192(12), 191(10),

179(19), 178(78), 165(10), 116(30), 115(39), 91(17), 57(24).

2-(o-Tolyl)indan (69)

Recombination of column fractions of which 69 was a major component

and then flash chromatography[136] with hexane as the elutent gave pure

69. ^{1}H NMR (CD$_2$Cl$_2$) δ 7.35-7.00 (m, 8H), 3.92 (dd, J = 7.70, 8.12 Hz,

1H), 3.32 (dd, J = 8.12, 15.41 Hz, 2H), 3.03 (dd, J = 7.70, 15.41 Hz,

2H), 2.40 (s, 3H); ^{13}C NMR (CD$_2$Cl$_2$) δ 127.81, 127.73, 127.38, 126.75,

125.71, 125.63, 125.25, 124.70, 123.59, 42.30, 40.56, 38.80, 20.86.

IR (NaCl, neat) 1605, 1480, 1455, 1012, 750, 745 (s), 720 cm^{-1}; ms

(70 eV) 208(38), 193(37), 179(14), 178(52), 117(15), 116(100), 115(38),

91(16), 57(14).

2-(m-Tolyl)indan (75)

This compound was not isolated (see results): gc/ms (70 eV) 208(75),

207(16), 194(15), 193(92), 192(10), 191(11), 179(12), 178(40), 165(17),

117(50), 116(93), 115(100), 91(33), 57(20).

5,6,7,12-Tetrahydrodibenzo[a,d]cyclooctene (70)

Compound 70 was obtained directly off the column and recrystallized

from EtOH mp 80-81°C (lit. 81.5-83.5,[70] 77-78°C[71]); ^{1}H NMR (CD$_2$Cl$_2$) δ

7.32-7.25 (m, 2H), 7.12-6.99 (m, 6H), 4.36-4.20 (br s, 1H), 3.72-3.50

(br s, 1H), 3.31-3.07 (br s, 2H), 3.02-2.82 (br s, 3H), 2.46-2.22 (br

s, 1H) (lit.[70] (CCl$_4$) δ 7.69-6.99 (m, 8H), 3.56-4.70 (br s, 4H), 3.50-

2.68 (br s, 4H), 2.60-1.10 (br s, 2H)); ^{13}C NMR (CD$_2$Cl$_2$) δ 142.95, 140.98, 130.74, 128.88, 127.05, 126.74, 30.64, 38.22, 39.90. IR (NaCl) 1480, 1450, 1000, 735 (s); ms (70 eV) 208(100), 193(48), 180(43), 179(66), 178(60), 165(25), 131(10), 130(49), 129(16), 128(10), 117(73), 116(37), 115(65), 104(60), 103(14), 92(11), 91(61), 78(15), 77(16), 57(11).

trans-2,2'-Dimethylstilbene (71)[72]

Compound 71 was obtained off the column in sufficient purity and was recrystallized from EtOH mp 80-82.5°C (lit.[72] 81.7°C). ^{1}H NMR (CD$_2$Cl$_2$) δ 7.78-7.49 (m, 2H), 7.52-7.30 (m, 6H), 7.19 (s, 2H), 2.42 (s, 6H); ms (70 eV) 208(100), 194(15), 193(88), 192(20), 191(17), 179(24), 180(95), 165(13), 117(11), 116(51), 115(65), 104(10), 103(15), 102(13), 91(27).

1-Methylanthracene (76) and 9-Methylanthracene (77)

These compounds were obtained as a mixture with anthracene (13). Gc/ms analysis indicated a molecular weight of 192. ^{1}H NMR clearly determined their identity.[61,80] For 1-methylanthracene (76) ^{1}H NMR (CD$_2$Cl$_2$) δ 2.77 (s) (lit.[80] 2.72 (s)); ms (70 eV) 192(100), 191(43), 190(12), 189(25), 165(12), 96(19), 57(14). For 9-methylanthracene (77) ^{1}H NMR (CD$_2$Cl$_2$) 3.04 (s) (lit.[61] 3.0 (s)); ms (70 eV) 192(53), 191(26), 189(13), 178(28), 115(10), 96(11), 95(10), 91(12), 85(15), 83(13), 81(10), 71(36), 70(17), 69(25), 67(10), 58(28), 57(100), 56(39), 55(36).

4,4'-Dimethyldibenzyl (79)

Compound 79 was prepared by the method of Trahanovsky and Brixius,[81] mp 79-81°C (lit.[81] 80-81°C); ^{1}H NMR (CDCl$_3$) δ 7.08 (s, 8H), 2.85 (s, 4H), 2.32 (s, 6H) (lit.[81] (CCl$_4$) δ 6.98 (s, 8H), 2.80 (s, 4H), 2.30 (s, 6H)).

2,9-Dimethyldibenzosuberone (38)

To a rapidly stirred (mechanically) suspension of 1.25 g (9.37 mmol) of AlCl$_3$ in 200 mL of dry CS$_2$ at 0°C was added over a 2.5 h period a solution of 79 (1.79 g, 8.52 mmol) and oxalyl chloride (80) (1.2 g, 9.4 mmol) in 50 mL dry CS$_2$. The reaction mixture was heated to reflux for 2 h and was then allowed to cool to room temperature.

The reaction mixture was poured into a beaker containing cracked ice and 10% HCl while leaving the sludge in the reaction flask. The reaction flask was then rinsed with generous portions of CCl$_4$ and the washings were added to the beaker. The mixture was poured into a separatory funnel and the water layer was removed. The organic layer was washed with water and then 10% NaOH, dried (MgSO$_4$), and concentrated. Column chromatography (alumina, Et$_2$O-hexane 1:20) gave a colorless oil which solidified upon standing. Recrystallization from MeOH gave 0.16 g (0.68 mmol, 8.0%) of 38 as colorless plates: mp 70-71°C; ^{1}H NMR (CDCl$_3$) δ 7.80 (s, 2H), 7.31-7.20 (m, 2H), 7.10-7.05 (m, 2h), 3.17 (s, 4H), 2.35 (s, 6H) (Figures 15 and 16); ^{13}C NMR (CDCl$_3$) δ 195.97 (s), 139.08 (s), 138.50 (s), 136.08 (s), 133.05 (d, J = 10.9 Hz), 130.74 (d, J = 19.6 Hz), 129.28 (d, J = 9.8 Hz), 34.64 (m), 20.83 (q, J = 16.4 Hz)

(Figure 17); IR (CCl_4) 3100, 3000, 2960, 1650, 1600, 1305, 1286 cm^{-1};

ms (70 eV) 236(100), 235(28), 222(12), 221(76), 208(31), 207(21), 193(69),

192(37), 191(32), 189(19), 179(13), 178(60), 165(20), 117(13), 115(22),

104(11), 103(33), 102(17), 96(15), 94(15), 91(19), 89(34), 82(15),

78(22), 77(34), 76(15), 65(16), 63(20), 51(26). Anal. Calcd for

$C_{17}H_{16}O$: C, 86.40; H, 6.85. Found: C, 86.54; H, 6.98.

2,9-Dinitrodibenzosuberone (82)[86]

To 26.74 g (0.128 mmol) of 37 in a 1,000 mL RB flask at 0°C was

added dropwise over a 30 min period 500 mL of chilled fuming nitric

acid (90%). After a reflux condensor was attached to the flask, the

reaction mixture was heated slowly to 100°C for 2 h. The oil bath was

removed, and the reaction was allowed to cool to room temperature.

The reaction solution was carefully poured into 3 L of water and the

product was collected on a buchner funnel. The crude material was

stirred in 100 mL of boiling EtOH and the insoluble product was removed

by filtration of the hot mixture. The treatment was repeated and then

the product was recrystallized from CH_3NO_2 to give 25.6 g (85.8 mmol,

67%) of 82: ^{1}H NMR (acetone-d_6/DMSO-d_6) δ 8.78 (d, J = 2.39 Hz, 2H),

8.41 (dd, J = 2.39, 8.32 Hz, 2H), 7.75 (d, J = 8.32 Hz, 2H), 3.46

(s, 4H); ^{13}C NMR (acetone-d_6/DMSO-d_6) δ 190.18, 148.92, 146.76, 137.90,

131.38, 126.70, 125.50, 33.78. IR (KBr) 3078, 1651, 1610, 1520, 1418,

1344, 1265, 1236, 1094, 931, 922, 899, 856, 845, 796, 781, 750 (s),

717, 679, 617 (s) cm^{-1}; ms (70 eV) 299(16), 298(P, 100), 281(22),

270(37), 252(11), 251(27), 223(11), 206(13), 205(20), 178(51), 177(42),

176(57), 166(12), 165(13), 152(22), 151(27), 150(14), 89(21), 88(20), 77(11), 76(33), 75(16), 63(38), 51(15).

<div align="center">2,9-Diaminodibenzosuberone (40)</div>

To 2.0 g (9 mmol) of SnCl$_2$·2H$_2$O in a 25 mL RB flask was added sequentially 1.6 mL of conc HCl and 2.9 mL of glacial acetic acid. Cautiously, 0.32 g (1.07 mmol) of 82 was added with stirring. A reflux condensor was attached and the reaction mixture was heated to reflux for 1 h.

After the reaction mixture was allowed to cool, it was diluted with 15 mL of water. The solution was gravity filtered through paper. The reaction flask was rinsed with conc HCl which was used to wash the precipitate. The precipitate was then washed with water. The filtrate was cooled to 0°C and made basic to litmus using 10% NaOH. The yellow colloidal precipitate was collected by suction filtration and the product was washed well with water. After drying, the product was recrystallized from EtOH to give 0.23·g (0.96 mmol, 90%) of 40 as floculent yellow needles: mp 171-171.5°C; ^{1}H NMR (CD$_2$Cl$_2$) δ 7.23 (d, J = 2.57 Hz, 2H), 7.01 (d, J = 8.08 Hz, 2H), 6.77 (dd, J = 2.57, 8.08 Hz, 2H), 3.72 (br s, 4H), 3.02 (s, 4H) (Figures 25 and 26); ^{13}C NMR (CD$_2$Cl$_2$/DMSO-d$_6$) 195.56, 146.21, 138.95, 130.57, 129.93, 118.59, 115.03, 34.23; IR (KBr) 3848 (br), 3697 (br), 1597, 1574, 1312, 1217, 895, 830, 816, 789, 710, 673 cm^{-1}; ms (70 eV) 239(16), 238(P, 100), 237(23), 223(17), 222(10), 221(16), 210(14), 209(58), 208(15), 195(12),

194(16), 193(22), 180(10), 165(12), 119(10), 104(62), 90(12), 51(11).

High resolution ms: calculated for $C_{15}H_{14}N_2O$, 238.1109; found, 238.1110.

2,9-Dichlorodibenzosuberone (39)

To 0.540 g, (2.27 mmol) of 40 was added 15 mL of conc HCl and

the flask was heated gently until 40 dissolved. The reaction mixture

was cooled to 0°C. To the heterogeneous reaction mixture was added an

aqueous solution of $NaNO_2$ (0.41 g in 4 mL H_2O) by pipette making sure

that the pipette tip was beneath the surface of the solution.

After stirring the solution for 5 min, an additional 125 mL of

conc HCl cooled to 0°C was added. The resulting solution was stirred

at 0°C for 20 min. A quantity of CuCl 0.50 g (5.0 mmol) in 100 mL of

H_2O cooled to 0°C was added in one portion. After stirring the mixture

for 5 min, the ice bath was removed and the reaction mixture was allowed

to warm to room temperature. After the reaction solution was stirred

at room temperature for 3 h, it was heated slowly to 55-60°C where it

was kept for 4 h. Upon cooling, the product was collected on a buchner

funnel and washed well with water. Column chromatography (silica gel,

Et_2O-hexane 1:10) gave 0.26 g (1.0 mmol, 44%) of 39 as colorless

needles: mp 119-121°C (lit.[90] 78-79°C); ^{1}H NMR (CDCl$_3$) δ 7.98 (d, J =

2.5 Hz, 2H), 7.43 (dd, J = 2.5, 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H),

3.17 (s, 4H) (Figures 21 and 22); ^{13}C NMR (CDCl$_3$) δ 192.38, 140.26,

139.18, 132.95, 132.49, 130.97, 130.57, 34.29; ms (70 eV) 280(9),

279(12), 278(56), 277(36), 276(88), 275(40), 248(16), 243(27), 242(16),

241(79), 240(13), 215(12), 214(16), 213(36), 212(37), 206(21), 179(15), 178(100), 177(27), 176(50), 151(14), 120(12), 106(17), 103(30), 102(30), 93(14), 89(56), 88(68), 87(15), 76(18), 75(29), 63(24), 51(11); IR (KBr) 2951, 2862, 1637, 1583, 1477, 1296, 1261, 1231, 1042, 835, 785, 625 cm^{-1} (lit.[90] (nujol mull) 1650, 1595, 1295, 1270, 845, 785 cm^{-1}).

FVP of 2,9-Dimethyldibenzosuberone (38)

A quantity of compound 38 (5-20 mg) was pyrolyzed with an oven temperature of 950°C which gave optimum results (see Table 28). The sample head temperature was kept between 60-80°C and this gave an acceptable pyrolysis rate. Under these conditions, the pressure remained between 0.001-0.004 mm Hg. The average time for a pyrolysis was on the order of 2 h.

The pyrolysis was worked-up as follows. The pyrolysis trap was rinsed with 4 hefty portions of CH_2Cl_2. The rinsings were combined and concentrated. The last trace of solvent was removed on a vacuum line. The pyrolyzate was taken up in hot CD_2Cl_2, and $CDCl_3$ was added. The solution was allowed to cool. If precipitation ensued, more $CDCl_3$ was added as necessary.

The internal standard, s-$CHCl_2CHCl_2$, which was purified immediately before use by passing it through a short column of alumina, was added by syringe. The amount added was obtained by weighing the syringe before and after the transfer.

TMS was added, before the sample was submitted to ^{1}H NMR analysis. The yields were calculated by integrating the internal standard absorptions vs. the absorption for the 9,10 hydrogens and vs. the methyl group hydrogens of 25. The yield of unreacted starting material was determined by integrating the internal standard vs. the 5,6 hydrogens and vs. the methyl group hydrogens of 38.

Several runs were combined and the product was purified by recrystallization from $CHCl_3$: mp 239-243°C (lit.[84] 248°C); ^{1}H NMR ($CDCl_3$) δ 8.26 (s, 2H), 7.88 (d, J = 8.56 Hz, 2H), 7.73 (d, J = 1.33 Hz, 2H), 7.29 (dd, J = 1.33, 8.56 Hz, 2H), 2.53 (s, 6H) (Figures 18 and 19); ^{13}C NMR ($CDCl_3$/CD_2Cl_2) δ 134.40, 131.38, 130.32, 127.95, 127.52, 126.02, 124.58, 21.48 (Figure 20); IR (KBr) 2907, 1471, 1375, 1301, 925, 903 (s), 872, 791 cm^{-1} (lit.[82] (KBr) 1474, 1460, 1449, 1378, 1305, 1273, 1171, 1139, 1041, 963, 942, 905 (s), 873, 793 cm^{-1}.)

FVP of 2,9-Dichlorodibenzosuberone (39)

This compound was pyrolyzed under the same conditions used for 38. For 2,6-dichloroanthracene (41): mp 263-266°C (lit[91] 273-274°C); ^{1}H NMR ($CDCl_3$) δ 8.31 (s, 2H), 7.97 (d, J = 1.9 Hz, 2H), 7.93 (d, J = 9.0 Hz, 2H), 7.42 (dd, J = 1.9, 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 131.92, 131.56, 130.30, 129.81, 127.36, 126.47, 125.71; ms (70 eV) 250(9), 249(9), 248(65), 247(15), 246(100), 176(43), 175(13), 174(11), 124(18), 123(27), 105(13), 88(44), 87(26), 75(13); IR (KBr) 926, 901 (s), 800 cm^{-1} (lit.[91] (nujol mull) 901, 799 cm^{-1}).

FVP of 2,9-Diaminodibenzosuberone (40)

The diamine 40 (0.048 g, 20.1 mmol) was pyrolyzed at an oven temperature of 950°C and a pressure of 0.001-0.004 mm Hg. The sample head temperature was kept between 100-120°C. The brilliant yellow product was scraped out of the pyrolysis trap with a spatula to give 24 mg (11.5 mmol, 57%) of 42:. mp (dec) > 300°C; ^{1}H NMR (acetone-d_6/-DMSO-d_6) δ 7.86 (s, 2H), 7.66 (d, J = 8.9 Hz, 2H), 7.01 (dd, J = 1.32, 8.9 Hz, 2H), 6.92 (d, J = 1.32 Hz, 2H), 4.94 (br s, 4H); IR (KBr) 3323 (br), 1637, 1477, 1018, 891, 800 cm^{-1}. High resolution ms for $C_{14}H_{12}N_2$: calculated, 208.1002; found, 208.1002.

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