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# Studies of the pyrolysis of hydroaromatic compounds with an emphasis on reactions of ortho-quinodimethanes

Michael Eugene Scribner  
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**Scribner, Michael Eugene**

**STUDIES OF THE PYROLYSIS OF HYDROAROMATIC COMPOUNDS WITH  
AN EMPHASIS ON REACTIONS OF ORTHO-QUINODIMETHANES**

*Iowa State University*

PH.D. 1985

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Studies of the pyrolysis of hydroaromatic compounds with  
an emphasis on reactions of ortho-quinodimethanes

by

Michael Eugene Scribner

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## GENERAL INTRODUCTION

The studies described herein are the results of questions raised concerning the pyrolysis of simple hydroaromatic compounds. A key compound within this group is tetralin which is presumed to thermally eject ethylene to produce ortho-quinodimethane, which then isomerizes to benzocyclobutene. It is also known that styrene is produced in this thermolysis and a possible source was hypothesized to be benzocyclobutene. Thus, in Part I we sought to delineate the mechanistic pathways operating in the isomerization of benzocyclobutene to styrene.

In Part II, a further study of a reaction of ortho-quinodimethane was pursued, the reaction of hydrogen gas with the exocyclic diene system of ortho-quinodimethane. Our grounds for pursuing this unprecedented reaction were: the well-documented reactivity of ortho-quinodimethane as a potent eneophile, the relative stability of ortho-xylene which would be the expected product of this reaction and the extreme importance of such an unusual find which would have a major effect on the way in which hydrogenations are thought about in industrial and laboratory applications.

The subject matter of Part III again deals with an ortho-quinodimethane, in this case 2,3-dihydronaphthalene. We wished to determine its role in the formation of the products of the pyrolysis of tetralin. More specifically, we attempted to determine its place among its other  $C_{10}H_{10}$  isomers, 1,2-dihydronaphthalene and ortho-divinylbenzene.

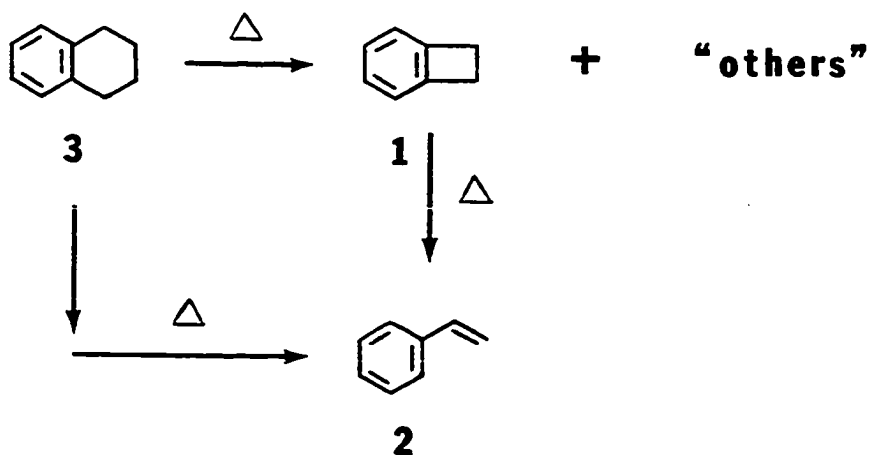
The last section deals with the effect that active pyrolysis packings have on the products and product distributions resulting from the pyrolysis of simple hydroaromatic compounds. We also wanted to determine to what extent the quartz chips used in our "normal" flash vacuum pyrolyses were influencing the chemistry which we observed.



PART I. DEUTERIUM ATOM AND METHYL-GROUP LABELING IN THE THERMAL  
ISOMERIZATION OF BENZOCYCLOBUTENE TO STYRENE

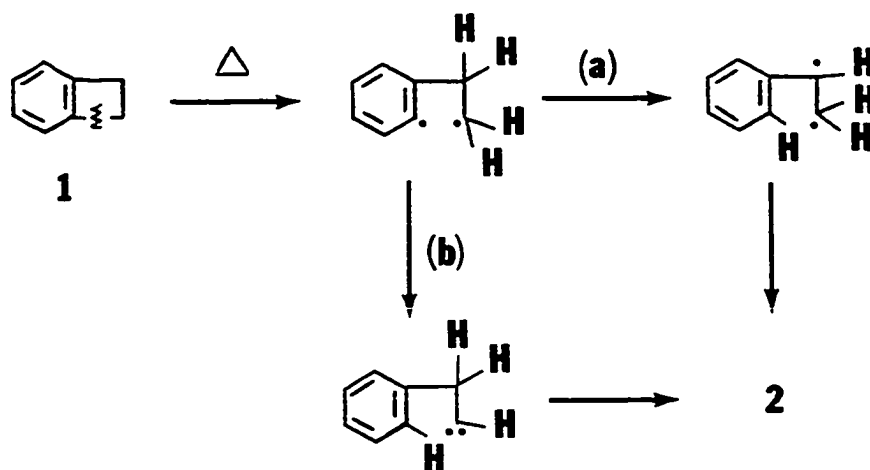
## INTRODUCTION

The observation that benzocyclobutene (1) thermally isomerizes to styrene (2) has been cited by several research groups. However, it has been mainly of passing interest and only recently [1,2] has it become the subject of a directed research effort aimed at determining the mechanistic pathway(s) involved. The generalized observations concerning the isomerization have been described by Baron and DeCamp [3] and Loudon et al. [4]. Similar mention has been made by Berman et al. [5] and Trahanovsky and Swenson [6] in pyrolysis studies involving tetralin (3). Results revealed that at elevated temperatures an



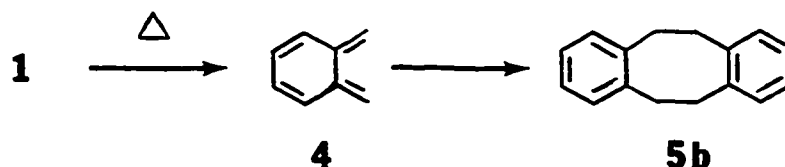
increased yield of styrene (2) was observed and that one of its sources was the thermal isomerization of benzocyclobutene (1).

In its simplest form, the isomerization involves the homolysis of the carbon-carbon bond resulting in the formation of a diradical which upon hydrogen atom transfer from the alpha position (pathway a) would give styrene (2). This simple mechanism may also have a perturbation in which the hydrogen atom may be transferred from the radical center (pathway b) to give a carbene which may C-H insert to give styrene (2). These two mechanisms invoke an initial homolysis which would result in a high energy phenyl radical, thus, making the entire scheme less reasonable.

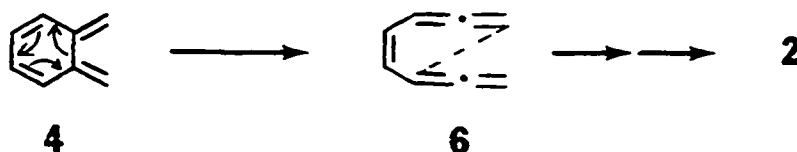


The thermal electrocyclic opening of benzocyclobutene (1) to ortho-quinodimethane (4) has been well established [7,8]. Research by Trahanovsky and Surber [9] and Surber [10] concerning the formation of

anthracene (5a) via the [4+4] dimer (5b) from the FVP of benzocyclobutene (1) indicates that 4 is produced under our pyrolysis conditions.

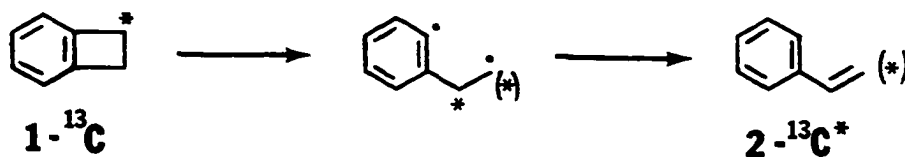


A plausible intermediate resulting from a second electrocyclic ring opening of ortho-quinodimethane (4) is the bisallene 6 [11,12,13]. One may envision that closure of the bisallene 6 across the terminus of one allene with the internal portion of the opposing allene, followed by multiple hydrogen shifts could lead to styrene (2).



Concurrently with this study, an investigation was being made by Chapman and Tsou utilizing a  $^{13}\text{C}$ -labeled benzocyclobutene ( $1\text{-}^{13}\text{C}$ ) [1]. They proposed two mechanisms, one involving a simple cleavage resulting

in the formation of a phenyl radical and homobenzylic radical, the other involving the formation of ortho-xylylene (4) and a series of



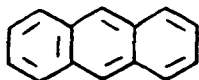
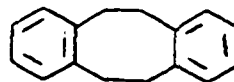
isomerizations involving cycloheptatetraene/arylcabene intermediates. Analysis of the pyrolyzate of <sup>13</sup>C labeled benzocyclobutene 1-<sup>13</sup>C determined that the label was present in the beta position and one of the ortho positions and not in the alpha and beta positions, thus, it was concluded that the cycloheptatetraene/arylcabene pathway was the major one involved.

In order to test the viability of the proposed mechanisms, we undertook the synthesis and flash vacuum pyrolysis (FVP) of methyl-group and deuterium-atom labeled benzocyclobutenes. Additional findings concerning the chemistry of the intermediates involved in the isomerization of benzocyclobutene (1) to styrene (2) will also be presented.

## RESULTS

Benzocyclobutene (1)

The synthesis of compound 1 was based on the elimination of HCl from a substituted ortho-methylbenzyl chloride to form a benzocyclobutene, the first report of which was made by Hart and Fish [14a] and Hart et al. [14b]. Our FVP route was derived from the flow pyrolysis route of Loudon et al. [15], beginning with commercially available ortho-methylbenzyl chloride (7). FVP at ca. 800°C using a cooled sample head (-35°C, CCl<sub>4</sub>/Dry Ice) produced a mixture containing > 70% benzocyclobutene (1), ca. 20% (7) and ca. 10% "heavy" compounds which included anthracene (5a) and the [4+4] dimer 5b. The starting material

**5a****5b**

7 was removed by forming the pyridinium chloride salt which was then filtered. The residue was then distilled to give pure 1 which was identified by its <sup>1</sup>H NMR and mass spectra.

FVP of Benzocyclobutene (1)

Compound 1 was pyrolyzed from 800-900°C, again utilizing a cooled sample head, to produce styrene (2) in good yields. The

highly informative  $^1\text{H}$  NMR spectrum, which was identical to that obtained from a commercial sample, is shown in Figure 1. Each of the vinyl protons are in distinct areas of the spectrum (6.8, 5.8 and 5.2 ppm) and have specific splitting patterns. The alpha proton is characterized by the doublet of doublet pattern ( $J_{\text{trans}} = 18$  Hz,  $J_{\text{cis}} = 11$  Hz) and the two beta protons are characterized by the doublet of doublet pattern ( $J_{\text{trans}} = 18$  Hz,  $J_{\text{gem}} = 2$  Hz) and ( $J_{\text{cis}} = 11$  Hz,  $J_{\text{gem}} = 2$  Hz). These protons reflect any changes due to substitution of the benzene ring as well as deuterium labeling of the vinyl positions.

#### 4-Methylbenzocyclobutene (8)

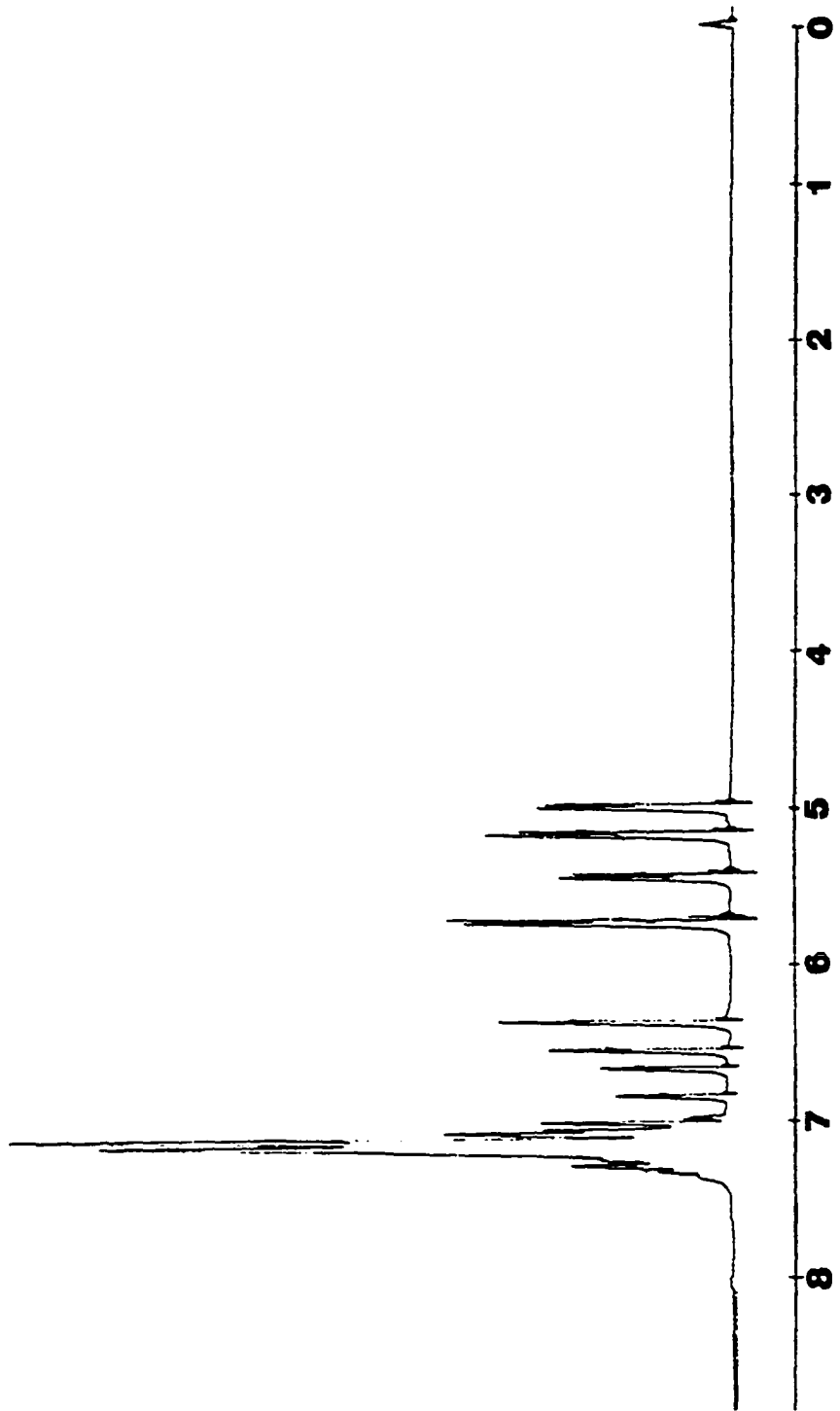
The methyl substituted benzocyclobutene 8 used for this study was produced by the FVP (780°C) of 2,5-dimethylbenzyl chloride (9), which was obtained by chloromethylation [16] of para-xylene (10). Compound 8 was purified in a manner similar to the parent compound 1. The product was identified by its  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectrum.

#### FVP of 4-Methylbenzocyclobutene (8)

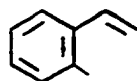
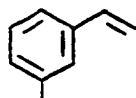
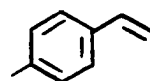
The FVP of 4-methylbenzocyclobutene (8) at 800°C resulted in the formation of two methylstyrenes which, by GLPC analysis, gave two peaks in the ratio of 1:1. Interpretation of the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the pyrolyzate did not yield conclusive evidence as to the isomeric identity of the two methylstyrenes.

Figure 1.  $^1\text{H}$  NMR spectrum of styrene (2)





Commercial samples of the ortho-, meta- and para-methylstyrenes (11-13) were obtained and co-injected with the pyrolyzate. This analysis revealed that the ortho- and meta-substituted styrenes (11 and 12) have exactly the same retention times under our GLPC conditions, therefore, it was concluded the pyrolyzate mixture was made up of either the ortho- and para-methylstyrene (11 and 13) or the meta- and the para-methylstyrene (12 and 13).

**11****12****13**

A comparison of the <sup>1</sup>H NMR spectra of the pyrolyzate versus a 40:60 mixture of 11 and 13 revealed significant differences in the chemical shift and splitting of the protons in the vinyl region (6.8-5.2 ppm) as shown in Figure 2. However, the <sup>1</sup>H NMR of a 40:60 mixture of 12 and 13 gave a sufficiently close match to the unknown mixture, Figure 3.

To further verify this result, the <sup>13</sup>C NMR spectra of each of the three samples were obtained and compared (Figures 4 and 5). The β-carbon of the vinyl moiety is especially sensitive to the position

Figure 2.  $^1\text{H}$  NMR spectra of: (a) the pyrolyzate from the FVP of 4-methylbenzocyclobutene (8) and (b) a 40:60 mixture of ortho- and para-methylstyrene (11 and 13)

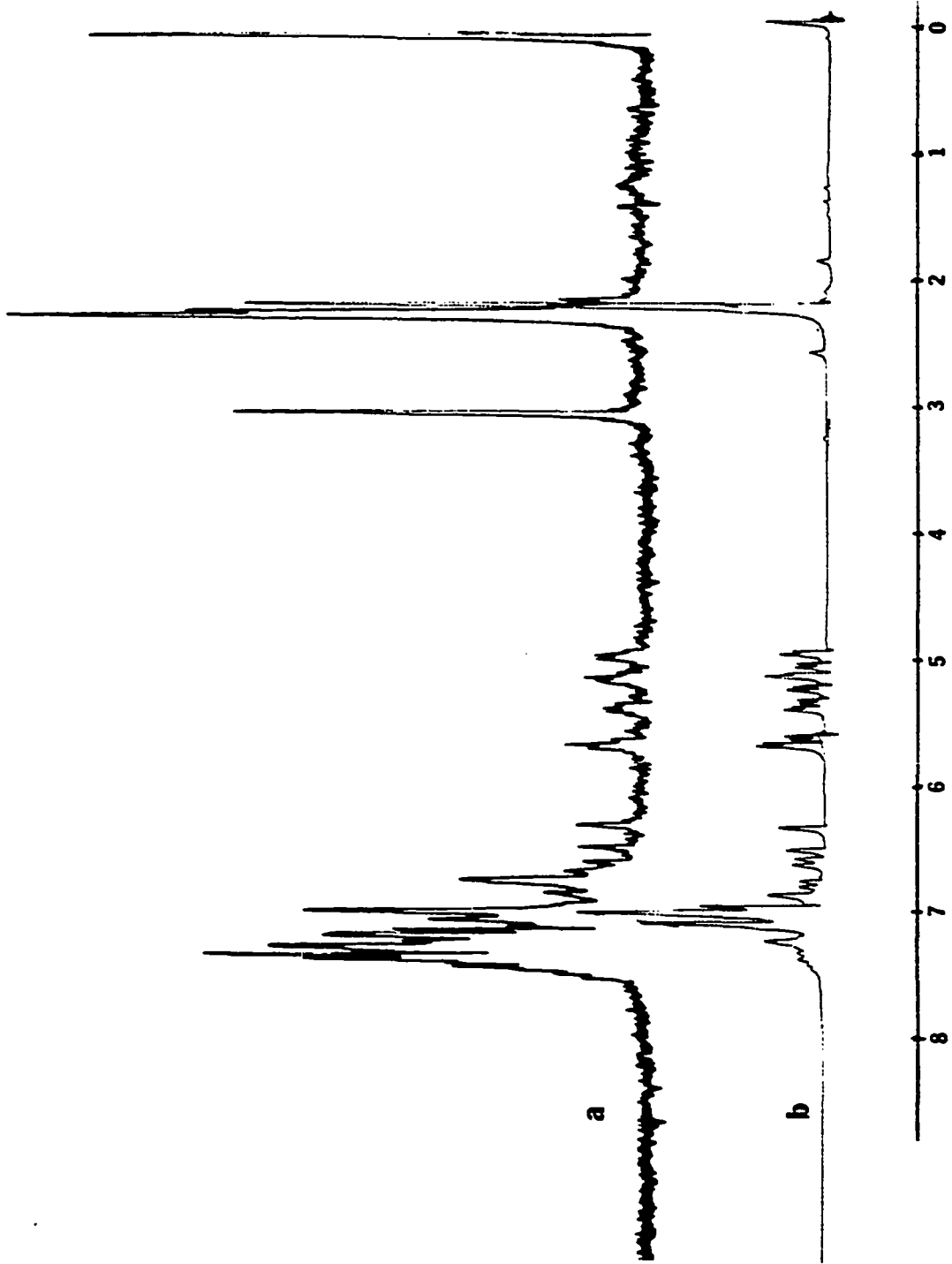


Figure 3.  $^1\text{H}$  NMR spectra of: (a) the pyrolyzate from the FVP of 4-methylbenzocyclobutene (8) and (b) a 40:60 mixture of meta- and para-methylstyrene (12 and 13)

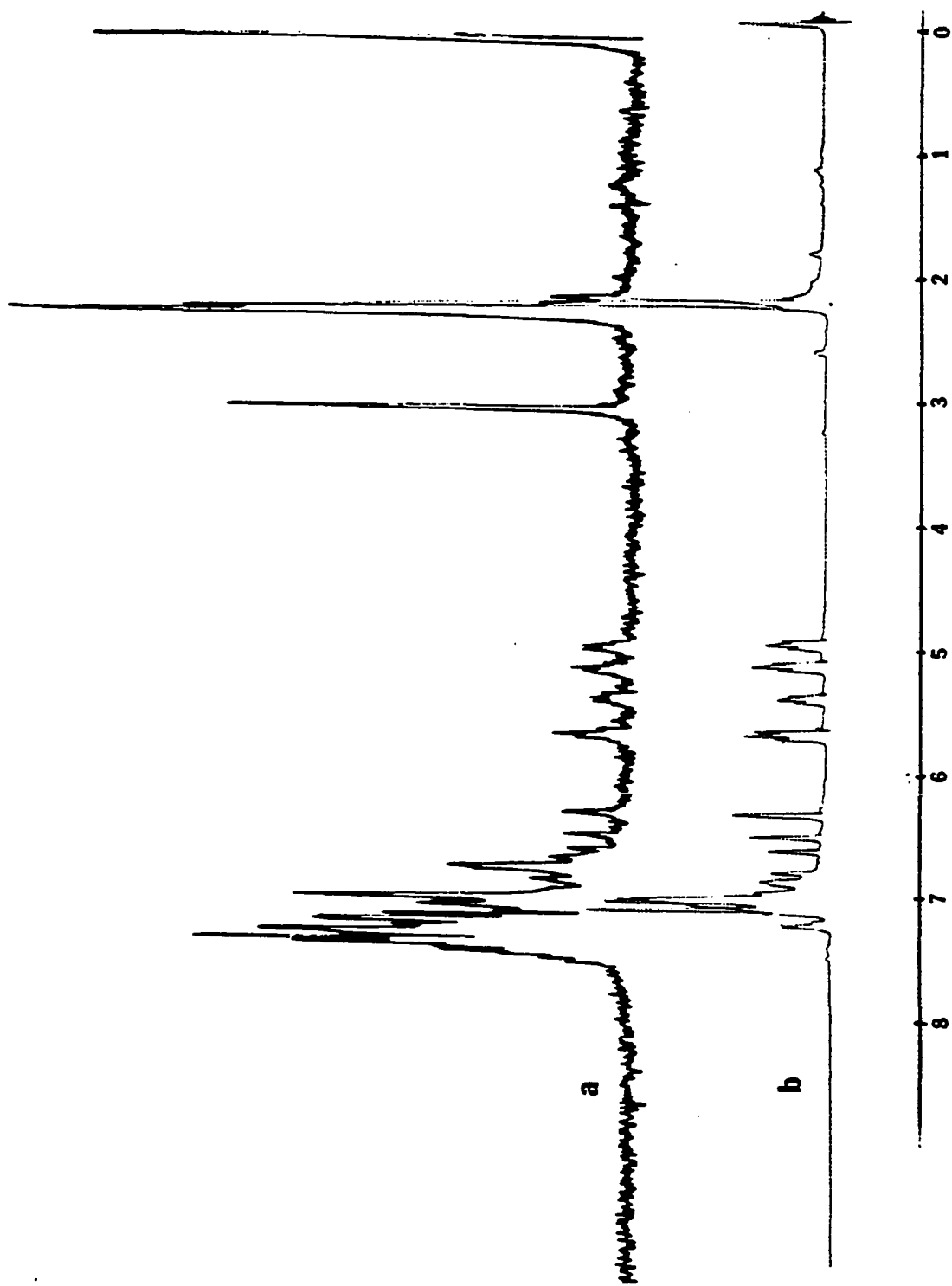


Figure 4.  $^{13}\text{C}$  NMR spectra of: (a) a 40:60 mixture of ortho- and para-methylstyrene (11 and 13) and (b) the pyrolyzate from the FVP of 4-methylbenzocyclobutene (8)

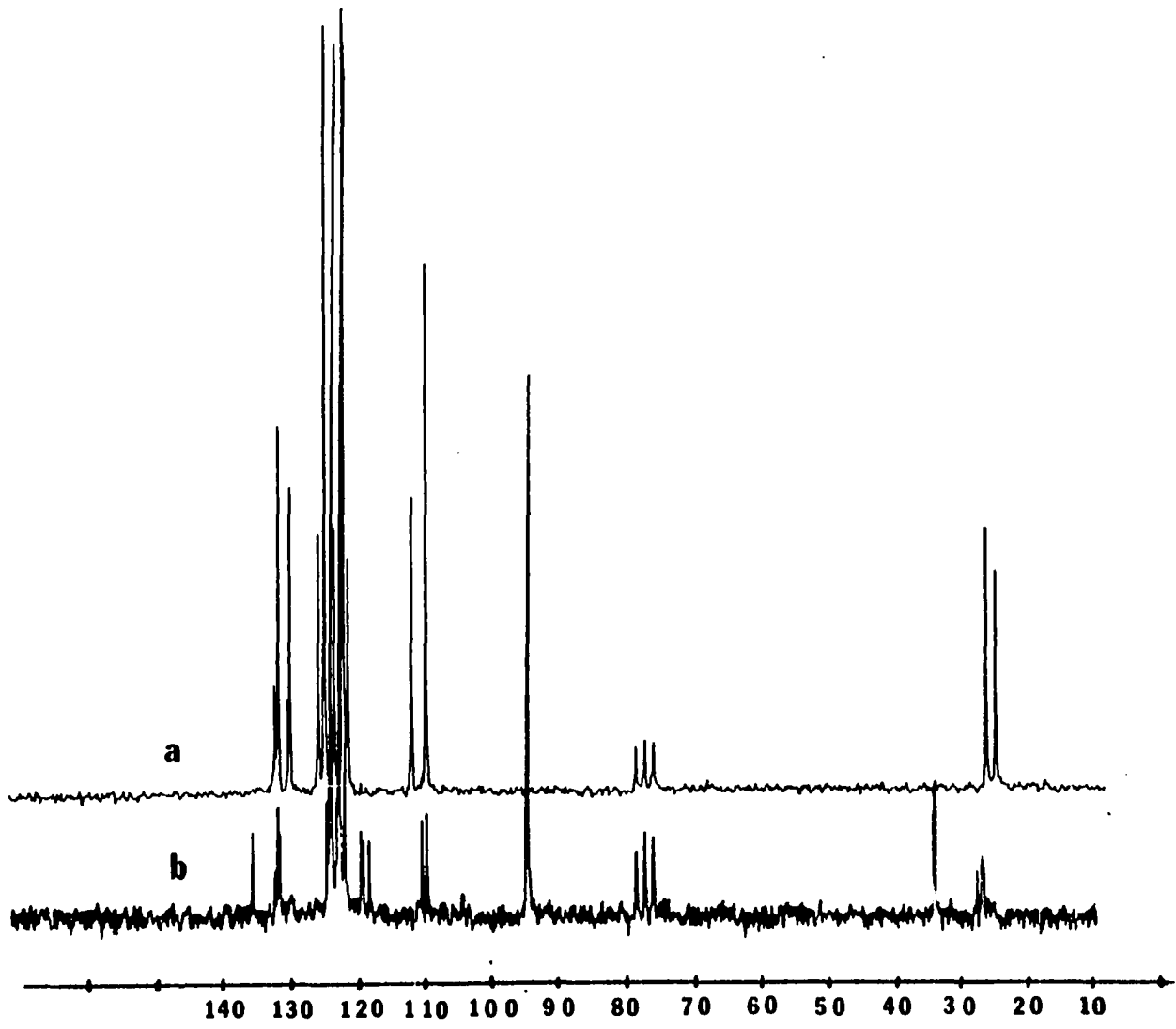
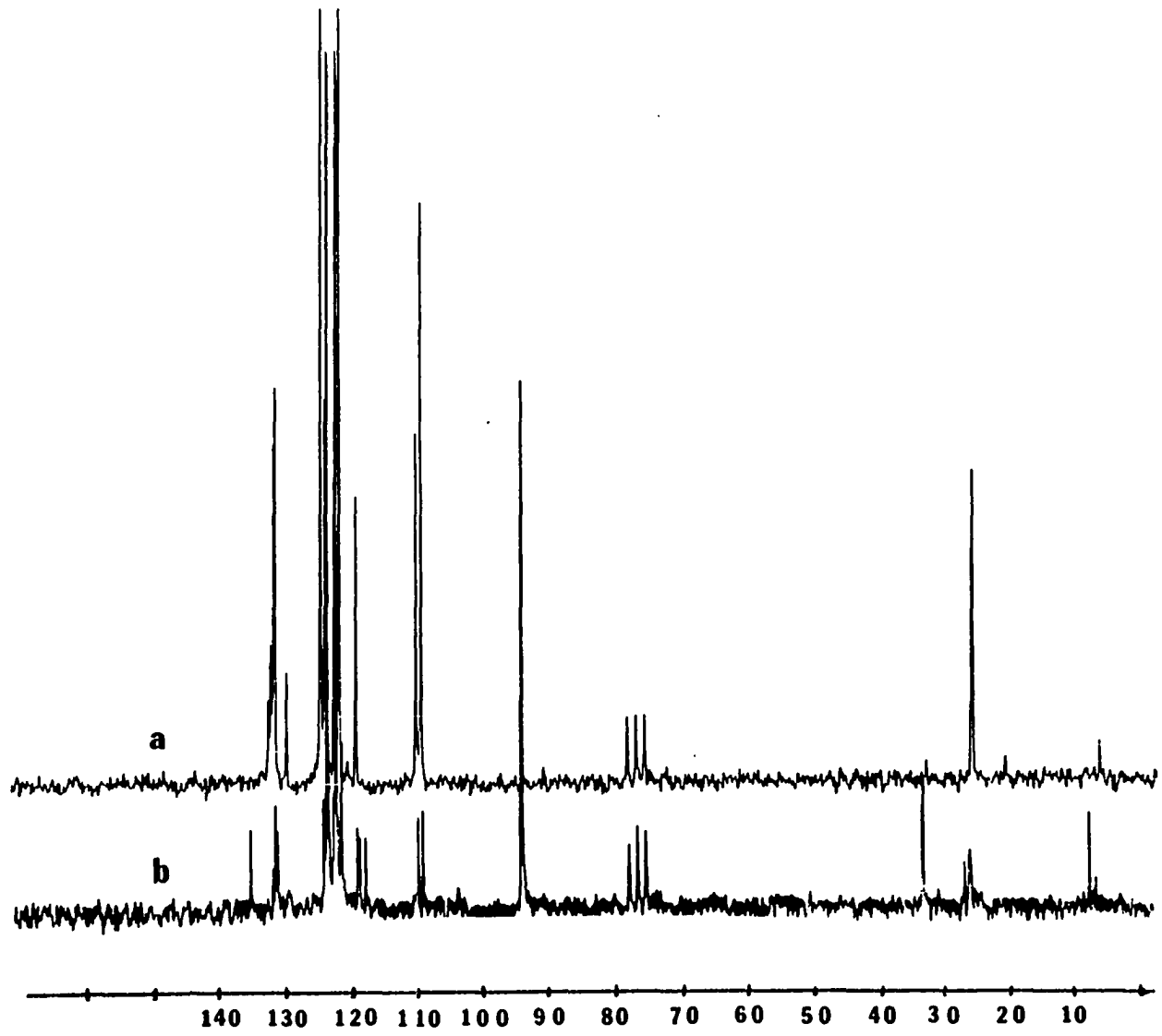




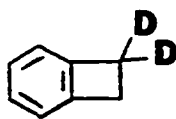
Figure 5.  $^{13}\text{C}$  NMR spectra of: (a) a 40:60 mixture of meta- and para-methylstyrene (12 and 13) and (b) the pyrolyzate from the FVP of 4-methylbenzocyclobutene (8)



of the arylmethyl substituent thus causing a far downfield shift (115 ppm) of the ortho-methylstyrene  $\beta$ -carbon, which was not observed in the pyrolyzate. In fact, there was once again a very good match between the  $^{13}\text{C}$  NMR spectrum of the unknown mixture and the 40:60 mixture of the meta- and para-methylstyrenes (12 and 13), shown in Figure 5.

Benzocyclobutene-1,1- $\underline{\text{d}}_2$  (1-d<sub>2</sub>)

Benzocyclobutene-1,1- $\underline{\text{d}}_2$  (1-d<sub>2</sub>) was produced by the method outlined by Morello and Trahanovsky [17]. FVP (780°C of ortho-methylbenzyl chloride- $\alpha,\alpha$ - $\underline{\text{d}}_2$  (7-d<sub>2</sub>) utilizing a cooled sample head yielded 1-d<sub>2</sub> (70% GLPC yield). The benzyl chloride 7-d<sub>2</sub> was obtained by the action of  $\text{SOCl}_2$  on ortho-methylbenzyl alcohol- $\alpha,\alpha$ - $\underline{\text{d}}_2$  (14) which was obtained by lithium aluminum deuteride (LAD) reduction of methyl ortho-toluate (15). The aromatic ester was produced by esterification of commercially available ortho-toluic acid.



**1-d<sub>2</sub>**

FVP of Benzocyclobutene-1,1-d<sub>2</sub> (1-d<sub>2</sub>)

Pyrolysis of 1-d<sub>2</sub>, which was found to be > 93% d<sub>2</sub> by GCMS (Table 1), at temperatures ranging from 800-900°C produced only styrene (2), as determined by analytical GLPC. The yield of styrene (2) was found to increase with increasing temperature. The <sup>1</sup>H NMR spectrum revealed complex absorbances centered around 7.40 ppm (aromatics), 6.80 ppm (α-vinyl), 5.82 ppm and 5.20 ppm (two β-vinyls) indicative of 2. Analysis of the <sup>2</sup>H NMR spectrum revealed absorbances centered around 7.50 ppm, 6.80 ppm, 5.80 ppm and 5.20 ppm also indicative of a mixture of deuterated styrenes.

In order to determine the amount of d<sub>2</sub>-styrene present in the pyrolyzate, a GCMS determination was made versus "light" styrene (2) (undeuterated). The results are tabulated in Table 2. It may be seen that there is no significant loss of the deuterium label due to the FVP experiment.

Due to the complex nature of the spectra associated with the pyrolyzate, a series of deuterated styrenes was synthesized and their spectra were compared with the pyrolyzate. E-Styrene-α,β-d<sub>2</sub> (16) and Z-styrene-β-d<sub>1</sub> (17) were prepared by Lindlar catalyzed [18] deuteration of phenylacetylene (18) and hydrogenation of phenylacetylene-2-d<sub>1</sub> (18-d<sub>1</sub>), respectively. Additionally, extra information was gained due to the formation of the opposing geometrical isomers produced by: 1) pyrolysis of 16 to give Z-styrene-α,β-d<sub>2</sub> (19)

Table 1. Mass spectral data for the distribution of deuterium in benzocyclobutene-1,1-d<sub>2</sub> (1-d<sub>2</sub>), measured at 18 eV

m/e	Peak Intensity of 1	Peak Intensity of 1-d <sub>2</sub>	Calculated deuterium content <sup>a</sup>		
			d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>
103	--	--	--	--	--
104	100.0	1.2	1.1	--	--
105	8.8	5.6	--	5.6	--
106	0.03	100.0	--	0.5	99.5
107	--	9.6	--	--	9.0
108	--	0.3	--	--	--

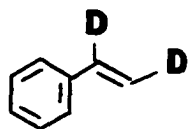
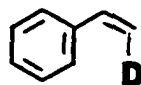
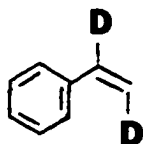
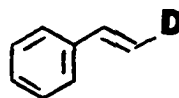
<sup>a</sup>The % of each of the species is as follows: d<sub>0</sub> = 1.0, d<sub>1</sub> = 5.3 and d<sub>2</sub> = 93.7

Table 2. Mass spectral data for styrene-d<sub>2</sub> (2-d<sub>2</sub>) formed from the FVP of 1-d<sub>2</sub> at 805°C

m/e	Peak Intensity of 2	Peak Intensity of 2-d <sub>2</sub>	Calculated deuterium content <sup>a</sup>		
			d <sub>0</sub>	d <sub>1</sub>	d <sub>2</sub>
103	--	--	--	--	--
104	100.0	1.8	1.8	--	--
105	9.8	8.9	--	8.9	--
106	0.05	100.0	--	0.9	99.1
107	--	9.8	--	--	9.8
108	--	0.5	--	--	--

<sup>a</sup>The % of each of the species is as follows: d<sub>0</sub> = 1.6, d<sub>1</sub> = 8.1 and d<sub>2</sub> = 90.3.

2) E-styrene- $\beta$ - $\underline{d}_1$  (20) being formed as a significant by-product of the hydrogenation of (18- $\underline{d}_1$ ). The spectrum of each compound matched that expected for the deuterated styrenes produced and are compared to the pyrolyzate mixture in Figures 6, 7 and 8.

**16****17****19****20**

The remaining styrenes, styrene- $\beta,\beta$ - $\underline{d}_2$  (21) and styrene- $\alpha$ - $\underline{d}_1$  (22), were synthesized utilizing pyrolytic acetate elimination of phenethyl acetate- $\beta,\beta,\beta$ - $\underline{d}_3$  (23) and phenethyl acetate- $\alpha$ - $\underline{d}_1$  (24). The pyrolysis method employed was that of flash vacuum pyrolysis, however, previously reported results on pyrolytic acetate eliminations [19,20] were helpful in determining favorable reaction conditions. The  $^1\text{H}$  NMR (Figure 9) and  $^2\text{H}$  NMR (Figure 10 and 11) are illustrated along with the pyrolyzate spectrum added for comparison.

Figure 6.  $^1\text{H}$  NMR spectra of: (a) the pyrolyzate from the FVP of benzocyclobutene-1,1- $\text{d}_2$  ( $\text{1-d}_2$ ) (b) a mixture of E- and Z-styrene- $\alpha,\beta$ - $\text{d}_2$  ( $\text{16}$  and  $\text{19}$ ) (c) Z-styrene- $\beta$ - $\text{d}_1$  ( $\text{17}$ )

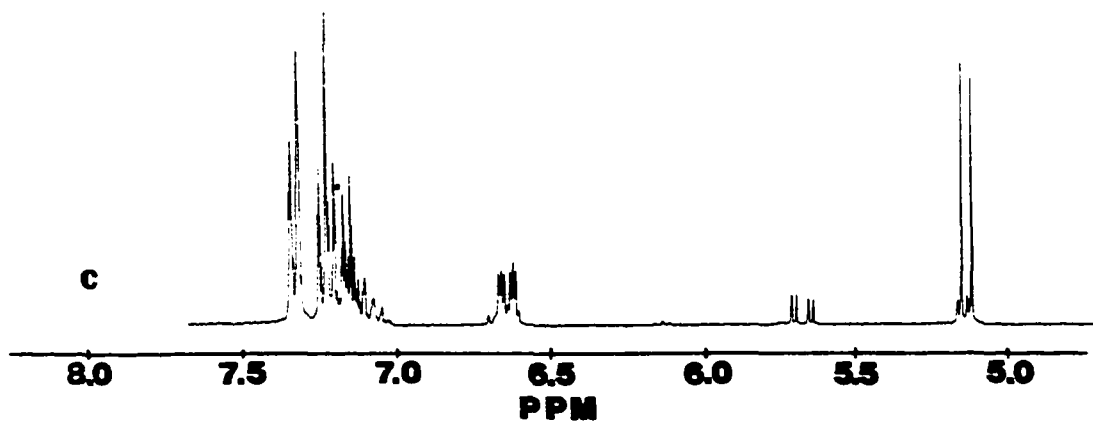
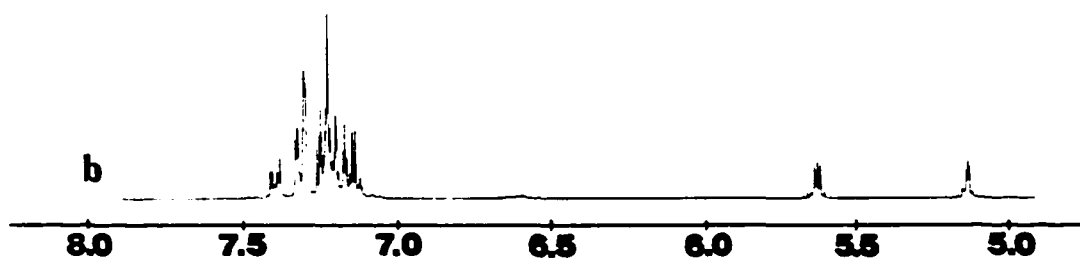
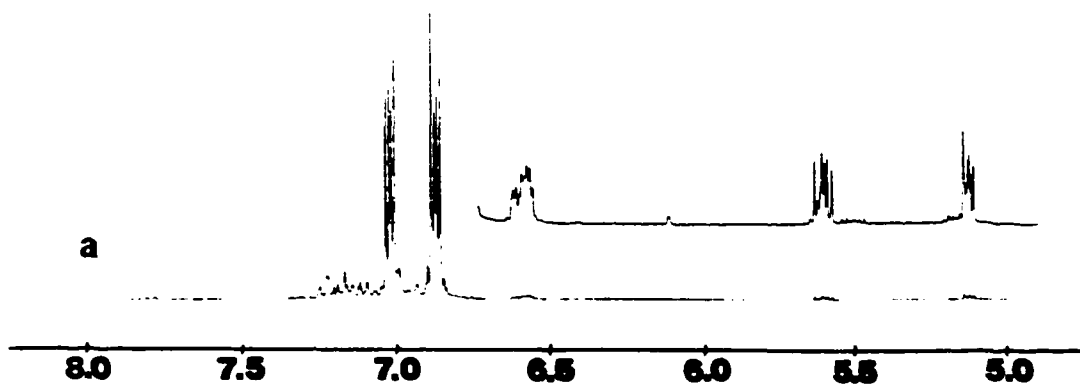




Figure 7.  $^2\text{H}$  NMR spectra of: (a) the pyrolyzate from the FVP of benzocyclobutene-1,1- $\underline{d}_2$  ( $\underline{1-d}_2$ ) and (b) E-styrene- $\alpha,\beta$ - $\underline{d}_2$  ( $\underline{16}$ )

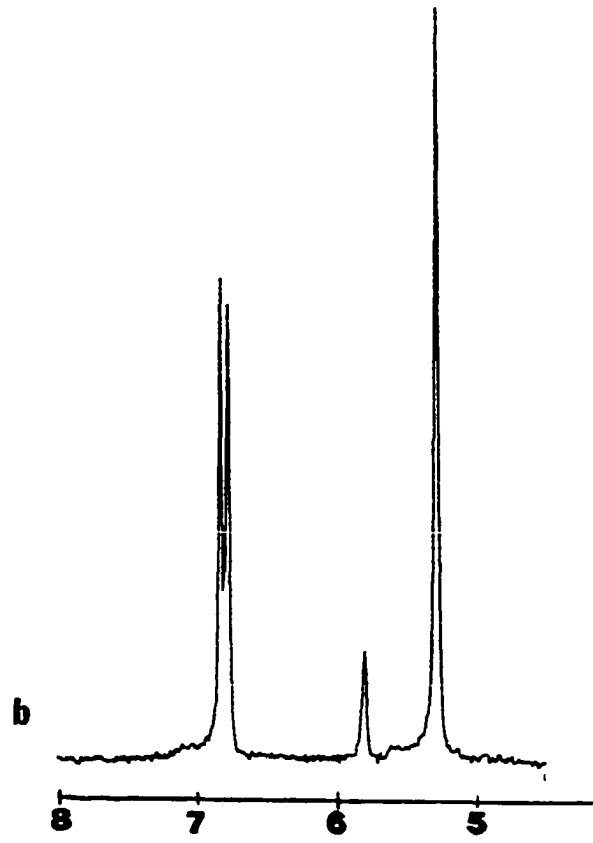
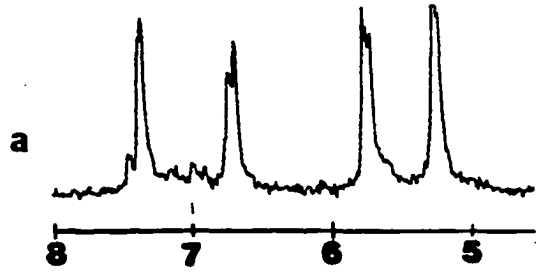


Figure 8.  $^2\text{H}$  NMR spectra of: (a) the pyrolyzate from the FVP of benzocyclobutene-1,1- $\underline{d}_2$  ( $\underline{1-d}_2$ ) and (b) Z-styrene- $\beta$ - $\underline{d}_1$  ( $\underline{17}$ )

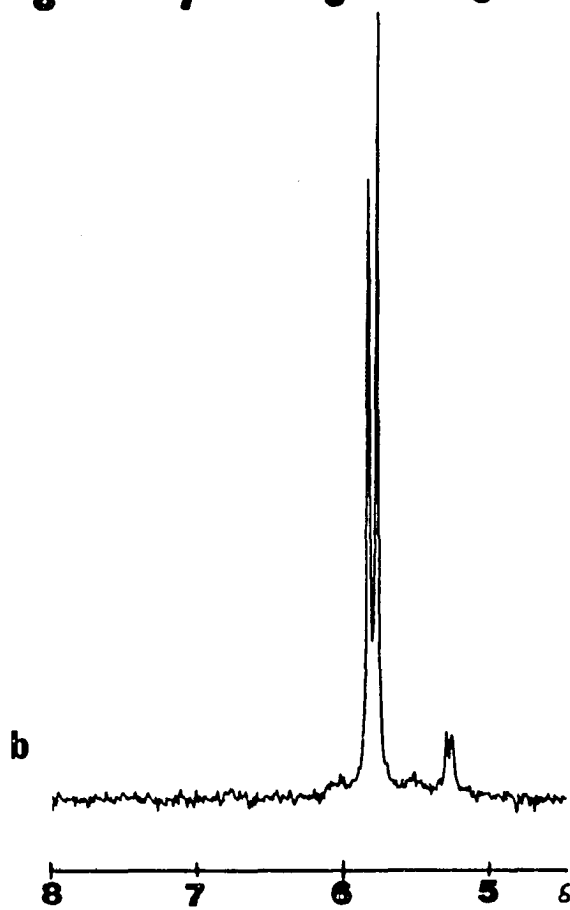
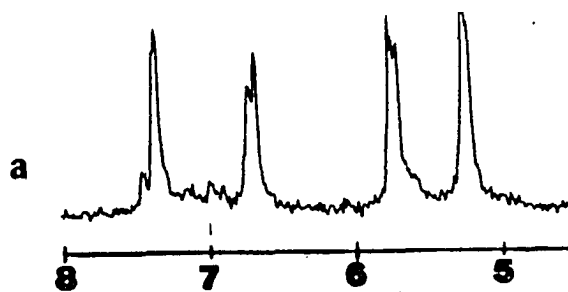


Figure 9.  $^1\text{H}$  NMR spectra of: (a) the pyrolyzate from the FVP of benzocyclobutene-1,1- $\underline{d}_2$  ( $\underline{1-d}_2$ ), (b) styrene- $\alpha$ - $\underline{d}_1$  ( $\underline{22}$ ) and (c) styrene- $\beta$ , $\beta$ - $\underline{d}_2$  ( $\underline{21}$ )

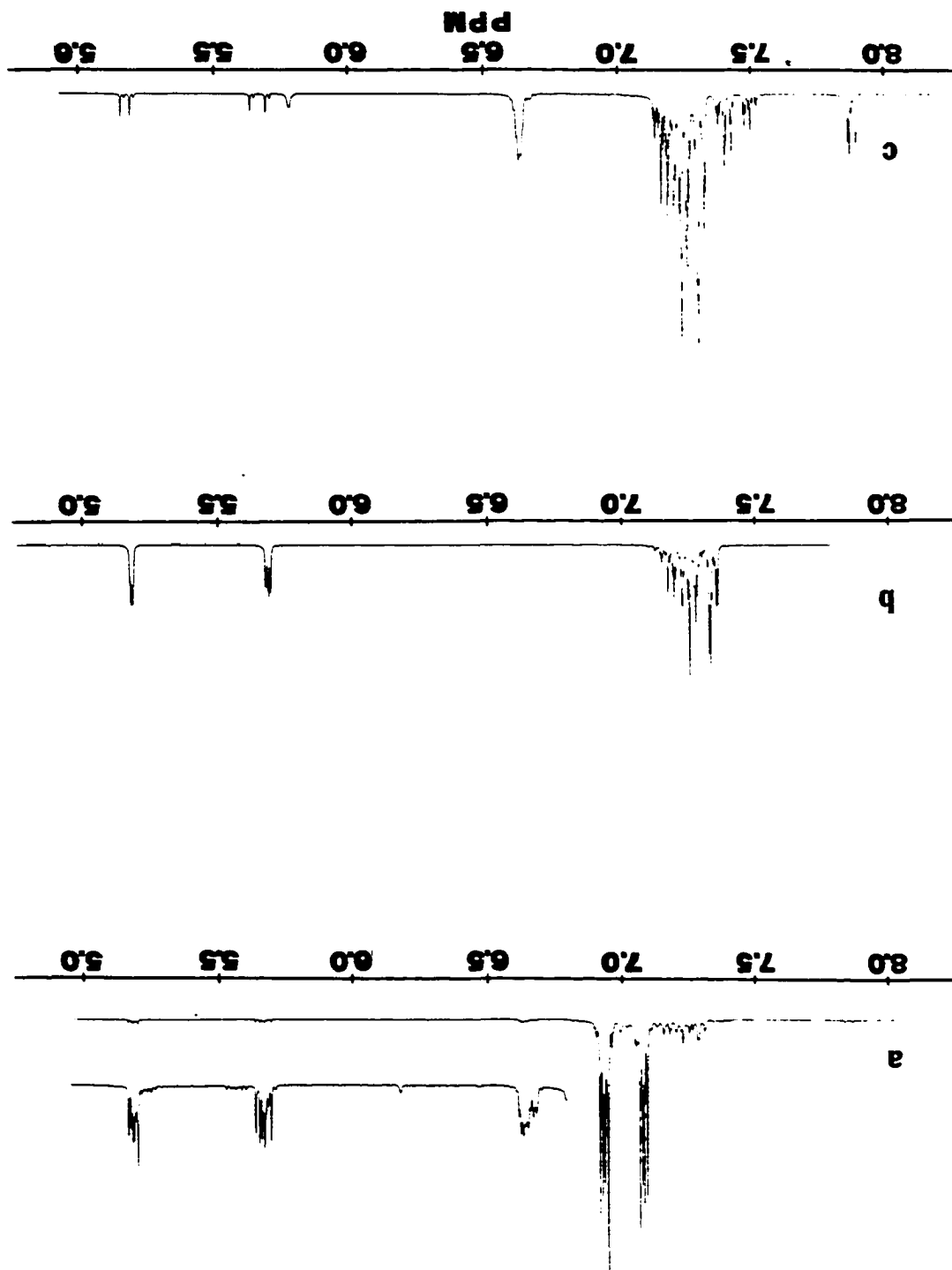


Figure 10.  $^2\text{H}$  NMR spectra of: (a) the pyrolyzate from the FVP of benzocyclobutene-1,1- $\text{d}_2$  ( $\text{1-d}_2$ ) and (b) styrene- $\alpha$ - $\text{d}_1$  ( $\text{22}$ )

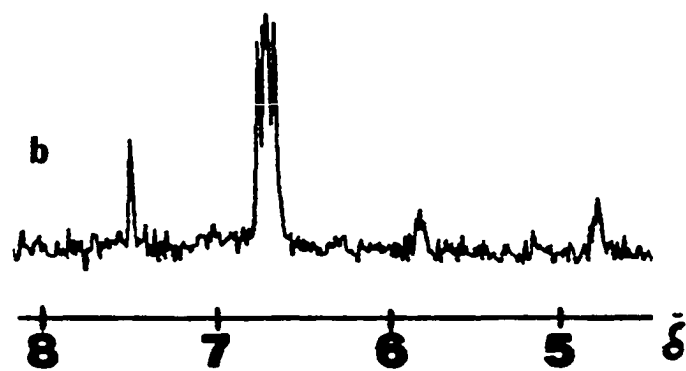
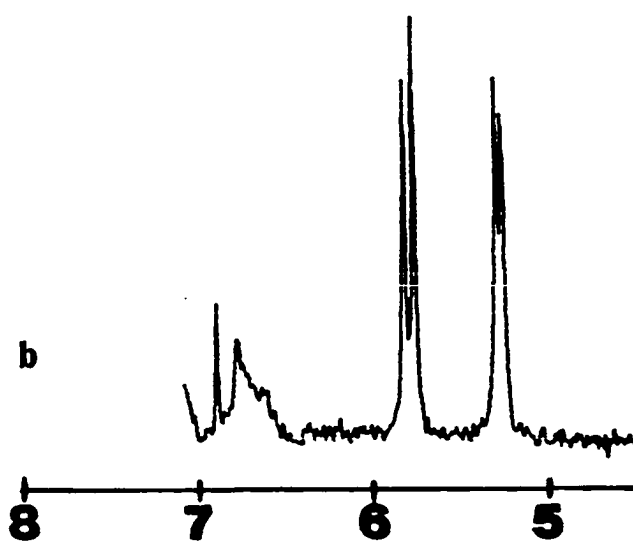
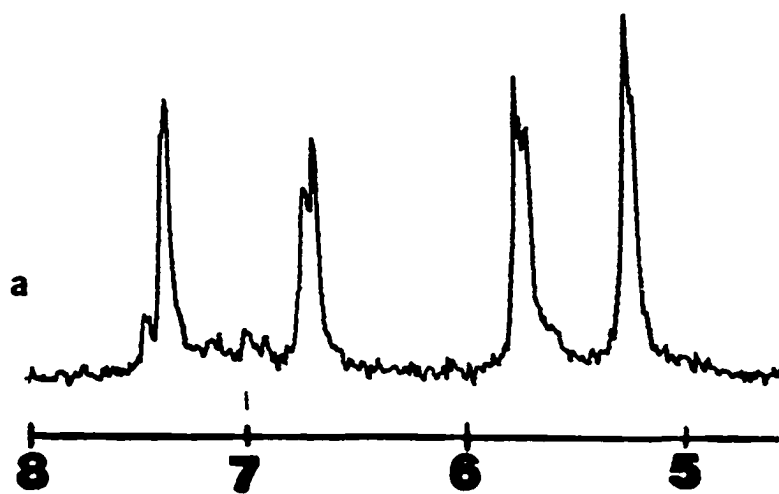




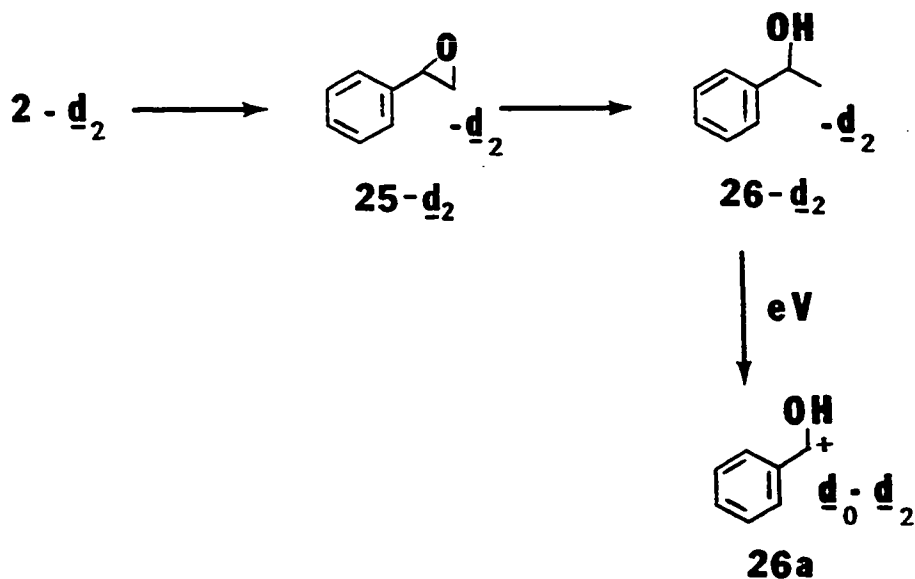
Figure 11.  $^2\text{H}$  NMR spectra of: (a) the pyrolyzate from the FVP of benzocyclobutene-1,1- $\underline{d}_2$  ( $\underline{1-d}_2$ ) and (b) styrene- $\beta,\beta$ - $\underline{d}_2$  ( $\underline{21}$ )





### Mass Spectral Analysis of the $\underline{d}_2$ -Styrenes ( $\underline{2-d}_2$ )

The mixture of  $\underline{d}_2$ -styrenes resulting from the pyrolysis of benzocyclobutene-1,1- $\underline{d}_2$  ( $\underline{1-d}_2$ ) was epoxidized using meta-chloroperbenzoic acid (MCPBA) [21]. The  $\underline{d}_2$ -styrene oxides  $\underline{25-d}_2$  were then opened using LAH (lithium aluminum hydride) to give the various deuterated  $\alpha$ -phenethyl alcohols ( $\underline{26-d}_2$ ) which were analyzed by GCMS.



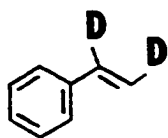
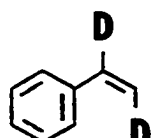
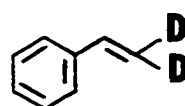
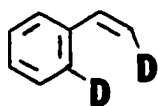
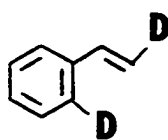
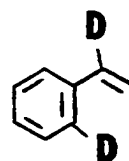
Upon electron impact, it has been shown that  $\alpha$ -phenethanol cleaves such that the benzyloxy cation ( $\underline{26a}$ ) is produced as the base peak [22]. It was also shown that the cleavage occurs at a rate faster than the rate of deuterium scrambling, thus, preserving the positional integrity of the deuterium atoms. It was possible to determine the distribution of the deuterium label by measuring the benzyloxy cation peaks resulting from the  $\underline{d_0}$ ,  $\underline{d_1}$  and  $\underline{d_2}$  species of  $\underline{26-d_2}$ , as shown in Table 3. Analysis of the spectrum revealed the

Table 3. Mass spectral data of the hydroxybenzyl radical formed by cleavage of  $\alpha$ -phenethanol- $\alpha,\alpha$ - $\underline{d_2}$  ( $\underline{26-d_2}$ )

m/e	Peak Intensity of $\underline{26}$	Peak Intensity of $\underline{26-d_2}$	Calculated deuterium content <sup>a</sup>		
			$\underline{d_0}$	$\underline{d_1}$	$\underline{d_2}$
106	--	--	--	--	--
107	100.0	99.2	99.2	--	--
108	4.8	100.0	4.8	95.2	--
109	0.2	18.5	--	4.6	13.9
110	--	1.1	--	--	0.7

<sup>a</sup>The % of each of the species is as follows:  $\underline{d_0}$  = 47.6,  $\underline{d_1}$  = 45.7 and  $\underline{d_2}$  = 6.7.

presence of compounds 16, 19, 27 and 28 which produced a  $d_1$ -benzyloxy cation peak (45.7%). Compound 21 produced a  $d_0$  species (47.6%), while a  $d_2$ -benzyloxy cation (6.7%) was produced by 29.

**16****19****21****27****28****29**

#### Acetophenone- $\beta$ - $d_1$ Tosylhydrazone (30)

Compound 30 was the result of the reaction of acetophenone- $d_1$  (31) and tosylhydrazine. Recrystallization (2 X) from  $H_2O/EtOH$  gave colorless plates which were identified by their spectral and physical properties. The  $^1H$  NMR spectrum revealed absorbances which were expected for the tosylhydrazone. The IR spectrum proved to be more informative since the  $C=O$  ( $1685\text{ cm}^{-1}$ ) absorption was absent and new absorbances for the  $C=N$  and  $SO_2$  moieties were present. Lastly, the observed melting point of  $146-147^\circ C$  is in good agreement with the literature value of  $145-147^\circ C$  [23].

The regiospecific deuteration of acetophenone was accomplished by first forming the enolate of acetophenone with KH, then quenching with deuterioacetic acid [24]. The use of deuterioacetic acid was of the utmost importance since the use of D<sub>2</sub>O caused considerable scrambling of the deuterium label due to further enolization by the KOD by-product.

#### Pyrolysis of the Sodium Salt of 30

The formation of the sodium salt and the pyrolysis of same is based on a general method reported by Kaufmann et al. [25]. The sodium tosylhydrazide 32 formed from proton abstraction by sodium methoxide in MeOH, was thermolyzed in the FVP sample head at ca. 100°C generating the diazo compound in situ. The volatile diazo compound 33 was then carried across the hot zone at which point it was thermolyzed to produce N<sub>2</sub> and methyl-d<sub>1</sub> phenylcarbene (34). GLPC analysis of the pyrolyzate revealed a single peak which had the same retention time as co-injected styrene (2).

The <sup>1</sup>H NMR spectrum produced absorbances at 7.40 ppm (aromatics), 6.80 ppm (alpha vinyl proton), 5.81 ppm and 5.20 ppm (beta vinyl protons) each of which were integrated to determine the value of  $k_H/k_D = 2.1$ . The calculation involves a correction factor which is derived from the GCMS analysis concerning the distribution of the d<sub>0</sub>, d<sub>1</sub> and d<sub>2</sub> styrenes, as shown in Table 4.

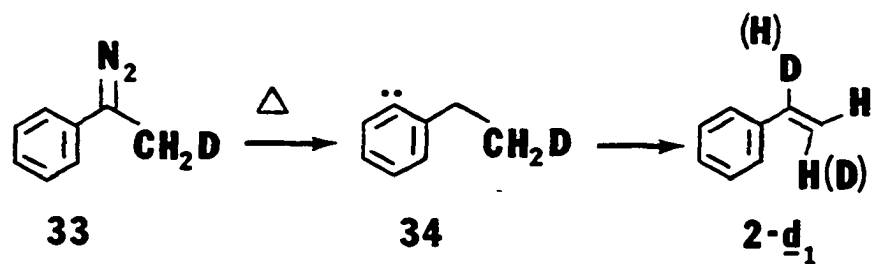


Table 4. Mass spectral data of styrene- $\underline{d}_1$  (**2- $\underline{d}_1$** ) formed from the FVP of diazo compound **33**

m/e	Peak Intensity of <b>2</b>	Peak Intensity of <b>2-<math>\underline{d}_1</math></b>	Calculated deuterium content <sup>a</sup>			
			$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$
103	0.6	--	--	--	--	--
104	100.0	26.7	26.7	--	--	--
105	9.2	100.0	2.1	97.5	--	--
106	0.02	14.4	--	9.0	5.4	--
107	--	1.6	--	--	0.5	1.1

<sup>a</sup>The % of each of the species is as follows:  $\underline{d}_0 = 20.4$ ,  $\underline{d}_1 = 74.6$ ,  $\underline{d}_2 = 4.2$  and  $\underline{d}_3 = 0.8$ .

### Acetophenone- $\beta,\beta$ - $d_2$ Tosylhydrazone (37)

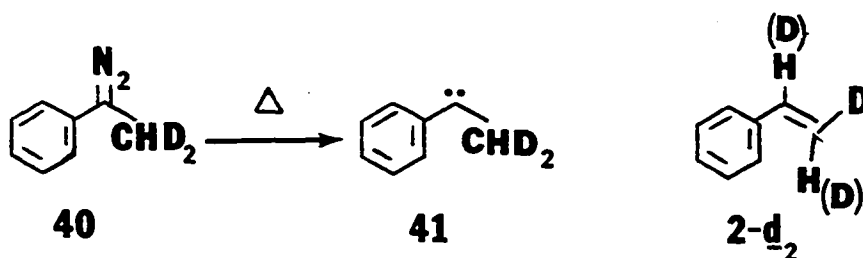
Tosylhydrazone 37 was the result of the reaction of acetophenone- $d_2$  (38) and tosylhydrazine. Recrystallization (2 X) from  $H_2O/EtOH$  gave colorless plates which were identified by their spectral and physical properties. The  $^1H$  NMR spectrum revealed absorbances which were expected for the tosylhydrazone. The IR spectrum revealed similar results as above, that of new absorbances for the C=N and  $SO_2$  moieties. Lastly, the observed melting point of 145-147°C is in good agreement with the literature value of 145-147°C [23].

The regiospecific deuteration was accomplished by deuterating acetophenone via basic exchange utilizing  $D_2O/K_2CO_3$  [26], the > 98%  $d_3$ -acetophenone (38- $d_3$ ) was then enolized using KH in THF. The enolate was then quenched with HOAC. Again, the use of acetic acid was important to prevent scrambling of the deuterium label.

### Pyrolysis of the Sodium Salt of 37

The general method outlined by Kaufmann et al. [25] was followed. The sodium tosylhydrazide 39 formed from proton abstraction by sodium methoxide in MeOH, was thermolyzed in the FVP sample head at ca. 100°C producing the diazo compound 40 in situ. The volatile diazo compound was then carried across the hot zone at which point it was thermolyzed to produce  $N_2$  and methyl- $d_2$ -phenylcarbene (41). GLPC analysis of the pyrolyzate revealed a single peak which had the same retention time as co-injected styrene (2).





The  $^1\text{H}$  NMR spectrum produced absorbances at 7.40 ppm (aromatics), 6.80 ppm (alpha vinyl proton), 5.81 ppm and 5.20 ppm (beta vinyl protons) which were integrated to determine the value of  $k_{\text{H}}/k_{\text{D}} = 2.3$ . The calculation involves a correction factor which is derived from the GCMS analysis concerning the distribution of the  $\underline{d}_1$ ,  $\underline{d}_2$  and  $\underline{d}_3$  styrenes (Table 5).

#### 4-Methyl- $\underline{d}_3$ -benzocyclobutene (44)

The deuterium labeled benzocyclobutene 44 was prepared by the reaction of lithium aluminum deuteride (LAD) on the tosylate 45, adapted from a method described by Streitweiser [27], resulting from the reaction of para-toluenesulfonyl chloride and the sodium alkoxide of 4-(hydroxymethyl- $\alpha, \alpha$ - $\underline{d}_2$ )-benzocyclobutene (46). The deuterated alcohol was prepared by the LAD reduction of 4-carbomethoxybenzocyclobutene (47). The deuterium content of 44 was determined to be > 72% by mass spectral analysis as shown in Table 6.

Table 5. Mass spectral data of styrene- $\underline{d}_2$  ( $\underline{2-d}_2$ ) formed from the FVP of diazo compound  $\underline{40}$

m/e	Peak Intensity of $\underline{2}$	Peak Intensity of $\underline{2-d}_2$	Calculated deuterium content <sup>a</sup>			
			$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$
103	0.6	--	--	--	--	--
104	100.0	1.1	1.1	--	--	--
105	9.2	12.2	--	12.2	--	--
106	0.02	100.0	--	1.1	98.9	--
107	--	28.4	--	--	9.1	19.3
108	--	2.4	--	--	--	1.8

<sup>a</sup>The % of each of the species is as follows:  $\underline{d}_0 = 0.8$ ,  $\underline{d}_1 = 9.3$ ,  $\underline{d}_2 = 75.2$  and  $\underline{d}_3 = 14.7$ .

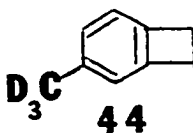


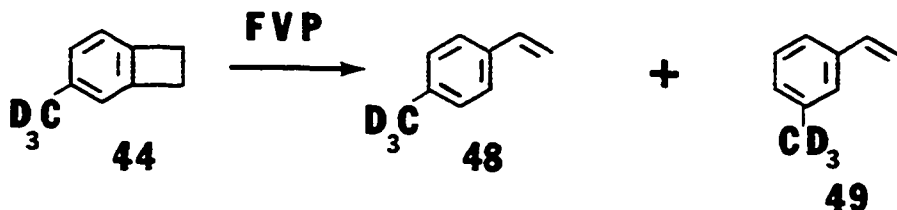
Table 6. Mass spectral data of the deuterium distribution in 4-methyl- $\underline{d}_3$ -benzocyclobutene ( $\underline{44}$ )

m/e	Peak Intensity of $\underline{44-d}_0$	Peak Intensity of $\underline{44}$	Calculated deuterium content <sup>a</sup>			
			$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$
117	--	--	--	--	--	--
118	100.0	3.4	3.4	--	--	--
119	9.9	7.1	--	7.1	--	--
120	0.04	28.8	--	0.7	28.1	--
121	--	100.0	--	--	2.8	97.2
122	--	10.1	--	--	--	9.6
123	--	0.5	--	--	--	--

<sup>a</sup>The % of each of the species is as follows:  $\underline{d}_0 = 2.5$ ,  $\underline{d}_1 = 5.2$ ,  $\underline{d}_2 = 21.3$  and  $\underline{d}_3 = 72.0$ .

#### FVP of 4-Methyl- $\underline{d}_3$ -benzocyclobutene ( $\underline{44}$ )

The deuterium labeled methylbenzocyclobutene  $\underline{44}$  was pyrolyzed at ca. 850°C resulting in slightly greater than 50% conversion. Isolation of the  $\underline{d}_3$ -methylstyrenes ( $\underline{48}$  and  $\underline{49}$ ) by GLPC collection gave a mixture of the isomeric methylstyrenes which was shown by  $^2\text{H}$  NMR to contain the deuterium label in only the methyl position and none of the vinyl positions. This result was corroborated by  $^1\text{H}$  NMR and mass spectral analysis of the GLPC collected sample as well as the crude pyrolyzate.



#### 2-Methyl-5-methyl- $\underline{\underline{d}}_3$ -benzaldehyde Tosylhydrazone (50)

The  $\underline{\underline{d}}_3$ -tosylhydrazone 50 was formed by the reaction of tosylhydrazine [25] on 2-methyl-5-methyl- $\underline{\underline{d}}_3$ -benzaldehyde (51) which was found to be > 95%  $\underline{\underline{d}}_3$ -species (Table 7). The reaction of ceric ammonium nitrate in acetic acid [28] on the corresponding alcohol 52 gave the benzaldehyde 51. The benzyl alcohol 52 was obtained by the deprotection of the *t*-butyldimethylsilyl benzyl ether 53 using  $(n\text{-Bu})_4\text{NF}$  [29]. The silyl benzyl ether 53 was obtained by the lithiation [30,31] and subsequent quenching with methyl- $\underline{\underline{d}}_3$  iodide of the 5-bromobenzyl silyl ether (54) which was formed by protection of 2-methyl-5-bromobenzyl alcohol (55) using *t*-butyldimethylsilyl chloride following the method of Corey and Snider [29]. Compound 55 was obtained by the LAH reduction of 2-methyl-5-bromobenzoic acid (56) which was produced by the bromination of ortho-toluic acid [32,33].

Table 7. Mass spectral data of the deuterium distribution of 2-methyl-5-methyl-d<sub>3</sub>-benzaldehyde (51)

m/e	Peak Intensity of <u>51</u> -d <sub>0</sub>	Peak Intensity of <u>51</u>	Calculated deuterium content <sup>a</sup>		
			<u>d</u> <sub>1</sub>	<u>d</u> <sub>2</sub>	<u>d</u> <sub>3</sub>
132	--	--	--	--	--
133	42.0	--	--	--	--
134	100.0	--	--	--	--
135	9.5	0.7	0.7	--	--
136	0.6	46.3	--	4.3	--
137	--	100.0	--	0.4	99.6
138	--	9.7	--	--	9.5
139	--	0.6	--	--	--

<sup>a</sup>The % of each of the species is as follows: d<sub>1</sub> = 0.7, d<sub>2</sub> = 4.1 and d<sub>3</sub> = 95.2.

FVP of the Sodium Salt of 2-Methyl-5-methyl-d<sub>3</sub>-benzaldehyde  
Tosylhydrazone (50)

The sodium salt was obtained by the action of sodium methoxide on the tosylhydrazone (50) as outlined by Kaufmann et al. [25]. Heating of the salt in the sample head liberated the corresponding diazo compound 58 which upon pyrolysis at 815°C gave a mixture of four major products.

The products were identified by comparison of  $^1\text{H}$  NMR, GC retention times and mass spectral cleavage with the respective non-deuterated methylstyrenes 11-13 and 4-methylbenzocyclobutene (10). The  $^1\text{H}$  NMR of the deuterated styrenes 48 and 49 showed no absorbance which would arise from a protio-methylstyrene. In addition, the  $^2\text{H}$  NMR gave a singlet at 2.41 ppm indicative of the deuterio-methyl group but more importantly, no olefinic deuterium signals were observed. The deuterium content determined by mass spectral means indicated  $> 95\%$   $\text{d}_3$ -methylstyrene (Table 8).

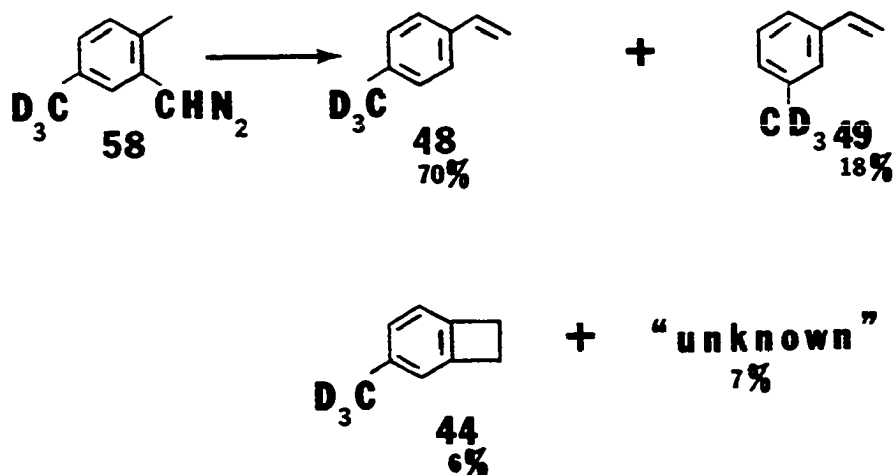


Table 8. Mass spectral data of methyl- $\underline{d}_3$ -styrene ( $\underline{48}$ ) resulting from the FVP of diazo compound  $\underline{58}$

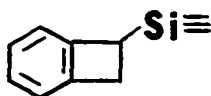
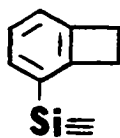
m/e	Peak Intensity of $\underline{48-d}_0$	Peak Intensity of $\underline{48}$	Calculated deuterium content <sup>a</sup>		
			$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$
117	2.0	--	--	--	--
118	100.0	--	--	--	--
119	9.6	--	--	--	--
120	0.1	3.2	3.2	--	--
121	--	100.0	--	100.0	--
122	--	12.0	--	9.6	2.4
123	--	0.3	--	--	--

<sup>a</sup>The % of each of the species is as follows:  $\underline{d}_2 = 3.0$ ,  $\underline{d}_3 = 94.7$  and  $\underline{d}_4 = 2.3$ .

### 3-Methyl- $\underline{d}_3$ -benzocyclobutene ( $\underline{61}$ )

The synthesis of  $\underline{61}$  employed the methodology of Eaborn et al. [34,35] beginning with the lithiation of benzocyclobutene ( $\underline{1}$ ) using  $n$ -BuLi/hexanes in TMEDA/THF. The lithium bonded to the three possible positions since quenching with trimethylsilyl chloride gave the 1-, 3- and 4-trimethylsilylbenzocyclobutenes ( $\underline{62-64}$ ). The three silylbenzocyclobutenes were formed as liquids at room temperature which were inseparable by preparative scale chromatography methods. They were

separable via capillary GLPC and were shown to be produced in the following distribution: 62 (9%), 63 (78%) and 64 (12%).

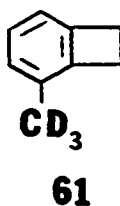
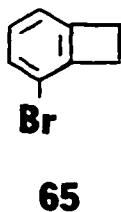
**62****63****64**

The method which was adopted for purification involved the selective destruction of each of the unwanted isomers leaving the desired 3-isomer 63. Sequential use of  $\text{H}_3\text{PO}_4/\text{MeOH}$  and  $\text{KOH}/\text{DMSO}$  removed isomers 62 and 64, respectively.

The desired 3-trimethylsilylbenzocyclobutene (63) was identified primarily by its  $^1\text{H}$  NMR spectrum. The aromatic protons were particularly informative in that the splitting patterns for each isomer are quite different. The 1-isomer 62 would be expected to produce a doublet of doublet pattern of 4 protons, the 3-isomer 63 would produce two doublets and a triplet of 3 protons and the 4-isomer 64 would produce two doublets and a singlet. The  $^1\text{H}$  NMR of the purified product exhibited two doublets of a proton each and a triplet of one proton indicative of 3-trimethylsilylbenzocyclobutene (63).



Compound 63 was treated with  $\text{Br}_2$  to give the bromide 65 which was lithiated using  $n\text{-BuLi}$ . The aryl lithium was then treated with methyl- $\text{d}_3$  iodide to give 3-methyl- $\text{d}_3$ -benzocyclobutene (61) which was identified by GCMS,  $^1\text{H}$  NMR and  $^2\text{H}$  NMR. Upon electron impact in the mass spectrometer, compound 61 produced a parent ion of mass 121 and a primary loss of mass 18 ( $-\text{CD}_3$ ). The proton spectrum recorded two doublets and a triplet indicative of the 4-, 5- and 6-protons as well as the ethano bridge at 3.18 ppm. Lastly, the  $^2\text{H}$  NMR spectrum produced a single absorbance at 2.30 ppm indicative of the tolyl deuteriomethyl group.

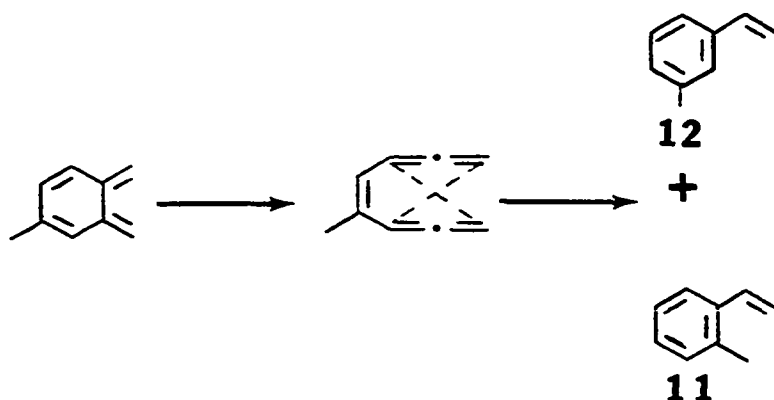


FVP of 3-Methyl- $\text{d}_3$ -benzocyclobutene (61)

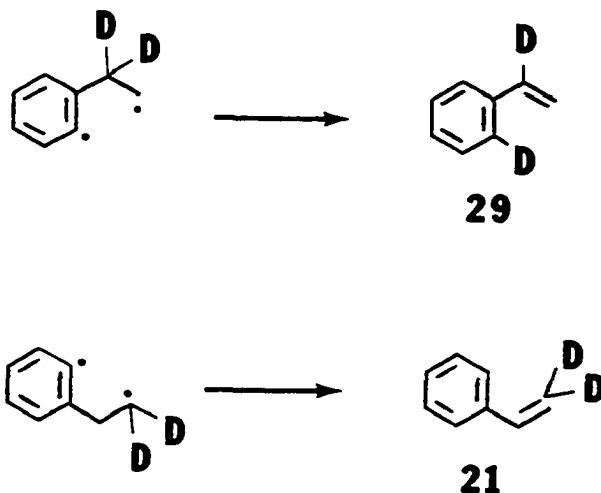
Pyrolysis of 61 at ca. 850°C produced what appeared to be a mixture of two isomeric methylstyrenes (by GC co-injection) which had masses of 121 amu indicating that the deuterium label was still present. The  $^1\text{H}$  NMR spectrum revealed extensive scrambling across the vinyl (6.8-5.2 ppm) and methyl groups (2.3 ppm). The  $^2\text{H}$  NMR spectrum also exhibited a complex pattern in the vinyl and methyl groups again indicative of scrambling of the label.

## DISCUSSION

The FVP of the two labeled compounds, 4-methylbenzocyclobutene (8) and benzocyclobutene-1,1-d<sub>2</sub> (1-d<sub>2</sub>), produced results which are able to clearly rule out the involvement of some of the proposed mechanisms. The bisallene mechanism would have predicted a mixture of ortho- and meta-methylstyrenes (11 and 12) in a ratio of 1:1 from the FVP of 8. However, this possibility was negated by meta- and para-methylstyrene (12 and 13) being produced in a 1:1 ratio from the pyrolysis.

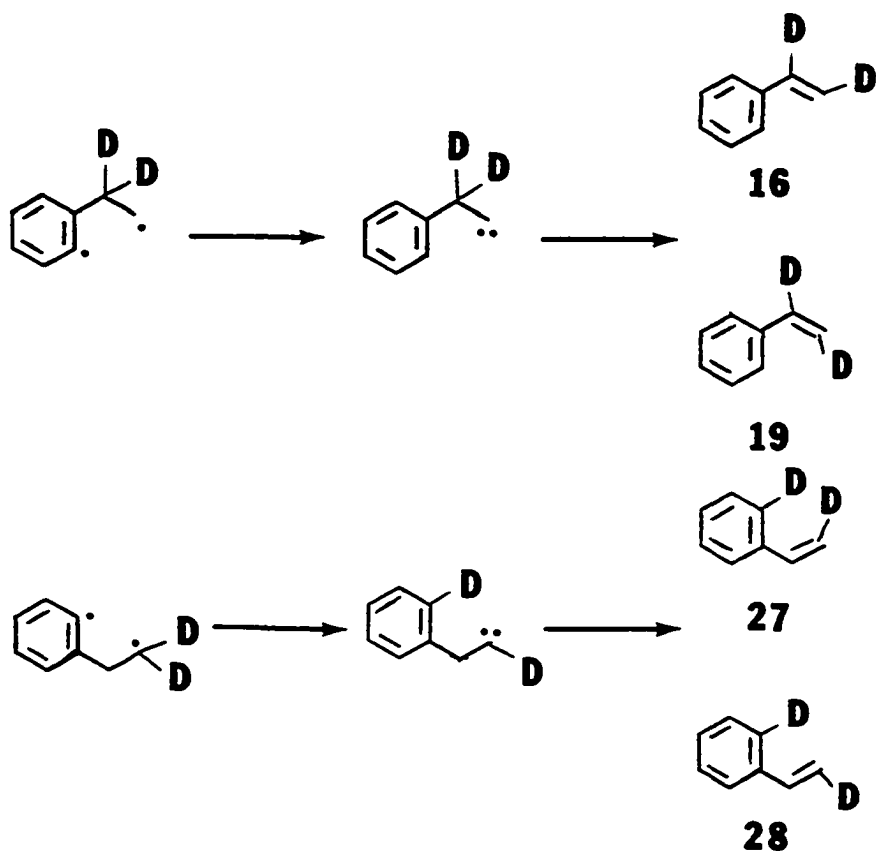


The elimination of the radical-involving mechanisms was realized following the pyrolysis of benzocyclobutene-1,1-d<sub>2</sub> (1-d<sub>2</sub>). If the "simple" homolysis reaction was occurring, a product distribution consisting of only 21 and 29 would be observed. Such a simple mixture would be easily identifiable, however, the obvious complexity of the pyrolyzate spectra rules out this alternative.



A slightly more complex mixture of four dideuteriostyrenes is predicted to be produced by the complex radical mechanism. Via this route, the initial diradical is converted to a carbene through a hydrogen atom shift. The carbene then C-H(D) inserts to form 16, 19, 27 and 28.

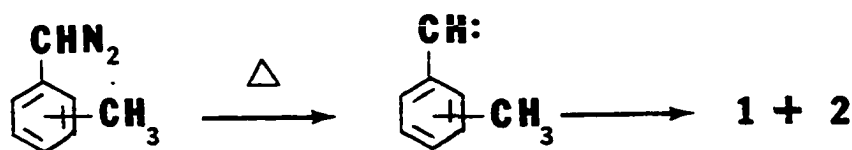
It was not possible to rule out the radical/carbene mechanism with absolute certainty, based only on the spectral information gleaned from the pyrolyzate. The  $^1\text{H}$  and  $^2\text{H}$  NMR spectra indicated sufficient complexity for the presence of the 4 previously mentioned  $\text{d}_2$ -styrenes, however, it was possible that styrene- $\beta,\beta\text{-d}_2$  (21) and styrene- $\alpha,2\text{-d}_2$  (29) were also present.



The GCMS experiment performed on the  $d_2$ -phenethanols  $\underline{26-d_2}$ , derived from the pyrolyzate mixture, provided key evidence for ruling out the "complex" radical mechanism. Upon electron impact, the  $d_2$ -phenethanols  $\underline{26-d_2}$  produced peaks indicating the existence of styrenes  $\underline{21}$  and  $\underline{29}$  as well as confirming the existence of  $\underline{16}$ ,  $\underline{19}$ ,  $\underline{27}$  and  $\underline{28}$ .

Since a product mixture consisting of all six  $d_2$ -styrenes is observed, it is obvious that an alternative mechanism must be operating. The observation that pyrolysis of benzocyclobutene (1) at a sufficiently high temperature produces styrene in good yield has been reported earlier [3,4]. It is also well established that at lower temperatures 1 opens to ortho-quinodimethane (4) which has been observed to form a [4+4] dimer 5b [9,10], a [4+2] dimer and has also been trapped as [4+2] Diels-Alder adducts using various dienophiles [36-38]. These facts imply that the initially formed ortho-xylylene (4) must be undergoing a higher energy process which leads it towards the final product, styrene (2).

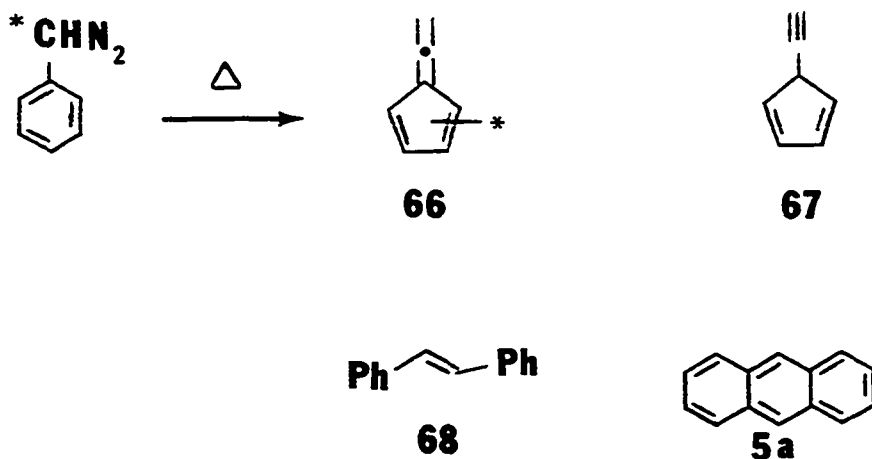
Several research groups have reported data which showed that benzocyclobutene (1) and styrene (2) were produced by the pyrolysis



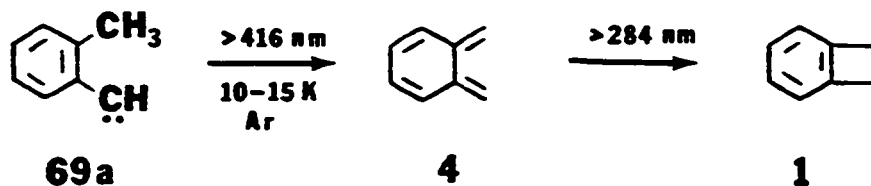
	<b>1</b>		<b>2</b>
<b>ortho</b>	1	:	3
<b>meta</b>	1	:	1
<b>para</b>	1	:	1

of tolyldiazomethanes [39-44]. In particular, Baron et al. [39] has shown that the ortho-, meta- and para-methylbenzylidenes gave comparable yields of benzocyclobutene (1) and styrene (2). A mechanism was proposed which accounted for the migration of the carbene by invoking arylcarbene/cycloheptatetraene isomerizations which ultimately led to an ortho-tolylcarbene producing both 1 and 2.

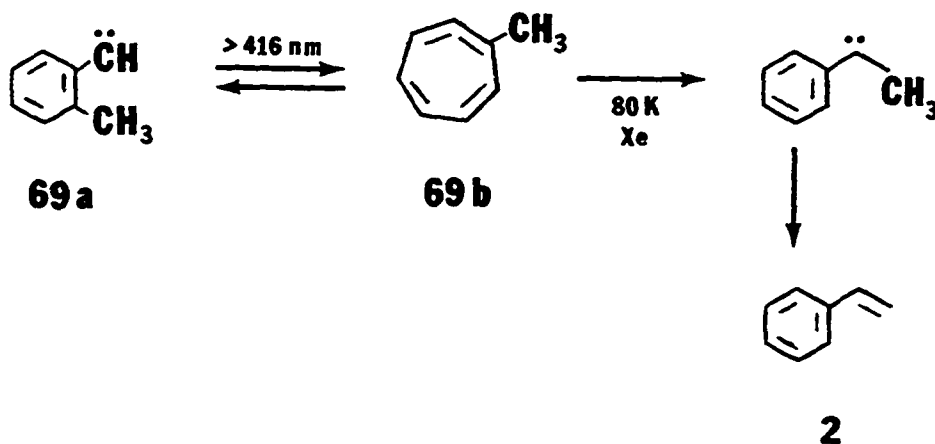
Experimental results concerning phenylcarbene have also offered evidence for the existence of the arylcarbene/cycloheptatetraene isomerizations to be operant in the pyrolysis of diazabenzylidene [45,46a]. The pyrolysis of phenyldiazomethane-<sup>13</sup>C produces phenylcarbene which gives as isolable products fulvene allene (66) (10%), ethynylcyclopentadiene (67) (5%), E-stilbene (68) (3%) and anthracene (4a) (14%). <sup>13</sup>C NMR Analysis of the pyrolyzate revealed extensive scrambling of the label due to multiple carbene/cycloheptatetraene isomerizations.



Strong evidence for the intermediates involved was furnished by Chapman et al. [46b] in matrix isolation studies of tolylmethylenes generated by irradiation of precursor diazo compounds. The work furnished a strong link between ortho-tolylcarbene 69a, cyclohepta-tetraene 69b, ortho-xylylene 4, benzocyclobutene 1 and styrene 2. It was found that matrix isolated ortho-tolylmethylene 69a gave predominately ortho-xylylene 4 upon irradiation at wavelengths  $> 416$  nm.



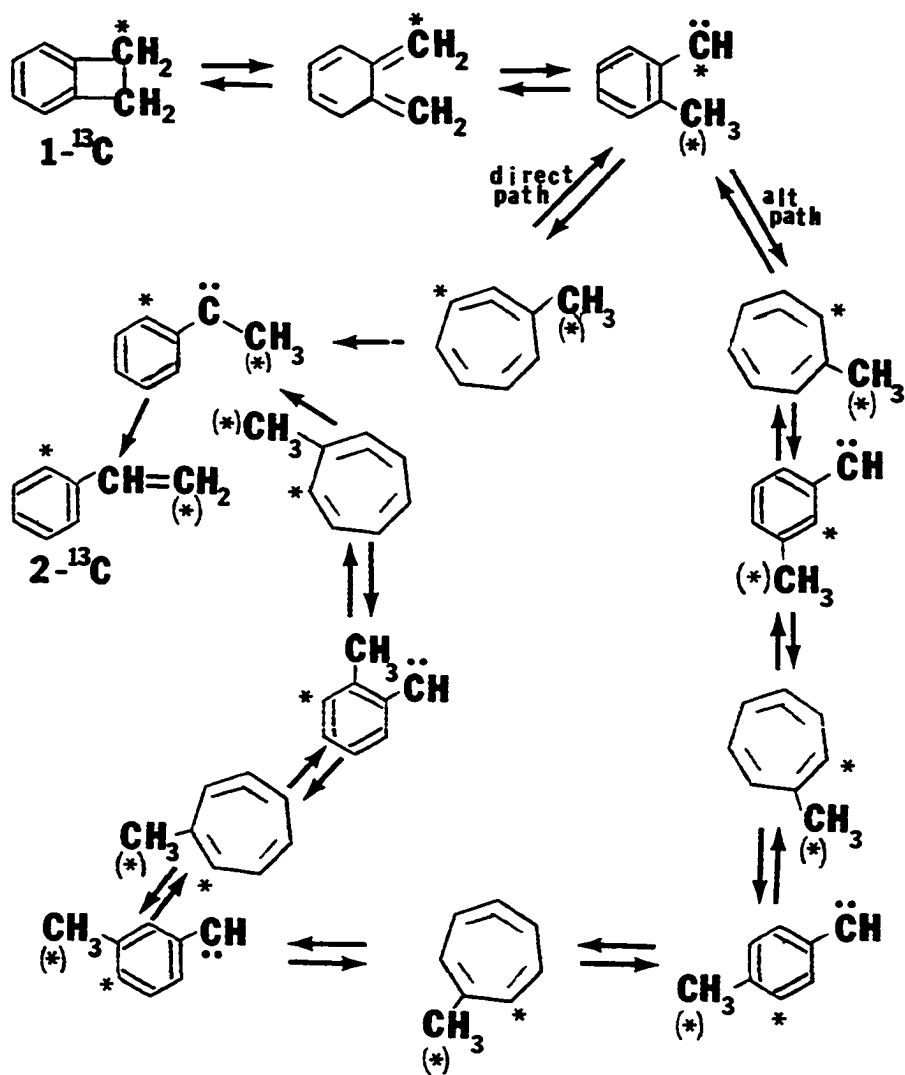
Subsequent irradiation ( $>284$  nm) produced the ring-closed isomer 1. The irradiation of ortho-tolylmethylene 69a also produced a small amount of ring-expanded 1-methyl-1,2,4,6-cycloheptatetraene 69b. Further irradiation or warming to 80 K in a xenon matrix 69b produced styrene 2.



Through a private communication, concurrent with our preliminary investigations, we learned that Chapman and Tsou were investigating the pyrolysis of benzocyclobutene utilizing a  $^{13}\text{C}$ -labeled benzocyclobutene. Their recently published [1] results outline the synthesis and pyrolysis of  $1\text{-}^{13}\text{C}$ -benzocyclobutene ( $1\text{-}^{13}\text{C}$ ) under FVP conditions similar to our own. Analysis of the pyrolyzate revealed that the  $^{13}\text{C}$  label was in the beta- and one of the ortho-positions of the styrene ( $2\text{-}^{13}\text{C}$ ). The "simple" mechanism predicted that the label should have been in the alpha- and beta-positions, thus, it was easily ruled out. It was concluded that only the mechanism involving arylcarbene/cycloheptatetraene isomerizations could account for the observed labeling pattern as shown in Scheme I.

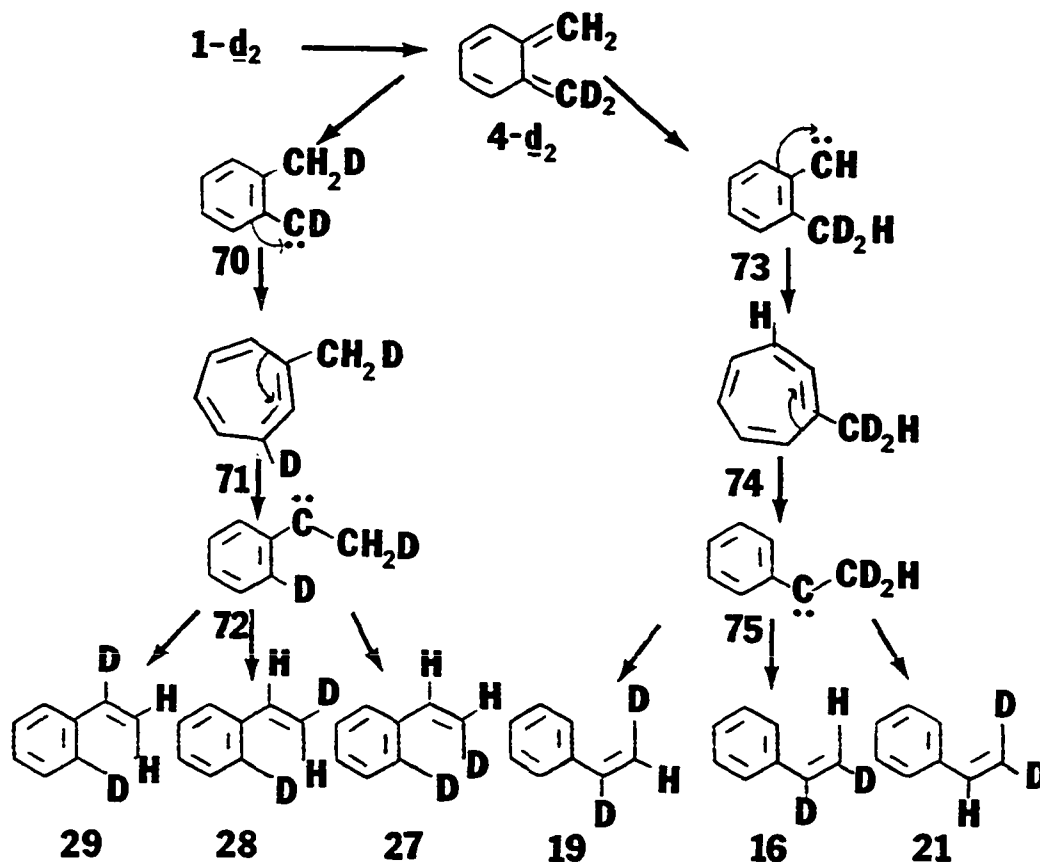


Scheme I



Examining our results (Scheme II) concerning the pyrolysis of benzocyclobutene-1,1-d<sub>2</sub> (1-d<sub>2</sub>), it may be seen that the arylcarbene mechanism accurately predicts the product distribution which we

Scheme II

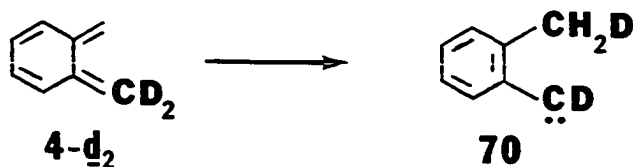


observed. Benzocyclobutene (**1**) opens to ortho-quinodimethane (**4-d<sub>2</sub>**) which then undergoes a hydrogen shift to give the benzylidene **70** which inserts and ring-expands to give cycloheptatetraene **71**. The cycloheptatetraene **71** may then open (non-degeneratively) to produce the methylphenylcarbene **72**, which may then either C-H or C-D insert

to give the observed products 27, 28 and 29. Likewise, the other three dideuteriostyrenes 16, 19 and 21 are produced by the parallel pathway.

#### Deuterium Isotope Effect

If one examines the overall scheme for the pyrolysis of benzo-cyclobutene-1,1-d<sub>2</sub> (1-d<sub>2</sub>), it may be noted that there are several occasions wherein a deuterium isotope effect may be measured. The first instance involves the conversion of ortho-quinodimethane (4) to the tolylcarbene 70 or 73 in which a formal 1,3-H shift occurs. In this instance, there are no analogous cases which may be cited from the literature, nor are there any experimental schemes which may be devised to test it.

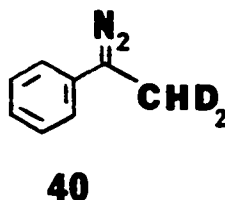
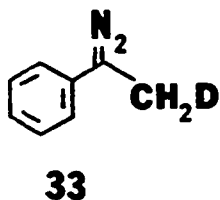


The second shift, wherein a deuterium isotope effect may be seen, involves the C-H(D) insertion of the carbene 72 or 75. In fact, by noting the relative yields of the six styrene-d<sub>2</sub> species it may be seen that styrene 21 which is formed by the shift of two

hydrogen (protium) atoms is present in the largest amount (47.6%). Examining the other end of the scale, the styrene 29 which results from the shift of two deuterium atoms is the lowest yield species (6.7%). A simple computer analysis [47] reveals that the observed distribution will result if a value of ca. 2.5 is given for both of the isotope effects which may be involved.

The literature precedent for an isotope effect of this magnitude, at elevated temperatures [48-52], is not totally unique. However, the observation of a significant isotope effect at elevated temperatures is somewhat unique. Significantly, it has been theoretically shown that as the temperature is increased the isotope effect should approach unity [48]. A kinetic isotope effect of 2.8 has been reported [52] for the pyrolytic acetate elimination of a deuterated phenyl substituted acetate. A result reported by Trahanovsky and Ong [51] indicates a deuterium isotope effect of 2.9 for the pyrolysis of a deuterated dicinnamyl oxalate at 570°C. Thus, our value of ca. 2.2 is certainly within the established bounds for such an isotope effect.

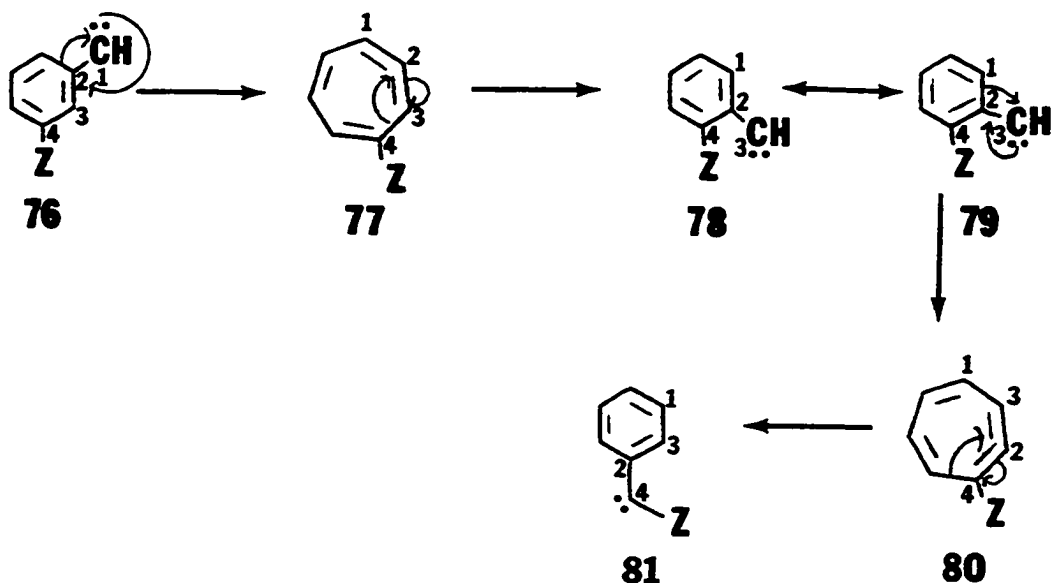
The generation of one of the carbene intermediates which we postulated to be present gave corroborative evidence for an isotope effect of the observed magnitude. The pyrolytic formation of both  $\beta$ -d<sub>1</sub>- and  $\beta$ , $\beta$ -d<sub>2</sub>-methylphenylcarbene, from their respective diazo compounds (33 and 40), showed that styrene (2) is the sole product and that an isotope effect of ca. 2.2 was observed for each of the



carbenes. This important result also gives further confirmation of the isotope effect value found in the pyrolysis of benzocyclobutene-1,1-d<sub>2</sub> (1-d<sub>2</sub>).

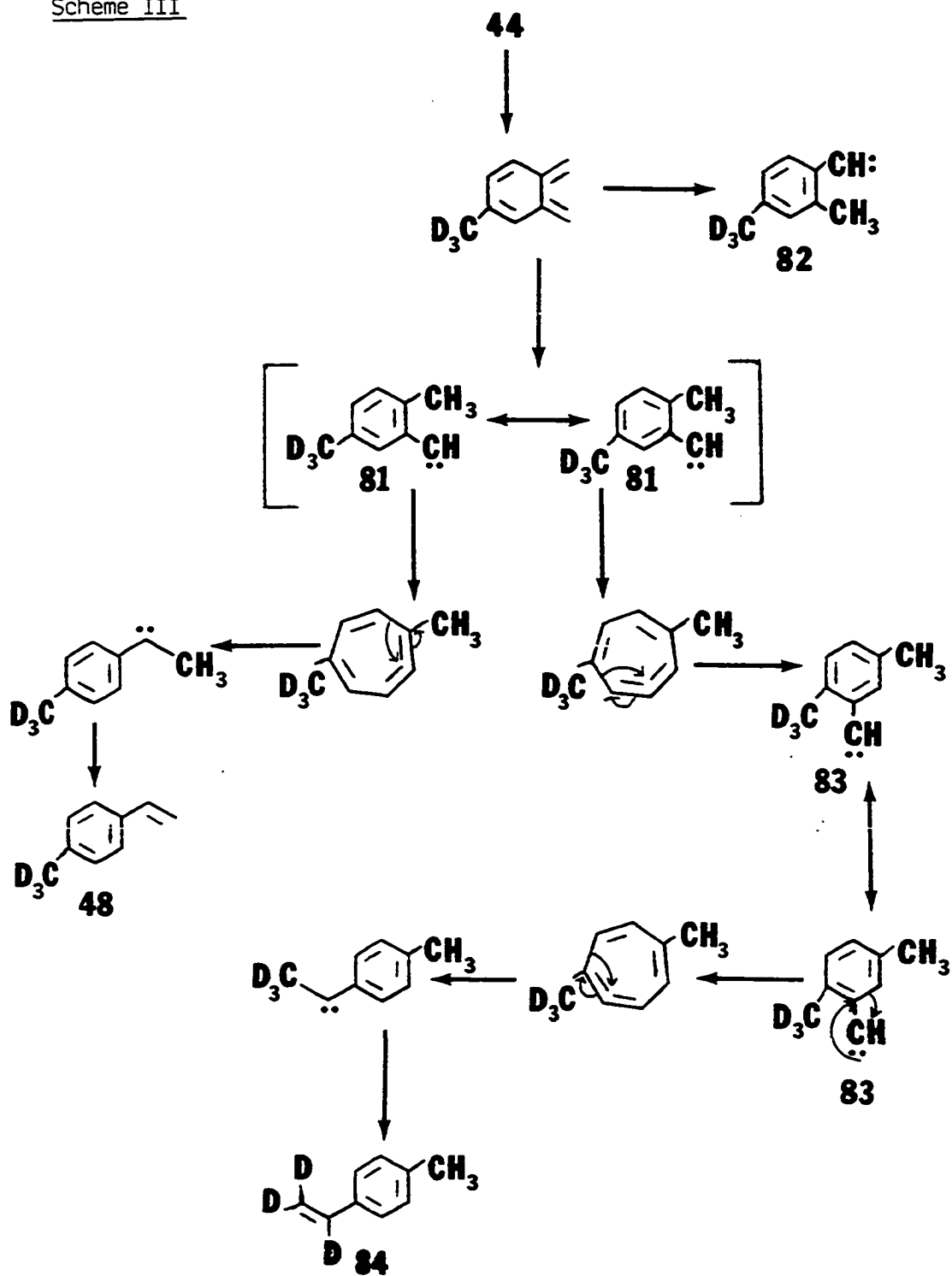
#### Phenylcarbene Migration

One of the more unusual aspects of the chemistry surrounding arylcarbenes is their propensity for migrating around an aromatic nucleus. Work has shown that the carbene undergoes a "walk" around the aromatic ring [39-46] (76-80), if no other avenues of reaction are open to it. The "walk" pertains to the perceived illusion of the initially formed carbene migrating toward adjacent unoccupied locations on the aromatic ring, hence, walking around the ring. Our interest in this phenomenon led us to perform several experiments which involved the pyrolysis of specifically labeled benzocyclobutenes as well as presumed carbene intermediates.



We expected the pyrolysis of 4-methyl- $d_3$ -benzocyclobutene (44) to produce a mixture of deuterated methylstyrenes in which the deuterium label was in the tolylmethyl group and more importantly, in the vinyl group. In Scheme III are outlined the two possible directions for migration of carbene 81. The most direct route (to 48) involves ring expansion of 81 away from the "light" methyl group. The alternative path involves ring-expansion toward the light methyl group and closure to give carbene 83. A second ring-expansion and closure leads to the production of para-methylstyrene- $\alpha,\beta,\beta$ - $d_3$  (84). If compound 84 was formed it would be immediately identifiable through its  $^2\text{H}$  NMR spectrum due to the vinyl- $d_3$  group. A similar treatment of arylcarbene 82 would produce meta-methyl- $d_3$ -styrene 49, the other expected product.

Scheme III

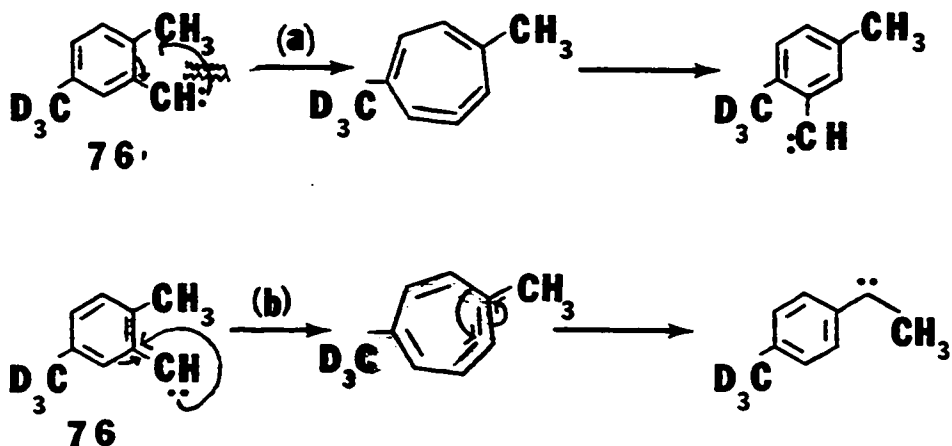


It was with great surprise that we failed to observe any deuterium signals in the vinyl region of the  $^2\text{H}$  NMR spectrum. This result meant that either the proposed carbene mechanism was not operative or that for some reason the direction of migration was being influenced to produce only the methyl- $\text{d}_3$ -styrenes. Of the two carbene intermediates which we had postulated, 2-methyl-5-methyl- $\text{d}_3$ -phenylcarbene (81) was the one which we reasoned would have the highest probability of exhibiting migration toward the methyl- $\text{d}_3$  group.

The pyrolyzate resulting from the thermal decomposition of the diazo precursor of 2-methyl-5-methyl- $\text{d}_3$ -phenylcarbene (81) had deuteria in only the methyl region and none in the vinyl region as proven by both the  $^1\text{H}$  and  $^2\text{H}$  NMR spectra. This allowed the retention of the originally proposed carbene mechanism since these results corroborated the previous results of the pyrolysis of 4-methyl- $\text{d}_3$ -benzocyclobutene (44). However, it did necessitate a change in the proposed mechanism concerning the mobility of the carbene. The experimental results indicated that the presence of the ortho-methyl group effectively blocked one direction of the "walk" so that the carbene ring-expanded in a manner such that only the undeuterated methyl group was attacked.

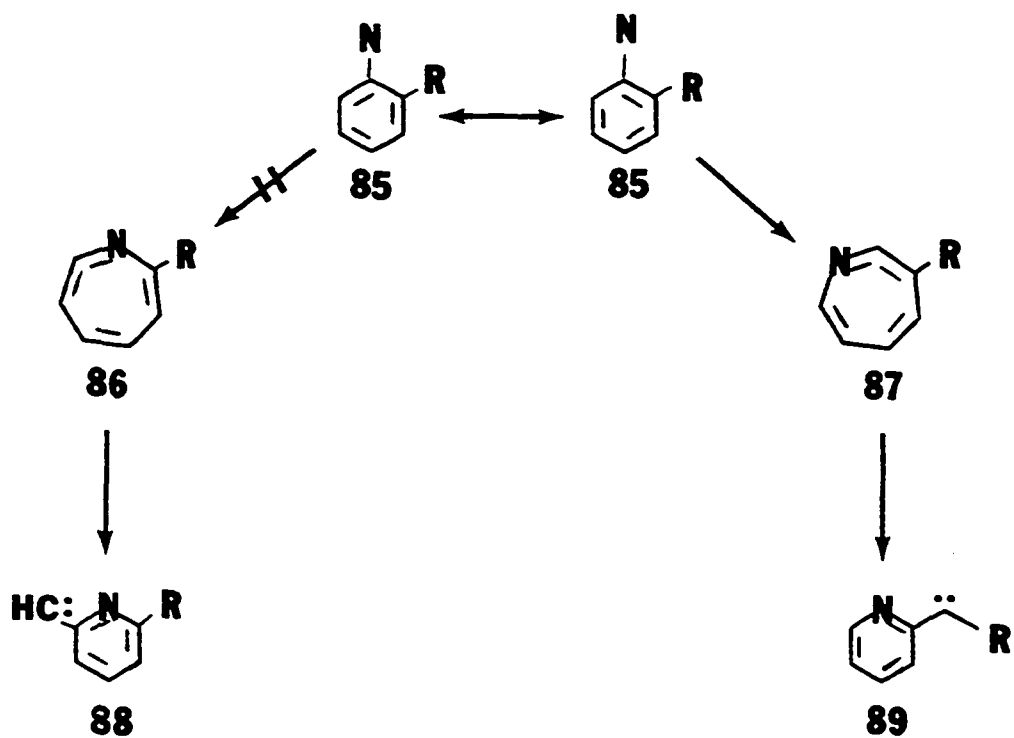
A possible explanation involves the movement of the tolylcarbene relative to the ortho-methyl group. In the pathway (a) it may be seen that the carbene must move towards the methyl group, thus, setting up a situation of increased steric strain. However, the





second pathway (b) requires that the carbene move away from the ortho-methyl group, creating a situation of alleviated steric strain. Thus, the avoidance of steric strain appears to influence the direction of attack such that only reaction with the "close" methyl group occurs.

A similar migrational preference has been cited by Gleiter et al. in an article concerning ring-expansion in aromatic nitrenes and carbenes [53]. In this case, the migration involves the movement of a phenylnitrene either towards or away from a substituent R. Their experimental results show that the nitrene 85 undergoes a unidirectional migration away from the R group to give 87. Their explanation involves the interaction between the nitrene center and the R substituent. They state that if the nitrene moves towards R (to give 86), there

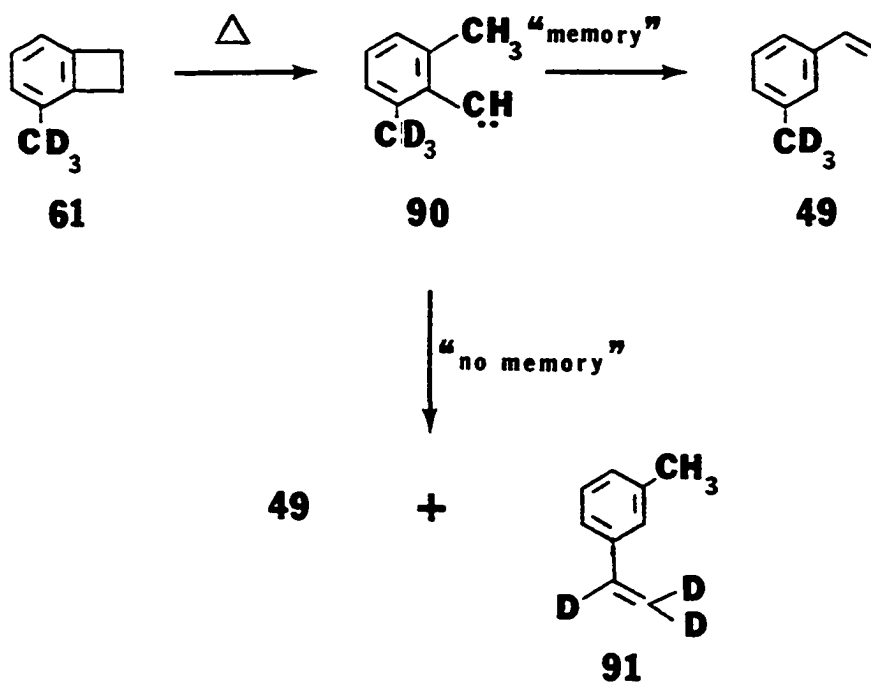


is a high probability that the nitrene will react with R or transfer kinetic energy to R, losing the necessary momentum for ring expansion.

We feel that our argument for steric control of the migrational selectivity is a strong one and beyond that is a very straightforward one which explains the facts concisely. It is this simplicity that makes our mechanism so universal, not only does it explain our

results but it also can easily apply to Gleiter's nitrene case. That is, the steric interaction between the nitrene and R substituent will be alleviated by movement away from each other to give 87 and not 86.

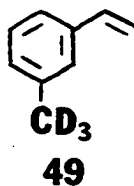
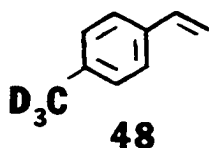
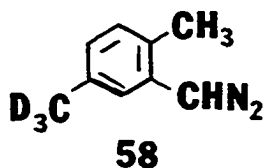
An effort to further extend the unusual migrational control shown with the FVP of 4-methyl-d<sub>3</sub>-benzocyclobutene (44) was made by studying the pyrolysis of 3-methyl-d<sub>3</sub>-benzocyclobutene (61). It was felt that 2-methyl-d<sub>3</sub>-6-methyl phenyl carbene (90) formed during the pyrolysis might exhibit a "memory effect" displayed by a preferential insertion into the non-deuterated methyl group resulting from the first hydrogen migration. Such a preferential migration



would produce only meta-methyl-d<sub>3</sub>-styrene (49), however, given a lack of memory, meta-methylstyrene- $\alpha,\beta,\beta$ -d<sub>3</sub> (91) would also be formed in addition to the aforementioned 49. Thus, any vinyl signals present in the <sup>2</sup>H NMR would necessitate the "no memory" pathway.

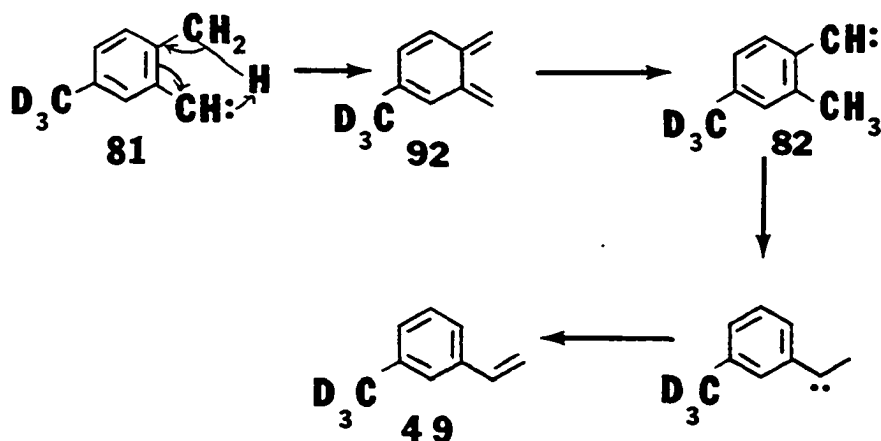
The pyrolyzate's <sup>2</sup>H NMR spectrum did, in fact, contain absorbances at 6.8, 5.8 and 5.2 ppm indicative of deuterium incorporation in the vinyl group. It appears that there is no interaction that remains between the undeuterated methyl group (from which the carbene was parented) and the carbene which allows it to differentiate between the deuterated methyl group and the undeuterated one.

An interesting secondary observation of the pyrolysis of 2-methyl-5-methyl-d<sub>3</sub>-diazabenzylidene (58) was the formation of two methyl-d<sub>3</sub>-styrenes, the expected para- isomer 48 (70%) as well as the meta-methyl-d<sub>3</sub>-styrene (49) (18%). A possible source of the unexpected isomer could have been the secondary pyrolysis of 4-methyl-d<sub>3</sub>-benzocyclobutene (44) which we already had established gave both 48 and 49



upon pyrolysis. However, in view of the low temperatures (810°C) employed, the extent of secondary pyrolysis would have been < 1.0%, hardly enough to explain the significant yield of the meta- compound.

In reviewing the mechanism, one may see that the methyl substituted carbene 81 could revert back to the ortho-quinodimethane 92 and form either of the two different carbenes (81 or 82). Following the non-degenerative pathway and carrying the process to its conclusion,

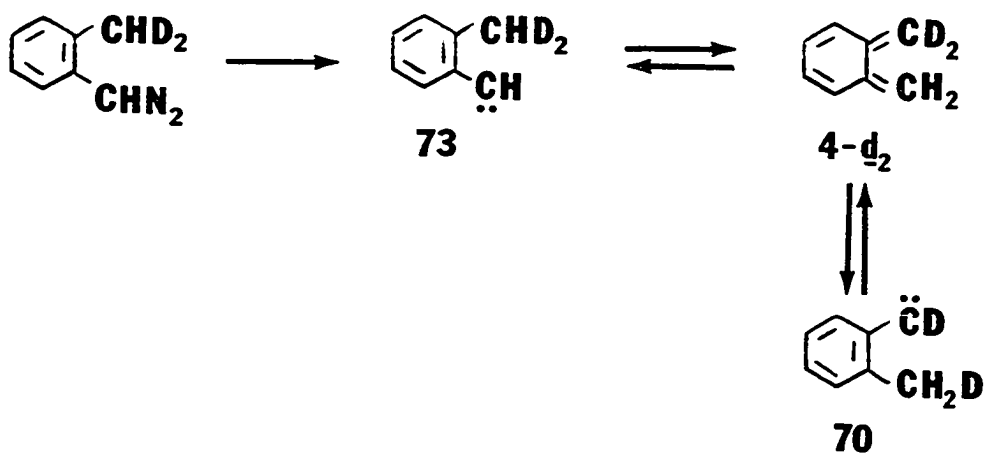
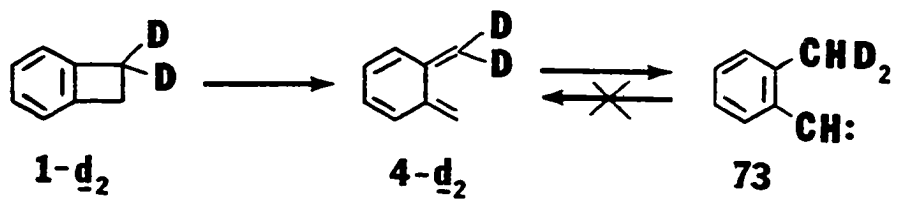


results in the formation of the meta-methyl- $d_3$ -styrene (49), which would not be produced if the reaction was not reversible.

A plausible extension of this conclusion is that experiments performed with the labeled benzocyclobutenes may also be interconverting between the ortho-quinodimethane and phenylcarbene intermediates. Such a condition would have dire consequences on the distribution of the deuterium label in the pyrolysis of benzocyclobutene-1,1- $d_2$  ( $1-d_2$ ). If wholesale interconversion was occurring, the deuterium label would

be completely randomized, eliminating any evidence for a deuterium isotope effect. However, our results indicate an isotope effect of ca. 2.2 indicating that there is little or no reversibility occurring in this reaction.

A seeming contradiction is apparent in these two results, one which may be resolved by hypothesizing that the same carbene is formed at two distinctly different times (and therefore points) in the pyrolysis tube by the two different methods of generating the carbene. It may be assumed that under our FVP conditions the carbene formed by the diazo decomposition will be formed earlier in the hot tube than that from the FVP of benzocyclobutene (1). Evidently, it is this early formation that allows the diazo generated carbene to "react" further producing secondary compounds indicative of reversal of the carbene to ortho-quinodimethane (4). The carbene from the FVP of 1, generated later in the hot tube, has only enough energy to produce the styrenes resulting from a non-reversing mechanism.



## EXPERIMENTAL

## General

The general methods and apparatus for flash chromatography have been described [54a]. The flash vacuum pyrolysis (FVP) method and apparatus have been described [54b]. Gas chromatographic analysis was performed on a Hewlett Packard 5840-A gas chromatograph utilizing either a 20 m SP 2100 (methylsilicone fluid) or a 30 m DB-1 (methylsilicone fluid) fused silica capillary column and a flame ionization detector. Combined gas chromatographic/mass spectra (GCMS) analyses were performed on a Finnigan 4000 GCMS with an Incos 2500 data system and Finnigan 9610 gc. High resolution mass spectra and exact mass determinations were recorded with an Associated Electronics Industries MS-902 instrument.

$^1\text{H}$  NMR spectra were obtained on a Varian Associates EM-360 A/L, Bruker WM 300 or Nicolet NT 300.  $^2\text{H}$  NMR were obtained on a Bruker WM 300.  $^{13}\text{C}$  NMR were recorded on either a JEOL FX-90Q or a Nicolet NT 300 spectrometer.

Infrared spectra were recorded on a Beckman Acculab II spectrometer using NaCl plates or a micro solution cell (50  $\mu\text{L}$ ). FT-IR were recorded on an IBM FTIR model 98. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

The commercially available chemicals are listed in Table 9.



Table 9. Commercially available compounds

Compound	Source
Acetophenone	Fisher Scientific Company
Bromine	Baker Chemical Company
Tetra N-butyl ammonium fluoride	Aldrich Chemical Company
t-Butyldimethylsilyl chloride	Aldrich Chemical Company
2-Carbomethoxybenzyl chloride	Bruce Surber
Ceric ammonium nitrate	Baker Chemical Company
<u>meta</u> -Chloroperbenzoic acid	Aldrich Chemical Company
Chloroform- <u>d</u>	Aldrich Chemical Company
Deuterium gas	Air Products
Deuterium oxide	KOR
Imidazole	Aldrich Chemical Company
Lithium aluminum deuteride	Aldrich Chemical Company
Lindlar's catalyst	Aldrich Chemical Company
<u>ortho</u> -Methylbenzyl chloride	Aldrich Chemical Company
Methyl- <u>d</u> <sub>3</sub> iodide	Aldrich Chemical Company
<u>meta</u> -Methylstyrene	Aldrich Chemical Company
<u>ortho</u> -Methylstyrene	Aldrich Chemical Company
<u>para</u> -Methylstyrene	Aldrich Chemical Company
<u>para</u> -Toluenesulfonyl hydrazide	Aldrich Chemical Company
Perchloric acid	Baker Chemical Company
Phenylacetylene	Aldrich Chemical Company
Quinoline	Fisher Scientific Company
Styrene	Aldrich Chemical Company
<u>ortho</u> -Toluic acid	Aldrich Chemical Company
Trimethylsilyl chloride	Aldrich Chemical Company
<u>para</u> -Xylene	Aldrich Chemical Company

Benzocyclobutene (1)

The synthesis of 1 is based on the thermolysis route reported by Loudon et al. [15]. ortho-Methylbenzyl chloride (7) (1.2786 g, 9.0932 mmol) was placed in the sample head of the FVP system and pyrolyzed at 800°C. Upon completion of the pyrolysis, the product was taken up in pyridine (5 mL) and transferred to a round-bottomed flask with an attached reflux condenser and the contents were heated to 50°C for ca. 1 h. After the mixture was cooled to room temperature, the resulting precipitate was filtered and the liquid was drained into a separatory funnel containing 10% HCl (20 mL). Pentane (10 mL) was added to the mixture, the HCl solution was drained off, this procedure was repeated 2 more times then 10% CuSO<sub>4</sub> solution (2 x 10 mL) was substituted. The pentane solution was then dried over MgSO<sub>4</sub>, filtered, then concentrated and distilled (bp 52°C at 15 min) to give benzocyclobutene (1) (0.6614 g, 6.36 mmol, 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.02 (m, 4 H), 3.18 (s, 4 H); [lit. [55] <sup>1</sup>H NMR δ 7.05 (m, 4 H), 3.15 (s, 4 H)]; IR (cm<sup>-1</sup>, neat film) 3085 (m), 2980 (s), 2945 (s), 1465 (m), 715 (m).

Benzocyclobutene-1,1-d<sub>2</sub> (1-d<sub>2</sub>)

ortho-Toluic acid (20.00 g, 0.15 mole) was added to dried MeOH (250 mL) and stirred until dissolved. Acetyl chloride (25 mL) was then added dropwise to the ice bath cooled reaction flask. After 8 h, TLC showed there was no starting material present. Pentane (100 mL) was added and the mixture was transferred to a separatory funnel.

The organic portion was removed then the aqueous portion was extracted with 1:1 Et<sub>2</sub>O/pentane (2 x 100 mL), the organic portions were combined, washed with saturated NaHCO<sub>3</sub> (3 x 75 mL), H<sub>2</sub>O (1 x 75 mL), dried over MgSO<sub>4</sub>, filtered and concentrated. The residue was vacuum distilled (bp 104.5-5°C at 25 mm) to give methyl ortho-toluate 15 (15.24 g, 0.10 mole, 67% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.95 (m, 1 H), 7.30 (m, 3 H), 3.90 (s, 3 H), 2.65 (s, 3 H); [lit. [56] <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 7.86-7.27 (m, 4 H), 3.82 (s, 3 H), 2.55 (s, 3 H)].

To a stirred slurry of LAD (190 mg, 4.5 mmol) in Et<sub>2</sub>O (25 mL) was added methyl ortho-toluate (15) (1.07 g, 7.13 mmol), upon complete addition the mixture was stirred for 2 h before quenching with 0.2 mL H<sub>2</sub>O, 0.2 mL 15% NaOH and 0.4 mL H<sub>2</sub>O. The resultant solids were filtered and the total volume was increased to ca. 40 mL with Et<sub>2</sub>O prior to washing with saturated NaCl (2 x 20 mL). The ethereal layer was then dried over MgSO<sub>4</sub>, filtered and concentrated to give ortho-methylbenzyl alcohol- $\alpha,\alpha$ -d<sub>2</sub> (14) (1.01 g, 8.15 mmol, 114%). <sup>1</sup>H NMR δ (CDCl<sub>3</sub>) δ 7.10 (m, 4 H), 4.20 (br s, 1 H), 2.20 (s, 3 H); IR (CDCl<sub>3</sub>, cm<sup>-1</sup>) 3630, 3460, 3090, 3040, 2950, 2880, 2220, 2140, 2090.

To a stirred solution of ortho-methylbenzyl alcohol- $\alpha,\alpha$ -d<sub>2</sub> (14) (399.8 mg, 3.22 mmol) in benzene (6 mL), was added SOCl<sub>2</sub> (2.75 mL). The solution was stirred for 30 min at room temperature then heated to reflux for an additional 45 min. The SOCl<sub>2</sub> was removed with an H<sub>2</sub>O aspirator, the product was then concentrated to give ortho-methylbenzyl chloride- $\alpha,\alpha$ -d<sub>2</sub> (7-d<sub>2</sub>) (325.7 mg, 2.27 mmol, 70%).

Co-injection with a commercial sample of ortho-methylbenzyl chloride produced no new GLPC peaks.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.15 (s, 4 H), 2.30 (s, 3 H); [lit. [17]  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  7.15 (br s, 4 H), 2.40 (s, 3 H)].

The preparation of  $\underline{1-d}_2$  has been described by Morello and Trahanovsky [17]. The sample head of the pyrolysis apparatus was loaded with the deuterated ortho-methylbenzyl chloride ( $\underline{7-d}_2$ ) (ca. 300 mg) and pyrolyzed in the normal manner except that the sample head was cooled in a Dry Ice/ $\text{CCl}_4$  ( $-33^\circ\text{C}$ ) bath. Upon termination of the pyrolysis, the trap was disconnected and the contents were allowed to warm to room temperature. Pyridine (5 mL) was added to the mixture which was transferred to a round-bottomed flask with a condenser affixed, the solution was heated to  $60^\circ\text{C}$  for 2 h before cooling to room temperature. The solid pyridinium chloride was removed by filtration. The pyridine was removed by adding pentane (5 mL) then washing with 10% HCl (2 x 5 mL), 10%  $\text{CuSO}_4$  solution (2 x 5 mL), the pentane solution was dried over  $\text{MgSO}_4$ , filtered, then concentrated to give benzocyclobutene-1,1- $\underline{d}_2$  ( $\underline{1-d}_2$ ) (ca. 70% GLPC yield), which was identical to the undeuterated material in all expected respects.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.12 (m, 4 H), 3.21 (br s, 2 H); [lit. [17]  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  6.95 (m, 4 H), 3.10 (s, 2 H)];  $^2\text{H}$  NMR (pentane)  $\delta$  3.20 (s, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  126.63, 126.14, 122.40, 29.33 (singlet superimposed over a weaker quintet); Mass Spec (20 eV) m/e (rel. intensity) 106 ( $\text{P}^+$ , 100).

4-Methylbenzocyclobutene (8)

The procedure of von Braun and Nelles [16] was followed. To para-xylene (21.24 g, 0.20 mole), in a 250-mL round-bottomed flask, was added 36% formalin (21.38 g) and concentrated HCl (100 g). A reflux condenser was affixed and HCl gas was passed into the solution while heating for 7 h at 60-70°C. The mixture was cooled to room temperature then Et<sub>2</sub>O (100 mL) was added with stirring to take up the organic oil. The solution was then washed with saturated NaHCO<sub>3</sub> (3 x 25 mL), H<sub>2</sub>O (1 x 25 mL) and dried over MgSO<sub>4</sub>. The mixture was filtered, concentrated then the residue was vacuum distilled (bp 59-60°C at 0.1 mm) [lit. [16] 103°C at 12 mm] to give 9 (3.00 g, 0.02 moles, 10%), which was > 97.5% pure by GLPC. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.00 (m, 3 H), 4.50 (s, 2 H), 2.35 (s, 3 H), 2.28 (s, 3 H).

The sample head of the pyrolysis apparatus was loaded with 2,5-dimethylbenzyl chloride (9) (610.6 mg, 3.95 mmol) which was pyrolyzed at 710°C. Upon completion of the pyrolysis, the products were taken up in pentane (8 mL) and washed with saturated NaHCO<sub>3</sub> (3 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was dissolved in ca. 5 mL of pyridine and heated to reflux for 1 h. The resultant solids were filtered and the solution was washed with 10% HCl (2 x 10 mL), 10% CuSO<sub>4</sub> solution (2 x 10 mL), dried over MgSO<sub>4</sub>, filtered, concentrated then Kugelrohr distilled to give 8 (312.8 mg, 2.65 mmol, 67%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.02 (m, 3 H), 3.20 (s, 4 H), 2.30 (s, 3 H); [lit. [57] <sup>1</sup>H NMR δ 6.75 (br s, 1 H), 6.25 (br s, 2 H),

3.09 (s, 4 H), 2.28 (s, 3 H)];  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  145.70, 142.45, 136.22, 127.33, 123.16, 122.13, 29.22, 29.06, 21.91.

E-Styrene- $\alpha,\beta$ - $\text{d}_2$  (16)

The general procedure outlined by Lindlar and Dubuis [18] for the hydrogenation of acetylenes was followed. To a hydrogenation flask containing Lindlar's [18] catalyst (10 mg), quinoline (30  $\mu\text{L}$ ) and hexanes (7 mL), which had been thoroughly flushed with  $\text{D}_2$  gas, was added phenylacetylene (18) (167.5 mg, 1.32 mmol). The mixture was stirred and the  $\text{D}_2$  gas uptake was monitored via a leveling-bulb apparatus. When the uptake was judged to have slowed appreciably, the flask was disconnected and the catalyst was removed by filtration. The solution was then concentrated and the crude product was purified by flash chromatography (pentanes/ $\text{SiO}_2$ ), utilizing a water-cooled column. Careful removal of the pentanes by distillation gave predominantly the desired styrene isomer 16 (150.2 mg, 1.42 mmol, 108%) contaminated with a small amount of the Z-isomer.  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 7.40 (m, 5 H), 5.72 (t,  $J = 2.64$  Hz, 1 H);  $^2\text{H}$  NMR ( $\text{CHCl}_3$ )  $\delta$  6.80 (d,  $J = 2.52$  Hz, 1 D), 5.28 (s, 1 D).

Z-Styrene- $\beta$ - $\text{d}_1$  (17)

The procedure outlined by Brandsma [58] was followed. Phenylacetylene (18) (235.6 mg, 2.31 mmol) was weighed into a 10-mL round-bottomed flask containing a magnetic stir bar. After adding  $\text{Et}_2\text{O}$  (2 mL), the solution was then cooled to  $-78^\circ\text{C}$  in a Dry Ice/acetone bath. To the solution was added  $n$ -BuLi/hexanes (1.2 mL, 2.64 mmol)

in Et<sub>2</sub>O (2 mL) and the lithium acetylide was then quenched with D<sub>2</sub>O (50 μL). After warming to room temperature, H<sub>2</sub>O was added to dissolve the lithium salts and the product was extracted with pentanes (2 x 5 mL). The pentane solution was dried over MgSO<sub>4</sub>, filtered and concentrated by distillation to give phenylacetylene-2-d<sub>1</sub> (18-d<sub>1</sub>) (228.9 mg, 2.22 mmol, 96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.60–7.00 (m, 5 H), the acetylenic absorbance at 2.85 ppm was too small to integrate.

The general procedure outlined by Lindlar and Dubuis [18] for the hydrogenation of acetylenes was followed. To a hydrogenation flask containing Lindlar's [18] catalyst (10 mg), quinoline (20 μL) and hexanes (7 mL), which had been thoroughly flushed with H<sub>2</sub> gas, was added d<sub>1</sub>-phenylacetylene (18-d<sub>1</sub>) (130.0 mg, 1.02 mmol). The mixture was stirred and the H<sub>2</sub> gas uptake was monitored via a leveling-bulb apparatus. When the uptake was judged to have slowed appreciably, the flask was disconnected and the catalyst was removed by filtration. Concentration of the solution gave 17 (127.0 mg, 0.98 mmol, 96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.40 (m, 5 H), 6.67 (d t, J = 10.8, 2.6 Hz, 1 H), 5.15 (d, J = 10.8 Hz, 1 H); <sup>2</sup>H NMR (pentanes) δ 5.80 (d, J = 2.7 Hz, 1 D).

#### Z-Styrene-α,β-d<sub>2</sub> (19)

A small quantity of the E-isomer 16 (ca. 20 mg) was pyrolyzed in the normal FVP manner to give a 1:1 (by NMR) mixture of the Z- and E-isomers (19 and 16). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.40 (m, 5 H), 5.22 (t, J = 1.59 Hz, 1 H); <sup>2</sup>H NMR (CHCl<sub>3</sub>) δ 6.80 (d, J = 1.60 Hz, 1 D), 5.79 (s, 1 D).

Styrene- $\beta,\beta$ - $d_2$  (21)

The general procedure has been outlined before [26]. To acetophenone (1.9699 g, 16.34 mmol) in a round-bottomed flask was added  $D_2O$  (5 mL) and  $K_2CO_3$  (0.25 g), the mixture was then heated to maintain a gentle reflux for ca. 2 h. After two exchange cycles using fresh  $D_2O$  and  $K_2CO_3$ ,  $Et_2O$  (1 x 10 mL, 2 x 5 mL) was used to extract the product, the combined extracts were washed with  $H_2O$  (2 x 5 mL), dried over  $MgSO_4$ , filtered and then concentrated by distillation through a Vigreux column to give acetophenone- $\beta,\beta,\beta$ - $d_3$  (38- $d_3$ ) (1.84 g, 14.92 mmol, 91%).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.20 (m, 5 H); IR ( $CCl_4$ ,  $cm^{-1}$ ), 3080 (m), 2270 (w), 1685 (s).

To a stirred slurry of LAH (134.3 mg, 3.54 mmol) in  $Et_2O$  (25 mL) was added acetophenone- $\beta,\beta,\beta$ - $d_3$  (38- $d_3$ ) (920.5 mg, 7.48 mmol) in  $Et_2O$  (10 mL) over a period of ca. 10 min. After the reaction reached completion,  $H_2O$  (1 mL), 15% NaOH (2 mL) then  $H_2O$  (1 mL) were added, but no precipitate formed so more  $H_2O$  (10 mL) was added. The product was then extracted with  $Et_2O$  (3 x 10 mL), the extracts were combined, washed with saturated  $NaHCO_3$  (4 x 10 mL), dried over  $MgSO_4$ , filtered and concentrated to give  $\alpha$ -phenethanol- $\beta,\beta,\beta$ - $d_3$  (26- $d_3$ ) (0.8734 g, 6.98 mmol, 93%).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.35 (s, 5 H), 4.85 (br s, 1 H), 1.88 (br s, 1 H); FT-IR ( $cm^{-1}$ ), 3700 (m), 3100 (s), 3050 (s), 2970 (s), 2220 (w), 1258 (s), 1120 (s), 940 (s).



The method of Wissell and Tollens [59] was modified for this procedure.  $\alpha$ -Phenethanol- $\beta,\beta,\beta$ - $d_3$  ( $\underline{26-d_3}$ ) (852.0 mg, 6.81 mmol) was transferred to a round-bottomed flask and cooled to 0°C in an ice bath. After ca. 10 min,  $Ac_2O$  (0.6 mL) was added dropwise to the stirred solution. Upon complete addition, 1 drop of concentrated  $H_2SO_4$  was added and the solution was stirred for 3 h at room temperature before work up. Pentanes (10 mL) was added along with saturated  $Na_2CO_3$  (10 mL) and the mixture was stirred for ca. 15 min. The product mixture was transferred to a separatory funnel and the aqueous layer was drained off. The organic layer was then washed with  $Na_2CO_3$  (3 x 6 mL), dried over  $MgSO_4$ , filtered and concentrated. The crude material was vacuum distilled (bp 70–74°C at 6 mm) to give phenethylacetate- $\beta,\beta,\beta$ - $d_3$  ( $\underline{23}$ ) as a colorless liquid (560.6 mg, 3.35 mmol, 49%).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.44 (s, 5 H), 5.86 (br s, 1 H), 2.06 (s, 3 H); FT-IR ( $cm^{-1}$ ), 1765 (s), 1375 (m), 1245 (s), 1125 (w), 1095 (w).

$d_3$ -Phenethyl acetate ( $\underline{23}$ ) (38.0 mg, 0.23 mmol) was pyrolyzed at 416°C in the normal manner. The product  $\underline{21}$  was then dissolved in  $CS_2$ , washed with saturated  $Na_2CO_3$ , dried over  $MgSO_4$ , filtered and diluted with  $CDCl_3$ .  $^1H$  NMR ( $CS_2/CDCl_3$ )  $\delta$  7.20 (m, 5 H), 6.62 (m, 1 H);  $^2H$  NMR (pentanes)  $\delta$  5.80 (d,  $J = 2.5$  Hz, 1 D), 5.28 (d,  $J = 1.5$  Hz, 1 D).

Styrene- $\alpha$ - $\underline{d}_1$  ( $\underline{22}$ )

LAD (96.7 mg, 2.30 mmol) was transferred, utilizing an  $N_2$ -filled glove bag, to a septum-sealed 50-mL round-bottomed flask.  $Et_2O$  (5 mL) was then added with stirring, the stirring was continued for ca. 20 min. Acetophenone (637.5 mg, 5.30 mmol) was transferred to a 10-dr vial and dissolved in  $Et_2O$  (7 mL), and this solution was then added dropwise to the stirred deuteride slurry over a 15 min period. The mixture was allowed to stir for an additional 4 h afterwhich  $H_2O$  (0.1 mL), 15% NaOH (0.1 mL) then  $H_2O$  (0.2 mL) were added, the solids were then filtered and the ethereal layer was washed with saturated NaCl (2 x 15 mL), dried over  $MgSO_4$ , filtered and concentrated to give the deuterated alcohol  $\alpha$ -phenethanol- $\alpha$ - $\underline{d}_1$  ( $\underline{26-d}_1$ ) (599.7 mg, 4.90 mmol, 92%).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.30 (s, 5 H), 2.20 (br s, 1 H), 1.43 (s, 3 H); IR ( $cm^{-1}$ ,  $CCl_4$ ) 3700 (m), 3100-2950 (s), 1320 (s), 1150 (s), 940 (s).

The method of Wissell and Tollens [59] was modified for this procedure.  $\alpha$ -Phenethanol- $\alpha$ - $\underline{d}_1$  ( $\underline{26-d}_1$ ) (599.7 mg, 4.90 mmol) was stirred in a round-bottomed flask which was cooled in an ice bath,  $Ac_2O$  (0.4 mL) was added then 1 drop of concentrated  $H_2SO_4$ . After stirring for 3 h at room temperature, saturated  $NaHCO_3$  (3 mL) and  $Et_2O$  (2 mL) were added, the ether solution was then washed with saturated  $NaHCO_3$  (5 x 10 mL), dried over  $MgSO_4$ , filtered and concentrated to give phenethylacetate- $\alpha$ - $\underline{d}_1$  ( $\underline{24}$ ) (452.7 mg, 2.74 mmol, 56%).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.37 (s, 5 H), 2.05 (s, 3 H), 1.50 (br s, 3 H); IR (FT IR,  $cm^{-1}$ ) 3100-2990 (w), 1740 (m), 1250 (s).

Phenethyl acetate- $\alpha$ -d<sub>1</sub> (24) (41.9 mg, 0.25 mmol) was pyrolyzed at 416°C in the usual FVP manner. The pyrolysis trap was allowed to warm to room temperature after which CCl<sub>4</sub> (5 mL) was added to the trap. The solution was then washed with saturated Na<sub>2</sub>CO<sub>3</sub> (3 x 5 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give styrene- $\alpha$ -d<sub>1</sub> (22). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.28 (m, 5 H), 5.69 (t d, J = 2.5, 0.9 Hz, 1 H), 5.18 (m, 1 H); <sup>2</sup>H NMR (pentanes)  $\delta$  6.76 (m, 1 D).

$\alpha$ -Phenethanol-d<sub>2</sub> (26-d<sub>2</sub>)

The pyrolyzate from the FVP of 1-d<sub>2</sub>, in CDCl<sub>3</sub>, was treated with an excess of meta-chloroperbenzoic acid (12.75 mg). This solution was allowed to stand overnight after which the crystals of meta-chlorobenzoic acid were filtered on a cotton plug. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.30 (m, 4 H), 3.87 (m, 1 H), 3.30 (m, 1 H), 2.80 (m, 1 H); [lit. [60] <sup>1</sup>H NMR (neat), oxirane protons 3.62 (dd, J = 4.1, 2.5 Hz, 1 H), 2.82 (dd, J = 5.7, 4.1 Hz, 1 H), 2.52 (dd, J = 5.7, 2.5 Hz, 1 H)]; Mass Spec (70 eV) m/e (rel intensity) 122 (P<sup>+</sup>, 39), 106 (P<sup>+</sup> -CDH<sub>2</sub>, 3).

The styrene oxide 25 was dissolved in Et<sub>2</sub>O (1 mL) and added to a stirred slurry of LAH (10 mg, 0.26 mmol) in Et<sub>2</sub>O (1 mL). After 2 h, the reaction was quenched by adding 10% NaOH (1 mL) to the reaction mixture. Workup consisted of washing with saturated NaHCO<sub>3</sub> (3 x 2 mL), drying over MgSO<sub>4</sub>, filtering and removing the solvent by distillation. When co-injected with an authentic sample of  $\alpha$ -phenethanol, no new GLPC peaks were produced. <sup>1</sup>H NMR (CDCl<sub>3</sub>)

$\delta$  7.30 (m, 4 H), 4.72 (br s, 1 H), 1.82 (br s, 1 H), 1.26 (br s, 1 H);  
 Mass Spec (70 eV) m/e (rel intensity) 124 ( $P^+$ , 80), 109 ( $P^+$  -CH<sub>3</sub>,  
 23), 108 ( $P^+$  -CH<sub>2</sub>D, 100), 107 ( $P^+$  -CHD<sub>2</sub>, 98).

Acetophenone- $\beta$ -d<sub>3</sub> Tosylhydrazone (30)

KH (81.5 mg, 2.03 mmol) which had been washed with hexanes (3 x 10 mL) then dried under flowing N<sub>2</sub> was slurried with THF (20 mL) and stirred for ca. 15-min. Acetophenone (108.1 mg, 0.90 mmol) in THF (3 mL) was added dropwise to the stirred slurry. After allowing the solution to stir for a short period of time, DOAc (145  $\mu$ L, 2.50 mmol) was added in a single portion to quench the enolate. The solution was diluted with Et<sub>2</sub>O (10 mL), washed with saturated NaHCO<sub>3</sub> (3 x 7 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give acetophenone- $\beta$ -d<sub>1</sub> (31) (100.6 mg, 0.92 mmol, 99%), which was identical to commercial acetophenone in all the expected properties. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.94 (d, J = 7.2 Hz, 2 H), 7.57 (d, J = 7.2 Hz, 1 H), 7.47 (t, J = 7.4 Hz, 2 H), 2.59 (m, 2 H).

The general method of Kaufmann et al. [25] was followed. To a stirred solution of acetophenone- $\beta$ -d<sub>1</sub> (31) (68.0 mg, 0.62 mmol) in 95% EtOH (10 mL) was added para-toluenesulfonylhydrazide (196.6 mg, 1.06 mmol). The solution was heated at a gentle reflux for ca. 20 min before cooling to room temperature. Recrystallization of the crude product from EtOH/H<sub>2</sub>O gave colorless plates of 30 (146.4 mg, 0.51 mmol, 82%), mp 146-147°C [lit. [23] mp 145-147°C]; <sup>1</sup>H NMR

(CDCl<sub>3</sub>)  $\delta$  7.92 (d, 2 H), 7.65 (m, 2 H), 7.47 (br s, 1 H), 7.35 (m, 5 H), 2.42 (s, 3 H), 2.13 (m, 2 H); IR (CDCl<sub>3</sub>, cm<sup>-1</sup>) 2950, 2850, 1560, 1540, 1305, 1140, 1065.

Acetophenone- $\beta,\beta$ -d<sub>2</sub> Tosylhydrazone (37)

KH (185.9 mg, 4.60 mmol) which had been washed with hexanes (3 x 10 mL) then dried under flowing nitrogen was slurried with THF (10 mL) and stirred for ca. 5 min. The acetophenone-d<sub>3</sub> (38-d<sub>3</sub>) (190.3 mg, 1.55 mmol) in THF (10 mL) was added dropwise, to the rapidly stirred slurry. After allowing the mixture to stir for a short period of time, HOAc (287  $\mu$ L, 5.0 mmol) was added in one portion to quench the enolate. The solution was diluted with Et<sub>2</sub>O (10 mL), washed with saturated NaHCO<sub>3</sub> (3 x 7 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give the dideuterated ketone 38 (185.9 mg, 1.49 mmol, 96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.96 (d, J = 7.2 Hz, 2 H), 7.55 (d, J = 7.2 Hz, 1 H), 7.47 (t, J = 7.4 Hz, 2 H), 2.58 (s, 1 H).

The general method outlined by Kaufmann et al. [25] was followed. To a stirred solution of acetophenone- $\beta,\beta$ -d<sub>2</sub> (38) (63.5 mg, 0.52 mmol) in 95% EtOH was added para-toluenesulfonylhydrazide (96.9 mg, 0.52 mmol). The solution was heated at a gentle reflux for ca. 15 min before cooling to room temperature. Recrystallization of the crude product from EtOH/H<sub>2</sub>O gave colorless plates of 37 (135.8 mg, 0.47 mmol, 90%): mp 145–147°C [lit. [23] mp 145–147°C]; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.92 (d, 2 H), 7.65 (m, 2 H), 7.52 (br s, 1 H), 7.34 (m, 5 H), 2.42 (s, 3 H), 2.12 (m, 0.9 H); IR (CDCl<sub>3</sub>, cm<sup>-1</sup>) 2950, 2855, 1555, 1540, 1305, 1140, 1060.

4-Methyl- $d_3$ -benzocyclobutene (44)

The following pyrolysis method has been described by Surber [10]. The pyrolysis sample head was loaded with 2-methyl-4-carbomethoxybenzyl chloride (650.0 mg, 3.27 mmol) and pyrolyzed (830°C) in the usual manner. Et<sub>2</sub>O (3 mL) was added to the room temperature trap, this solution was then washed with saturated NaHCO<sub>3</sub> (3 x 2 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give a yellow liquid.

Since there was a noticeable amount of styrene impurity present, MCPBA was added to the sample to form the styrene oxide. The benzocyclobutene 47 was easily separated from the styrene oxide and other impurities by flash chromatography (5% Et<sub>2</sub>O/hexane/SiO<sub>2</sub>) to give 4-carbomethoxybenzocyclobutene (47) (190.2 mg, 1.17 mmol, 36%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.60 (m, 3 H), 3.82 (s, 3 H), 3.12 (s, 4 H); [lit. [10] <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.60 (m, 3 H), 3.80 (s, 3 H), 3.10 (s, 4 H)].

A solution of 4-carbomethoxybenzocyclobutene (47) (190.0 mg, 1.17 mmol) in Et<sub>2</sub>O (2 mL) was added to a stirred slurry of lithium aluminum deuteride (42.1 mg, 1.00 mmol) in Et<sub>2</sub>O (5 mL). The resulting mixture was stirred for 4 h before quenching with 0.1 mL H<sub>2</sub>O, 0.2 mL 10% NaOH and 0.1 mL H<sub>2</sub>O. The solids were filtered with a cotton plug, and the resultant solution was then washed with saturated NaHCO<sub>3</sub> (3 x 2 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give 4-hydroxymethyl- $\alpha,\alpha$ - $d_2$ -benzocyclobutene (46) (146.9 mg, 1.08 mmol, 92%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.20 (m, 3 H), 3.09 (s, 4 H).

NaH in oil was washed with hexanes (3 x 10 mL) to provide pure NaH (72.0 mg, 3.00 mmol). Et<sub>2</sub>O (10 mL) was added to the NaH to provide a thin slurry. A solution of 4-hydroxymethyl- $\alpha,\alpha$ -d<sub>2</sub>-benzocyclobutene (46) (288.3 mg, 2.12 mmol) dissolved in Et<sub>2</sub>O (2 mL) was added to the stirred NaH slurry. A reflux condenser was affixed and the mixture was heated at reflux for 12 h.

The alkoxide was then cooled to -22°C in a CCl<sub>4</sub>/Dry Ice slush, a solution of para-toluenesulfonyl chloride (189.2 mg, 0.99 mmol) in Et<sub>2</sub>O (3 mL) was added dropwise, and the mixture was stirred at low temperature for 2 h. The reflux condenser was removed, the flask was stoppered and stored in the freezer overnight. The resultant suspension was filtered through Fuller's Earth to give a clear, colorless solution of 4-(toluenesulfonatomethyl-d<sub>2</sub>)-benzocyclobutene (45) which was used without workup. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.80 (m, 2 H), 3.13 (s, 4 H), 2.44 (s, 3 H).

The following procedure is adapted from a method developed by Streitwieser [27]. A solution of 4-toluenesulfonatomethyl-d<sub>2</sub>-benzocyclobutene (45) in Et<sub>2</sub>O (5 mL) was slowly added to a stirred slurry of LAD (32.0 mg, 0.76 mmol) in Et<sub>2</sub>O (1 mL). This mixture was stirred overnight then quenched by adding H<sub>2</sub>O (0.1 mL), 15% NaOH (0.2 mL) and H<sub>2</sub>O (0.1 mL), the resulting precipitate was then filtered to give a colorless solution. The organic portion was washed with NaHCO<sub>3</sub> (3 x 1 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give a crude product. The product was purified by flash chromatography (pentane/SiO<sub>2</sub>) using a H<sub>2</sub>O-cooled jacketed

column. After removal of the pentanes through a Vigreux column, the product 44 was obtained as a colorless liquid (87.0 mg, 0.72 mmol, 95%) that was identical to 4-methylbenzocyclobutene (8) in all the expected respects.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.93 (m, 3 H), 3.14 (s, 4 H);  $^2\text{H NMR}$  (pentanes)  $\delta$  2.30 (br s, 3 D); Mass Spec (20 eV) m/e (rel intensity) 121 ( $\text{P}^+$ , 100).

2-Methyl-5-methyl- $\text{d}_3$ -benzaldehyde Tosylhydrazone (50)

The procedure described by Jacobsen and Wierss [33] was followed. Bromine (20 mL) was added in a single portion to ortho-toluic acid (5.00 g, 36.8 mmol), and the mixture was then stirred for 24 h. A trap consisting of an inverted funnel and a beaker of saturated NaOH solution was used to control the bromine vapor. After the bromine was removed, a solid mass remained which was dissolved in 95% EtOH and allowed to crystallize. Subsequent recrystallization from  $\text{CHCl}_3$  gave 2-methyl-5-bromobenzoic acid (56) (3.74 g, 17.4 mmol, 47%): mp 166–168.5°C [lit. [32] mp 170°C];  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J = 1.8$  Hz, 1 H), 7.56 (dd,  $J = 8.0, 1.8$  Hz, 1 H), 7.16 (d,  $J = 8.0$  Hz, 1 H), 2.60 (s, 3 H); IR ( $\text{cm}^{-1}$ ,  $\text{CCl}_4$ ) 3400–2850, 1700 (s), 1485 (w), 1415 (m), 1300 (m).

A solution of 2-methyl-5-bromobenzoic acid (56) (3.74 g, 17.39 mmol) in  $\text{Et}_2\text{O}$  (50 mL) was added to a stirred slurry of LAH (0.33 g, 8.70 mmol) in  $\text{Et}_2\text{O}$  (10 mL). The mixture was stirred for 3.5 h then quenched with 0.4 mL of  $\text{H}_2\text{O}$ , 0.4 mL of 15% NaOH solution and 0.8 mL of  $\text{H}_2\text{O}$ . The solid material was then filtered and the



solution was washed with saturated brine solution (3 x 10 mL).

The solvent was then removed to give 2-methyl-5-bromobenzyl alcohol (55) (3.08 g, 15.30 mmol, 88%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 1.7$  Hz, 1 H), 7.31 (dd,  $J = 8.0$  Hz, 1.7 Hz, 1 H), 7.03 (d,  $J = 8.0$  Hz, 1 H), 4.67 (s, 2 H), 2.27 (s, 3 H); IR ( $\text{cm}^{-1}$ ,  $\text{CCl}_4$ ) 3640 (s), 3600–3200, 3015 (w), 2940 (m), 2890 (m), 1480 (s), 1450 (m).

The general method outlined by Corey and Snider [29] was followed. To a cooled ( $0^\circ\text{C}$ ) flask containing *t*-butyldimethylsilyl chloride (1.85 g, 12.30 mmol) and imidazole (1.73 g, 25.40 mmol) was added a solution of 2-methyl-5-bromobenzyl alcohol (55) (2.02 g, 10.05 mmol) in DMF (5 mL). The solution was allowed to stir overnight. The reaction medium was then diluted with  $\text{Et}_2\text{O}$  (10 mL), transferred to a separatory funnel, and washed with saturated  $\text{NH}_4\text{Cl}$  solution (10 mL). The aqueous portion was then extracted with  $\text{Et}_2\text{O}$  (2 x 10 mL), the ethereal extracts were combined and washed with saturated  $\text{NH}_4\text{Cl}$  solution (2 x 10 mL), dried over  $\text{MgSO}_4$ , filtered and concentrated to give 2-methyl-5-bromobenzyl *t*-butyldimethylsilyl ether (54) (3.18 g, 10.09 mmol, 100%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 1.6$  Hz, 1 H), 7.26 (dd,  $J = 8.0$ , 1.6 Hz, 1 H), 6.96 (d,  $J = 8.0$  Hz, 1 H), 4.64 (s, 2 H), 2.18 (s, 3 H), 0.95 (s, 9 H), 0.11 (s, 6 H); IR ( $\text{cm}^{-1}$ ,  $\text{CCl}_4$ ) 2940 (s), 2880 (s), 2875 (s), 1480 (s), 1460 (s), 1400 (m), 1375 (m), 1175 (s), 1130 (s), 1070 (s).

To a solution of 2-methyl-5-bromobenzyl *t*-butyldimethylsilyl ether (54) (434.5 mg, 1.38 mmol) in THF (10 mL) at  $-78^{\circ}\text{C}$  (Dry Ice/*i*-PrOH) was slowly added *n*-BuLi/hexanes (1.1 mL, 2.76 mmol) [30, 31]. After 0.5 h  $\text{CD}_3\text{I}$  (97  $\mu\text{L}$ , 1.52 mmol) was added in two portions, and the mixture was then allowed to warm to room temperature by not replenishing the spent Dry Ice (ca. 3 h).

Once the mixture had warmed to room temperature, pentane (10 mL) was added and the solution was transferred to a separatory funnel.  $\text{Et}_2\text{O}$  (5 mL) was used to rinse all the residue into the funnel. The organic layer was washed with saturated brine solution (3 x 5 mL). The aqueous washes were combined then extracted with  $\text{Et}_2\text{O}$  (1 x 5 mL), and the organic extracts were combined then dried over  $\text{MgSO}_4$ , filtered and concentrated. The crude material was purified by flash chromatography (hexane/ $\text{SiO}_2$ ) to give 2-methyl-5-methyl- $\text{d}_3$ -benzyl *t*-butyldimethylsilyl ether (53) (197.2 mg, 0.78 mmol, 57%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.13 (br s, 1 H), 7.01 (d, 1 H), 6.95 (d, 1 H), 4.67 (s, 2 H), 2.24 (s, 3 H), 0.95 (s, 9 H), 0.10 (s, 6 H); IR ( $\text{cm}^{-1}$ , neat) 3800 (s), 2895 (m), 2865 (s), 1255 (m), 1075 (s), 830 (s), 770 (m).

The method of Corey and Snider [29] was utilized in the following procedure. 2-Methyl-5-methyl- $\text{d}_3$ -benzyl *t*-butyldimethylsilyl ether (53) (197.2 mg, 0.78 mmol) was stirred while  $(\text{n-Bu})_4\text{NF}$  in THF (0.86 mL, 0.78 mmol) was added in a single portion. The reaction ran to completion within 1 h,  $\text{Et}_2\text{O}$  (10 mL) was added, and then

solution was transferred to a separatory funnel. The organic portion was washed with saturated brine solution (2 x 3 mL), dried over  $\text{MgSO}_4$ , filtered and concentrated to give 2-methyl-5-methyl- $\text{d}_3$ -benzyl alcohol (52) (103.4 mg, 0.76 mmol, 97%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.17 (br s, 1 H), 7.06 (d, 1 H), 7.01 (d, 1 H), 4.65 (s, 2 H), 2.30 (s, 3 H), 1.82 (br s, 1 H); IR ( $\text{cm}^{-1}$ ,  $\text{CCl}_4$ ) 3705 (m), 3635 (m), 3500-3200 (m), 2980 (s), 2220 (w), 2140 (w), 2060 (w), 1465 (s), 1375 (m), 1030 (s), 905 (s); Mass Spec (70 eV) m/e (rel. intensity), 139 ( $\text{P}^+$ , 72), 121 ( $\text{P}^+ - \text{H}_2\text{O}$ , 100).

The general method of Trahanovsky and Young [28] was followed. A solution of 0.5 M ceric ammonium nitrate (4.7 mL) in 50% HOAc was added in a single portion to 2-methyl-5-methyl- $\text{d}_3$ -benzyl alcohol (52) (162.8 mg, 1.17 mmol), and the reaction was complete after ca. 15 min. The mixture was transferred to a separatory funnel with 10 mL of  $\text{Et}_2\text{O}$ , extracted with  $\text{Et}_2\text{O}$  (3 x 5 mL), and the combined extracts were then washed with 15% NaOH solution (4 x 5 mL), saturated brine solution (1 x 5 mL), dried over  $\text{MgSO}_4$ , filtered and concentrated. The crude reaction mixture was separated by flash chromatography (10%  $\text{Et}_2\text{O}$ /hexane/ $\text{SiO}_2$ ) to give the aldehyde 51 (37.1 mg, 0.27 mmol, 23%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  10.24 (s, 1 H), 7.60 (d,  $J = 1.6$  Hz, 1 H), 7.28 (dd,  $J = 7.7$  Hz, 1 H), 2.62 (s, 3 H); IR ( $\text{cm}^{-1}$ ,  $\text{CCl}_4$ ) 2960 (m), 2930 (m), 2860 (m), 2720 (w), 2200 (w), 2130 (w), 2050 (w), 1700 (s), 1670 (m), 1270 (m), 1060 (s); Mass Spec (70 eV) m/e (rel. intensity), 137 ( $\text{P}^+$ , 100), 136 ( $\text{P}^+ - \text{H}$ , 44), 108 ( $\text{P}^+ - \text{CHO}$ , 8).

The general method described by Kaufmann et al. [25] was followed. A solution of para-toluensulfonylhydrazine (50.4 mg, 0.28 mmol) in 95% EtOH (0.5 mL) was added to a solution of 2-methyl-5-methyl-d<sub>3</sub>-benzaldehyde (51) (37.1 mg, 0.27 mmol) in 95% EtOH (0.5 mL). The solution was heated to reflux for 15 min, cooled, and then flash chromatographed (50% EtOAc/hexane/SiO<sub>2</sub>) to give 50 (79.6 mg, 0.26 mmol, 93%) as a colorless crystalline solid mp 139–142°C [lit. [43] mp 145–146°C]. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.98 (s, 1 H), 7.87 (d, J = 8.3 Hz, 2 H), 7.74 (br s, 1 H), 7.48 (d, J = 1.3 Hz, 1 H), 7.32 (d, J = 8.3 Hz, 2 H), 7.07 (dd, J = 8.3, 1.3 Hz, 1 H), 7.03 (d, J = 8.3 Hz, 1 H), 2.41 (s, 3 H), 2.34 (s, 3 H); calcd. for C<sub>16</sub>H<sub>16</sub>D<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S calcd. C = 63.55, H = 6.01, N = 9.27; actual C = 63.66, H = 6.22, N = 9.16.

### 3-Methyl-d<sub>3</sub>-benzocyclobutene (61)

The method developed by Eaborn et al. [34,35] was followed. A solution of benzocyclobutene (189.7 mg, 1.82 mmol) in TMEDA (634.5 mg, 5.47 mmol) was cooled to -78°C in a Dry Ice/i-PrOH bath before adding n-BuLi/hexanes (2.2 mL, 5.47 mmol). The solution was stirred for ca. 10 min before allowing it to warm to room temperature. The solution was then heated to a gentle reflux and maintained at reflux for 10 h. The black solution was then cooled to 0°C in an ice bath before adding trimethylsilyl chloride (594.3 mg, 5.47 mmol) dropwise. Upon complete addition of the silyl chloride, the solution became non-homogeneous with a white precipitate

in a pale-yellow solution. The mixture was stirred for 1 h and then the reaction was quenched with 6 M HCl (15 mL). The resulting mixture of the 1-, 3- and 4-trimethylsilylbenzocyclobutenes was dissolved in MeOH (3 mL) and then 10 M HClO<sub>4</sub> (1.6 mL) was added and the solution was heated to 80°C for 15 min. Cold H<sub>2</sub>O was immediately added, the products were extracted with Et<sub>2</sub>O (3 x 1 mL), and the ethereal portions were combined, washed with saturated NaHCO<sub>3</sub> (3 x 2 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give a mixture of the 1- and 3-isomers.

This mixture was dissolved in DMSO (1 mL) and added to a solution of 10% NaOH (8 mL) in DMSO (10 mL). The resulting mixture was then heated to 50°C (under positive N<sub>2</sub> pressure) for 2 h. H<sub>2</sub>O (25 mL) was then added, the product was extracted with Et<sub>2</sub>O (3 x 5 mL), and the extracts were combined, washed with saturated NH<sub>4</sub>Cl (3 x 5 mL), H<sub>2</sub>O (1 x 5 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give the crude product which was further purified by flash chromatography (hexane/SiO<sub>2</sub>) to give 3-trimethylsilylbenzocyclobutene (63) (36.4 mg, 0.21 mmol, 12%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.30 (d, J = 8.22 Hz, 1 H), 7.17 (t, J = 8.22 Hz, 1 H), 7.04 (d, J = 8.22 Hz, 1 H), 3.20 (m, 4 H), 0.30 (s, 9 H); [lit. [35] <sup>1</sup>H NMR (neat) δ 6.90–6.30 (m, 3 H), 2.69 (s, 4 H), -0.17 (s, 9 H)]; Mass Spec (70 eV) m/e (rel. intensity) 176 (P<sup>+</sup>, 38), 161 (P<sup>+</sup> -CH<sub>3</sub>, 100).

The method of Eaborn et al. [35] was followed to produce 3-bromobenzocyclobutene (65). Bromine (33.0 mg, 0.21 mmol) in  $\text{CCl}_4$  (0.25 mL) was added to a solution of 3-trimethylsilylbenzocyclobutene (63) (36.4 mg, 0.21 mmol) in  $\text{CCl}_4$  (0.5 mL), the solution was then heated to a gentle reflux for 0.5 h, cooled to room temperature and worked up by adding  $\text{CCl}_4$  (5 mL) and then washing with 10%  $\text{NaHSO}_3$  (2 x 5 mL), and the solution was then dried over  $\text{MgSO}_4$ , filtered, concentrated, and then flash chromatographed (hexanes/ $\text{SiO}_2$ ) to give 3-bromobenzocyclobutene (65) (9.5 mg, 0.05 mmol, 24%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.28 (d,  $J = 7.9$  Hz, 1 H), 7.06 (t,  $J = 7.9$  Hz, 1 H), 6.99 (d,  $J = 7.9$  Hz, 1 H), 3.13 (s, 4 H); [lit. [35]  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  7.25–6.80 (m, 3 H), 3.10 (s, 4 H)].

#### 3-Methyl- $\text{d}_3$ -benzocyclobutene (61)

To a solution of 3-bromobenzocyclobutene (65) (134.5 mg, 0.74 mmol) in THF (5 mL) at  $-78^\circ\text{C}$  was added  $n\text{-BuLi}$ /hexanes (294  $\mu\text{L}$ , 0.74 mmol) with stirring. Stirring was continued for 15 min before adding  $\text{CD}_3\text{I}$  (47.1  $\mu\text{L}$ , 0.74 mmol), and the reaction mixture was then allowed to warm slowly to room temperature (ca. 2 h). The mixture was poured into  $\text{H}_2\text{O}$ , extracted with pentane (2 x 5 mL), and the extrates were combined and then washed with  $\text{H}_2\text{O}$  (1 x 5 mL), saturated  $\text{NaHCO}_3$  (1 x 5 mL), dried over  $\text{MgSO}_4$ , filtered and concentrated to give a crude mixture. Flash chromatography (hexane/ $\text{SiO}_2$ ) of the mixture yielded 61 (72.3 mg, 0.60 mmol, 81%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.10 (t,

$J = 7.6$  Hz, 1 H), 6.97 (d,  $J = 7.6$  Hz, 1 H), 6.87 (d,  $J = 7.6$  Hz, 1 H), 3.13 (s, 4 H); [lit. [35]  $^1\text{H}$  NMR  $\delta$  7.02 (m, 3 H), 3.10 (s, 4 H), 2.20 (s, 3 H)];  $^2\text{H}$  NMR ( $\text{CHCl}_3$ )  $\delta$  2.16 (s, 3 D); Mass Spec (20 eV)  $m/e$  (rel. intensity) 121 ( $\text{P}^+$ , 100).

#### General Pyrolysis Procedure

The sample (20 mg to gram quantities) was weighed into a round-bottomed flask. After purging the pyrolysis system with dry  $\text{N}_2$ , the sample flask was attached and the trap was immersed in liquid nitrogen. The system was opened to a vacuum pump (0.1 to 0.01 mm) and the sample was allowed to distill through the pyrolysis tube. The sample flask was usually kept at ambient temperature but it could be heated or cooled according to the volatility of the sample. Upon completion of the pyrolysis, the vacuum line was closed and dry  $\text{N}_2$  gas was slowly leaked into the system to facilitate removal of the trap. The trap was disconnected, stoppered and warmed to room temperature before adding a solvent for analysis. If a quantitative GC analysis was going to be made, the solution was transferred to a vial containing a weighed amount of biphenyl internal standard. Identification of the individual components of the pyrolyzate was based on molecular weight and fragmentation patterns, as determined by GCMS, co-injection with commercial samples,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR analysis. After each pyrolysis, the pyrolysis tube was cleaned by passing  $\text{O}_2$  gas through the tube while it was heated to  $> 800^\circ\text{C}$ .

FVP of Benzocyclobutene (1)

Benzocyclobutene (1) was transferred to the sample head and pyrolyzed as usual with the exception that the sample head was cooled in a Dry Ice/CCl<sub>4</sub> (-22°C) slurry. An oven temperature of ca. 865°C resulted in 32% conversion of 1 to styrene (2). An appropriate solvent was used depending on the analytical method. Co-injection with a commercial sample of styrene (2) produced no new GLPC peaks. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.02 (m, 5 H), 6.82 (dd, J<sub>trans</sub> = 18 Hz, J<sub>cis</sub> = 11 Hz, 1 H), 5.82 (dd, J<sub>trans</sub> = 18 Hz, J<sub>gem</sub> = 2.1 Hz, 1 H), 5.27 (J<sub>cis</sub> = 11 Hz, J<sub>gem</sub> = 2.1 Hz, 1 H).

FVP of Benzocyclobutene-1,1-d<sub>2</sub> (1-d<sub>2</sub>)

The benzocyclobutene 1-d<sub>2</sub> was pyrolyzed in the normal manner at temperatures ranging from 800-900°C to yield a complex mixture of d<sub>2</sub>-styrenes which were found to have the two deuterium atoms substituted on the vinyl positions and one of the ortho positions. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.20 (m), 6.82 (m), 5.80 (m), 5.21 (m); <sup>2</sup>H NMR (pentane) δ 7.20 (br s), 6.80 (m), 5.80 (m), 5.20 (m); Mass Spec (18 eV) m/e (rel. intensity) 106 (P<sup>+</sup>, 100).

FVP of 4-Methylbenzocyclobutene (8)

The sample head of the pyrolysis apparatus was loaded with 8 (ca. 40 mg) and the pyrolysis was carried out with a furnace temperature of 855°C. With the completion of the pyrolysis, the trap was disconnected and the contents were warmed to room temperature. The products were then dissolved in a solvent appropriate for the analytical method and compared with commercial samples.



For meta-methylstyrene (12):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.22 (m, 4 H), 6.68 (dd,  $J = 18, 11$  Hz, 1 H), 5.73 (dd,  $J = 18, 2$  Hz, 1 H), 5.21 (dd,  $J = 11, 2$  Hz, 1 H), 2.35;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  137.90, 137.57, 137.03, 128.53, 128.36, 126.95, 123.38, 113.41, 21.26.

For para-methylstyrene (13):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.30 (d, 8 Hz, 2 H), 7.13 (d, 8 Hz, 2 H), 6.68 (dd,  $J = 18, 11$  Hz, 1 H), 5.68 (d, 18 Hz, 1 H), 5.18 (d, 11 Hz, 1 H), 2.34 (s, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  137.46, 136.76, 134.92, 129.18, 126.14, 112.60, 21.10.

FVP of the Sodium Salt of d<sub>1</sub>-Tosylhydrazone (30)

The general method for the pyrolysis of the tosylhydrazone salts has been described by Kaufmann et al. [25]. The d<sub>1</sub>-hydrazone (30) (26.7 mg, 0.09 mmol) was weighed into a round-bottomed flask which was septum sealed and purged with  $\text{N}_2$  gas. MeOH (200  $\mu\text{L}$ ) was added with stirring then NaOMe/MeOH (25.0  $\mu\text{L}$ , 0.10 mmol) was added, after ca. 10 min of additional stirring the MeOH was removed on a rotary evaporator. The solid residue was washed with  $\text{Et}_2\text{O}$  (4 x 4 mL), the flask was covered with aluminum foil and the last trace of  $\text{Et}_2\text{O}$  was removed on the rotary evaporator.

The flask was then attached to the pyrolysis apparatus and wrapped with heat tape and aluminum foil. The wrapped sample head was slowly heated to 120°C and the liberated diazo compound was pyrolyzed at 820°C. The d<sub>1</sub>-styrene (2-d<sub>1</sub>) in the trap was dissolved in  $\text{CDCl}_3$  (400  $\mu\text{L}$ ) and analyzed.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.38 (m, 5 H), 6.82 (m, 100 units), 5.83 (m, 77.6 units), 5.33 (m, 74.9 units).

FVP of the Sodium Salt of  $\underline{d}_2$ -Tosylhydrazone (37)

The general method for the pyrolysis of tosylhydrazone salts has been described by Kaufmann et al. [25]. The  $\underline{d}_2$ -hydrazone (37) (18.7 mg, 0.06 mmol) was weighed into a round-bottomed flask which was septum sealed and purged with  $N_2$  gas. MeOH (200  $\mu$ L) was added with stirring then NaOMe/MeOH (22.3  $\mu$ L) was added, after ca. 10 min of additional stirring the MeOH was removed on the rotary evaporator. The solid residue was washed with  $Et_2O$  (4 x 4 mL), the flask was covered with aluminum foil and the last trace of  $Et_2O$  was removed on the rotary evaporator.

The flask was then attached to the pyrolysis apparatus and wrapped with heat tape and aluminum foil. The wrapped sample head was slowly heated to 120°C and the liberated diazo compound pyrolyzed at 820°C. The  $\underline{d}_2$ -styrene ( $\underline{2-d}_2$ ) in the trap was dissolved in  $CDCl_3$  (400  $\mu$ L) and analyzed.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.36 (m, 5 H), 6.72 (m, 100 units), 5.73 (m, 39 units), 5.23 (m, 36 units).

## Computer Estimate of the Kinetic Isotope Effect

An estimate of the isotope effects at the two unique steps was calculated using a short computer program [47]. The BASIC computer program was run on a VIC-20 microcomputer. The 4 equations which were used are given below:

$$Q = \frac{(A)(B)(100)}{(B+2)(A+1)} \quad Z = \frac{(A)(100)}{(B+2)(A+2)}$$

$$S = \frac{100}{(A+1)(1+2B)} \quad T = \frac{(100)(B)}{(A+1)(1+2B)}$$

Where A = 1st isotope effect, seen when ortho-quinodimethane isomerizes to ortho-tolylcarbene and B = 2nd isotope effect where the methyl phenyl carbene isomerizes to styrene. The variables Q, S, T and Z represent the percent amounts of the various dideuterated styrenes. The variable Q represents the amount of styrene (21) resulting from 2 protium shifts, the variable S represents the amount of styrene (29) resulting from 2 deuterium shifts. The sum of T and Z represents the amount of styrenes (16, 19, 27, 28) resulting from a deuterium and protium shift. The program was set up to generate values of Q, S, T and Z based upon values of A and B, the closest fit occurred when A = B = 2.5 giving S = 4.8, T + Z = 55.6 and Q = 39.7. The actual values found were: S = 6.7, T + Z = 45.7 and Q = 47.6.

Sample Calculation for Determining the Effect of the Deuterium  
Distribution on the Kinetic Isotope Effect

The following calculation provides a  $k_H/k_D = 2.3$  for the styrenes formed from the decomposition of the d<sub>2</sub>-diazo compound 40, a value of 2.1 is calculated in a similar manner for the d<sub>1</sub>-diazo compound 33.

Given by  $^1\text{H}$  NMR integration:

alpha protons = 100 units

beta protons = 75 units

Given by GCMS analysis:

$$\underline{d}_1 = 9\%$$

$$\underline{d}_2 = 75\%$$

Refigure % based on  $\underline{d}_1$  and  $\underline{d}_2$ :

$$9 + 75 = 84$$

$$\underline{d}_1 = 9/84 \times 100\% \quad \underline{d}_2 = 75/84 \times 100\%$$

$$\underline{d}_1 = 11\% \quad \underline{d}_2 = 89\%$$

Integral of  $\underline{d}_2$ :

$$\text{Total Integral} \times \% \underline{d}_2 = 175 \times 0.89 = 156.3$$

Integral of  $\underline{d}_1$ :

$$\text{Total Integral} \times \% \underline{d}_1 = 175 \times 0.11 = 18.7$$

Assign: X = alpha protons      Y = beta protons

$$\text{Integral of } \underline{d}_1 = 18.7 = X + Y$$

$$k_{\text{H}}/k_{\text{D}} = X/2Y = 2.5 \text{ (computer estimate)}$$

$$\text{from above: } X = 5Y$$

$$18.7 = 5Y + Y$$

$$18.7 = 6Y$$

$$3.1 = Y \text{ implies } X = 15.6$$

Returning to integral of  $\underline{d}_1 + \underline{d}_2$ :

Total alpha  $^1\text{H} = 100$       Total beta  $^1\text{H} = 75$

$$\frac{-15.6}{84.4}$$

$$\frac{-3.1}{71.9}$$

For the  $\underline{d}_2$  species:

$$k_{\text{H}}/k_{\text{D}} = 2(\text{alpha } ^1\text{H})/\text{beta } ^1\text{H}$$

$$= 2(84.4)/71.9$$

$$= 2.3$$

FVP of 4-Methyl- $\underline{d}_3$ -Benzocyclobutene (44)

The deuterium-labeled benzocyclobutene 44 was pyrolyzed at ca. 850°C producing a yellowish liquid which was dissolved in pentanes. The pyrolyzate was purified by preparative GLPC to give a > 90% relative yield of a mixture of 3- and 4-methyl- $\underline{d}_3$ -styrenes (49 and 48).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.10 (m, 3 H), 6.83 (m, 1 H), 5.72 (m, 1 H), 5.20 (m, 1 H);  $^2\text{H}$  NMR (pentanes)  $\delta$  2.30 (br s, 3 D); Mass Spec (20 eV) m/e (rel. intensity), 121 ( $\text{P}^+$ , 100).

FVP of the Sodium Salt of 2-Methyl-5-methyl- $\underline{d}_3$ -benzaldehyde  
Tosylhydrazone (50)

The pyrolysis of the undeuterated compound has been described by Van der Stouw et al. [43]. To a stirred solution of 50 (23.8 mg, 0.08 mmol) in MeOH (0.2 mL) was added a 25% solution of NaOMe/MeOH (30  $\mu\text{L}$ ) in a single portion. The solution was stirred for ca. 0.5 h before removing the MeOH under reduced pressure. Aliquots of  $\text{Et}_2\text{O}$  (3 x 2 mL) were syringed into the flask and withdrawn to

remove all traces of the MeOH. The Et<sub>2</sub>O was then removed in vacuo and the sodium salt was transferred to the pyrolysis sample head for immediate FVP.

The sodium salt of tosylhydrazone (50) was heated to ca. 90°C in the sample head, liberating the transient diazo compound. The resultant diazo compound was transferred through the hot zone by its vapor pressure, and the pyrolysis products were trapped in liquid N<sub>2</sub>. After the pyrolysis was completed the trap was disconnected (under N<sub>2</sub> gas) then allowed to warm to room temperature. A suitable <sup>1</sup>H NMR solvent (400 μL) was added, then the solution was transferred to a 5-mm tube for analysis, the solution was then concentrated, a suitable <sup>2</sup>H NMR solvent was added, and then the solution was transferred to a 10-mm NMR tube for <sup>2</sup>H NMR analysis.

For para-methyl-d<sub>3</sub>-styrene (48): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.31 (d, J = 8.1 Hz, 2 H), 7.13 (d, J = 8.1 Hz, 2 H), 6.68 (dd, J = 17.5, 10.8 Hz, 1 H), 5.69 (d, J = 17.5 Hz, 1 H), 5.17 (d, J = 10.8 Hz, 1 H); <sup>2</sup>H NMR (cyclohexane) δ 2.39 (s, 3 D); Mass Spec (20 eV) m/e (rel. intensity) 121 (P<sup>+</sup>, 100).

For the meta-methyl-d<sub>3</sub>-styrene (49): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.22 (m, 4 H), 6.68 (dd, J = 17.5, 10.8 Hz, 1 H), 5.73 (dd, J = 17.5, 2 Hz, 1 H), 5.73 (dd, J = 17.5 Hz, J = 0.6 Hz, 1 H), 5.22 (dd, J = 10.8, 0.6 Hz, 1 H); <sup>2</sup>H NMR (cyclohexane) δ 2.41 (s, 3 D); Mass Spec (20 eV) m/e (rel. intensity) 121 (P<sup>+</sup>, 100).

FVP of 3-Methyl- $\underline{\underline{d}}_3$ -benzocyclobutene (61)

The deuterated benzocyclobutene 61 (32.0 mg, 0.27 mmol) was pyrolyzed at 805°C under normal FVP conditions. The trap contents were dissolved in  $\text{CDCl}_3$  (0.5 mL) and analyzed.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.20 (m, 3 H), 6.80 (m), 5.7 (m), 5.25 (m), 2.30 (m);  $^2\text{H}$  NMR ( $\text{CHCl}_3$ )  $\delta$  6.80 (m), 5.65 (m), 5.25 (m), 2.32 (m).

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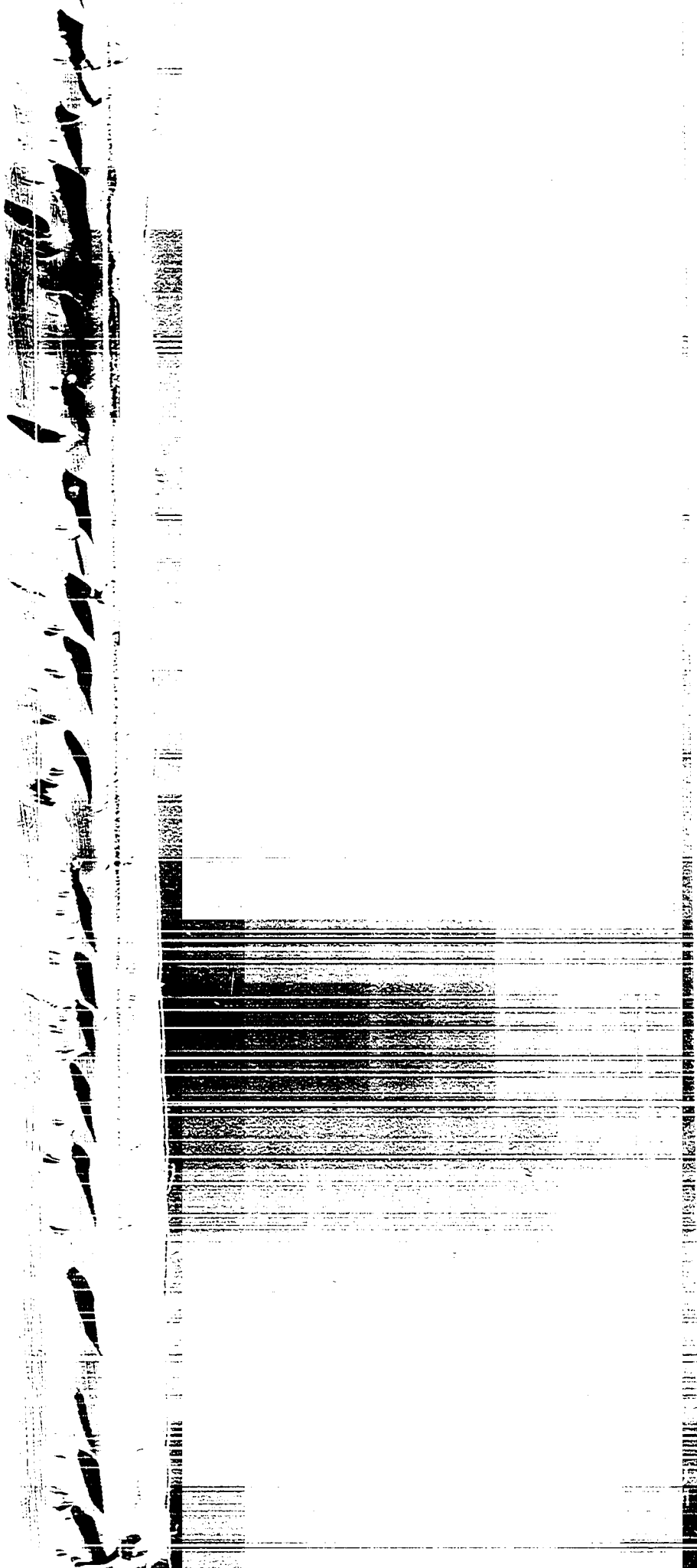
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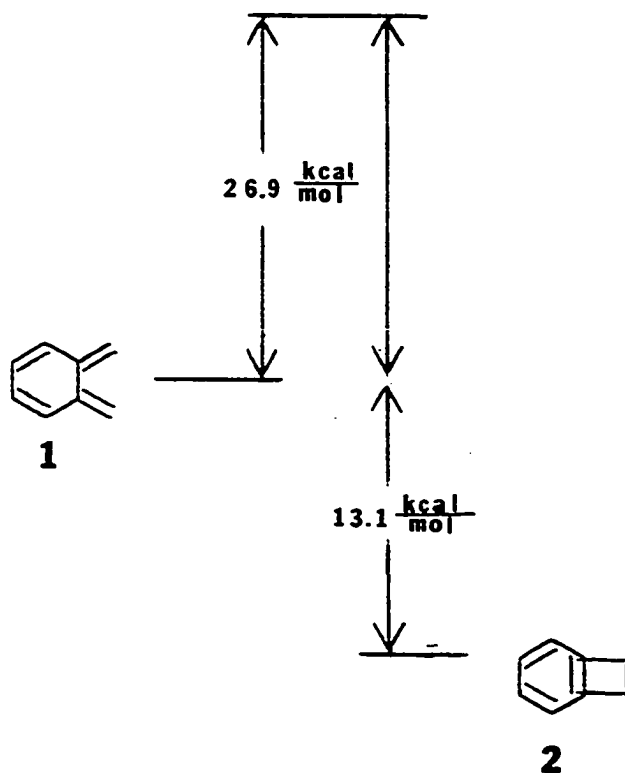
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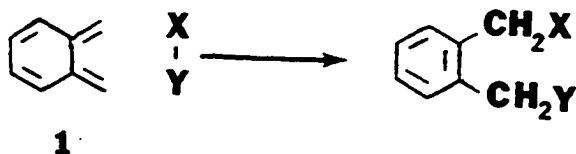


## INTRODUCTION

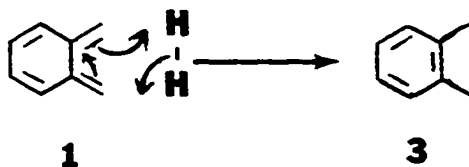
The high reactivity of ortho-xylylene (1) [1,2], a simple yet vastly interesting molecule, is without dispute. It has been generated via thermally and photochemically induced isomerizations as well as ion-induced methods [3]. Although it is formed as a transient species, its chemical reactivity and relative energetics with its isomer benzocyclobutene (2) are well known [4].



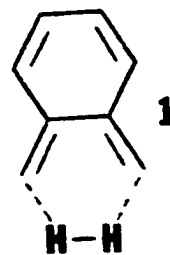
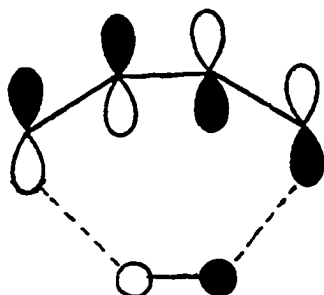
The highly reactive diene system exposed in ortho-quinodimethane (1) has led to many studies of its eneophilicity, both in an intra- and intermolecular sense [2,3,5,6]. This reactivity stems from the facts that the diene system is in a fixed cisoid conformation and also that a [4+2] addition will result in the formation of the aromatic benzene nucleus, which in itself accounts for ca. 36 kcal/mol of stability.



An intriguing possibility for study came to light when it was hypothesized that 1 might react with molecular  $H_2$  in a concerted [4+2] manner. That is, could it be possible that ortho-quinodimethane (1), generated under controlled conditions, might add hydrogen in a bimolecular, nonsurface controlled manner to give ortho-xylene (3)?



If one examines this reaction in terms of the Woodward - Hoffmann [7] selection rules, a strong argument for the reaction can be derived. The generalized statement which applies in our case is that for a  $[4q+2]$  cycloaddition (where  $q = \text{some integer}$ ) to be ground state allowed, the  $m + n$  components (where  $m$  and  $n$  are the electron components of the two interacting systems) must interact in an  $m_s + n_s$  or  $m_a + n_a$  orientation. The notation  $m_s + n_s$  denotes interaction of the two electron systems in a suprafacial orientation, the notation  $m_a + n_a$  denotes interaction of the two systems in an antarafacial manner. For our specific case, it will be necessary to consider only the exocyclic diene system of ortho-quinodimethane (1) which is a 4 electron system, thus  $m = 4$ . The molecule of hydrogen is a 2 electron system, thus  $n = 2$ . For the  $[4+2]$  addition (where  $q = 1$  and  $m + n = 6$ ), the Woodward - Hoffman rule states that the ground state (thermal) allowed interaction will either be  $[4_s+2_s]$  or  $[4_a+2_a]$ . Examination of the interacting orbitals reveals that the two electron systems will interact in an allowed  $[4_s + 2_s]$  manner.

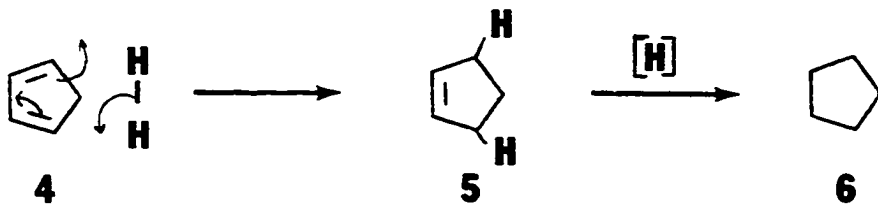


The existence of such an unprecedented reaction would have major ramifications in areas such as the petroleum industry and in coal liquefaction and gasification. Although the role of hydrogen donor solvents has been well established [8], and is certainly not going to be challenged herein, there exists the possibility that our proposed mechanism could be working in concert with the other modes of hydrogenation.

As our source of ortho-quinodimethane (1) we chose benzocyclobutene (2), since it is well known that it undergoes a thermal electrocyclic ring opening to give 1 and we were already familiar with most of the aspects of dealing with it. In order to attain high enough concentrations of H<sub>2</sub> relative to 1, the pyrolyses were run in a high pressure vessel at H<sub>2</sub> pressures between 1000 and 2000 psi at room temperature.

The hydrogenation of cyclopentadiene (cpd) (4) was also investigated when initial liquid phase pyrolyses (LPP) with the benzocyclobutene/ortho-quinodimethane system indicated that extension of the reaction seemed promising. Cyclopentadiene (4), like ortho-quinodimethane (1), has a constrained cisoid diene system amenable to the same hypothesized concerted hydrogenation as 1. However, it differs in that there is no resultant formation of an aromatic center and the product, cyclopentene (5), might also undergo further hydrogenation to give cyclopentane (6). Thus, 4 was pyrolyzed under high pressure atmospheres of H<sub>2</sub> and D<sub>2</sub> gas.



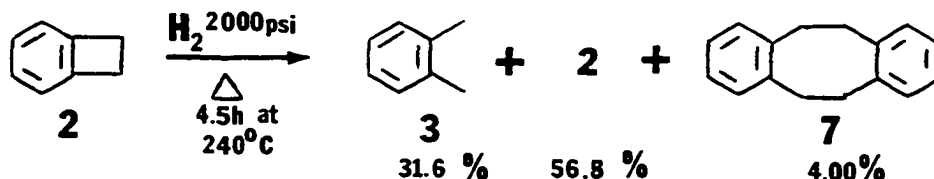


## RESULTS

## Liquid Phase Pyrolysis (LPP) of Benzocyclobutene (2)

in H<sub>2</sub> and He Gas

Freshly distilled 2, in cyclohexane or hexanes, was pyrolyzed at 240°C for 5 h in an autoclave with varying pressures of H<sub>2</sub> or He gas. The resulting clear, colorless solution was analyzed by GC co-injection and GCMS analysis of authentic samples. The simple product distribution consisted of ortho-xylene (3) and/or the [4+4] dimer of ortho-xylylene (7) [6], when 2 was pyrolyzed in an atmosphere of H<sub>2</sub> gas, (Table 1).



The yield of ortho-xylene (3) relative to the [4+4] dimer (7) plainly shows the effect of H<sub>2</sub> gas on the reactions of ortho-quinodimethane (1). In fact, when the concentration of H<sub>2</sub> gas was zero, as for the He gas liquid phase pyrolysis, the yield of 3 was zero and the sole product was the [4+4] dimer (7).

Table 1. Products and yields of the pyrolysis of benzocyclobutene (BCB) (2) in an atmosphere of H<sub>2</sub> and He gases

Product	Yields, % <sup>a</sup>				
	Run 1 <sup>b</sup>	Run 2 <sup>c</sup>	Run 3 <sup>d</sup>	Run 4 <sup>e</sup>	Run 5 <sup>f</sup>
<u>o</u> -xylene	31.6	22.5	13.2	--	--
BCB	56.8	53.7	41.6	85.4	77.8
4+4 dimer	4.00	13.7	2.80	5.20	10.6
% TRM <sup>g</sup>	92.4	89.9	64.6	90.6	88.4

<sup>a</sup>All yields are absolute GLPC yields using biphenyl as an internal standard.

<sup>b</sup>2000 psi H<sub>2</sub> gas, 240°C for 4.5 h.

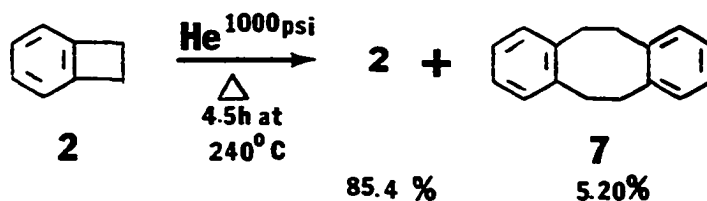
<sup>c</sup>1000 psi H<sub>2</sub> gas, 240°C for 5 h.

<sup>d</sup>1800 psi H<sub>2</sub> gas, 200°C for 24 h.

<sup>e</sup>1000 psi He gas, 240°C for 4.5 h.

<sup>f</sup>1000 psi He gas, repyrolyzed Run 4 for another 4.5 h.

<sup>g</sup>% TRM = % total recovered material =  $\Sigma$  absolute yields of all components.



#### LPP of Benzocyclobutene (2) in $D_2$ and $H_2/D_2$ Gas

The liquid phase pyrolysis was carried out with  $D_2$  gas that varied in pressure from 1700 to 1850 psi. The clear, colorless solutions contained only ortho-xylene (3) and [4+4] dimer 7. The yields of the products once again were influenced by the presence of the gas involved, as shown in Table 2.

Analysis of the low eV (14 eV) mass spectrum of the pyrolyzate in  $D_2$  gas revealed a high degree of deuterium incorporation in ortho-xylene (3). Also noteworthy was the complete lack of deuterium incorporation into the [4+4] dimer and the starting material 2. The yields of the  $d_0$ ,  $d_1$  and  $d_2$ -ortho-xylenes (3) are calculated and shown in Table 3.

The LPP of benzocyclobutene (2), in a mixture of  $D_2$  and  $H_2$  gas, produced the same products as those previously stated. The dimer 7 and 2 were again devoid of any deuterium incorporation. Analysis of the GCMS of ortho-xylene (3) revealed a mixture of  $d_0$ ,  $d_1$  and  $d_2$  species, shown in Table 4.

Table 2. Products and yields of the pyrolysis of benzocyclobutene (2) in an atmosphere of D<sub>2</sub> and H<sub>2</sub>/D<sub>2</sub> gases

Product	Yields, % <sup>a</sup>		
	Run 1 <sup>b</sup>	Run 2 <sup>c</sup>	Run 3 <sup>d</sup>
<u>o</u> -xylene	19.0	16.0	18.1
BCB	74.4	54.2	71.8
4+4 dimer	2.90	4.50	2.70
% TRM <sup>e</sup>	96.3	74.7	92.6

<sup>a</sup>All yields are absolute GLPC yields using biphenyl as an internal standard.

<sup>b</sup>1720 psi D<sub>2</sub> gas, 240°C for 5 h.

<sup>c</sup>1840 psi D<sub>2</sub> gas, 210°C for 12 h.

<sup>d</sup>100 psi H<sub>2</sub>/1900 psi D<sub>2</sub> gas, 235°C for 7 h.

<sup>e</sup>% TRM = % total recovered material =  $\Sigma$  absolute yields of all components.

#### LPP of Cyclopentadiene (4) in H<sub>2</sub> Gas

The pyrolysis of cyclopentadiene (4) in hexanes produced a clear, colorless solution which was analyzed by GLPC and GCMS means versus commercially available samples. The pyrolyzate was found to consist of starting material 4, cyclopentene (5) and cyclopentane (6) as well as the dimer of cyclopentadiene (8).

Table 3. Low eV (18 eV) GCMS analysis of *o*-xylene- $\underline{d}_2$  ( $\underline{3-d}_2$ ) resulting from the LPP of benzocyclobutene ( $\underline{2}$ ) in an atmosphere of  $D_2$  gas<sup>a</sup>

M/e	Peak Intensity of $\underline{3}$	Peak Intensity of $\underline{3-d}_2$	Calculated deuterium content <sup>b</sup>		
			$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$
105	1.2	--	--	--	--
106	100.0	2.5	2.5	--	--
107	9.0	6.4	--	6.4	--
108	0.3	100.0	--	0.6	99.4
109	--	9.0	--	--	9.0

<sup>a</sup>1720 psi  $D_2$  gas, 240°C for 5 h.

<sup>b</sup>The distribution of deuterated compounds is as follows:  $\underline{d}_0$  = 2.3,  $\underline{d}_1$  = 5.9 and  $\underline{d}_2$  = 91.8%.

In addition to comparison with commercial samples, a search of the Finnegan computer library of mass spectra also indentified the aforementioned products as those present within the pyrolyzate sample.

Table 4. Low eV (18 eV) mass spectral data of o-xylene (3-d) resulting from the LPP of benzocyclobutene (2) in an atmosphere of H<sub>2</sub> and D<sub>2</sub> gases<sup>a</sup>

M/e	Peak Intensity of <u>3</u>	Peak Intensity of <u>3-d</u>	Calculated deuterium content <sup>b</sup>		
			<u>d</u> <sub>0</sub>	<u>d</u> <sub>1</sub>	<u>d</u> <sub>2</sub>
105	1.2	--	--	--	--
106	100.0	14.1	14.1	--	--
107	9.0	36.4	1.3	35.1	--
108	0.3	100.0	--	3.2	96.8
109	--	9.2	--	--	8.7

<sup>a</sup>100 psi H<sub>2</sub>/1900 psi D<sub>2</sub> gases, 235°C for 7 h.

<sup>b</sup>The distribution of deuterated species is as follows: d<sub>0</sub> = 9.7, d<sub>1</sub> = 24.0 and d<sub>2</sub> = 66.3.

#### LPP of Cyclopentadiene (4) in D<sub>2</sub> Gas

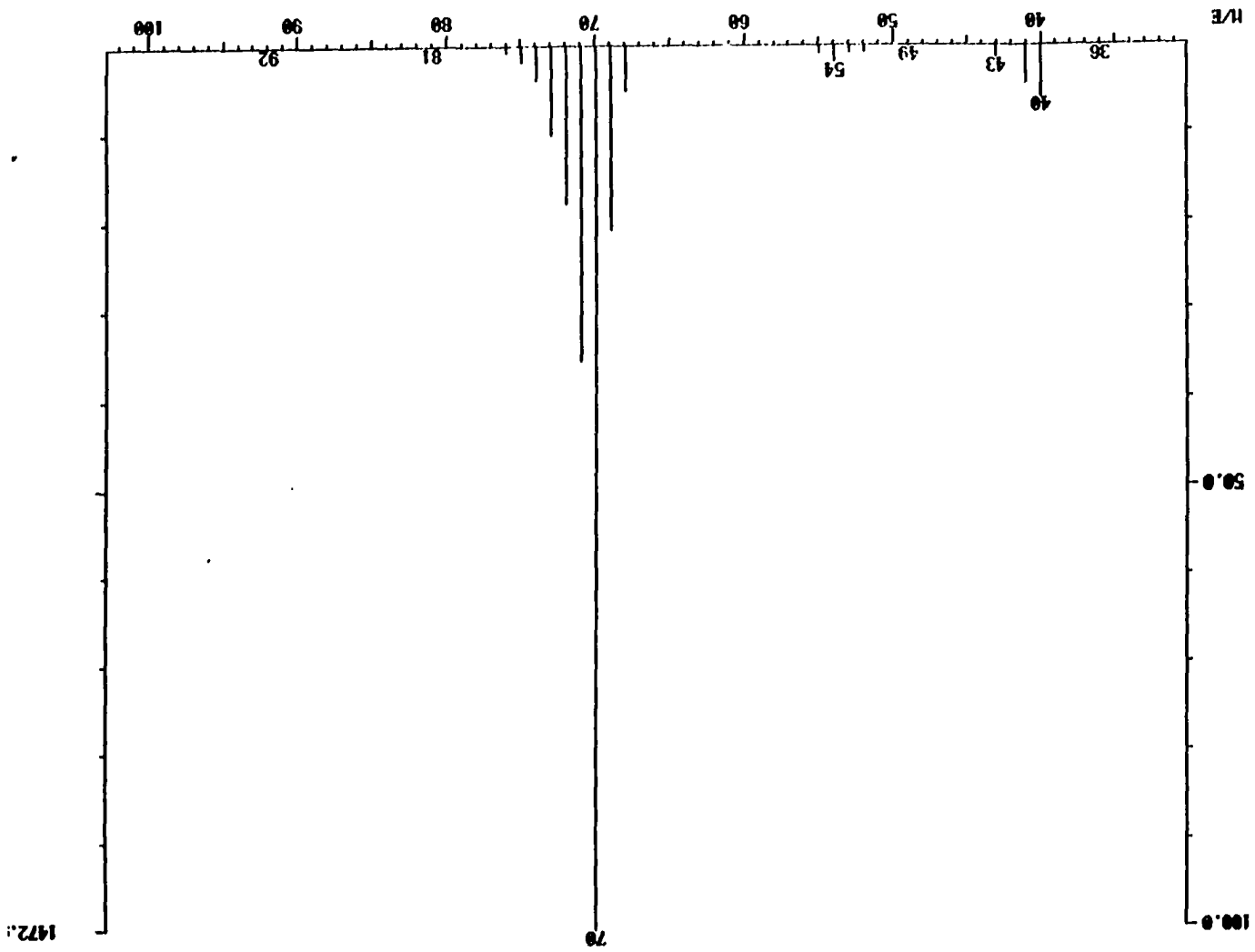
The liquid phase pyrolysis of 4 in deuterium gas produced the same product distribution (by GLPC) as that in H<sub>2</sub> gas. The compounds identified by GLPC and GCMS included cyclopentene (5), cyclopentane (6) and dicyclopentadiene (8).

Inspection of the low eV mass spectrum of the pyrolyzate revealed a collection of many deuterated species for both 5 and 6. The mass spectrum displays a skewed "bell" shaped distribution

ranging from  $d_0$  to  $d_8$  which is centered at cyclopentene- $d_2$  (70 amu) as shown in Figure 1. A similar statistical distribution was observed for the cyclopentane which was formed as a secondary product in the hydrogenation reaction.



Figure 1. GCMS (16 eV) of cyclopentene  $\text{-d}_1$  (5-d) from the pyrolysis of cyclopentadiene (4) in  $\text{D}_2$  gas



## DISCUSSION

The liquid phase pyrolysis of benzocyclobutene (2) at 240°C in an H<sub>2</sub> atmosphere results in the addition of 1 equivalent of H<sub>2</sub> to give ortho-xylene (3). The added hydrogen appears to come from the H<sub>2</sub> gas rather than radical abstraction from the hydrocarbon solvent. This hypothesis is substantiated by several separate experimental results.

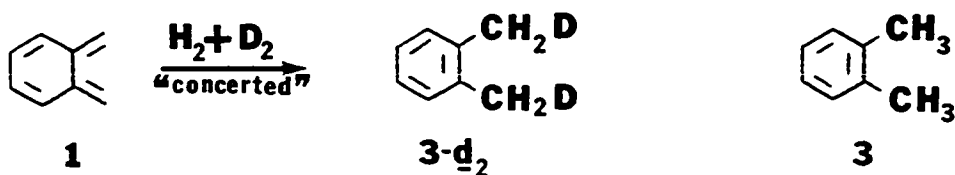
In the total absence of H<sub>2</sub> gas, the only product obtained was the [4+4] dimer of ortho-quinodimethane (7). The LPP of benzocyclobutene (2) in He gas did in fact produce ortho-quinodimethane (1), however, since there was no H<sub>2</sub> gas to react with 1, the only productive route was dimerization. Thus, the formation of ortho-xylene (3) in the presence of H<sub>2</sub> gas and the total lack of ortho-xylene in an atmosphere of He gas precludes the participation of the solvent in the hydrogenation.

The LPP of benzocyclobutene (2) in a pure D<sub>2</sub> atmosphere produced ortho-xylene-d (3-d) which was primarily a d<sub>2</sub>-species. The high yield of this particular isotopomer again indicates reaction solely from the gaseous atmosphere and not by the solvent which should be deuterium free under our conditions [9].

Finally, we do not observe products derived from radical coupling of ortho-xylene (3), benzocyclobutene (2) or the [4+4] dimer 7 with each other or the solvent. Again, this result provides further support for a hydrogenation resulting only from the gaseous atmosphere.

The aforementioned results provide credence for our original thesis, that of a concerted reaction between ortho-quinodimethane (1) and H<sub>2</sub> gas. Provided with only this information a lucid argument could be made for such a novel and interesting reaction. However, the possibility that a surface-catalyzed hydrogenation might be occurring led us to use a mixture of H<sub>2</sub> and D<sub>2</sub> gas under similar LPP conditions.

It was believed that if the reaction was indeed concerted, the ortho-xylene (3) formed from the pyrolysis of benzocyclobutene (2), in a mixture of H<sub>2</sub> and D<sub>2</sub> gas, should be solely d<sub>0</sub> and d<sub>2</sub> species. On the other hand, if GCMS analysis revealed a significant amount of d<sub>1</sub> species, an exchange mechanism would need to be invoked such as a surface catalyzed reaction. The LPP of



benzocyclobutene (2) under just such conditions produced ortho-xylene (3-d) which consisted of d<sub>0</sub>, d<sub>1</sub> and d<sub>2</sub> species in a statistically distributed pattern.

Although it is readily apparent that an exchange process is in effect, an important distinction must be realized. That is, could it be that the deuterium randomization is occurring before the hydrogenation rather than during the hydrogenation? It has been shown [10] that a mixture of  $H_2$  and  $D_2$  gas will randomize over a hydrogenation catalyst affording a mixture of  $H_2$ ,  $D_2$  and HD gases. Such a mixture, when added in a concerted manner to 1, would produce ortho-xylene (3) with an isotopic distribution exactly as we observed. Of course, at this point it is inarguable as to the equal likelihood that ortho-quinodimethane (1) is simply being hydrogenated by a surface-catalyzed mode which also would produce the observed distribution of deuterated ortho-xylenes.

Similar evidence was afforded from the liquid phase pyrolyses (LPP) of cyclopentadiene (4) with  $H_2$  and  $D_2$  gas. The hydrogenation of 4 resulted in the production of both cyclopentene (5) and cyclopentane (6). The presence of 6 presents strong evidence for a surface-controlled hydrogenation, since the hydrogenation of cyclopentene (5) could come about only by such means.

Further evidence for a surface-catalyzed reaction was gained by the LPP of cyclopentadiene (4) in a  $D_2$  atmosphere. Not only were cyclopentene-d (5-d) and cyclopentane-d (6-d) formed, but the deuterated species were statistically distributed over a range of  $d_0$ - $d_8$ . Unfortunately, in a like manner to ortho-quinodimethane (1), the possibility that the first hydrogenation step is a molecular, concerted process cannot be supported or ruled out.

The observed randomization process for cyclopentadiene (4) would be of a different nature than that involved with 1 since the distribution is observed with theoretically pure  $D_2$  gas. A possible scenario involving concerted addition of  $D_2$  to cyclopentadiene to give primarily cyclopentene- $d_2$  which is randomized via multiple adsorption/desorption steps might be in effect. Each of these cycles would necessarily increase the deuterium content of cyclopentene (5) since a deuterium atom would be added upon adsorption. Subsequent desorption would bring about the loss of either hydrogen or deuterium. The existence of a deuterium isotope effect would also favor the preferential loss of hydrogen, enriching the molecule with deuterium above and beyond that which statistical control would produce.

The results provide enough of a basis for us to support the occurrence of the proposed molecular addition of hydrogen to ortho-quinodimethane (1). Even if we did not support the idea, the unprecedented nature of such a result deserves a dedicated effort to determine the exact mechanism of the hydrogenation.

#### Future Work

The experimental evidence which has been presented still contains many unknown factors. However, these factors are valuable in that they indicate directions for future study. There are several possible directions of attack, each of which alone or in conjunction with the others might solve this puzzling issue. The

problems which need to be solved involve the 2° reaction of cyclopentene (5), the lack of stereochemistry in ortho-xylene (3) (from ortho-quinodimethane (1)) and the surface-catalyzed reactions we believe are occurring.

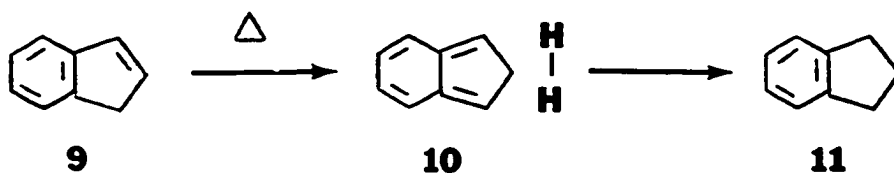
The last problem stated may perhaps be the easiest to solve. Since the autoclave is constructed of stainless steel, it may be viewed as a surface with potential catalytic activity. A possible method of destroying this activity would be to poison the catalyst. However, since this would involve the addition of extra chemical(s), it is certainly not an attractive alternative.

The use of an inert liner may provide the necessary means for alleviating the surface effect. The same hydrogenation could be carried out in the autoclave both lined and unlined. If upon analysis, the yield of the hydrogenated product varied markedly between the two experiments, a good argument could be made for a surface-catalyzed hydrogenation.

The other problems, both dealing with chemical properties of 1 and 4, could be solved by the use of related systems. One possibility exists in the form of indene (9).

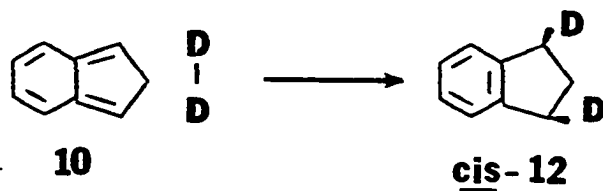
It is well documented [1,11] that indene (9) undergoes a thermal isomerization at 200°C to its valence isomer isoindene (10). Compound 10 has a key feature of ortho-quinodimethane (1), that being the formation of an aromatic nucleus upon hydrogenation to produce indan (11). A feature of cyclopentadiene (4), the

constrained cyclopentadienyl ring system, is also contained within isoindene (10). An added bonus of 10 which makes it a particularly



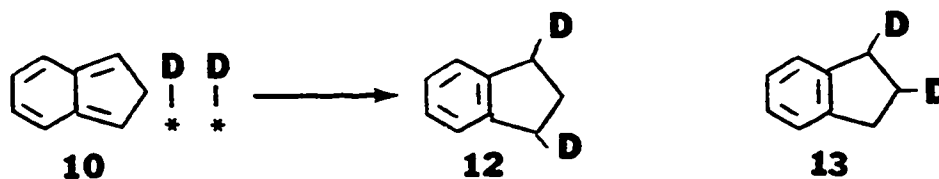
attractive molecule, is that the product of hydrogenation, indan (11), will not undergo further reaction under our conditions.

The presence of the constrained ring system is also beneficial in elucidating the stereochemistry of the hydrogenation. Whereas the addition of  $D_2$  gas to ortho-quinodimethane (1) to give ortho-xylene (3) gave no indication of stereochemistry, the addition of  $D_2$  to 10 should provide interesting evidence as to the regio-





and stereochemistry of the hydrogenation. Should the hydrogenation occur in a concerted manner, the sole product would be cis-indan-1,3-d<sub>2</sub> CB-(12). The <sup>1</sup>H and <sup>2</sup>H NMR spectra of this compound should be easily distinguished from the mixture formed by a surface-catalyzed reaction. A surface-catalyzed hydrogenation would produce the two regioisomers indan-1,3-d<sub>2</sub> (12) and indan-1,2-d<sub>2</sub> (13), which might not be formed as a single stereoisomer.



The specific difference in the <sup>1</sup>H NMR would be the presence of the benzylic proton at C-3 in 13. The key factor in the <sup>2</sup>H NMR would be an absorbance from the homobenzylic deuterium at C-2 also contained in 13. Other than these two specific points, a difference in complexity should also differentiate the two modes. On one hand, the concerted reaction should produce only 1 regio- and stereoisomer, which would produce simple <sup>1</sup>H and <sup>2</sup>H NMR spectra, whereas a surface mediated hydrogenation would produce two regiochemically different compounds, each of which would most likely be a mixture of stereoisomers, thus, producing a considerably more complex set of spectra.

## EXPERIMENTAL

## General

Gas chromatographic analysis was performed on a Hewlett Packard 5840-A gas chromatograph utilizing either a 20-m SP 2100 (methylsilicone fluid) or a 30-m DB-1 (methylsilicone fluid) fused-silica capillary column and a flame-ionization detector. Combined gas chromatographic/mass spectra (GCMS) analysis was performed on a Finnigan 4000 gc/ms with an Incos 2500 data system and Finnigan 9610 GC.

The commercially available chemicals are listed in Table 5.

Table 5. Commercially available compounds

Compound	Source
Cyclopentane	Aldrich Chemical Company
Cyclopentene	Loren E. Linder, T. J. Barton group, I.S.U.
Cyclohexane	Fisher Scientific Company
Deuterium gas	Air Products
Dicyclopentadiene	Eastman Kodak Company
Dimer of <u>ortho</u> -xylylene	Bruce Surber, I.S.U.
Hexanes	Baker Chemical Company
Hydrogen gas	I.S.U. Chemistry Stores
Pentanes	Eastman Kodak Company
<u>ortho</u> -Xylene	Aldrich Chemical Company

### General Pyrolysis Procedure

The autoclave employed was a bolted enclosure pressure vessel (300 mL) manufactured by Autoclave Engineers with an upper pressure limit of 4800 psi, as shown in Figures 2 and 3. Provisions were made for multiple flushing of the system with whichever gas was being employed in the LPP at the time. Controlled heating of the vessel was accomplished by a jacketed heater, available from Autoclave Engineers, specifically designed for this vessel. The contents were stirred utilizing a glass encased magnetic stirring bar which was used for each pyrolysis run.

Typically, 25 mL of solvent was added to the vessel before adding the compound to be pyrolyzed. The stirring bar was then deposited in the bomb and the vessel was then bolted closed. The bomb was then pressurized to ca. 60 psi and purged. This purging cycle was repeated 4 times and then the vessel was pressurized to the working pressure for the particular pyrolysis. The heating jacket was turned on and adjusted through a Variac to produce the desired working temperature. The stirring motor was also turned on and adjusted to maintain a medium rate of mixing. The temperature was monitored with an Omega pyrometer by a thermocouple inserted between the bomb and heating jacket. After the desired time for the particular run had passed, the power was turned off and the vessel was allowed to cool to room temperature. The bomb was then purged, opened and the contents were removed for GLPC analysis.

Figure 2. Design specifications for the body and bottom of the 300-mL high-pressure vessel

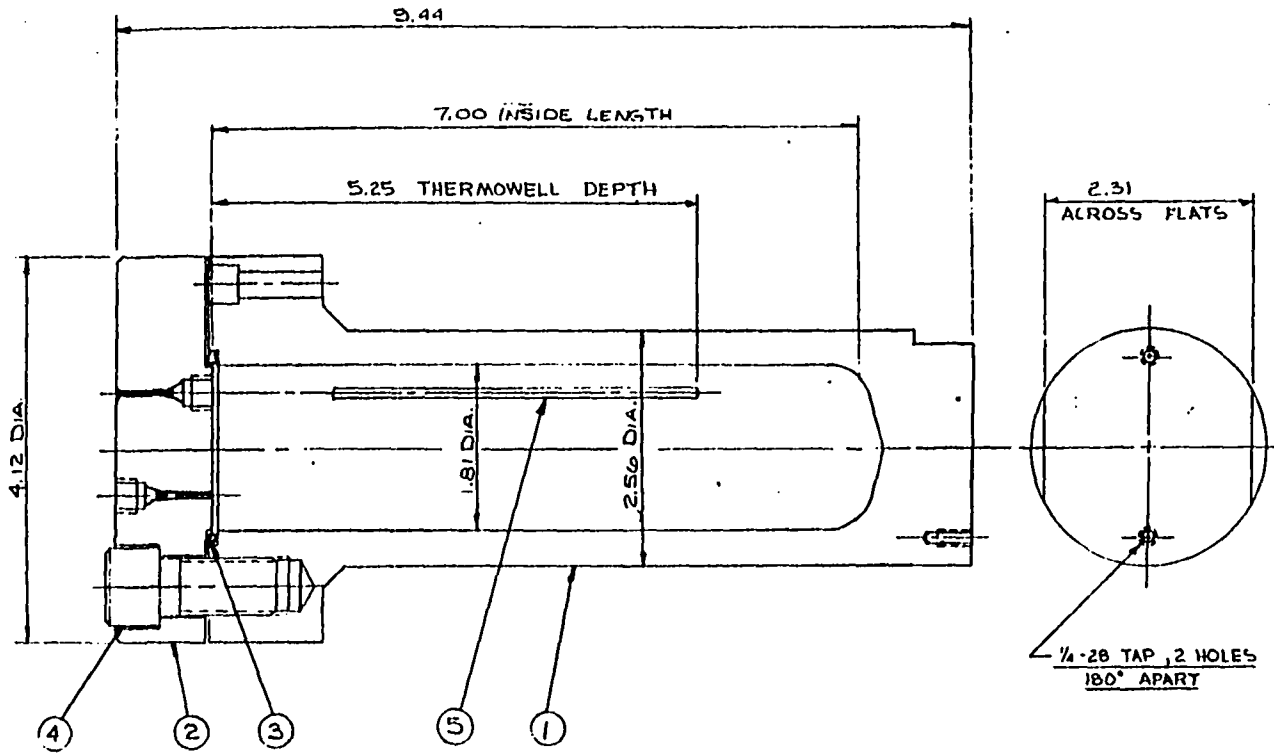
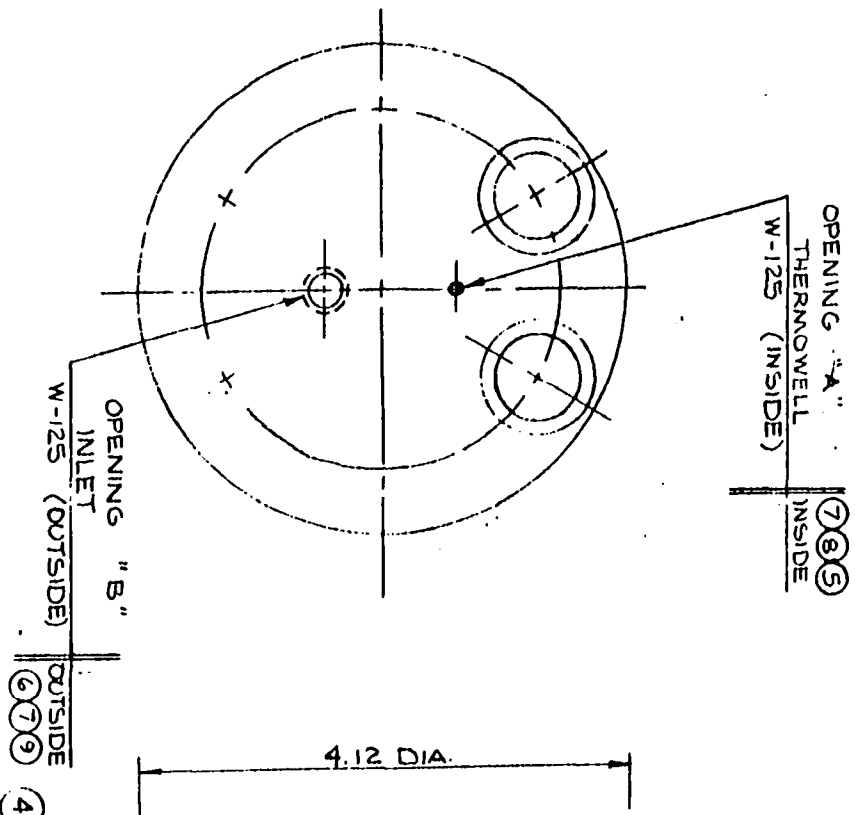


Figure 3. Design specifications for the top of the 300-mL high-pressure vessel and parts list for same



— PARTS LIST —

ITEM NO NO REQS	DESCRIPTION	PART NO.	MATERIAL
1	BODY	101B-9117	SA-182 F316
2	COVER	101B-9164	SA-182 F316
3	GASKET	1010-7717	316 SS
4	Hex Soc. Cap Screws	P-1093	SA-193-GR B16
5	THERMOWELL	101B-0274	316 SS
6	GLAND	5MN20-174	17-4PH
7	SLEEVE	5SL20-316	316 SS
8	GLAND	5MN20-316	316 SS
9	PLUG	5P20-316	316 SS

AE SERIAL NO. 84-06924-1

MAWP 5,400 PSI @ 650°F

HT \* TYPE

LPP (Liquid Phase Pyrolysis) of Benzocyclobutene (2) and H<sub>2</sub>

Typically, 9-10 mg of benzocyclobutene (2), prepared as described on pp 76, as outlined by Loudon et al. [12], was pyrolyzed in the previously described manner.

ortho-Xylene (3): Mass Spec (70 eV) m/e (rel. intensity) 106 (P<sup>+</sup>, 48), 105 (P<sup>+</sup> -H, 19), 91 (P<sup>+</sup> -CH<sub>3</sub>, 100).

Benzocyclobutene (2): Mass Spec (70 eV) m/e (rel. intensity) 104 (P<sup>+</sup>, 100), 103 (P<sup>+</sup> -H, 59), 78 (P<sup>+</sup> -C<sub>2</sub>H<sub>4</sub>, 60), 51 (P<sup>+</sup> -C<sub>4</sub>H<sub>5</sub>, 38).

[4+4] Dimer (7): Mass Spec (70 eV) m/e (rel. intensity) 208 (P<sup>+</sup>, 11), 193 (P<sup>+</sup> -CH<sub>3</sub>, 100), 178 (P<sup>+</sup> -C<sub>2</sub>H<sub>6</sub>, 39), 115 (P<sup>+</sup> -C<sub>7</sub>H<sub>6</sub>, 33), 104 (P<sup>+</sup> -C<sub>8</sub>H<sub>8</sub>, 55).

LPP of Cyclopentadiene (4) and H<sub>2</sub>

Typically, 8-9 mg of cyclopentadiene (4), freshly cracked from dicyclopentadiene, was pyrolyzed and analyzed in the previously described manner.

Cyclopentadiene (4): Mass Spec (70 eV) m/e (rel. intensity) 66 (P<sup>+</sup>, 100), 65 (P<sup>+</sup> -H, 57), 40 (P<sup>+</sup> -C<sub>2</sub>H<sub>2</sub>, 40), 39 (P<sup>+</sup> -C<sub>2</sub>H<sub>3</sub>, 48).

Cyclopentene (5): Mass Spec (70 eV) m/e (rel. intensity) 68 (P<sup>+</sup>, 38), 67 (P<sup>+</sup> -H, 100), 53 (P<sup>+</sup> -CH<sub>3</sub>, 20) 39 (P<sup>+</sup> -C<sub>2</sub>H<sub>5</sub>, 33).

Cyclopentane (6): Mass Spec (70 eV) m/e (rel. intensity) 70 (P<sup>+</sup>, 24), 55 (P<sup>+</sup> -CH<sub>3</sub>, 33), 42 (P<sup>+</sup> -C<sub>2</sub>H<sub>4</sub>, 100).



## Cyclopentadiene (4)

Compound 4 was prepared fresh each time a thermolysis was performed by cracking commercially available dicyclopentadiene. The dicyclopentadiene (ca. 50 mL) was added to a 250-mL round-bottomed flask which had a Vigreux column and a take-off arm attached. The flask and contents were heated to ca. 180°C to produce a smooth flow of 4. Mass Spec (70 eV) m/e (rel. intensity) 66 (P<sup>+</sup>, 100), 65 (P<sup>+</sup> -H, 57), 40 (P<sup>+</sup> -C<sub>2</sub>H<sub>2</sub>, 40), 39 (P<sup>+</sup> -C<sub>2</sub>H<sub>3</sub>, 48).

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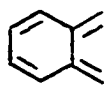
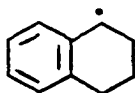
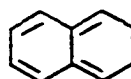
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PART III. ORTHO-QUINODIMETHANES AND RADICAL INTERMEDIATES INVOLVED  
IN THE PYROLYSIS OF TETRALIN

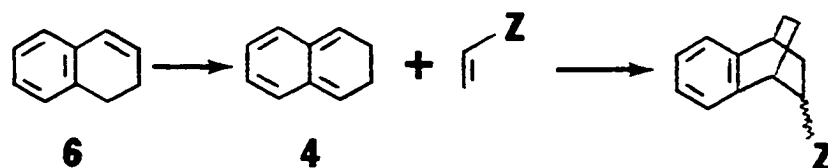
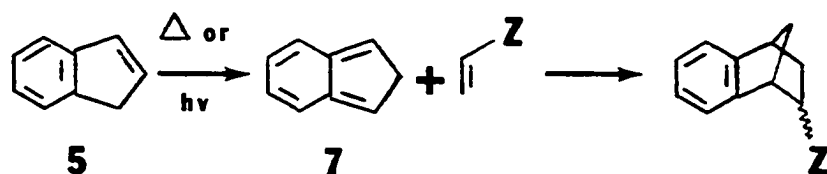
## INTRODUCTION

The thermal reactions of 1,2,3,4-tetrahydronaphthalene (tetralin) (1) have been extensively studied such that the identities of the products and their ratios are predictably known [1]. Very little work, on the other hand, has been done to delineate the reaction pathways and identify reactive intermediates involved in the formation of the products. Compounds such as ortho-quinodimethane (2) [2] and the 1-tetralyl radical (3) [1a,b] have been cited repeatedly in the literature as intermediates in the pyrolysis of 1. We wished to determine the possibility that 2,3-dihydronaphthalene (4), may be a transient species in the pyrolysis of tetralin (1) and we also re-examined the chemistry surrounding the 1-tetralyl radical (3).

**2****3****4**

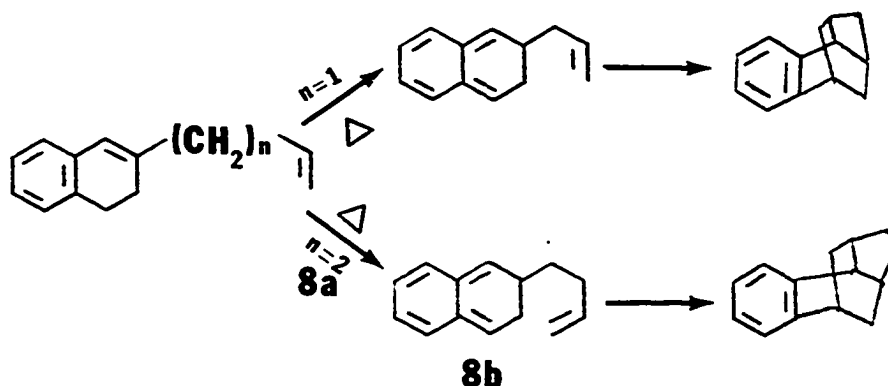
As the initial stage of the study of the involvement of 2,3-dihydronaphthalene (4) in the thermal reactions of 1, we chose to study concurrently the pyrolysis of indene (5) and 1,2-dihydronaphthalene (6). Due to the similarities between 5 and 6, we felt a strong analogy could be drawn between the thermal reactions

of these two molecules. Specifically, it is well known that 1H-indene (5) will isomerize to 2H-indene (isoindene) (7) both under thermal and photochemical excitation [2,3,4]. We then postulated that schemes designed to trap isoindene (7) could be applied to the trapping of 2,3-dihydronaphthalene (4).

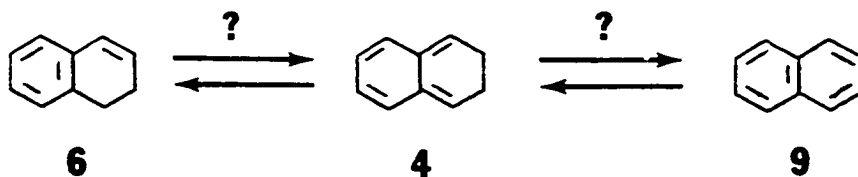


In an attempt to extend and improve the trapping scheme of 2,3-dihydronaphthalene (4), it was also decided to employ an intramolecular Diels-Alder trap. A logical choice involved a terminal double bond connected to the 1,2-dihydronaphthalene/2,3-dihydronaphthalene ring system by an alkyl side chain. Examination of framework models of each of the two possible intramolecular adducts provided reason to believe the adduct formed from an alkyl chain of  $n = 2$ , would be the most stable and most likely to perform

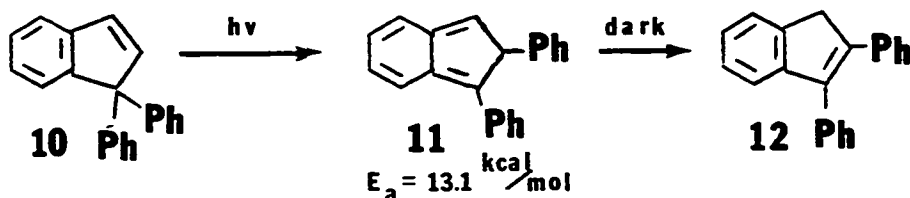
as desired. Thus, it was decided to synthesize and pyrolyze the precursor to 8 to provide evidence for 2,3-dihydronaphthalene (4).



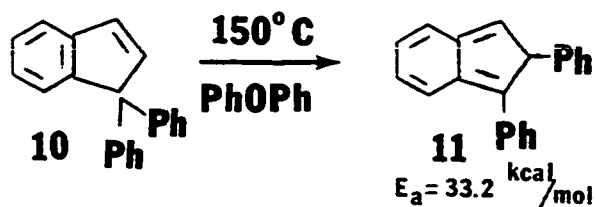
The thermal reaction of ortho-divinylbenzene (9), another  $C_{10}H_{10}$  molecule, was also studied to determine its relationship to 2,3-dihydronaphthalene (4) and 1,2-dihydronaphthalene (6) and to attempt to draw conclusions as to its bearing on the pyrolysis of tetralin (1). In fact, a scheme may be hypothesized which interconverts these three molecules by concerted rearrangements, thus making it an interesting system to study.



de Fonseca et al. [4b], studied the energetics of the isoindene (7) to indene (5) isomerization by photochemically producing 1,2-diphenylisoindene (11) and then measuring the decay to 1,2-di-



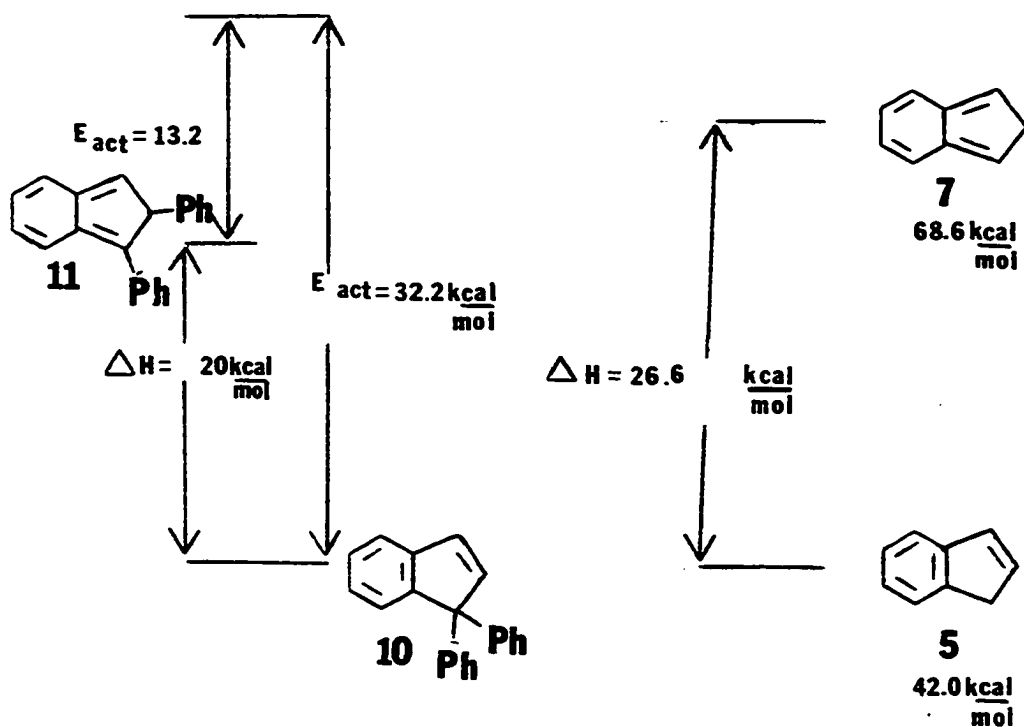
phenylindene (12) in the absence of light. From the kinetic data he established that the energy of activation for the 1,2-H shift was 13.1 kcal/mol. These measurements coupled with their data on the thermal generation of 11 from 1,1-diphenylindene (10) allowed the



calculation of the activation parameters and the ground state energy differences given in Scheme I. The calculated values using Benson's [5] group additivity methods were used to obtain values for the parent indene/isoindene interconversion and are also presented in Scheme I.

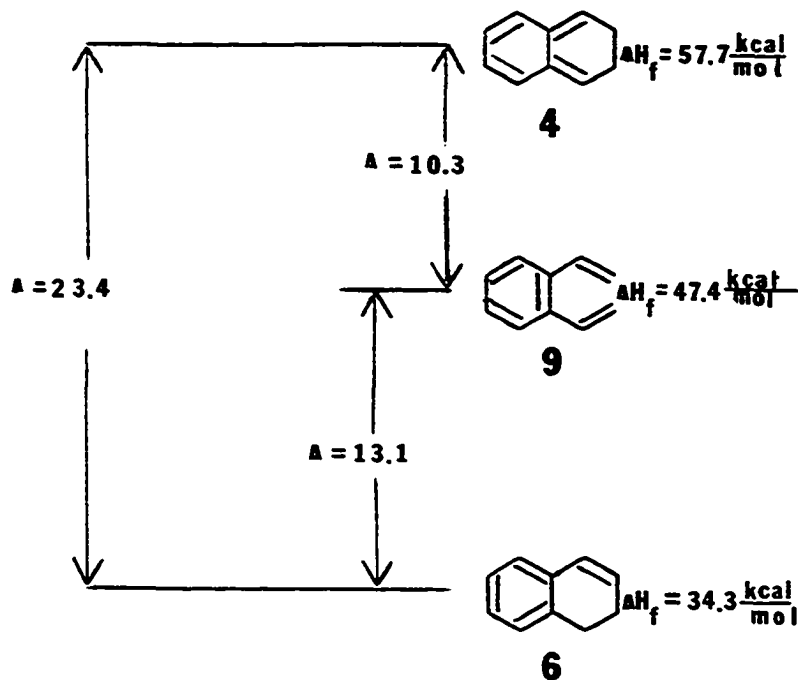


Scheme I



There is no experimental comparison for the 1,2-dihydronaphthalene (6) to 2,3-dihydronaphthalene (4) system, but ground state parameters may be calculated by Benson's [5,6] methods to arrive at a scheme providing the differences in ground state energy between 6 and 4, the energy difference of ortho-divinylbenzene (9) is also given in Scheme II.

Scheme II



The evidence for the existence of 7 as indicated by trapping (4+2 Diels-Alder) is voluminous [2a,7] and will not be covered here. The single case that could be found of the parent 2,3-dihydronaphthalene (4) being trapped by a dienophile was that reported by Dinulescu et al. [8a,b] in 1960. From the metal-mediated 1,4-dihalo elimination of 1,4-dibromotetralin they reported an adduct of N-phenylmaleimide formed in 51%. The researchers also reported that in the absence of N-phenylmaleimide a polymer of 1,2-dihydronaphthalene was formed.

The FVP of ortho-divinylbenzene (9) has been previously investigated [9] to determine if it was a precursor to indene (5). The results are outlined in Table 1 for a variety of temperatures. The high yield of 1,2-dihydronaphthalene (6) observed might be a consequence of the existence of 2,3-dihydronaphthalene (4) formed by electrocyclic ring closure of ortho-divinylbenzene (9).

Table 1. Products and yields from the FVP of ortho-divinylbenzene (9)

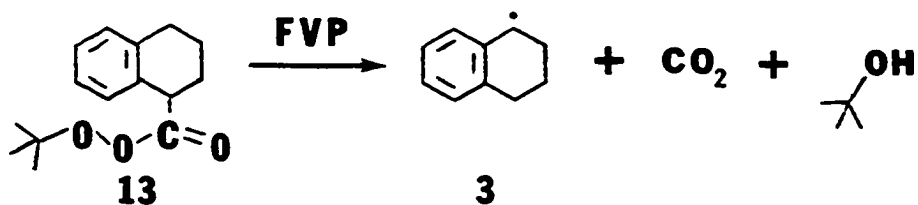
Products	Yields, % <sup>a</sup>					
	793°C	734°C	652°C	588°C	567°C	554°C
Tetralin	1.7	1.4	0.6	0.1	0.1	0.05
1,2-DHN <sup>b</sup>	54.2	84.0	82.7	97.0	68.1	53.6
Naphthalene	41.0	15.2	4.2	0.5	0.2	0.1
<u>ortho</u> -DVB <sup>b</sup>	--	--	--	10.1	35.0	51.1

<sup>a</sup>The yields are absolute GLPC yields using biphenyl as an internal standard.

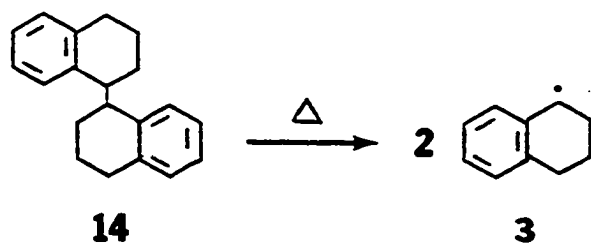
<sup>b</sup>1,2-DHN is 1,2-dihydronaphthalene and DVB is divinylbenzene.

Shifting now to the possible radical intermediates in the tetralin pyrolysis, one of our intentions was to determine the pathway of decomposition of the 1-tetralyl radical (3). The pyrolysis of tetralin (1) may generate 3, but we felt as others have [1a,b],

that concurrent concerted reactions might be clouding the issue. Franz's research group chose to study the pyrolytic decompositions of 1-tert-butyl tetralinpercarboxylate (13) [1a] under FVP conditions. They postulated that 13 should decompose to give the 1-tetralyl radical (3) whose subsequent decompositions could be studied at various temperatures.



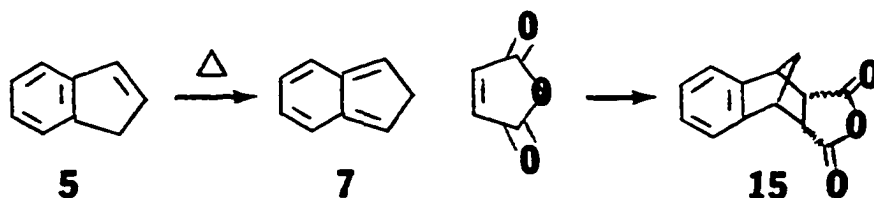
We chose as our precursor of 3 to be 1,1'-bitetralyl (14) which is synthesized as a mixture of diastereomers. The favored thermal process, homolytic cleavage at the 1,1'-junction, would produce two 1-tetralyl radicals. This, coupled with its relative stability and lack of by-products over the tert-butyl peresters made it an especially attractive source of the radical intermediate 3.



## RESULTS

## Indene (5) Pyrolyses

The reaction of 5 with maleic anhydride proceeds at temperatures between 200-210°C for a reaction time of 5 h to produce up to 30% of the Diels-Alder adduct (15) [3a]. The majority of the remaining



material is converted to polymer with very little of the starting indene remaining (less than 1%), as shown in Table 2. The yields were higher when hydroquinone was added to the mixture and the yields were lowered when a large excess of maleic anhydride was used. However, the use of hydroquinone was ultimately abandoned since we were interested in only the thermal processes and did not wish to introduce any source of acid catalysis.

When indene (5) and N-phenylmaleimide were heated together for 5 h at 200°C, a new [4+2] adduct (16) was formed in 51% yield. The new compound was a crystalline solid which melted at 178-178.5°C with  $^1\text{H}$  NMR spectral data as follows;  $^1\text{H}$  NMR  $\delta$  7.35-7.00 (m, 7 H), 6.50-6.20 (m, 2 H), 4.00-3.75 (m, 2 H), 3.70-3.50 (m, 2 H), 2.30-1.85 (m, 2 H). The compound was shown to result from isindene (7) and N-phenylmaleimide in a 1:1 ratio by GCMS and  $^{13}\text{C}$  NMR, Figure 1.

Table 2. Products and yields from the sealed tube pyrolyses of indene (5) and various dienophiles

Product	Solvent	Other	Adduct Yield, % <sup>a</sup>
<u>Maleic Anhydride</u>			
Indene (5)			
1:1	tetralin	hydroquinone	23%
"	phenyl ether	"	27%
"	"	--	13.7%
"	"	benzoic acid	15.6%
2:1	"	--	7.7%
5:1	"	--	--
2:1	"	hydroquinone	21%
1:1	"	benzoquinone	2.2%
"	"	"	1.8%
<u>Methyl Acrylate</u>			
Indene (5)			
1:1	phenyl ether	--	--
<u>N-Phenylmaleimide</u>			
Indene (5)			
1:1	phenyl ether	--	15% <sup>b</sup>
1.3:1	benzene	--	51%
Indene (5) (neat)	phenyl ether	other	0% <sup>c</sup>
Indene (5) (neat)	"	hydroquinone	0% <sup>d</sup>

<sup>a</sup>Determined by <sup>1</sup>H NMR yield with s-tetrachloroethane internal standard.

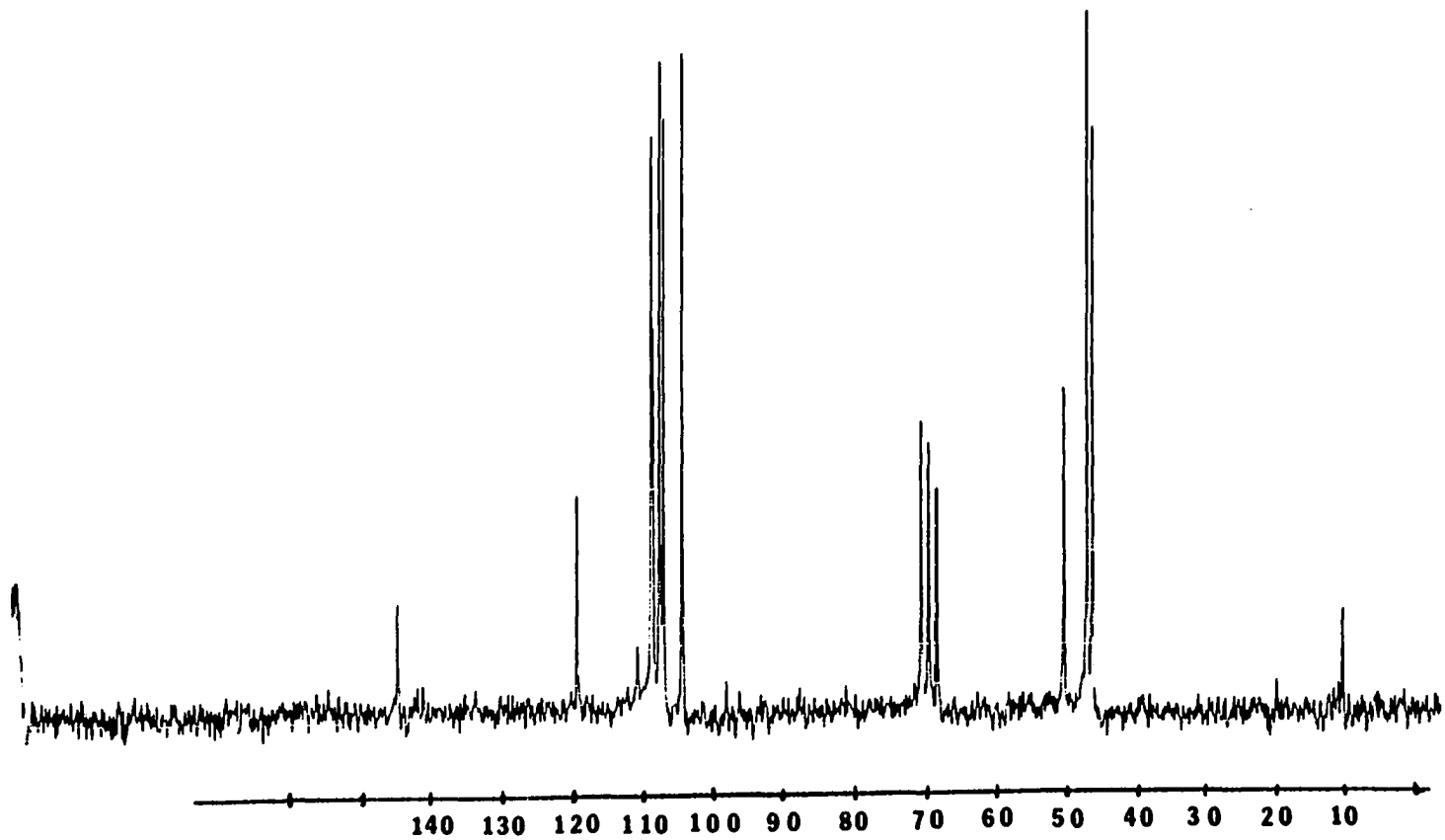
<sup>b</sup>Isolated yield from column chromatography then recrystallization, weighed.

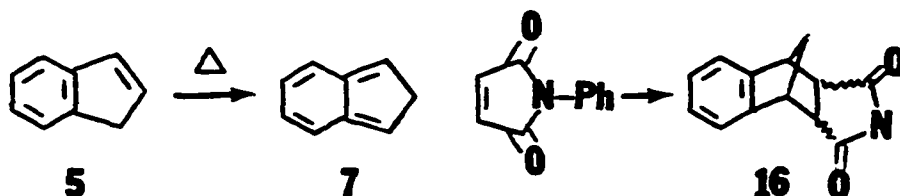
<sup>c</sup>No products were formed, only indene (91%).

<sup>d</sup>No products were formed, only indene (83%).

Figure 1.  $^{13}\text{C}$  NMR of the [4+2] adduct of isoindene (10) and N-phenylmaleimide







### 1,2-Dihydronaphthalene Pyrolyses (6)

With a general understanding of the indene/isoindene system we felt we could proceed to the 1,2-dihydronaphthalene/2,3-dihydronaphthalene system. Under similar pyrolysis conditions (for indene), 1,2-dihydronaphthalene (6) failed to give any products indicative of the 2,3-dihydronaphthalene (4) species. The pyrolyses are summarized in Table 3. When maleic anhydride was used as the dienophile, a polymeric mass formed which presumably consumed 6 since after 5 h at 205°C only 54% of the starting dihydronaphthalene 6 was present.

The reaction of 6 with dimethyl acetylenedicarboxylate (DMAD) gave an interesting 1:1 adduct. The adduct was puzzling in that the melting point was very low (82-84°C) and the  $^1\text{H}$  NMR spectrum did not indicate a benzobicyclo-[2.2.2]octane system. Instead, the  $^1\text{H}$  NMR produced a six hydrogen multiplet from 8.00-7.20 ppm and two upfield singlets of three protons each at 4.05 and 3.90 ppm.

Table 3. Sealed tube pyrolyses of 1,2-dihydronaphthalene (6) under various conditions

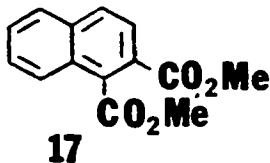
Product	Conditions	Comments
<u>Maleic Anhydride</u>		
<u>1,2-DHN (<u>6</u>)</u>		
1:1	205°C, 5 h	no adduct
"	205°C, 5 h	no adduct, 54% of <u>6</u> <sup>a</sup>
2:3	210°C, 25 h	no adduct, 20% of <u>18</u> <sup>a,b,c</sup>
<u>N-Phenylmaleimide</u>		
<u>1,2-DHN (<u>6</u>)</u>		
1:1	200°C, 5 h	no adduct
1:1	200°C, 89 h	no adduct
<u>DMAD</u>		
<u>1,2-DHN (<u>6</u>)</u>		
1:1	270°C, 17 h	32% of <u>17</u> <sup>c</sup>
1,2-DHN ( <u>6</u> ) (neat)	205°C, 5 h	1% of <u>18</u> <sup>c</sup>
1,2-DHN ( <u>6</u> ) (neat)	230°C, 1 h	10% of <u>18</u> <sup>c</sup>
1,2-DHN ( <u>6</u> ) (neat)	230°C, 2 h	15% of <u>18</u> <sup>c</sup>

<sup>a</sup>Yield determined by <sup>1</sup>H NMR using s-tetrachloroethane as internal standard.

<sup>b</sup>Yield determined by GLPC using biphenyl as internal standard.

<sup>c</sup>Compound 17 is 1,2-dicarbomethoxynaphthalene and compound 18 is naphthalene.

This evidence suggested an unsymmetrical naphthalenedicarboxylate which indicated that if an adduct of 1,2-dihydronaphthalene (6) and DMAD had been formed, it had to lose a  $C_2H_4$  unit. The only adduct that fit the criteria was 1,2-dicarbomethoxynaphthalene (17) and in fact the literature values [10] for the  $^1H$  NMR spectra and melting point matched very well.



Thus, DMAD attacks the diene system without prior isomerization of 6, forming a transient 1:1 adduct. The driving force for aromatization resulted in a loss of ethylene to give 1,2-dicarbomethoxynaphthalene (17) in a 30% yield. The major product, which resulted from dehydrogenation of the starting material, was naphthalene (18) in 36% yield.

The liquid phase thermolysis of 1,2-dihydronaphthalene (6) in phenyl ether followed quite nicely from what was seen in the previously cited FVP experiments. The pyrolysis resulted in the formation of only naphthalene (18) Table 3. There were no dimeric products formed nor any products which indicated the transient existence of 2,3-dihydronaphthalene (4).

Pyrolysis of ortho-Divinylbenzene (9)

The liquid phase sealed tube pyrolysis of ortho-divinylbenzene (9) was carried out in the presence of a dienophile and in the absence of one. The choice of the dienophile was guided by Noland and Kameswaran's [7] work with isoindene (7), as well as Dinulescu et al. [8a,b] trapping of 2,3-dihydronaphthalene (4).

The trapping experiments all produced polymer with no evidence of a [4+2] adduct by  $^1\text{H}$  NMR or GLPC analysis. The various reactions including changes in temperature, dienophile, concentration, and reaction time are summarized in Table 4.

In the liquid phase pyrolysis of 9 in the absence of dienophile, there was no reaction until the temperature reached 230-240°C. At this temperature five unidentified dimers (by GCMS) and 1,2-dihydronaphthalene (6) were observed. At a longer reaction time, more 6 was formed in preference to the five dimers. In addition, no indene (5) was identified under these reaction conditions.

3-Homoallyl-1,2-dihydronaphthalene (8)

Base-induced elimination, following the general procedure of Lipton and Shapiro [11], of 2-homoallyl-1-tetralone tosylhydrazone (19) produced compound 8. The tosylhydrazone 19 resulted from the reaction of tosylhydrazine and 2-homoallyl-1-tetralone (20).

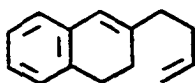
The substituted tetralone 20 was produced by quenching the potassium enolate of 1-tetralone with homoallyl bromide.

Table 4. Sealed tube pyrolyses of ortho-divinylbenzene (9) under various conditions

Products	Conditions	Comments
<u>Maleic Anhydride</u>		
<u>o-Divinylbenzene (9)</u>		
1:1	200°C, 5 h	insoluble white powder
10:1	200°C, 5 h	polymer
<u>N-Phenylmaleimide</u>		
<u>o-Divinylbenzene (9)</u>		
1:1	200°C, 5 h	no reaction
1:1	200°C, 5 h	no reaction
1:1	230°C, 6 h	solid white powder
1:1	220°C, 3 h	polymer
1:1	215°C, 6 h	polymer
o-Divinylbenzene (9) (neat)		
repyrolyzed sample	210°C, 17 h	no reaction
	230°C, 6 h	1,2-DHN, five dimers <sup>a</sup>

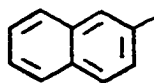
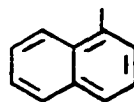
<sup>a</sup>Area % yield by GLPC: 1,2-DHN (6), 7.12%; o-divinylbenzene (9), 14.61%; dimers, 23.86, 3.00, 10.49, 24.86 and 19.05%.

The  $^1\text{H}$  NMR spectrum of the clear, colorless liquid 8 was clearly indicative of the desired compound. Although the aliphatic protons at  $\delta$  2.80 (t, 2 H) and 2.28 (m, 6 H) were difficult to distinguish due to their complex splitting patterns, the integration relative to the aromatic and vinyl protons was as expected for the compound. The vinyl protons of the homallyl group absorbed at  $\delta$  5.85 (m, 1 H) for the  $\alpha$ -proton and  $\delta$  5.01 (m, 2 H) for the 2  $\beta$ -protons. The absorption at  $\delta$  6.22 (s, 1 H) corresponded to the lone vinyl proton of the 1,2-dihydronaphthalene moiety.

**8**

FVP of 8

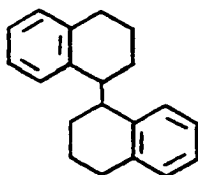
The pyrolysis of 8 at temperatures ranging from 530–800°C produced a mixture of 3 major products all of which had GC retention times appreciably shorter than the starting material, indicating lower molecular weight compounds. True to this prediction, GCMS analysis allowed the identification of naphthalene (18) (21%) and two other compounds 2-methylnaphthalene (21) (49%) and 1-methylnaphthalene (22) (10%), both with a molecular weight of 142 amu.

**21****22**

The  $^1\text{H}$  NMR spectrum of the pyrolyzate contained aromatic absorbances indicative of naphthalene (18) plus other similar condensed aromatic structures. The only major aliphatic absorbances were at  $\delta$  2.70 and 2.50, both of which were resolved singlets, also indicative of 21 and 22. There was no product formed with a mass greater than 142 amu.

#### 1,1'-Bitetralyl (14) Pyrolysis

The FVP of 14 led to the production of the 1-tetralyl radical (3), the decomposition of which, produced mainly 1,2-dihydronaphthalene (6). At lower temperatures where secondary pyrolysis of tetralin (1) and 6 was minimized, the yields of styrene (23), indene (5), 1-methylindan (24) and naphthalene (18) were lower (Table 5). The consistent yield of 1 tended to indicate either a long lived 1-tetralyl species which abstracted a hydrogen atom or an intramolecular process which led to equal amounts of 1 and 6.



**14**



Table 5. Relative yields of the products from the FVP of 1,1'-bitetralyl (14)<sup>a</sup>

Products	430°C	508°C	515°C	538°C	540°C	627°C	650°C
Styrene	trace	trace	0.62	1.60	1.03	2.11	3.32
Indene	trace	trace	2.47	3.80	2.90	5.27	6.07
1-Methylindan	--	--	0.75	0.72	0.87	0.98	1.01
Tetralin	23.4	15.2	14.7	14.2	12.3	10.1	8.02
1-Methylindene	--	3.23	3.32	3.40	3.49	1.64	4.45
1,2-DHN	59.5	67.2	67.1	66.9	69.2	53.2	54.6
Naphthalene	10.7	2.89	3.06	4.99	4.40	18.6	17.4
1-Methyltetralin	--	0.21	0.23	0.61	0.21	0.90	0.35
% conversion	18.7	100.0	100.0	100.0	100.0	100.0	100.0
% TRM <sup>b</sup>	88.2	78.2	76.3	77.7	77.1	80.9	78.0

<sup>a</sup>All yields are relative GLPC yields with biphenyl used as the internal standard, where relative yield = (absolute yield of product/Σ absolute yields of all products) × 100%.

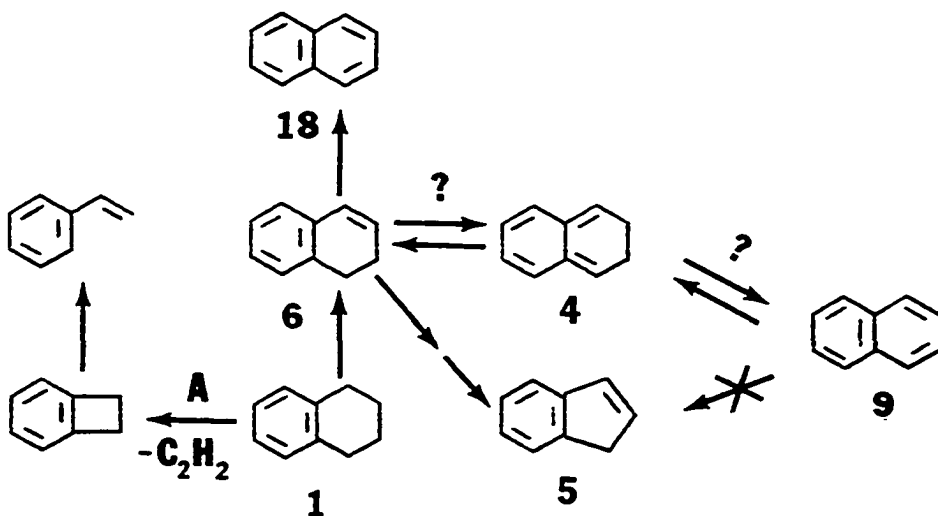
<sup>b</sup>% TRM = % total recovered material = absolute yields of all components.

## DISCUSSION

The  $C_{10}H_{10}$  System

Of the three  $C_{10}H_{10}$  hydrocarbons which may be involved in the pyrolysis of tetralin (1), this work indicates that 1,2-dihydronaphthalene (6) plays the most important role in the formation of the products not resulting from path A, shown in Scheme IV. Since Bergman et al. [1b] has shown by deuterium labeling that the dehydrogenation of 1 occurs 1,2- rather than 1,4- to give 6 rather than 2,3-dihydronaphthalene (4), the only conceivable route to 4 and ortho-divinylbenzene (9) must go through 1,2-dihydronaphthalene

Scheme III



(6). Interestingly enough, the other products they observed were naphthalene (18) and other minor products such as indene (5), toluene (25) and ortho-xylene (26). It might be possible that 5 could come from ortho-divinylbenzene (9) and that 4 was not being trapped. Although our work both with and without a [4+2] trap gave no direct evidence for 2,3-dihydronaphthalene (4), some circumstantial evidence was found. The liquid phase pyrolysis of 9 (neat) did not produce indene (5) but it did produce a small amount of 6 as well as five dimers. It is the presence of 1,2-dihydronaphthalene (6), which must be produced solely through the intermediacy of 2,3-dihydronaphthalene (4), that offers our proof for ortho-quinodimethane 4.

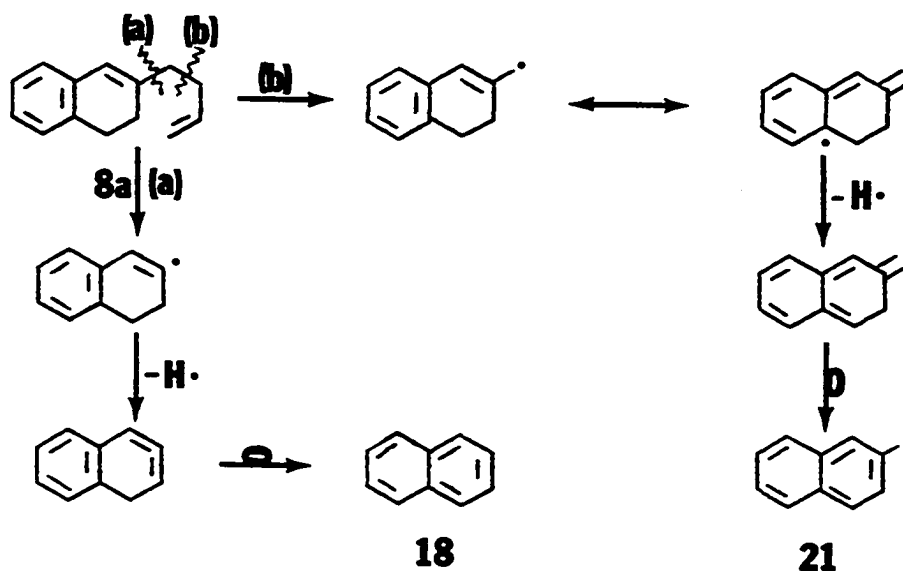
It is still perplexing that there is no evidence for 2,3-dihydronaphthalene (4) from the trapping experiments done with ortho-divinylbenzene (9). Possible explanations for these observations are: 1. 2,3-Dihydronaphthalene (4) is not formed from either of these species. 2. The 1,5-H shift of 2,3-dihydronaphthalene (4) to 1,2-dihydronaphthalene (6) is so rapid that trapping cannot compete. 3. A retro Diels-Alder reaction of the [4+2] adduct is occurring.

It does seem plausible that 6 will not isomerize to 4 because of the loss of resonance stabilization effected by disrupting the aromatic ring [5,6]. It prefers instead to dehydrogenate, a process which could occur without loss of aromatic stabilization.

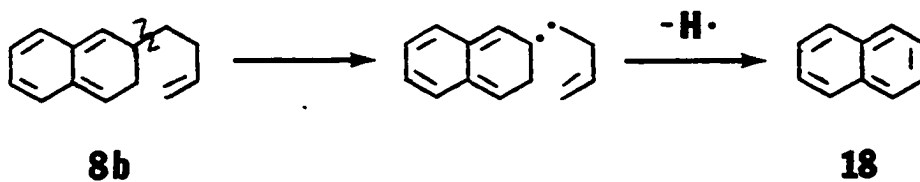
The situation with ortho-divinylbenzene (9) does not appear to be so straightforward in view of the formation of 1,2-dihydro-naphthalene (6). The most satisfactory way to explain the formation is via electrocyclic ring closure to 4 and then a 1,5-H shift to give 6. Thus, at least ortho-divinylbenzene (9) does appear to form 2,3-dihydronaphthalene (4) as an intermediate on the way to forming 6.

The Diels-Alder trapping of 4 is under a major handicap from enthalpy and entropy factors. Not only must the higher energy 2,3-dihydronaphthalene (4) be present, it also has to be in a proper orientation with a dienophile in order for the [4+2] adduct to be formed. While these two requirements need to be satisfied there is another much simpler process, that of the 1,5-H shift to give 1,2-dihydronaphthalene (6).

The attempted intramolecular trapping of 4 by FVP of 8a, resulted in products with molecular weights less than that of the starting material. This result points toward a fatal shortcoming of this experiment, the ease of cleavage of the homoallyl side chain. Due to the stability of the two allylic radicals, it is apparent that fragmentation would be a dominant reaction, in fact, it is the predominant reaction.



The formation of naphthalene (18) may be solely from the cleavage of the 1,2-dihydronaphthalene derivative 8a, however, it might also arise from cleavage of the quinodimethane intermediate 8b. The cleavage illustrated would be favorable since it produces an endocyclic allylic radical and a homo-allylic radical. Subsequent loss of H-atom would give 18, the major product observed at elevated temperature.



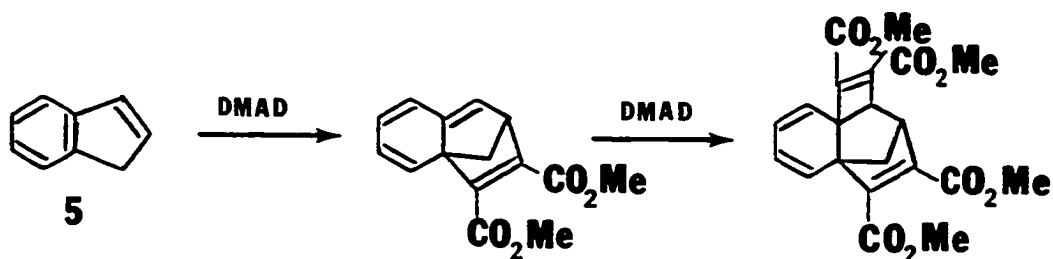
Although these results do not refute the existence of 2,3-dihydronaphthalene (4), they certainly do not support it. All indications are that the system prefers to homolyze (fragment) no matter whether it does so from the 1,2- or 2,3-dihydronaphthalene isomer (8a or 8b). It is obvious that the formation of 18 is a higher energy process since the yield increases with temperature. The important question is whether the extra energy is required to isomerize 1,2-dihydronaphthalene to 2,3-dihydronaphthalene or to bring about a less favorable (higher energy) cleavage such as in (a).

The possibility that a methylnaphthalene is undergoing secondary pyrolysis to form naphthalene (18), though possible is improbable. It has been shown [12], that temperatures in excess of 900°C are required to cleave the methyl group of 9-methylanthracene. In view of this fact, it appears reasonable that the formation of 18 will not involve the pyrolysis of a methylnaphthalene species.

Whether or not a retro-reaction is occurring is a hard question to answer. Evidence given by the heating of [4+2] adducts of isoindene (7) shows that a retro-grade Diels-Alder reaction does not occur. By analogy, if an adduct of 2,3-dihydronaphthalene (4) were to form it would be even less likely to retrograde due to the formation of a higher energy species.

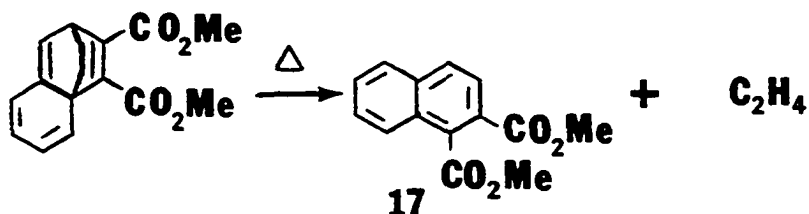
The Diels-Alder reaction of dimethyl acetylenedicarboxylate (DMAD) with 1H-indene (5) and several other substituted indenenes has been reported by Noland et al. [13,14] and Noland and Kameswaran [15]. It was reported that DMAD undergoes reaction across the 2-

and 7a- positions to break up the aromatic ring. This is in opposition to the reaction of maleic anhydride which reacts only after the 1H-indene (5) isomerizes to isoindene (7). The 1:1 adduct then reacts further in refluxing benzene to give a 1:2 adduct resulting from a [2+2] addition of the second molecule of DMAD. If the reaction is carried out in refluxing xylenes and a 3 X molar excess of DMAD, a 1:3 adduct was formed in 40% isolated yield.

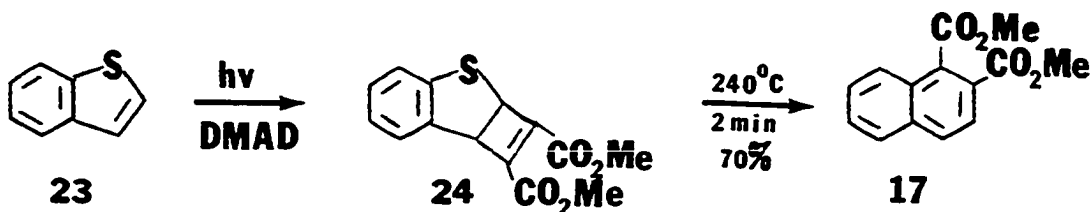


Our own results with 1,2-dihydronaphthalene (6) and DMAD show a similar reaction with the non-isomerized compound. However, addition of another mole of DMAD is not observed as in Noland's work. The work done with the Diels-Alder reaction of 6 and DMAD tends to suggest a retro-process would eject the ethano bridge of the adduct and not the original dienophile. The important difference is that the acetylenic dienophile provides for facile subsequent aromatization by extrusion of ethylene. The same loss in a quino-

dimethane derived adduct would yield another 2,3-dihydronaphthalene species which could aromatize by losing 2 hydrogen atoms or react with another molecule of dienophile.



A similar extrusion reaction has been reported by Neckers and Dopfer [16] in their study of the photochemical addition of acetylenes to benzo[b]thiophene 23. It was found that DMAD adds in a [2+2] photochemical process to give a cyclobutene derivative 24. The

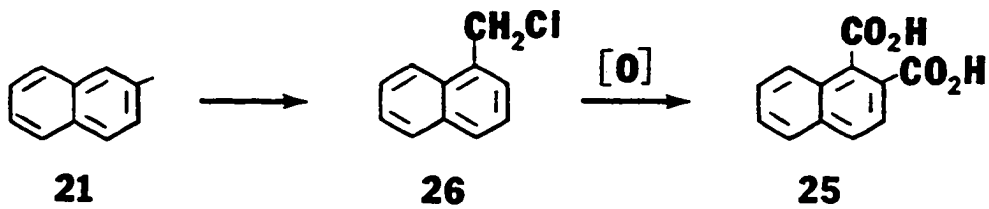


adduct 24 is thermally unstable and extrudes sulfur to produce dimethyl 1,2-naphthalenedicarboxylate 17 in good yields.

A method [17] for the bulk production of 1,2-naphthalene-dicarboxylic acid 25 involves the heating of crude anthracenes in an O<sub>2</sub> atmosphere. After heating at 250°C for variable periods of time, 25 is produced in 0.4–6.0% in combination with other aromatic acids.



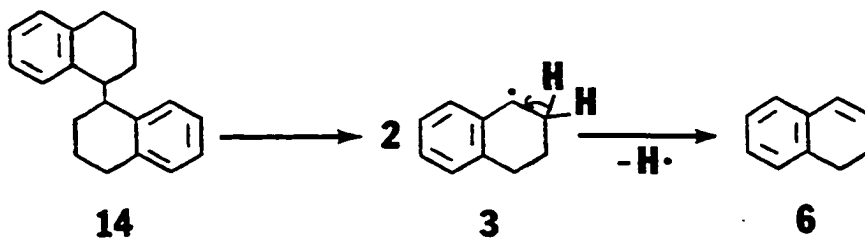
A smaller scale preparation of 25 has been outlined by Szadewski [18] starting with available 2-methylnaphthalene (21). The starting



material 21 is chloromethylated to give 26 which is treated with  $\text{Na}_2\text{Cr}_2\text{O}_7$  at  $200^\circ\text{C}$  to produce 25 in an overall yield of 60%.

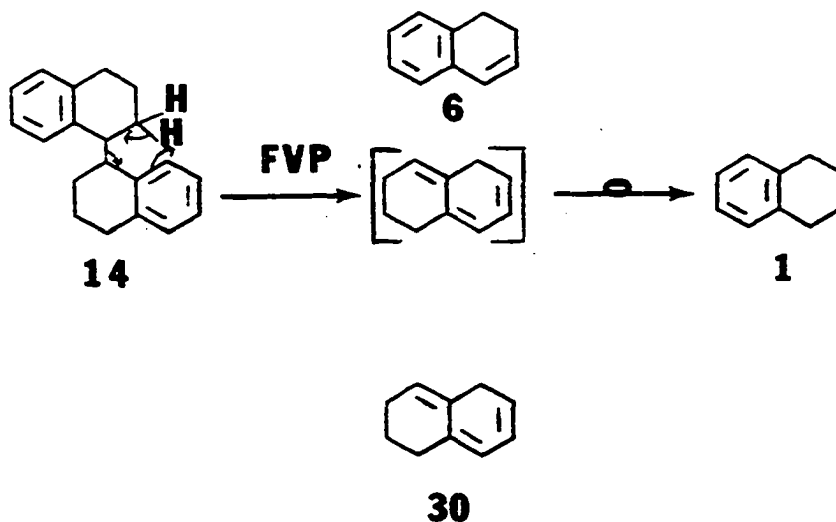
#### FVP of 1,1'-Bitetralyl (14)

The two most notable results of the bitetralyl pyrolyses were the consistently high relative yield of 1,2-dihydronaphthalene (6) and the presence of tetralin (1) at all pyrolysis temperatures. The most obvious explanation for the formation of 1,2-dihydronaphthalene (6) would be loss of H-radical alpha to the benzylic radical. The formation of other products such as indene (5),



1-methylindan (27), ortho-xylene (28) and toluene (29) may arise from the decomposition of the 1-tetralyl radical (3). However, the possibility of secondary pyrolysis of 1 and/or 6 cannot be ignored and is probably quite likely at elevated temperatures.

The fact that tetralin (1) was always present in the pyrolysis of 1,1'-bitetralyl (14) was rather surprising. We felt that either the 1-tetralyl radical (3) was able to efficiently scavenge H-radical or that some other unique process was occurring. The likelihood of 3 being able to scavenge H atoms was quite remote since our FVP conditions are designed to optimize unimolecular reactions. It occurred to us that the operation of a retro-ene reaction could account for both the tetralin (1) and a second source of 1,2-dihydronaphthalene (6). The formation of the isotetralin derivative 30 [19] would most certainly result in the formation of tetralin (1) by either a formal 1,3-H shift or 1,7-H shift.



## EXPERIMENTAL

## General

The flash vacuum pyrolysis (FVP) method and apparatus have been described [20]. The flash chromatography procedure has been described by Still et al. [21]. Gas chromatographic analysis was performed on a Hewlett Packard 5840-A gas chromatograph utilizing either a 20-m SP 2100 (methylsilicone fluid) or a 30-m DB-1 (methylsilicone fluid) fused-silica capillary column and a flame-ionization detector. Combined gas chromatographic/mass spectra (gc/ms) analysis was performed on a Finnigan 4000 gc/ms with and IncoS 2500 data system and Finnigan 9610 gc. High resolution mass spectra and exact mass determinations were recorded with an Associated Electronics Industries MS-902 instrument.

$^1\text{H}$  NMR spectra were obtained on a Varian Associates EM-360 A/L, Bruker WM 300 or Nicolet NT 300.  $^{13}\text{C}$  NMR were recorded on either a JEOL FX-90Q or a Nicolet NT 300 spectrometer.

Infrared spectra were recorded on a Beckman Acculab II spectrometer using NaCl plates or a micro solution cell (50  $\mu\text{L}$ ). Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

The commercially available chemicals are listed in Table 6.

Table 6. Commercially available chemicals

Compound	Source
Acetic anhydride	Eastman Kodak Company
Benzene	Fisher Scientific Company
1,2-Dihydronaphthalene	Aldrich Chemical Company
<u>ortho</u> -Diphthalaldehyde	Aldrich Chemical Company
Dimethyl acetylenedicarboxylate	Aldrich Chemical Company
Ethyl ether	Fisher Scientific Company
Indene	Aldrich Chemical Company
Maleic anhydride	Aldrich Chemical Company
McMurry's reagent ( $\text{TiCl}_3 \cdot \text{LAH}$ )	Aldrich Chemical Company
Methyltriphenylphosphonium bromide	Aldrich Chemical Company
Naphthalene	Baker Chemical Company
Potassium hydride	Aldrich Chemical Company
Tetrahydrofuran	Fisher Scientific Company
Tetralin	Aldrich Chemical Company
1-Tetralone	Aldrich Chemical Company
Toluene	Fisher Scientific Company
<u>para</u> -Toluenesulfonic acid	Aldrich Chemical Company
<u>para</u> -Toluenesulfonylhydrazide	Aldrich Chemical Company
<u>ortho</u> -Xylene	Aldrich Chemical Company

1,2-Dihydronaphthalene (6)

To 1-tetralone (9.97 g, 68.2 mmol) was added 95% EtOH (200 mL), the mixture was stirred to attain homogeneity. With continued stirring, NaBH<sub>4</sub> (1.23 g, 32.5 mmol) was added to the solution. After 6 h TLC analysis revealed some remaining starting ketone. More NaBH<sub>4</sub> (0.17 g, 4.49 mmol) was added and a second TLC analysis showed no starting material. The alcohol was liberated by the dropwise addition of 6 M HCl until the mixture was shown to be neutral by pH paper. The solution was then diluted with H<sub>2</sub>O (250 mL) and extracted with Et<sub>2</sub>O (3 x 150 mL). The combined extracts was washed with H<sub>2</sub>O (1 x 100 mL), saturated brine solution (3 x 100 mL), dried over MgSO<sub>4</sub>, filtered and concentrated. The residue was vacuum distilled to give the product 1-tetralol (27) (6.25 g, 42.2 mmol, 62%) bp 67-68°C at 0.3 mm. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.10 (m, 4 H), 4.65 (br t, J = 4 Hz, 1 H), 3.60 (m, 3 H), 1.85 (m, 4 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 138.764, 136.868, 128.688, 127.225, 125.871, 128.525, 67.796, 32.096, 29.115, 18.768; [lit. [22]]. <sup>13</sup>C NMR δ 138.87, 136.87, 128.68, 128.68, 125.89, 67.70, 32.15, 29.18, 18.99.

Compound 6 was prepared following the method of Senda [23]. To 1-tetralol (27) (9.30 g, 62.75 mmol) was added Ac<sub>2</sub>O (40 mL) and para-toluenesulfonic acid (20 mg). The resulting solution was stirred for 15 min then heated to reflux for 3 h under an N<sub>2</sub> blanket. The solution was cooled to room temperature, poured into

H<sub>2</sub>O (150 mL), extracted with Et<sub>2</sub>O (2 x 100 mL), and the extracts were combined, washed with H<sub>2</sub>O (6 x 75 mL), saturated NaHCO<sub>3</sub> solution (2 x 75 mL), and H<sub>2</sub>O (1 x 75 mL), dried over MgSO<sub>4</sub>, filtered and concentrated. The crude product was distilled under vacuum to give 1,2-dihydronaphthalene (6) (4.0 g, 30.7 mmol, 49%) bp 28-29°C at 0.3 mm which was essentially identical to the commercial compound [lit. [23b] 91°C at 20 mm]. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.10 (t, J = 2 Hz, 4 H), 6.35 (d t, J = 10, 2 Hz, 1 H), 5.95 (d t, J = 10, 4 Hz, 1 H), 3.85 (m, 2 H), 2.30 (m, 2 H).

#### 4-Homoallyl-1,2-dihydronaphthalene (8)

KH (521.5 mg, 13.0 mmol) was washed with hexanes (3 x 10 mL), the dried under a stream of flowing N<sub>2</sub> gas, and then weighed. THF (10 mL) was then added to form a thin slurry to which was added 1-tetralone (1.52 g, 10.4 mmol) in THF (5 mL). The insoluble enolate was dissolved by adding HMPA (2 mL), and this solution was then transferred to a round-bottomed flask containing DMSO (60 mL). The color of the enolate progressed from yellow to black as the concentration increased. The solution was stirred at room temperature for 0.5 h before adding homoallyl bromide (5.27 g, 40.0 mmol) in a single portion. The solution changed color from black to yellow in ca. 25 min. H<sub>2</sub>O (80 mL) was added and the organic products were extracted with Et<sub>2</sub>O (3 x 25 mL). The extracts were combined, washed with 10% HCl solution (2 x 20 mL) and saturated

NaHCO<sub>3</sub> solution (2 x 20 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give a mixture of mono-, di- and o-alkylated adducts. The crude mixture was separated via flash chromatography (5% Et<sub>2</sub>O/hexanes/SiO<sub>2</sub>) and yielded the desired mono-adduct 2-homoallyl-1-tetralone (20) (176.7 mg, 0.90 mmol, 9%): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.03 (d, J = 7.2 Hz, 1 H), 7.45 (t, J = 7.2 Hz, 1 H), 7.29 (t, J = 7.2 Hz, 1 H), 7.22 (d, J = 7.2 Hz, 1 H), 5.84 (m, 1 H), 5.02 (m, 2 H), 2.99 (t, J = 7.0 Hz, 2 H), 2.50 (m, 1 H), 2.20 (m, 5 H), 1.89 (m, 1 H).

The tosylhydrazone 19 was prepared according to the general method of Van der Stouw et al. [24]. 2-Homoallyl-1-tetralone (20) (138.6 mg, 0.69 mmol) and p-toluenesulfonyl hydrazide (128.9 mg, 0.69 mmol) were dissolved in 95% EtOH (5 mL) and the solution then heated to a slow reflux for 20 min, cooled to room temperature, and then concentrated to give white crystals. 2-Homoallyl-1-tetralone tosylhydrazone (19) was recrystallized in Et<sub>2</sub>O to give white plates (212.4 mg, 0.57 mmol, 83%) (dec. 151-153°C): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.0-7.75 (m, 3 H), 7.40-7.05 (m, 7 H), 5.78 (m, 1 H), 5.09 (m, 2 H), 3.00-2.80 (m, 2 H), 2.75-2.70 (m, 1 H), 2.41 (s, 3 H), 2.10-1.80 (m, 4 H), 1.65-1.40 (m, 2 H).

The general procedure has been adapted from a method developed by Lipton and Shapiro [11]. 2-Homoallyl-1-tetralone tosylhydrazone (19) (91.1 mg, 0.25 mmol) was dissolved in THF (10 mL) and then cooled to -78°C using a Dry Ice/*i*-PrOH slurry bath. After ca. 15 min, *n*-BuLi/hexanes (0.30 mL, 0.75 mmol) was added, and the resulting orange

solution was stirred for 2 h at  $-78^{\circ}\text{C}$  before allowing it to warm slowly to room temperature. As the solution warmed, the color deepened (red/orange) and a gas presumed to be  $\text{N}_2$  was produced, as shown by an attached oil bubbler. The solution was allowed to stir overnight, after which a 10% HCl solution (4 mL) was added causing the red/brown solution to immediately turn pale yellow. The aqueous solution was extended with  $\text{H}_2\text{O}$  (10 mL) and then extracted with pentanes (2 x 15 mL). The extracts were combined, washed with saturated  $\text{NaHCO}_3$  solution (1 x 10 mL) and  $\text{H}_2\text{O}$  (2 x 20 mL), and then dried over  $\text{MgSO}_4$ , filtered and concentrated to give a yellow/orange liquid. The crude product was purified by flash chromatography (hexane/ $\text{SiO}_2$ ) and yielded the desired alkenyl 1,2-dihydronaphthalene **8** (36.9 mg, 0.20 mmol, 80%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.10 (m, 4 H), 6.22 (s, 1 H), 5.85 (m, 1 H), 5.01 (m, 2 H), 2.80 (t,  $J = 2$  Hz, 2 H), 2.28 (m, 6 H). Mass Spec (70 eV)  $m/e$ , 184 ( $\text{P}^+$ , 67), 169 ( $\text{P}^+ - \text{CH}_3$ , 100), 142 ( $\text{P}^+ - \text{C}_3\text{H}_6$ , 40). High resolution mass spec for  $\text{C}_{14}\text{H}_{16}$ : calculated, 184.2829, found 184.2291.

#### ortho-Divinylbenzene (**9**)

The synthesis was adapted from the methods of Wittig and Schoelkopf [25a] and Moercker [25b]. Methyltriphenylphosphonium bromide [23.58 g, 66 mmol] was weighed into an Erlenmeyer flask connected to a 500-mL round-bottomed flask via Gooch tubing.  $\text{Et}_2\text{O}$  [200 mL] was added to the flask via a transfer needle, and then *n*-butyl



lithium [41.0 mL, 68 mmol] was added to the stirred solution. The phosphonium salt was added slowly over a 30-min period. The mixture attained a deep yellow color and was stirred for ca. 4 h. At the end of this period, ortho-diphthalaldehyde [3.75 g, 28 mmol] dissolved in Et<sub>2</sub>O [75 mL] was added over a 30-min period. The mixture was then heated to reflux for 2 h with continued stirring, afterwhich a large quantity of white precipitate formed. The solids were filtered to give a pale yellow solution which was reduced in volume to ca. 50 mL, cooled in the refrigerator, and filtered and the remainder of the solvent was removed by distillation. The crude product was vacuum distilled (77-80°C at 15 mm) to give 9 (420 mg, 3.23 mmol, 12%) as a colorless liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.20 (s, 4 H), 6.85 (dd, J = 18, 11 Hz, 2 H), 5.40 (dd, J = 18, 2 Hz, 2 H), 5.10 (dd, J = 11, 2 Hz, 2 H). [Lit. [9]] <sup>1</sup>H NMR δ 7.21 (m, 4 H), 6.93 (dd, J = 18, 11 Hz, 2 H), 5.48 (dd, J = 18, 2 Hz, 2 H), 5.20 (dd, J = 11, 2 Hz).

#### 1,1'-Bitetralyl (14)

McMurry's reagent [26] (TiCl<sub>4</sub>/LAH) (9.36 g, 14.29) was put into a 250-mL round-bottomed flask into which dry glyme (175 mL) was added with stirring and cooling. 1-Tetralol (27) (6.26 g, 42.2 mmol) was dissolved in dry glyme (20 mL) and transferred to an addition funnel attached to the reaction flask. The alcohol solution was added dropwise to the now black suspension. Once

addition was complete, the mixture was heated at a gentle reflux for 4.5 h. The flask was then cooled to room temperature and the contents were diluted with H<sub>2</sub>O (300 mL). The solution was then extracted with Et<sub>2</sub>O (3 x 200 mL), the extracts were combined, washed with H<sub>2</sub>O (3 x 150 mL), dried over MgSO<sub>4</sub>, filtered and concentrated to give (2.50 g, 9.53 mmol, 23%) of the product 14. The crude material was vacuum distilled (bp 125-128°C at 0.3 mm) and purified by preparative gas chromatography. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.50-7.00 (m, 4 H), 3.80-3.30 (m, 2 H), 2.80-2.50 (br t, J = 7 Hz, 4 H), 2.20-1.10 (m, 8 H). [Lit. [1a]] <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.5-7.0 (m, 4 H), 3.8-3.3 (m, 2 H), 2.8-2.5 (t, J = 6 Hz, 4 H), 2.1-1.2 (m, 8 H).

#### Pyrolysis of Indene (5) and Maleic Anhydride,

##### General Pyrolysis Method

A mixture of distilled indene (5) (194.0 mg, 1.70 mmol), maleic anhydride (327.5 mg, 3.30 mmol) and toluene (3 mL) was transferred into a drawn 25 x 75-mm tube which was attached to an evacuated "cow" apparatus to facilitate freeze/thaw degassing of the solution. The sample was subjected to 5 cycles of degassing before the tube was sealed under vacuum.

The sample was lowered into a heated air bath which was equilibrated to the desired temperature (205°C). After 5.5 h in the air bath, the sample was removed and allowed to cool to room temperature. The tube was scored with a file around the top section

to allow opening of the tube. Once the tube was opened, the toluene was removed by rotary evaporation to leave a crystalline residue and a viscous yellow oil. Recrystallization from EtOAc yielded the [4+2] adduct 15 (37.6 mg, 0.18 mmol, 10%): melting point 184.5–185.5°C [lit. [3a] mp 185.5–187.0°C];  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.30 (s, 4 H), 3.95–3.60 (m, 4 H), 2.30–1.80 (m, 2 H); IR ( $\text{CDCl}_3$ ,  $\text{cm}^{-1}$ ) 1873, 1785, 1083.

#### Pyrolysis of Indene (5) and N-Phenylmaleimide

Indene (5) (141.8 mg, 1.22 mmol), N-phenylmaleimide (211.4 mg, 1.22 mmol) and phenyl ether (0.7 mL) were added to a constricted tube, the tube was sealed and the mixture was pyrolyzed at 200°C for 5 h. The [4+2] adduct was isolated by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{SiO}_2$ ). Recrystallization of the product (26.8 mg, 0.09 mmol, 8%) gave a melting point of 178.0–178.5°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.35–7.00 (m, 7 H), 6.50–6.20 (m, 2 H), 4.00–3.75 (m, 2 H), 3.70–3.50 (m, 2 H), 2.30–1.85 (m, 2 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  175.97 (carbonyl), 142.55, 131.36, 128.89, 128.50, 127.26, 126.61, 123.10 (aromatics), 52.02, 47.73, 46.76 (aliphatics); IR ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ) 2925, 1710, 1500, 1255, 1185; Mass Spec (70 eV) m/e, 289 ( $\text{P}^+$ , 100), 116 ( $\text{P}^+ - \text{C}_{10}\text{H}_7\text{NO}_2$ , 23). High resolution mass spec for  $\text{C}_{19}\text{H}_{15}\text{NO}_2$ : calculated, 289.3360, found 289.3363.

Pyrolysis of 1,2-Dihydronaphthalene (6) and  
Dimethyl Acetylenedicarboxylate

1,2-Dihydronaphthalene (6) (145.0 mg, 1.11 mmol), DMAD (0.2 mL) and toluene (0.5 mL) were added to a constricted tube, the tube was sealed and the mixture was pyrolyzed at 270°C for 30 h. The resultant solid material was crystallized from EtOAc to give 1,2-dicarbomethoxynaphthalene (17), mp 82–84°C [lit. [10] mp 85°C].  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.00–7.20 (m, 6 H), 4.05 (s, 3 H), 3.90 (s, 3 H); IR ( $\text{CDCl}_3$ ,  $\text{cm}^{-1}$ ) 1745, 1455, 1310, 1285, 1255, 1155, 1055.

Pyrolysis of ortho-Divinylbenzene (9)

ortho-Divinylbenzene (9) was pyrolyzed neat for 6 h at 230°C. Analysis by GCMS revealed that 6 products were formed, five dimers that were not identified and 1,2-dihydronaphthalene (6).

General Flash Vacuum Pyrolysis Procedure

The sample (20 mg to gram quantities) was weighed into a round-bottomed flask. After purging the pyrolysis system with dry  $\text{N}_2$ , the sample flask was attached and the trap was immersed in liquid nitrogen. The system was opened to a vacuum pump (0.1 to 0.01 mm) and the sample was allowed to distill through the pyrolysis tube. The sample flask was usually kept at ambient temperature but it could be heated or cooled according to the volatility of the sample. Upon completion of the pyrolysis, the vacuum line was closed and dry  $\text{N}_2$  gas was slowly leaked into the system to facilitate

removal of the trap. The trap was disconnected, stoppered and warmed to room temperature before a solvent was added for analysis. If a quantitative GC analysis was going to be made, the solution was transferred to a vial containing a weighed amount of biphenyl internal standard. Identification of the individual components of the pyrolyzate was based on molecular weight and fragmentation patterns, as determined by GCMS, co-injection with commercial samples, and  $^1\text{H}$  NMR analysis. After each pyrolysis, the pyrolysis tube was cleaned by passing  $\text{O}_2$  gas through the tube while it was heated to  $> 800^\circ\text{C}$ .

FVP of 4-Homoallyl-1,2-dihydronaphthalene (8)

The substituted dihydronaphthalene 8 was pyrolyzed in the "normal" fashion to give a mixture of 3 major products which were identified by  $^1\text{H}$  NMR and GCMS.

For naphthalene (18):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J = 6.2$  Hz, 4 H), 7.48 (t,  $J = 6.2$  Hz, 4 H); Mass Spec (70 eV) m/e (rel. intensity) 128 ( $\text{P}^+$ , 100), 102 ( $\text{P}^+ - \text{C}_2\text{H}_2$ , 9).

For 2-methylnaphthalene (21):  $\delta$  7.80-7.35 (m, 7 H), 2.50 (s, 3 H); Mass Spec (70 eV) m/e 142 ( $\text{P}^+$ , 100), 141 ( $\text{P}^+ - \text{H}$ , 12), 115 ( $\text{P}^+ - \text{C}_2\text{H}_3$ , 32).

For 1-methylnaphthalene (22):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.80-7.35 (m, 7 H), 2.69 (s, 3 H); Mass Spec (70 eV) m/e 142 ( $\text{P}^+$ , 100), 141 ( $\text{P}^+ - \text{H}$ , 12), 115 ( $\text{P}^+ - \text{C}_2\text{H}_3$ , 31).

FVP of 1,1'-Bitetralyl (14)

Compound 14 (ca. 30 mg) was pyrolyzed under normal FVP conditions at temperatures ranging from 450-650°C. The products were identified by co-injection with commercial samples and mass spectral analyses. The product yields and other pertinent information are tabulated in the results section.

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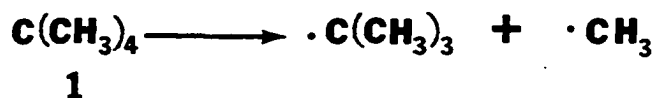
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PART IV. THE ROLE OF ACTIVE PACKINGS IN FLASH VACUUM PYROLYSIS

## INTRODUCTION

The difficulties with obtaining totally gas-phase unimolecular pyrolysis reactions are great [1]. In practically every experiment, the molecule under study is confined in a walled apparatus of some design. To further complicate matters, a packing material of some "inert" material is often added to provide added avenues for the transfer of thermal energy [2]. With the addition of this material comes the increased likelihood of the thermochemistry being controlled by surface catalysis rather than simple thermal transfer.

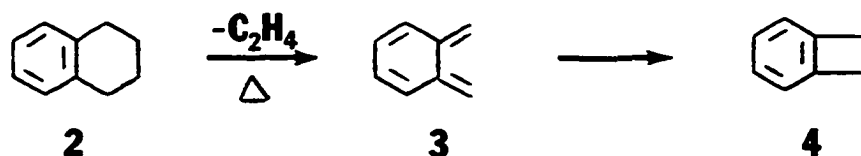
One approach to the problem has been to develop a pyrolysis procedure which does not involve "walls". In 1968, Taylor et al. [2] developed what they termed a wall-less reactor for the homogeneous gas-phase pyrolysis of neopentane (1). The reactor, in



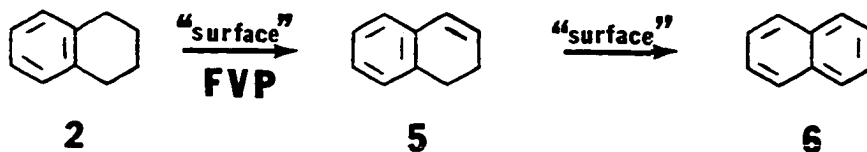
idealized form, utilizes a flowing stream of hydrocarbon inside a protective cylinder of inert carrier gas. Thus, the plug flow sample is rapidly heated to the desired pyrolysis temperature (650-800°C), sampled downstream, and then analyzed by gas chromatography. Sections of screening set perpendicular to the flow could be inserted to simulate the effect of a heterogeneous surface without significantly

disturbing the plug flow. In a comparison of the thermolysis of 1, between a static system and the wall-less reactor, Taylor cited a report by Anderson and Benson [3] in which a reaction order of  $3/2$  with an activation energy of 51.6 kcal/mol for the static system was found. These numbers change to a 1st order reaction with an activation energy of 80.5 kcal/mol when utilizing Taylor's wall-less reactor. Thus, it was concluded that the activation barrier was being lowered by some heterogeneous catalytic effect. In a later report, Taylor et al. [4], using insertable screens or rods of stainless steel, quartz or carbon, stated that pre-conditioning of the surface by allowing the substrate to flow over the hot surface for a few minutes may be the most important factor for controlling the surface chemistry. The deposition of an active carbon coating on each of the three surfaces resulted in product distributions which were essentially identical.

A similar effort to eliminate surface effects was demonstrated by Berman et al. [5]. They utilized direct pulsed IR laser and  $\text{SiF}_4$ -sensitized IR irradiation to pyrolyze tetralin (2) and thus, determine its true thermal reactions. They found that the laser thermolyses resulted in a presumed concerted elimination of ethylene to give ortho-quinodimethane (3) which then isomerizes to benzo-cyclobutene (4).



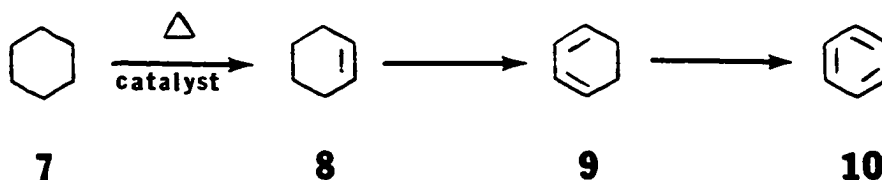
This result is in contrast to their flash vacuum pyrolysis (FVP) studies which produced primarily dehydrogenation products such as 1,2-dihydronaphthalene (5) and naphthalene (6). They cited the interference of heterogeneous surface effects causing the dehydrogenation and thus, masking the concerted loss of ethylene.



An alternative approach to this problem is to determine the changes in product distributions when the packing material in the pyrolysis system is changed. The industrial use of dehydrogenation/dealkylation catalysts in pressurized flow reactors is quite extensive [6]. Among the catalysts employed are  $\text{Cr}_2\text{O}_3$ ,

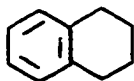
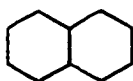
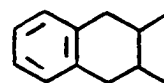
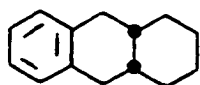
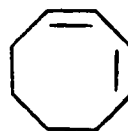
$\text{Na}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$  and other metal oxides, sulfur, zeolites, carbon supported metals and activated carbon. Laboratory applications are sparse owing to the relatively high operating temperatures employed (300–800°C). Most of the research has been done on relatively simple model systems containing simple cycloalkyl and hydroaromatic structures.

In all cases when using activated surfaces, the dehydrogenation or dealkylation reaction proceeds best when forming an aromatic nucleus. Therefore, cyclohexanes (7) [enes (8), dienes (9)] give the highest yields of dehydrogenated products [7,8,9,10], and alkyl substituents tended to lower the yields by introducing fragmentation [10,11]. Cyclopentanes also tended to undergo less dehydrogenation and more fragmentation [11,12,13,14].



In an effort to understand the surface effects involved in the FVP of tetralin (2), a variety of pyrolysis packings were employed under our thermolysis conditions. These packings included quartz, copper metal, oxidized copper, zeolite and carbon which were used in the pyrolysis of 2. Due to the interesting results obtained with tetralin, the compounds decalin (11), 2,3-dimethyltetralin (12), *cis*-

and trans-octahydroanthracene (13 and 14), 1,2- and 1,5-cyclooctadiene (15 and 16) and ortho-xylene (17) were also pyrolyzed over carbon to determine the extent of the unique dehydrogenating abilities of carbon.

**2****11****12****13****14****15****16**

## RESULTS

FVP of Tetralin (2) Over Copper Metal

The pyrolysis resulted in a distribution of products similar to that seen when the pyrolysis is carried out on quartz chips [15] as seen in Table 1. The products were identified by co-injection with authentic samples and by analysis of their mass spectra. The relative yields of the major products of the pyrolysis of 2 over copper and other pertinent data are listed in Table 2. At 820°C where there was ca. 6% conversion, the predominant products were 1,2-dihydronaphthalene (5) (37.5%) and benzocyclobutene (4) (26.3%) with naphthalene (6) (12.5%), styrene (18) (8.39%) and indene (19) (2.92%) being formed in noticeably smaller amounts. As the pyrolysis temperature was increased, small amounts of benzene (10), toluene (20), and ethylbenzene (21) were formed. The combined yield of these minor products was never > 5%. 1,2-Dihydronaphthalene (5) and benzocyclobutene (4), originally formed in the greatest amount, decreased with increasing temperature to 14.7% and 12.1%, respectively. Compound 6, which is expected to increase at the expense of 1,2-dihydronaphthalene (5), was produced in 29.9% yield at 876°C, styrene (18) also increased in yield to 17.1% at 876°C. The relative yield of indene (19) increased to 10.7% at the highest pyrolysis temperature examined.



Table 1. Relative yields of products of the flash vacuum pyrolysis (FVP) of tetralin (2) over quartz chips at various temperatures

Product	Yields, % <sup>a</sup>		
	737°C	806°C	860°C
Benzene	0.99	1.44	2.71
Toluene	2.19	1.18	3.33
Ethylbenzene	--	0.37	0.78
Styrene	9.87	12.2	18.4
Benzocyclobutene	6.09	9.97	8.87
Indene	5.19	9.21	12.9
1,2-DHN	55.5	34.6	12.4
Naphthalene	9.80	22.3	30.9
% Conversion	6.39	34.2	71.0
% TRM <sup>b</sup>	103.0	99.5	88.8

<sup>a</sup>The yields are relative GLPC yields using biphenyl as an internal standard, where relative yield = (absolute yield of product/ $\Sigma$  of absolute yields of all products)  $\times$  100%.

<sup>b</sup>% TRM = % total recovered material =  $\Sigma$  absolute yields of all the components.

Table 2. Relative yields of the products of the FVP of tetralin (2) over copper metal

Product	Yields, % <sup>a</sup>		
	820°C	834°C	876°C
Benzene	--	0.71	2.38
Toluene	--	0.53	1.56
Ethylbenzene	--	--	0.63
Styrene	8.39	11.6	17.1
Benzocyclobutene	26.3	20.0	12.1
Indene	2.92	4.45	10.7
1,2-DHN	37.5	26.7	14.7
Naphthalene	12.5	19.9	29.9
% Conversion	5.70	34.8	62.3

<sup>a</sup>The yields are relative GLPC yields using biphenyl as an internal standard where relative yield = (absolute yield of product/ $\Sigma$  absolute yields of all products) x 100%.

#### FVP of Tetralin (2) Over Copper Oxide

The oxidized copper packing, prepared by passing O<sub>2</sub> gas over copper turnings packed in the hot pyrolysis tube, changed the distribution of products markedly. The FVP of tetralin (2) resulted in a mixture of only 1,2-dihydronaphthalene (5) and naphthalene (6) at low to moderate temperatures, at temperatures

in excess of 580°C only naphthalene (6) is formed, (Table 3). A significant degree of scatter was observed for some of the data, although the general trend was an increased yield of the more highly unsaturated 6 with increasing temperature.

#### FVP of Tetralin (2) Over Zeolite

The pyrolysis of tetralin (2) not only produced different product amounts, it also produced 2- and 1-methylnaphthalene (22 and 23), both of which have one more carbon atom than the starting material. The zeolite (type LZ-Y82, size 1/8) packing proved to be highly active in that % conversions were always > 95% in the temperature range of 200 to 784°C. At both temperature extremes, the amount of total recovered material (% TRM) was observed to decrease. The formation of 22 and 23 also showed signs of temperature dependence since the highest yield occurred at ca. 450°C and decreased to zero at both temperature extremes, as shown in Table 4.

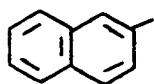
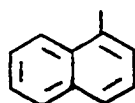
**22****23**

Table 3. Relative yields of 1,2-dihydronaphthalene (5) and naphthalene (6) from the FVP of tetralin (2) over oxidized copper<sup>a</sup>

Temperature °C	5	6	% conversion	% TRM <sup>b</sup>
354	4.21	95.0	36.8	77.4
420	0.53	99.2	80.9	42.1
530	1.45	97.50	91.5	22.0
532	13.7	84.1	52.9	58.0
580	2.04	98.0	68.3	14.4
588 <sup>c</sup>	--	quant.	quant.	0.38
592 <sup>c</sup>	--	quant.	quant.	0.10
700	--	94.7	99.7	5.53
822	8.49	87.9	97.4	3.20

<sup>a</sup>Relative yield = (absolute yield of the product/ $\Sigma$  of the absolute yields of all of the products)  $\times$  100%.

<sup>b</sup>% TRM = % total recovered material =  $\Sigma$  of the absolute yields of all of the components.

<sup>c</sup>The oxidized copper was used immediately after a preceding pyrolysis run without passing O<sub>2</sub> gas over it.

Table 4. Relative yields of naphthalene (6) 2- and 1-methyl-naphthalene (22 and 23) from the pyrolysis of tetralin (2) over zeolite at various temperatures<sup>a</sup>

Temperature, °C	<u>6</u>	<u>22</u>	<u>23</u>	% conversion	% TRM <sup>b</sup>
200	quant.	--	--	95.8	4.35
320	90.9	2.83	1.17	99.3	79.9
434	83.8	5.16	2.23	99.4	72.8
508	91.9	4.12	2.02	99.9	68.0
564	94.8	2.21	0.61	99.9	61.8
616	98.0	0.64	0.32	quant.	58.7
700	97.5	1.06	0.49	quant.	22.0
784	quant.	--	--	quant.	8.47

<sup>a</sup>Relative yield = (absolute yield of product/ $\Sigma$  of the absolute yields of the products)  $\times$  100%.

<sup>b</sup>% TRM = % total recovered material =  $\Sigma$  of the absolute yields of all of the components.

#### FVP of Tetralin (2) Over Carbon

The sole reaction of the pyrolyses was dehydrogenation to form 1,2-dihydronaphthalene (5) and naphthalene (6). Naphthalene (6) was always the major product, never < 84% of the product mixture, as shown by GLPC. At temperatures above 700°C, it is the sole product, see Table 5.

Table 5. Relative yields of 1,2-dihydronaphthalene (5) and naphthalene (6) from the FVP of tetralin (2) over carbon at various temperatures<sup>a</sup>

Temperature, °C	<u>5</u>	<u>6</u>	% conversion	% TRM <sup>b</sup>
436 <sup>c</sup>	9.21	85.0	9.59	99.1
550 <sup>c</sup>	2.33	96.5	46.5	105.0
706 <sup>c</sup>	--	quant.	99.8	80.2
625 <sup>d</sup>	--	quant.	97.7	82.8

<sup>a</sup>Relative yield = (absolute yield of product/ $\Sigma$  absolute yield of all products)  $\times$  100%.

<sup>b</sup>% TRM = % total recovered material =  $\Sigma$  of the absolute yields of all of the components.

<sup>c</sup>Charcoal lumps were used as the pyrolysis packing.

<sup>d</sup>A ca. 1:5 mixture of active carbon pellets and quartz chips was used as the pyrolysis packing.

The % conversion and % TRM meshed nicely to produce a very efficient reaction wherein most of the starting material was consumed and most of the naphthalene (6) was recovered. For instance, with > 99% of the starting tetralin (2) consumed, naphthalene (6) was recovered in 80%, the highest yield of any of the previous active packings.

## Pyrolytic Dehydrogenation Over Carbon

The yields from the pyrolysis of some selected hydroaromatic compounds are listed in Table 6. It may be seen that the expected high yields of the fully aromatized compounds do in fact result from the use of carbon as the pyrolysis packing. The pyrolysis of

Table 6. Relative yields of dimethylnaphthalene (24) and anthracene (25) from the pyrolysis of selected hydroaromatic compounds over charcoal<sup>a</sup>

Compound	<u>24</u>	<u>25</u>	% conversion	% TRM <sup>b</sup>
2,3-dimethyltetralin ( <u>12</u> ) <sup>c</sup>	75.0	--	82.1	88.4 <sup>d</sup>
<u>cis</u> -octahydroanthracene ( <u>13</u> ) <sup>c</sup>	--	99.4	quant.	92.2
<u>trans</u> -octahydroanthracene ( <u>14</u> ) <sup>c</sup>	--	quant.	quant.	90.8

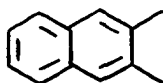
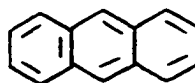
<sup>a</sup>Relative yield = (absolute yield of product/ $\Sigma$  absolute yields of all products) x 100%.

<sup>b</sup>% TRM = % total recovered material =  $\Sigma$  of absolute yields of all the components.

<sup>c</sup>The pyrolyses were carried out at 638, 664 and 654°C, respectively.

<sup>d</sup>Also formed were naphthalene, 2- and 1-methylnaphthalene (22 and 23) in 7% combined yield.

2,3-dimethyltetralin (12) resulted in the formation of 2,3-dimethylnaphthalene (24) in 75% yield. An expected cleavage to form methyl radical, resulted in the low yield of 24 and the formation of 2-methylnaphthalene (22) as determined by GCMS analyses. Pyrolytic dehydrogenation of cis- and trans-octahydroanthracene (13 and 14), resulted in high yields of anthracene (25) from both compounds.

**24****25**

The pyrolysis of 1,3- and 1,5-cyclooctadiene (15 and 16) resulted in a complex mixture of products upon GLPC analysis. Analysis by GCMS revealed no products resulting from dehydrogenation only, such as cyclooctatriene (26) or cyclooctatetraene (27).

The pyrolysis of ortho-xylene (17) over carbon was carried out at 664 and 778°C. There were no products detected by GLPC at either one of the temperatures. The starting material was recovered in ca. 95% absolute yield.

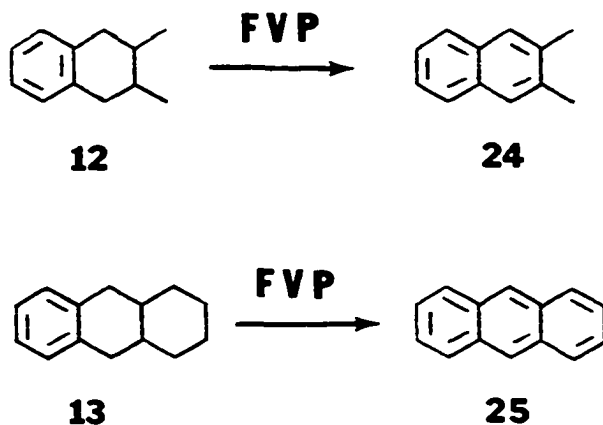


## DISCUSSION

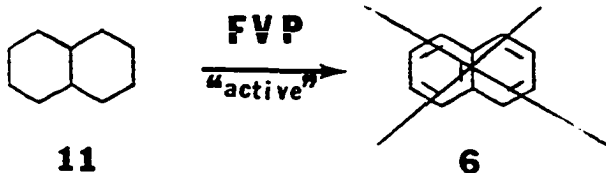
The differences in activity of the packings employed are clear-cut and extreme. They range from that observed with quartz which seems to provide a fairly "inactive" surface functioning to transfer thermal energy, to oxidized copper which directly influences the thermochemistry by affecting the products and % TRM. The primary reaction of the "active" packings is that of dehydrogenation especially when it will result in the formation of an aromatic nucleus. The pyrolyses of tetralin (2) over oxidized copper, zeolites and carbon all yielded naphthalene (6) in excess of 80% and quite often in the realm of 95%. The amount of recovered



material was very different for each, carbon gave the highest return with ca. 90% then zeolite and oxidized copper with ca. 70% for each. The production of the fully aromatized substituted naphthalene (24) and anthracene (25) from the thermolyses over carbon of 2,3-dimethyltetralin (12) and cis- and trans-octahydroanthracene (13 and 14) provided further proof of the dehydrogenating capability initially observed with tetralin (2).



However, the presence of at least 1 aromatic ring appears to be important under our conditions. A case in point is the pyrolysis of decalin (11) over carbon which did not produce any naphthalene (6). Even though 11 contains two fused six-membered rings, similar to tetralin (2), it did not aromatize due to its lack of an "initiating" aromatic system.

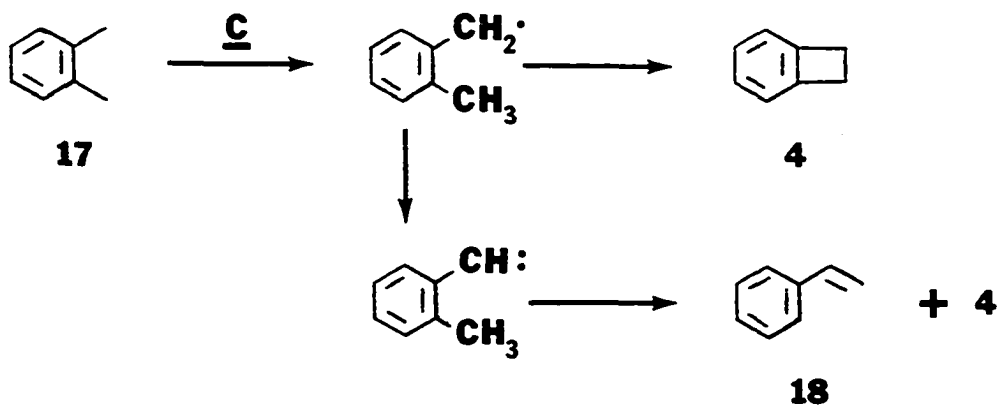


Further proof of this rule was gained from the pyrolyses of 1,3- and 1,5-cyclooctadiene (15 and 16). It was hoped that the cyclooctadienes 15 and 16 might be further dehydrogenated to

either cyclooctatriene (26) or cyclooctatetraene (27). However, the lack of any compounds of mass 106 or 104 amu, that of either desired product, laid to rest the possibility that this method could be used for the dehydrogenation of a non-aromatic system.

An additional complication involves the thermal instability of cyclooctatetraene (27). In 1961, Nenitzescu [14] showed that 27 is unstable at temperatures in excess of 400°C. Therefore, it is likely that even if cyclooctatetraene (27) were formed under our conditions, it would not survive the thermal conditions necessary to bring about pyrolytic dehydrogenation.

The possibility that a benzylic hydrogen might be more susceptible to pyrolytic dehydrogenation prompted the pyrolysis of ortho-xylene (17). If such a dehydrogenation were to take place, one might expect the formation of benzocyclobutene (4) or possibly styrene (18). Since only ortho-xylene (17) was recovered, it may be concluded that a longer alkyl chain or even a fused ring system is necessary to bring about the reaction.



These results indicate that although the active packings do exhibit unique reactivity compared to quartz chips, they do not provide a truly useful reaction. The active packings produced only dehydrogenated compounds at relatively low temperatures, whereas the pyrolyses of tetralin (2) over quartz [15] required higher temperatures ( $> 800^{\circ}\text{C}$ ) for significant reaction and produced compounds resulting from fragmentation as well as dehydrogenation. Thus, a comforting feeling arises from the realization that the quartz chips do not strongly attenuate the "true" thermal reaction. In fact, the specific reproducible reactivity or rather non-reactivity of the quartz packing could be maintained by a cleaning process consisting of flowing  $\text{O}_2$  gas over the hot chips.

## EXPERIMENTAL

## General

The flash vacuum pyrolysis (FVP) method and apparatus have been described [16]. Gas chromatographic analysis was performed on a Hewlett Packard 5840-A gas chromatograph utilizing either a 20-m SP 2100 (methylsilicone fluid) or a 30-m DB-1 (methylsilicone fluid) fused-silica capillary column and a flame-ionization detector. Combined gas chromatographic/mass spectra (GCMS) analysis was performed on a Finnigan 4000 GCMS with an Incos 2500 data system and Finnigan 9610 gc.

The commercially available chemicals are listed in Table 7.

## General Pyrolysis Procedure

The sample (20 mg to gram quantities) was weighed into a round-bottomed flask. After purging the pyrolysis system with dry  $N_2$ , the sample flask was attached and the trap was immersed in liquid nitrogen. The system was opened to a vacuum pump (0.1 to 0.01 mm) and the sample was allowed to distill through the pyrolysis tube. The sample flask was usually kept at ambient temperature but it could be heated or cooled according to the volatility of the sample. Upon completion of the pyrolysis, the vacuum line was closed and dry  $N_2$  gas was slowly leaked into the system to facilitate removal of the trap. The trap was disconnected, stoppered and warmed to room temperature before a solvent was added for analysis. If a

Table 7. Commercially available compounds

Compound	Source
Anthracene	Aldrich Chemical Company
Benzene	Fisher Scientific Company
Carbon dust	Baker Chemical Company
Carbon pellets	Roy Laboratory
Charcoal	Walter S. Trahanovsky
Copper metal	Baker Chemical Company
1,3- and 1,5-Cyclooctadiene	Aldrich Chemical Company
Decalin	Aldrich Chemical Company
1,2-Dihydronaphthalene	Aldrich Chemical Company
2,3-Dimethyltetralin	Karl Swenson, W. S. Trahanovsky group
Ethylbenzene	Aldrich Chemical Company
Indene	Aldrich Chemical Company
Naphthalene	Baker Chemical Company
<u>cis</u> -Octahydroanthracene	Karl Swenson, W. S. Trahanovsky group
<u>trans</u> -Octahydroanthracene	Karl Swenson, W. S. Trahanovsky group
Styrene	Aldrich Chemical Company
Toluene	Baker Chemical Company
<u>ortho</u> -Xylene	Aldrich Chemical Company
Zeolite (type LZ-Y82, size 1/8)	Linde/Union Carbide Corporation

quantitative GC analysis was going to be made, the solution was transferred to a vial containing a weighed amount of biphenyl internal standard. Identification of the individual components of the pyrolyzate was based on molecular weight and fragmentation patterns, as determined by GCMS and co-injection with commercial samples. After each pyrolysis, the pyrolysis tube was cleaned by passing  $O_2$  gas through the tube while it was heated to  $> 800^\circ C$ .

#### Preparation of the Pyrolysis Packings

The copper metal turnings were loosely packed into a room temperature pyrolysis tube, connected to the FVP apparatus and evacuated. The power to the furnace was then turned on and then controlled so as to sustain the desired pyrolysis temperature (ca. 4 h). The apparatus was then brought to atmospheric pressure with dried  $N_2$  gas and the sample was then added and pyrolyzed as usual.

The copper was oxidized by passing  $O_2$  gas through a loose packing of the metal while the tube was heated in the furnace to ca.  $900^\circ C$ . The tube was then cooled to the desired temperature and the pyrolysis was carried out as usual.

The carbon surfaces, whether they were present as charcoal, powdered carbon or pelletized carbon, were added to a room temperature pyrolysis tube which was then attached to the pyrolysis

apparatus. The apparatus was evacuated and the power to the furnace was turned on. Upon reaching the desired pyrolysis temperature, the apparatus was brought to atmospheric pressure with dried N<sub>2</sub> gas and the pyrolysis was continued as usual.

#### FVP of Tetralin (2) Over Copper Turnings

FVP of 2 resulted in a mixture of 8 major products which were identified by co-injection of an authentic sample and comparison of the GCMS of the products with authentic samples. The compounds identified in this manner were benzene (5), toluene (19), ethylbenzene (20), styrene (17), benzocyclobutene (15), indene (18), 1,2-dihydronaphthalene (5) and naphthalene (6). The yields and other data are tabulated in the results section.

#### FVP of Tetralin (2) Over Oxidized Copper

The FVP of 6, when executed over oxidized copper, yielded only 1,2-DHN (5) and naphthalene (6). These compounds were identified as outlined above. The relative yields and other data are tabulated in the results section.

#### FVP of Tetralin (2) Over Zeolite

The FVP of 2 resulted in the production of mostly naphthalene (6) with some 2- and 1-methylnaphthalene (22 and 23) as minor products. The relative yields and other pertinent data are tabulated in the results section.



FVP of Tetralin (2) Over Carbon

The FVP of 2 over carbon produced only 1,2-DHN (5) and naphthalene (6). The relative yields and associated data are tabulated in the results section.

FVP of 2,3-Dimethyltetralin (12)

The FVP of 12 at 638°C resulted in the formation of 2,3-dimethylnaphthalene (24) in 74.95% and 2-methylnaphthalene (22) and naphthalene (16) in a combined yield of 7%. The % conversion and % TRM are tabulated in the results section.

FVP of cis- and trans-Octahydroanthracene (13 and 14)

The FVP of 13 and 14 both resulted in > 99% formation of anthracene (25) as the sole product. Other relevant data are tabulated in the results section.

Attempted Formation of Benzocyclobutene (4) from  
the FVP of ortho-Xylene (17)

The FVP of 17 did not produce any benzocyclobutene (4) up to the maximum temperature employed (778°C). The only recovered material was the starting compound 17.

FVP of 1,3- and 1,5-Cyclooctadiene (COD) (15 and 16)

The FVP of 1,3-COD (15) is representative of the procedure used for both 15 and 16. The pyrolysis of 15 over carbon resulted in a pale-yellow pyrolyzate, the GCMS analysis of which disclosed only products resulting from fragmentation of the starting material. There were no parent ions indicative of cyclooctatriene (26) or COT (27). The pyrolysis of 1,5-COD 16 produced similar results.

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## GENERAL SUMMARY

For Part I, the thermal isomerization of benzocyclobutene to styrene was found to involve the intermediacy of tolylcarbenes and cycloheptatetraenes, as shown by the flash vacuum pyrolysis (FVP) of benzocyclobutene-1,1- $d_2$ . A kinetic deuterium isotope effect of ca. 2.2 was established for the C-H (D) insertion of an arylcarbene species involved in the isomerization. The pyrolysis of 4-methyl- $d_3$ -benzocyclobutene and 2-methyl-5-methyl- $d_3$  benzyldiazomethane established a migratory preference for an intermediate arylcarbene which was explained on the grounds of steric interactions.

For Part II, the pyrolysis of ortho-xylylene in an  $H_2$  atmosphere produced ortho-xylene. The pyrolysis of ortho-xylylene in an atmosphere of  $D_2$  gas produced ortho-xylene- $d_2$  which is  $> 92\%$   $d_2$ . We interpret the data as indicating that ortho-xylene adds  $H_2$  and  $D_2$  gas in a [4+2] concerted reaction.

In Part III, the pyrolysis of 1,2-dihydronaphthalene and ortho-divinylbenzene did not produce direct evidence for the ortho-quinodimethane 2,3-dihydronaphthalene. However, indirect evidence was found in that the pyrolysis of ortho-divinylbenzene produced 1,2-dihydronaphthalene. This could occur only through the intermediacy of 2,3-dihydronaphthalene.

For Part IV, the pyrolysis of several simple hydroaromatic compounds over active packings of oxidized copper, zeolites and carbon produced fully aromatized compounds. It was found that

compounds which did not contain an initiating aromatic center did not dehydrogenate but fragmented instead. It was also concluded that the quartz chips which we use in our normal FVP procedures provided a reproducibly inert surface for the transfer of thermal energy.

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