1987

I. Gas-phase intramolecular Diels-Alder reactions of 2,3-dimethylene-2,3-dihydrofurans; II. Formation of anthracene and other polycyclic aromatic compounds in the pyrolysis of 1,5-dibenzocyclooctadienes and related compounds; III. Formation of 9-methylanthracene and anthracene in the pyrolysis of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene and other related compounds; IV. Preparation of cyclopentadienones by flash vacuum pyrolysis and their dimerization and intramolecular reactions

Suk Kyu Lee
Iowa State University

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Lee, Suk Kyu

I. GAS-PHASE INTRAMOLECULAR DIELS-ALDER REACTIONS OF 2,3-DIMETHYLENE-2,3-DIHYDROFURANS. II. FORMATION OF ANTHRACENE AND OTHER POLYCYCLIC AROMATIC COMPOUNDS IN THE PYROLYSIS OF 1,5-DIBENZOCYCLOOCTADIENES AND RELATED COMPOUNDS. III. FORMATION OF 9-METHYLANTHRACENE AND ANTHRACENE IN THE PYROLYSIS OF 5,6,11,12-TETRAHYDRODIBENZO(A,E)CYCLOOCTENE AND OTHER RELATED COMPOUNDS. IV. PREPARATION OF CYCLOPENTADIENONES BY FLASH VACUUM PYROLYSIS AND THEIR DIMERIZATION AND INTRAMOLECULAR REACTIONS

Iowa State University PH.D. 1987

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by

Suk Kyu Lee

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Major: Organic Chemistry

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Ames, Iowa

1987

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For Part IV

GENERAL INTRODUCTION

The pyrolysis of benzoates and hydrocarbons has been carried out by our research group to obtain novel intermediates as well as to discover novel thermal reactions. As parts of these studies, we investigated the areas summarized below.

In Part I, intramolecular Diels-Alder reactions of 2,3-dimethylene-2,3-dihydrofurans were investigated to establish the scope of the reaction and to explore its use in the synthesis of polycyclic compounds. The preparation and the flash vacuum pyrolysis (FVP) of 2-alkenyl-3-furylmethyl benzoates are presented.

In Part II, FVP of 1,5-dibenzocyclooctadienes containing heteroatoms and dibenzosuberanes were carried out in order to obtain a better understanding of the formation of anthracene from the FVP of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1).

Part III presents a mechanistic study of the formation of 9-methylanthracene from the sealed tube pyrolysis of 1. This study was carried out by pyrolyzing several possible precursors for 9-methylanthracene.

Part IV presents a new method of preparing cyclopentadienones by the pyrolysis of cyclic diethers. Intramolecular Diels-Alder reactions of cyclopentadienones were investigated

to develop a new way of preparing polycyclic compounds as well as to prove the transient existence of cyclopentadienones.

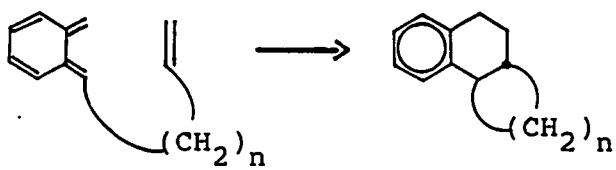
Explanation of Dissertation Format

This dissertation has been written using the alternate dissertation format and consists of four parts written as complete papers in a style suitable for publication in journals published by the American Chemical Society. All of the experimental results presented in Parts I through IV were contributed by the candidate.

PART I. GAS-PHASE INTRAMOLECULAR DIELS-ALDER REACTIONS OF 2,3-DIMETHYLENE-2,3-DIHYDROFURANS

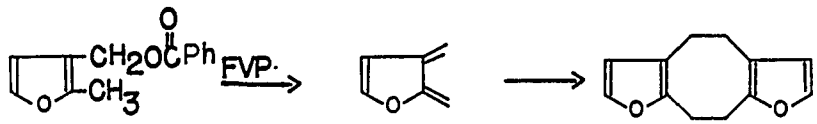
INTRODUCTION

o-Xylylene and its derivatives have been the subject of both mechanistic and synthetic studies.[1] o-Quinodimethanes have been generated by various methods such as the ring opening of benzocyclobutenes,[2-5] cheletropic desulfurization from 1,3-dihydrobenzo[c]thiophene-2,2-dioxides,[6,7] the flash vacuum pyrolysis of acetates or benzoates,[8] the Hoffman elimination method,[9] and the fluoride anion induced 1,4-elimination of o-(α-trimethylsilylallyl)benzyltrimethylammonium halides.[10] o-Quinodimethanes have been utilized in intramolecular Diels-Alder reactions that are key steps in regio- and stereoselective syntheses of polycyclic compounds including steroids[11-16] and alkaloids.[17-19] Equation (1) is the generalized reaction used in the synthesis of polycyclic



n = 3,4 (1)

compounds. For the past several years, 2,3-dimethylene-2,3-dihydrofuran (1), the furan analogue of o-xylylene which can be prepared by the flash vacuum pyrolysis (FVP) of 2-methyl-3-furylmethyl benzoate (2) and has been under study by our research group.[8,20] Compound 1 in solution at temperatures

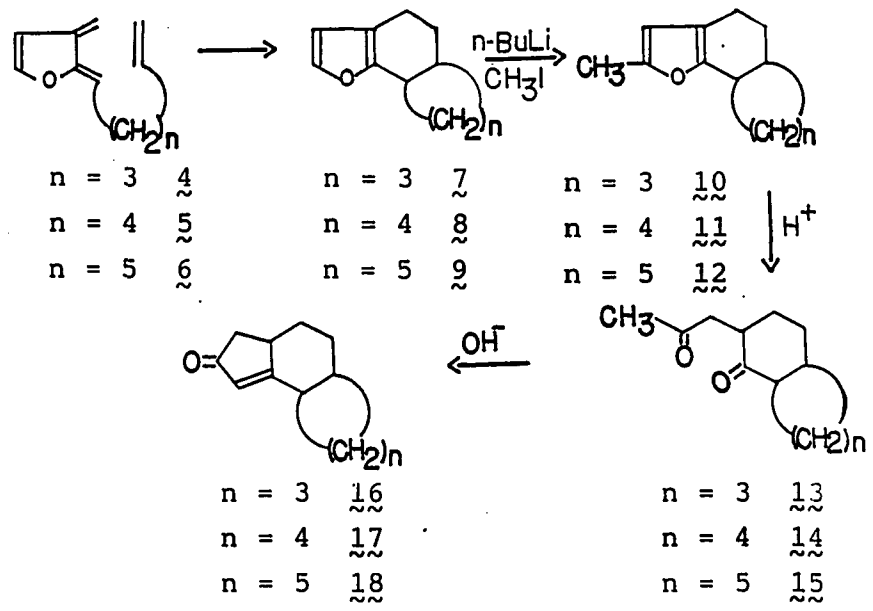


2 1 3

above -30°C dimerizes rapidly and quantitatively to the head to head [4+4] dimer 3.[8]

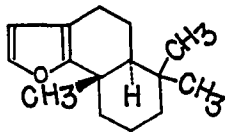
As part of our study of 2,3-dimethylene-2,3-dihydrofurans, we set out to investigate their use in intramolecular Diels-Alder reactions. We anticipated that each of the 2,3-dimethylene-2,3-dihydrofurans 4, 5, and 6 would undergo an intramolecular Diels-Alder reaction to give furan-containing

Scheme 1



tricyclic compounds 7, 8, and 9, respectively. These products could be converted to cyclopentenone-containing tricyclic compounds 16, 17, and 18, respectively, by methylation using n-butyllithium followed by furan ring opening and reclosing[21]

(Scheme 1). Compounds 16, 17, and 18 are important skeletons for steroids and these could be utilized in the synthesis of naturally occurring tricyclic compounds. Compound 8 also has the ring system of naturally occurring furanosesquiterpenes such as pallascensin A (19)[22] and microcionin-1 (20).[23] The synthesis of 19 has been reported in both racemic[24,25] and



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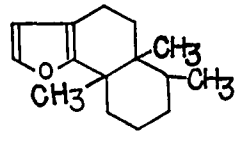
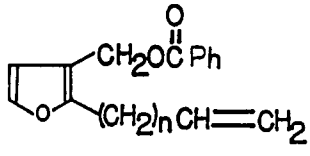


20

chiral forms,[26-28] but the synthesis of 20 has not been reported to date. In this paper the study of the intramolecular Diels-Alder reactions of 2,3-dimethylene-2,3-dihydrofurans generated by the pyrolysis of 2-alkenyl-3-furylmethyl benzoates 21, 22, and 23 will be presented.

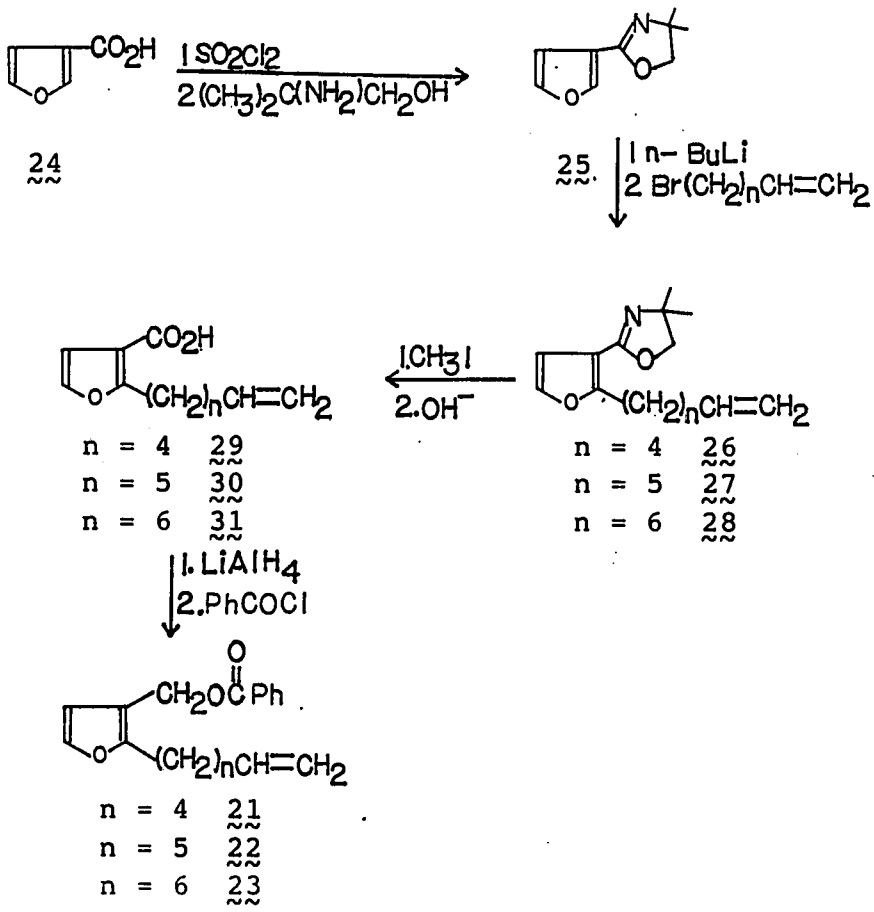


n = 4 21
n = 5 22
n = 6 23

RESULTS

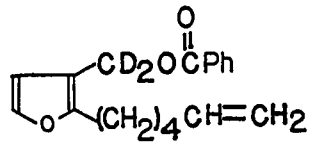
The syntheses of 2-alkenyl-3-furylmethyl benzoates 21, 22, and 23 were carried out using the o-metalation reaction of the oxazoline protecting group[29] as a key step and are summarized in Scheme 2. 2-(5-Hexenyl)-3-furylmethyl-α,α-d_2 benzoate

Scheme 2



(21-d_2) was prepared by reducing 29 with lithium aluminum

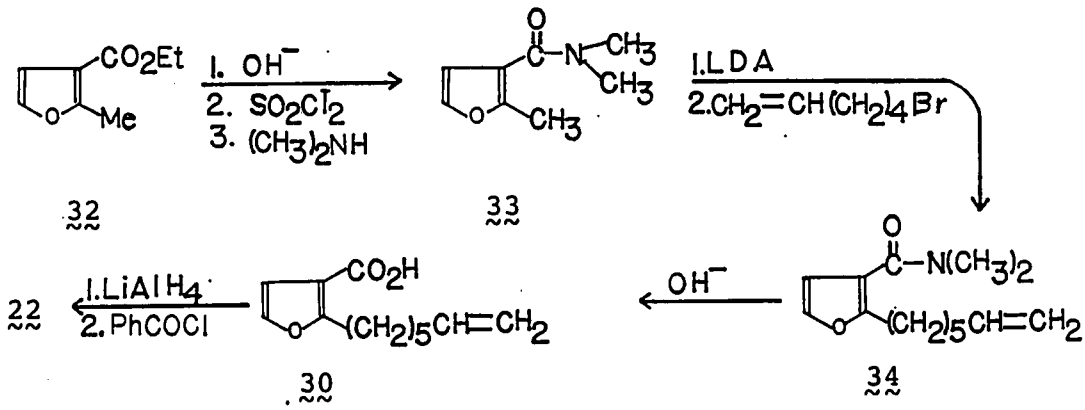
deuteride followed by esterification of the alcohol with benzoyl chloride.



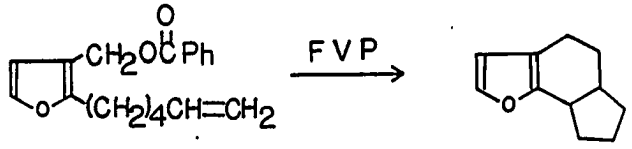
21-d_2

The synthesis of 2-(6-heptenyl)-3-furylmethyl benzoate (22) was also carried out using the o-metalation reaction of the amide group[30] as a key step and this sequence is summarized in Scheme 3.

Scheme 3



The flash vacuum pyrolysis (FVP) of 21 at 650°C gave a 99% relative yield of a 3:7 mixture of cis-7 and trans-7 (7c,t). The structures of 7c,t were determined by their spectral



21 7c,t

properties. The ^{1}H NMR spectrum of a 3:7 mixture of cis-7 and trans-7 (Fig. 1) included doublets at δ 7.16 (J = 1.76 Hz), 7.14 (J = 0.84 Hz), 6.13 (J = 1.74 Hz) and 6.08 (J = 1.73 Hz) for the furan group, a quartet at δ 2.9 (J = 6 Hz) for the CH group adjacent to the furan ring and a multiplet at δ 2.6-0.7 for the protons of the 5- and 6-membered rings. The ^{13}C NMR spectrum (Fig. 2) included signals at δ 152.93, 152.81, 139.31, 139.06, 115.28, 115.00, 109.36, and 108.87 for the furan groups, and at δ 46.04, 42.25, 38.27, 36.73, 29.81, 29.41, 28.77, 28.37, 26.64, 25.82, 25.68, 23.62, 22.36, 21.71, and 19.36 for the carbons of the 5- and 6-membered rings. GC/MS and high resolution mass spectral data were consistent with the molecular formula $C_{11}H_{14}O$. The FVP of 21-d_2 at 650°C also gave a 99% relative yield of a 1:3 mixture of cis-35 and trans-35 (35c,t). The deuterium NMR spectrum of 35c,t included a broad singlet at δ 2.4. The ^{1}H NMR spectrum (Fig. 3) also showed reduced intensity around δ 2.4.

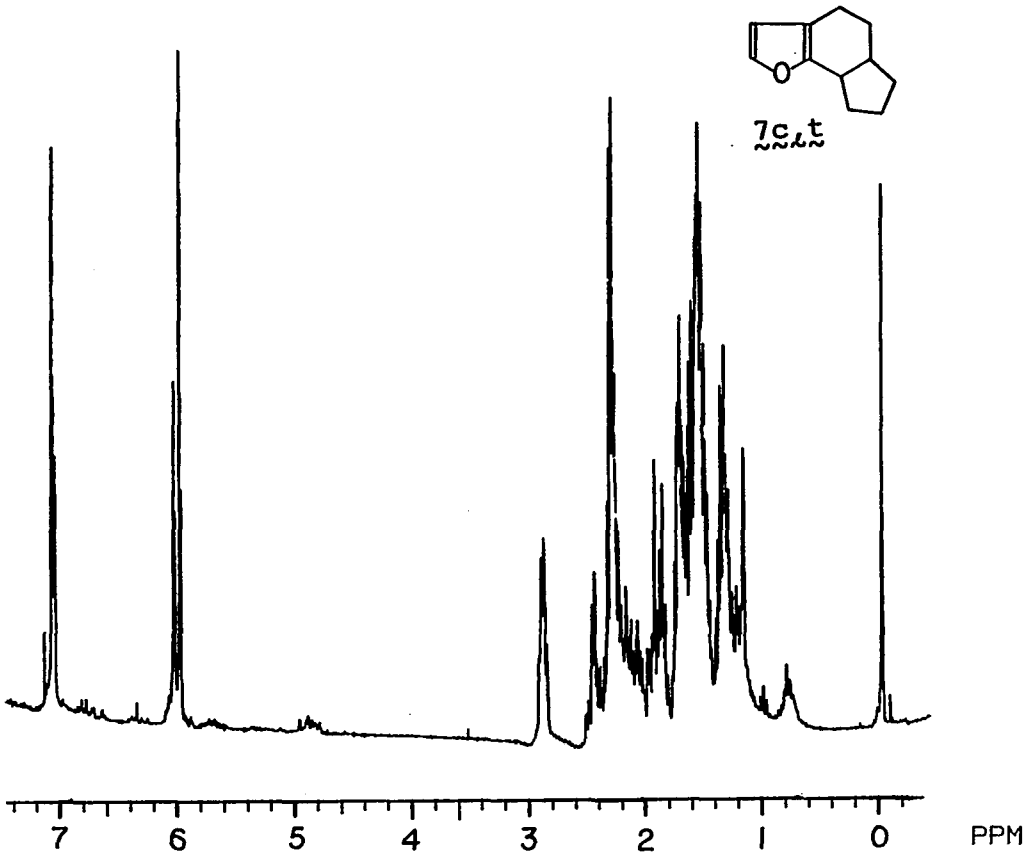


Figure 1 ^{1}H NMR spectrum of a 3:7 mixture of cis- and trans-4,5,5a,6,7,8a-hexahydro-8H-indeno[4,5-b]furans (7c,t)

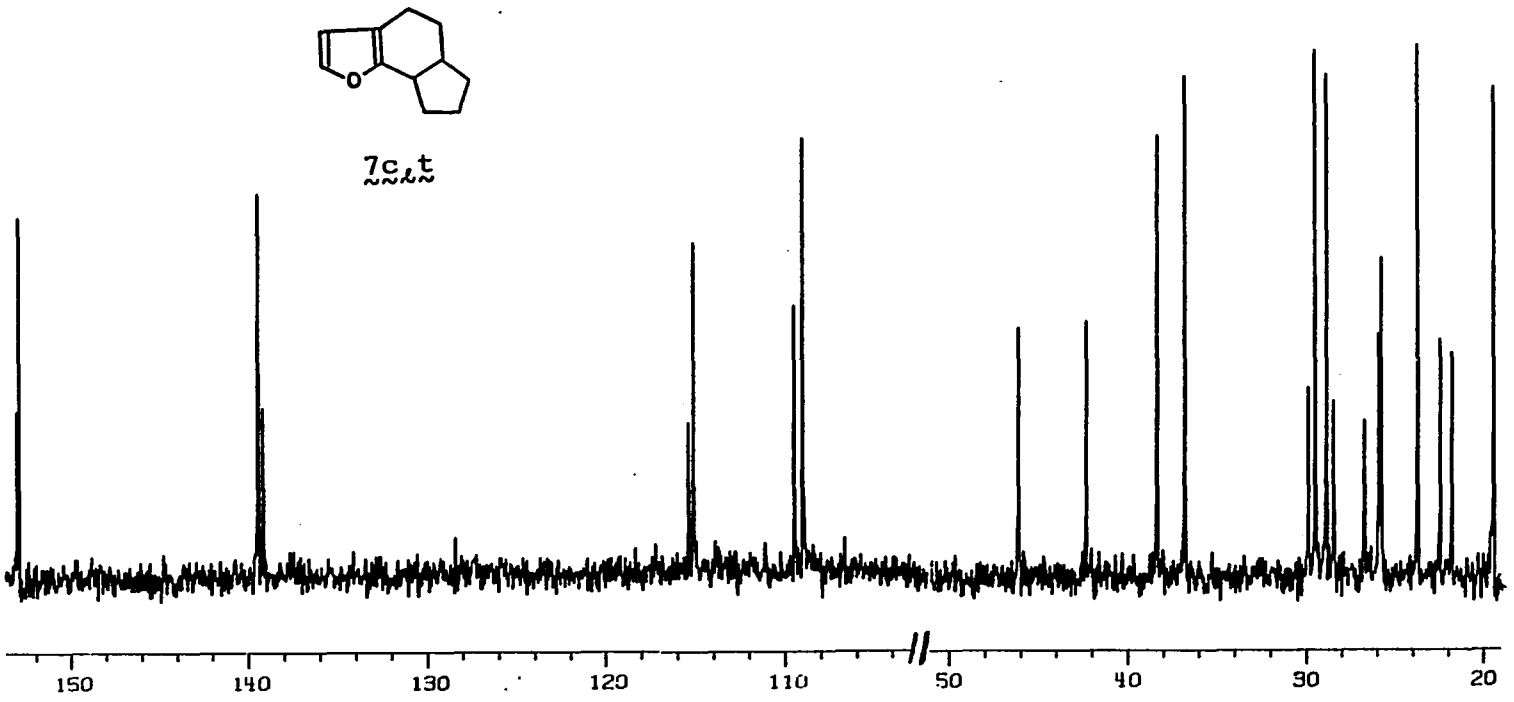


Figure 2. ^{13}C NMR spectrum of a 3:7 mixture of cis- and trans-4,5,5a,6,7,8a-hexahydro-8H-indeno[4,5-b]furans (7c,t)

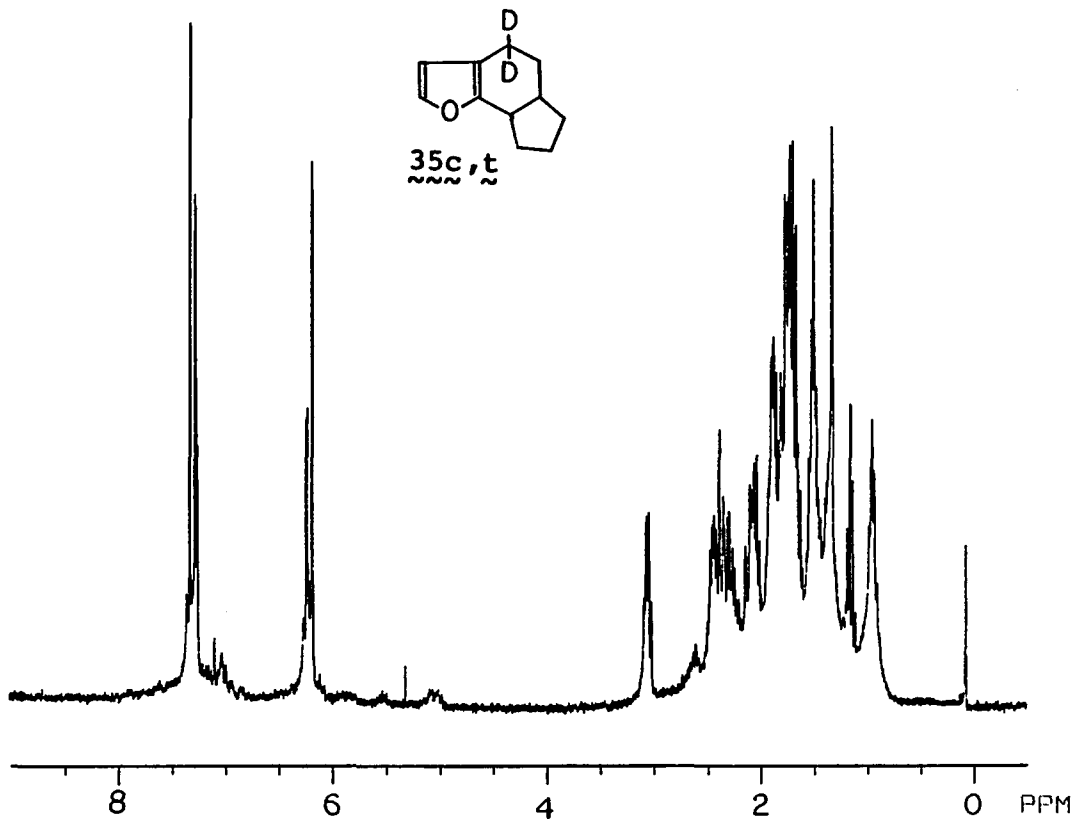
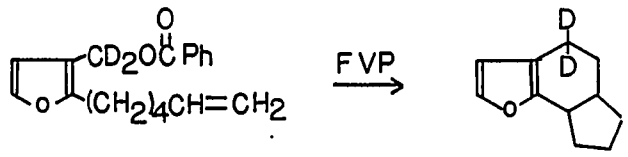
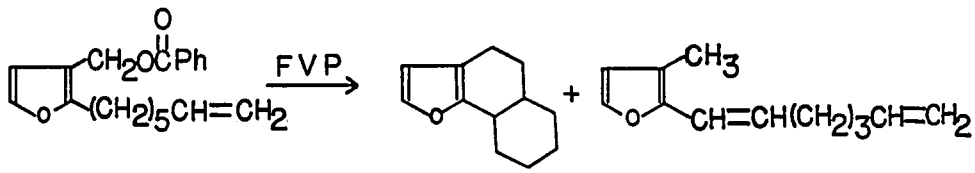


Figure 3. ^{1}H NMR spectrum of a mixture of cis- and trans-4,5,5a,6,7,8a-hexahydro-4,4-dideutero-8H-indeno[4,5-b]furans (35c,t)



21-d_4 35c,t

The FVP of 22 at 640°C gave an 82% relative yield of a 47:53 mixture of cis-8 and trans-8 (8c,t), and an 18% relative yield of a 4:14 mixture of cis-36 and trans-36 (36c,t). The ^{1}H NMR spectrum of the mixture of cis-8 and trans-8 (Fig. 4)



22 8c,t 36c,t

included doublets at δ 7.17 (J = 2 Hz) and 6.09 (J = 2 Hz) for the furan group, a quartet at δ 2.81 for the CH group adjacent to the furan ring, and a multiplet at δ 2.6-0.8 for the protons of the 6-membered rings. ^{13}C NMR spectrum (Fig. 5) included signals at δ 153.42, 140.27, 115.82, 115.50, 110.36 and 110.23 for the furan groups and at δ 41.67, 41.64, 35.23, 34.91, 33.66, 31.10, 28.95, 28.93, 26.97, 26.79, 26.24, 24.00, 23.94, 22.21, and 20.76 for the carbons of the 6-membered rings. GC/MS data were consistent with the molecular formula $C_{12}H_{16}O$. The ^{1}H NMR spectrum of a 6:4 mixture of 36c,t and

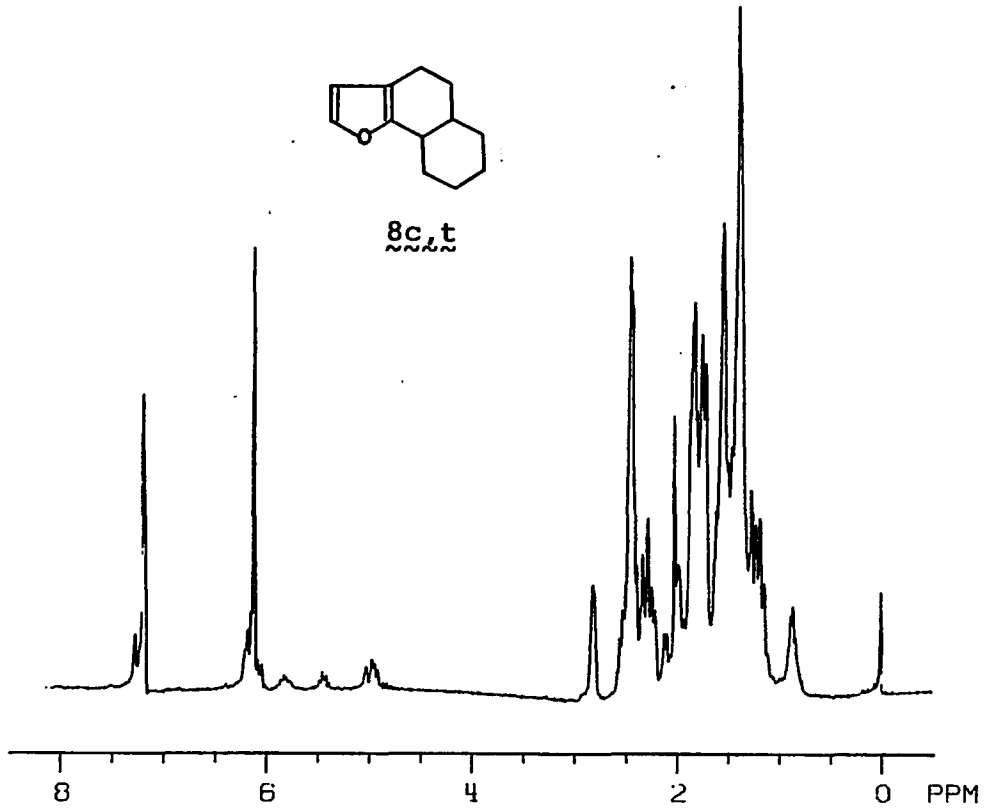


Figure 4. ^{1}H NMR spectrum of a mixture of cis- and trans-4,5,5a,6,7,8,9,9a-octahydronaphtho[1,2-b]furans (8c,t)

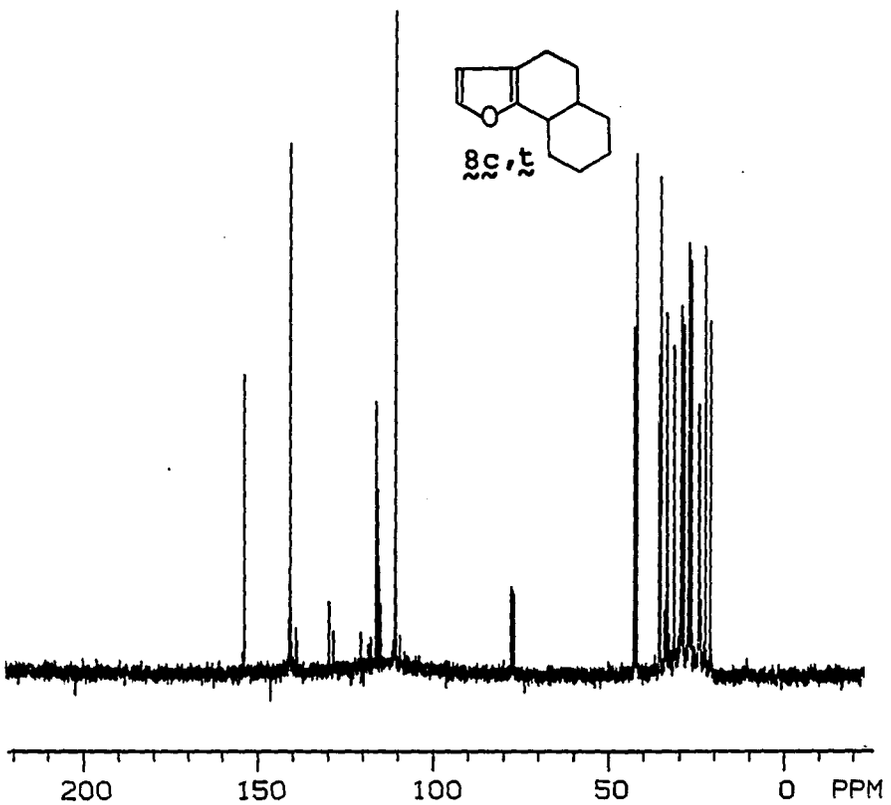
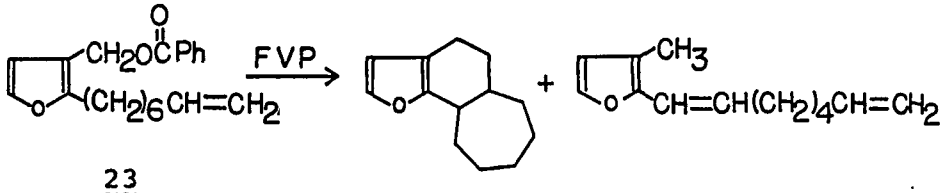


Figure 5. ^{13}C NMR spectrum of 8c,t

8c,t (Fig. 6) included a doublet at δ 7.15 (J = 1.7 Hz), and multiplets at δ 6.29-5.65, 5.15-4.82, and 2.2-1.0.

The FVP of 23 at 640°C gave about a 36% relative yield of 1:1 mixture of cis-9 and trans-9 (9c,t), and a 64% relative yield of a 1:3 mixture of cis-37 and trans-37 (37c,t). The



23 9c,t 37c,t

structures of 9c,t were determined by their spectral properties. The ^{1}H NMR spectrum of an 82:18 mixture of 9c,t and 37c,t (Fig. 7) included doublets at δ 7.2 and 6.1 for the furan group, a quartet at δ 3.4 (J = 6 Hz) for the CH group adjacent to the furan group, and a multiplet at δ 2.6-1.0 for the protons of the 6- and 7-membered rings. The ^{13}C NMR (Fig. 8) also included two sets of signals. GC/MS data were consistent with the molecular formula $C_{13}H_{18}O$. The structures of 37c,t were also determined by spectral properties. The ^{1}H NMR of an 89:11 mixture of 37c,t and 9c,t (Fig. 9) included doublets at δ 7.15 (J = 1.7 Hz) and 6.17 (J = 1.7 Hz) for the furan group, multiplets at δ 6.15-6.10, 6.09-5.95, 5.85-5.65 and 5.05-4.85 for the olefinic groups, and multiplets at δ 2.25-1.95 and 1.55-0.75 for the protons of the 6- and 7-membered rings. The ^{13}C NMR spectrum also included signals

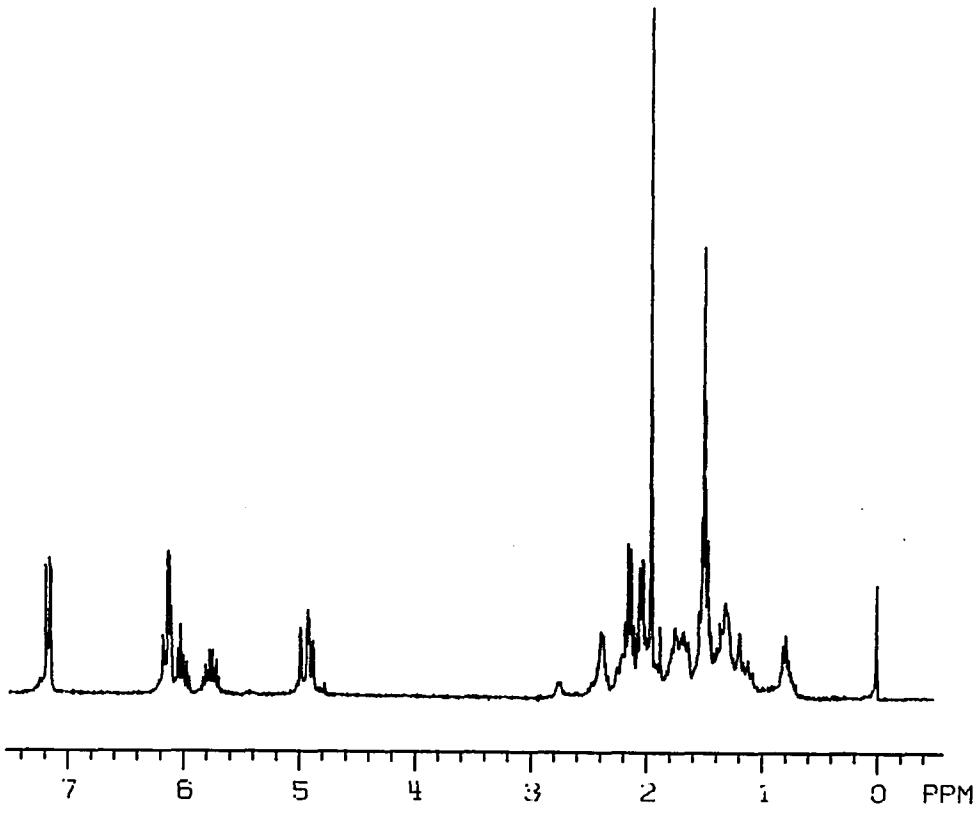


Figure 6. ^{1}H NMR spectrum of a 6:4 mixture of cis- and trans-2-(1,6-heptadienyl)-3-methylfurans (36c,t) and cis- and trans-4,5,5a,6,7,8,9,9a-octahydronaphtho[1,2-b]furans (8c,t)

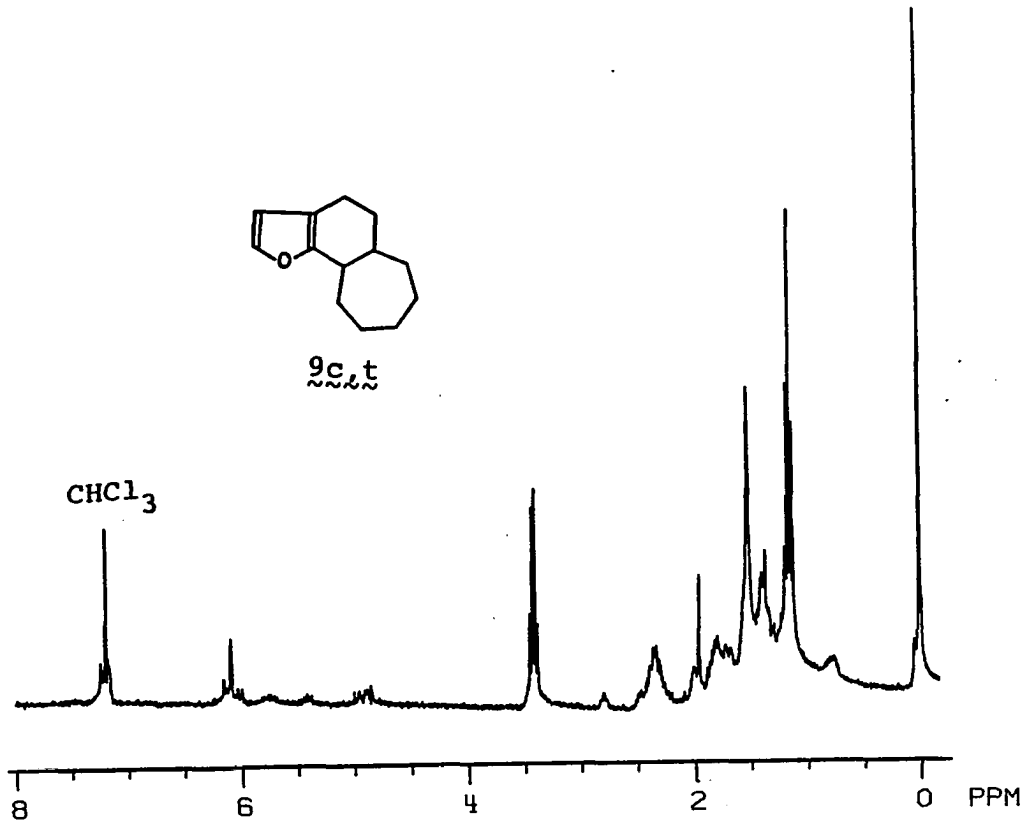


Figure 7. ^{1}H NMR spectrum of a 82:18 mixture of 9c,t and cis- and trans-2-(1,7-octadienyl)-3-methylfurans (37c,t)

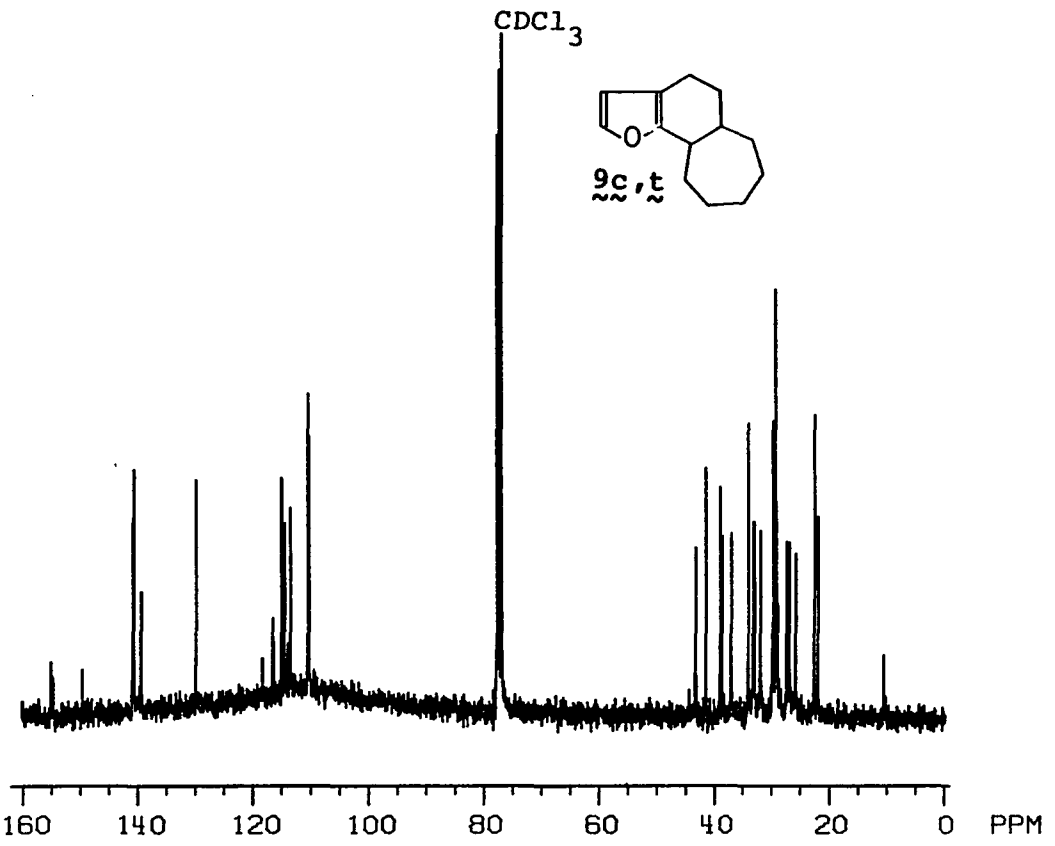


Figure 8. ^{13}C NMR spectrum of a 82:18 mixture of 9c,t and cis- and trans-2-(1,7-octadienyl)-3-methylfurans (37c,t)

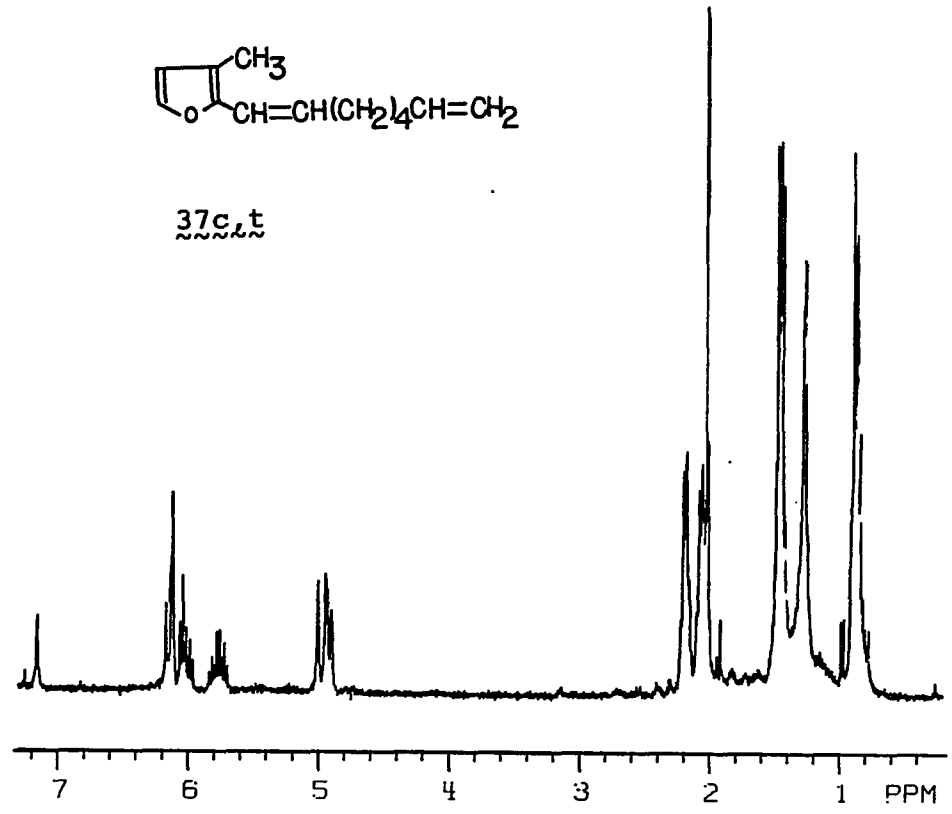


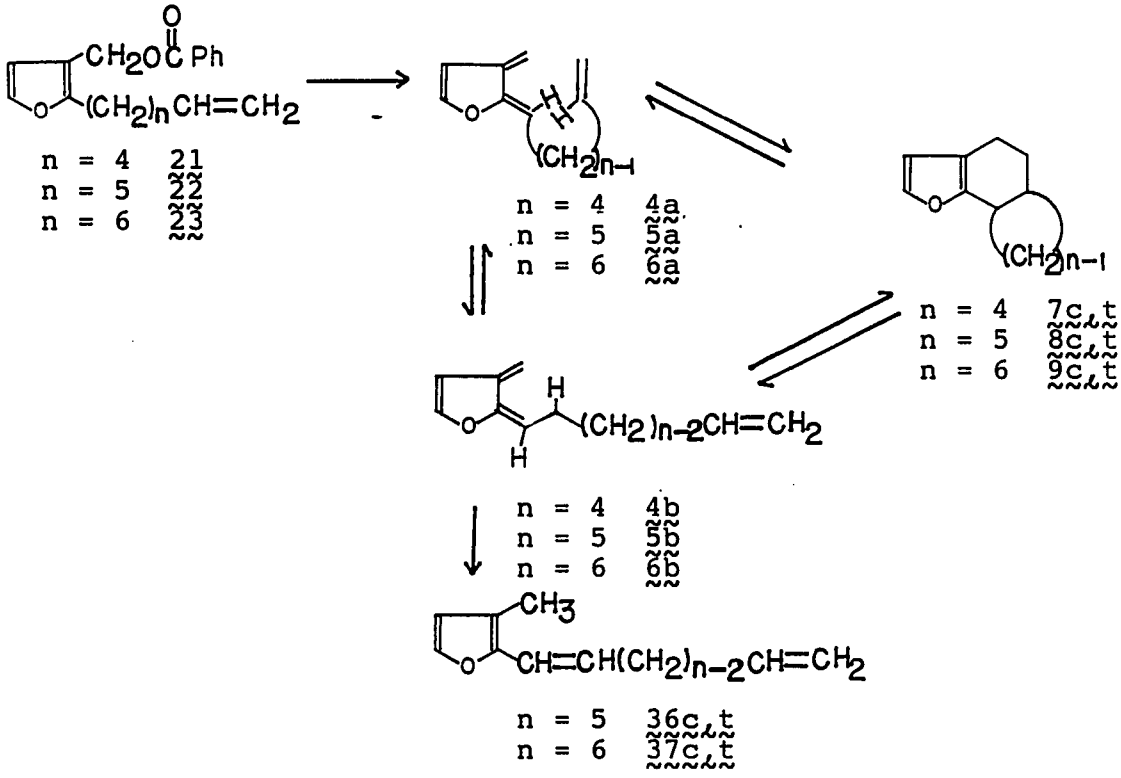
Figure 9. ^{1}H NMR spectrum of a 9:1 mixture of 37c,t and cis- and trans-4,5,5a,6,7,8,9,10a-octahydrocyclohepta[g]benzofurans (9c,t)

at δ 140.31, 139.08, 128.41, 116.86, 114.72, 114.67, 114.33, 113.68 for the furans and olefin groups, and at δ 33.68, 33.59, 32.93, 32.71, 28.98 and 28.47 for the hydrocarbon group. GC/MS data were also consistent with the molecular formula $C_{13}H_{18}O$.

DISCUSSION

The FVP of 2-alkenyl-3-furylmethyl benzoates 21, 22, and 23 at ca 640°C gave the corresponding tricyclic compounds 7c,t, 8c,t, and 9c,t and 1,5-hydrogen shift products 36c,t, and 37c,t. In Scheme 4, mechanistic pathways which account for the formation of pyrolysis products are presented. The

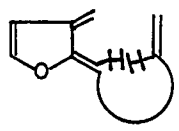
Scheme 4



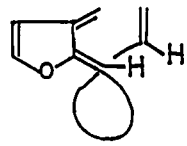
formation of tricyclic compounds 7c,t, 8c,t, and 9c,t can be explained by the initial formation of the corresponding

2,3-dimethylene-2,3-dihydrofurans, 4a,b, 5a,b, and 6a,b, which undergo intramolecular Diels-Alder reactions to form tricyclic compounds. The loss of benzoic acid from the benzoates could be by a direct δ-elimination or by a stepwise mechanism involving a [3,3] shift followed by a β-elimination.[8] The 1,5-hydrogen shift products 36c,t, and 37c,t can be formed from the cis-o-quinodimethanes, 5b and 6b, which have a good geometry for the 1,5-hydrogen shift reaction.[31] The amount of 1,5-hydrogen shift products increased as the size of the chain increases (n = 4, 0% < n = 5, 18% < n = 6, 64%). This can be explained by the rate of the intramolecular Diels-Alder reactions of 2,3-dimethylene-2,3-difurans. If the intramolecular Diels-Alder reaction takes place efficiently, there are no 1,5-hydrogen shift products. As the intramolecular Diels-Alder reaction becomes slower as the chain length increases, the 1,5-hydrogen shift products increase in importance.

The stereoselective formation of trans-polycyclic compounds over cis-polycyclic compounds was anticipated on the basis of previous o-quinodimethane-based syntheses,[14,32] and it reveals a distinct preference for the exo-transition state (38a) rather than the endo-transition state (38b) in the intramolecular Diels-Alder reaction. In a short-chain (n = 4) 2,3-dimethylene-2,3-dihydrofuran, the exo-transition state is



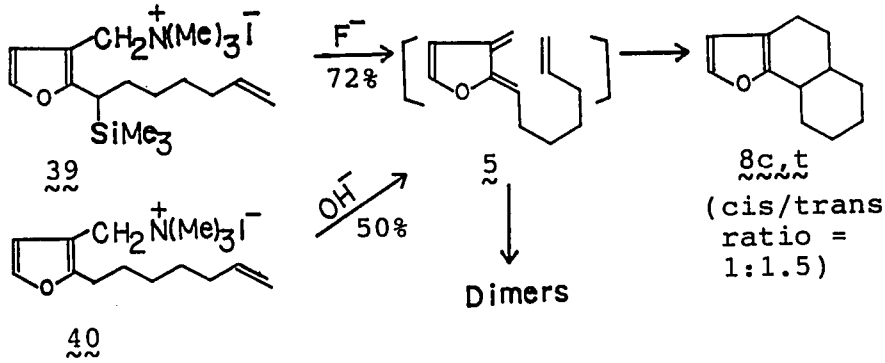
38a



38b

preferred over the endo-transition state to give trans-predominant tricyclic compounds 7c,t (cis/trans = 3/7). While in a longer-chain (n = 6) 2,3-dimethylene-2,3-dihydrofuran, either exo- or endo-transition state can be equally formed because of the flexibility of long chain producing nearly equal amounts of cis- and trans-tricyclic compounds 9c,t.

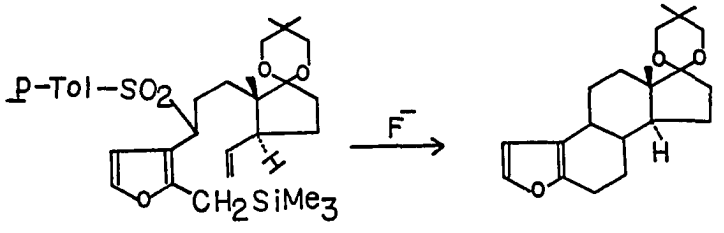
Recently, Gregor and Wiseman also reported[33] the preparation of 2,3-dimethylene-2,3-dihydrofurans by using the fluoride anion induced 1,4-elimination method[10] and the Hoffman elimination method.[9] These compounds have been used in investigations of intramolecular Diels-Alder reactions. Tricyclic compounds 8c,t have also been prepared from 39 and 40 by using a fluoride anion induced 1,4-elimination method and a Hoffman elimination method, respectively.[33] They observed the formation of dimers in addition to tricyclic



39

40

compounds 8c,t, but they did not observe 1,5-H shift products 36c,t. They also reported the synthesis of an A-furanosteroid 42 from 41 by using the fluoride anion induced 1,4-elimination method.



41 42

Although the flash vacuum pyrolysis of benzoates 22 and 23 gave the 1,5-hydrogen shift products 36c,t and 37c,t, we have demonstrated that 2,3-dimethylene-2,3-dihydrofurans such as 4 and 5, when generated under the condition of FVP, undergo intramolecular Diels-Alder reactions leading to polycyclic compounds 7c,t and 8c,t. This method is superior to that used by Gregor and Wiseman, because the dimerization reaction of 4 and 5 do not occur in the gas-phase.

EXPERIMENTAL

Methods and Materials

The pyrolysis apparatus has been previously described.[34] ^{1}H NMR spectra were recorded on a Varian A-60 or a Nicolet-300 spectrometer. Deuterium NMR spectrum was recorded on a Bruker WM300 spectrometer. ^{13}C NMR spectra were recorded on a Nicolet-300 spectrometer. Chemical shifts are reported in parts per million (δ) from tetramethylsilane (TMS). Gas chromatographic analysis was performed on a Hewlett Packard Model 5840-A gas chromatograph (GC) with a fused silica column coated with methyl silicone fluid (J and W scientific DB-1) and a flame ionization detector. Combined gas chromatographic/mass spectra (GC/MS) analysis was performed on a Finnigan 4000 GC/MS with Incos data system. High resolution mass spectra were measured with either an Associated Electronics Industries MS-902 instrument or an MS 50 mass spectrometer. Infrared spectra (IR) were recorded on either a Beckman Acculab II or a Beckman 4250 spectrophotometer. GC/IR analysis was performed on an IBM FT/IR model 98. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Melting points were determined on a Hoover Thomas melting point apparatus and are uncorrected. 2-Amino-2-methyl-1-propanol, 6-bromo-1-hexene, 8-bromo-1-octene, 3-furoic acid, and 1,7-dibromoheptane were purchased

from Aldrich Chemical Company. Dimethylamine was purchased from Eastman Kodak Company.

4,4-Dimethyl-2-(3-furyl)-2-oxazoline (25)

Compound 25 was prepared by reacting 15 g (0.13 mol) of 3-furoic acid with 50 g of thionyl chloride followed by reaction with 2-amino-2-methyl-1-propanol using the method of Chou and Trahanovsky.[20] 25 (yield; 72%): ^{1}H NMR ($CDCl_3$) δ 8.0 (s, 1 H), 7.4 (d, 1 H, J = 2 Hz), 6.8 (d, 1 H, J = 2 Hz), 4.1 (s, 2 H), 1.4 (s, 6 H); IR (CS_2) 1678, 1324, 1165, 1110, 1010, 1000, 985 cm^{-1}; GC/MS (70eV) m/e (% base peak) 165 (13.5), 150 (100), 135 (15), 122 (27), 94 (93), 66 (8), 65 (6), 57 (11), 53 (3). (These data were well matched with the reported values.[20])

7-Bromo-1-heptene (43)

To 10 g (39 mmol) of 1,7-dibromoheptane 15 ml of hexamethylphosphoric triamide (HMPA) was added dropwise at 200-205°C with stirring under nitrogen over a 1 h period. The product, 7-bromo-1-heptene, was collected by distillation. As the product was volatile, distillation was facilitated by a flow of nitrogen from the distillation flask into the receiving flask where it was collected by cooling the flask with dry ice. The crude product was washed successively with saturated $NaHCO_3$ (3 x 5 ml) and saturated NaCl (3 x 5 ml), and then dried ($MgSO_4$) and concentrated. The crude product was

purified by vacuum distillation to give 1.6 g (9 mmol; 23%) of 43: bp 55-60°C (1 torr) (Lit.[35] bp 64°C, 10 torr); ^{1}H NMR ($CDCl_3$) δ 6.1-5.4 (m, 1 H), 5.2-4.7 (m, 2 H), 3.4 (t, 2 H, J = 6 Hz), 2.2-1.3 (m, 8 H); GC/MS (70eV) m/e (% base peak) 178 (0.22), 176 (0.23), 148 (2), 150 (2), 137 (4), 136 (4), 135 (4), 134 (4), 97 (27), 81 (6), 69 (27), 55 (100).

4,4-Dimethyl-2-[2-(5-hexenyl)-3-furyl]-2-oxazoline (26)

To a solution of 5.6 ml of n-BuLi (2.0 M) in hexanes, 1.85 g (11.2 mmol) of 4,4-dimethyl-2-(3-furyl)-2-oxazoline (25) in 20 ml of THF was added dropwise at -78°C with stirring under nitrogen. The mixture was stirred at -78°C for 1 h and at 0°C for another 1 h. A 2.0 g (12 mmol) quantity of 6-bromo-1-hexene in 15 ml of THF was added at -78°C and the mixture was slowly warmed to room temperature and stirred for 15 h. Work up with saturated NH_4Cl at -78°C, followed by ether extraction (3 x 20 ml) and purification by column chromatography on silica gel (10% ether in hexanes) gave an oil 26 (621 mg, 22%): ^{1}H NMR (CCl_4) δ 7.1 (d, 1 H, J = 2 Hz), 6.4 (d, 1 H, J = 2 Hz), 5.9-5.3 (m, 1 H), 5.0-4.7 (m, 2 H), 3.8 (s, 2 H), 2.8 (t, 2 H, J = 6 Hz), 2.2-1.0 (m, 12 H); GC/MS (70eV) m/e (% base peak) 247 (17.38), 232 (9), 218 (25), 206 (44), 193 (18), 192 (100), 180 (10), 179 (90), 178 (10), 164 (25), 163 (7), 162 (10), 121 (36), 120 (19), 108 (16), 107 (19), 106 (58), 91 (14), 81 (8), 80 (13), 79 (13), 78 (11), 77 (14), 65 (17), 55

(39), 53 (15), 52 (17), 51 (16); high resolution mass spectrum calculated for $C_{15}H_{21}NO_2$ 247.15723, measured 247.15692.

4,4-Dimethyl-2-[2-(6-heptenyl)-3-furyl]-2-oxazoline (27)

Compound 27 was prepared by reacting 4,4-dimethyl-2-(3-furyl)-2-oxazoline anion with 7-bromo-1-heptene, as described in the preparation of 26. 27 (yield; 21%): ^{1}H NMR (CCl_4) δ 7.2 (d, 1 H, J = 2 Hz), 6.6 (d, 1 H, J = 2 Hz), 5.9-5.3 (m, 1 H), 5.2-4.8 (m, 2 H), 3.9 (s, 2 H), 3.0 (t, 2 H, J = 7 Hz), 2.4-0.9 (m, 14 H); GC/MS (70eV) m/e (% base peak) 261 (4.72), 232 (19), 218 (16), 205 (11), 193 (15), 192 (94), 180 (11), 179 (100), 164 (27), 121 (32), 120 (16), 108 (13), 107 (14), 106 (49), 79 (9), 77 (10), 65 (11), 55 (36); high resolution mass spectrum calculated for $C_{16}H_{23}O_2N$ 261.17288, measured 261.17271.

4,4-Dimethyl-2-[2-(7-octenyl)-3-furyl]-2-oxazoline (28)

Compound 28 was prepared by reacting the o-anion of 25 with 8-bromo-1-octene as described in the preparation of 26. 28 (yield; 21%): ^{1}H NMR (CCl_4) δ 7.2 (d, 1 H, J = 2 Hz), 6.5 (d, 1 H, J = 2 Hz), 5.9-5.4 (m, 1 H), 5.1-4.7 (m, 2 H), 3.9 (s, 2 H), 2.9 (t, 2 H, J = 6 Hz), 2.2-1.2 (m, 16 H); GC/MS m/e (% base peak) 275 (26), 260 (21), 246 (12), 234 (12), 206 (13), 193 (16), 192 (100), 179 (34), 121 (11), 117 (11), 106 (18), 65 (8), 55 (16); high resolution mass spectrum, calculated for $C_{17}H_{25}NO_2$ 275.18853, measured 275.18847.

2-(5-Hexenyl)-3-furoic acid (29)

Compound 29 was prepared by converting 4,4-dimethyl-2-[2-(5-hexenyl)-3-furyl]-2-oxazoline (26) to 29 using the method of Chou and Trahanovsky.[20] A 300 mg (1.21 mmol) quantity of 26 was stirred in the presence of a 10-fold excess of iodomethane for a week and the excess iodomethane was removed in vacuum. To the crude methiodide was added 15 ml of a 1:1 solution of methanol and 20% sodium hydroxide, and the mixture was heated to reflux for 15 h. After cooling, the solution was extracted with ether and the ether extract was discarded. The aqueous phase was acidified with 9N HCl and extracted with ether. The solvent was dried ($MgSO_4$) and concentrated to give 188 mg (0.97 mmol, 80%) of 29: ^1H NMR ($CDCl_3$) δ 10.5 (s, 1 H), 7.3 (d, 1 H, J = 2 Hz), 6.7 (d, 1 H, J = 2 Hz), 6.2-5.4 (m, 1 H), 3.1 (t, 2 H, J = 7 Hz), 2.2-1.0 (m, 6 H); IR ($CDCl_3$) 3300-2800, 1690, 1640, 1600, 1460, 1260, 905 cm^{-1}.

2-(6-Heptenyl)-3-furoic acid (30)

Compound 30 was prepared from 4,4-dimethyl-2-[2-(6-heptenyl)-3-furyl]-2-oxazoline (27) as described in the preparation of 29. 30 (yield; 80%): ^1H NMR ($CDCl_3$) δ 10.5 (s, 1 H), 7.2 (d, 1 H, J = 2 Hz), 6.6 (d, 1 H, J = 2 Hz), 6.1-5.4 (m, 1 H), 5.1-4.7 (m, 2 H), 3.0 (t, 2 H, J = 7 Hz), 2.2-1.20 (m, 8 H); IR ($CDCl_3$) 3600-2400, 1680, 1640, 1600, 1460, 1300, 900 cm^{-1}.

2-(7-Octenyl)-3-furoic acid (31)

Compound 31 was prepared from 4,4-dimethyl-2-[2-(7-octenyl)-3-furyl]-2-oxazoline (28) as described in the preparation of 29. 31 (yield; 79%): ^{1}H NMR ($CDCl_3$) δ 10.3 (s, 1 H), 7.3 (d, 1 H, J = 2 Hz), 6.6 (d, 1 H, J = 2 Hz), 6.1-5.4 (m, 1 H), 5.1-4.7 (m, 2 H), 3.1 (t, 2 H, J = 7 Hz), 2.2-1.2 (m, 10 H); IR ($CDCl_3$) 3700-2400, 1690, 1640, 1600, 1460, 1300, 900 cm^{-1}.

2-(5-Hexenyl)-3-furylmethanol (44)

To a stirred slurry of 38 mg (1.0 mmol) of $LiAlH_4$ in 3 ml of THF at 0°C was added 188 mg (0.97 mmol) of 29 in 5 ml of THF over a 10-min period. The resulting mixture was stirred at room temperature for 18 h. A standard workup procedure[36] gave 44 (166 mg, 95%): ^{1}H NMR ($CDCl_3$) δ 7.2 (d, 1 H, J = 2 Hz), 6.3 (d, 1 H, J = 2 Hz), 6.0-5.4 (m, 1 H), 5.1-4.7 (m, 2 H), 4.4 (s, 2 H), 2.5 (t, 2 H, J = 7 Hz), 2.1-0.7 (m, 6 H); IR (neat, NaCl) 3680-3060, 3100, 2950, 2880, 1645, 1630, 1260, 770 cm^{-1}.

2-(6-Heptenyl)-3-furylmethanol (45)

Compound 45 was prepared by reducing 30 with $LiAlH_4$ as described in the preparation of 2-(5-hexenyl)-3-furylmethanol (44). 45: ^{1}H NMR ($CDCl_3$) δ 7.2 (d, 1 H, J = 2 Hz), 6.2 (d, 1 H, J = 2 Hz), 6.0-5.4 (m, 1 H), 5.1-4.7 (m, 2 H), 4.3 (s, 2 H), 2.5 (t, 2 H, J = 7 Hz), 2.1-1.0 (m, 8 H); IR (neat, NaCl)

3700-3100, 3090, 2950, 2880, 1650, 1630, 1050, 1000, 900, 910, 730 cm^{-1}.

2-(7-Octentyl)-3-furylmethanol (46)

Compound 46 was prepared by reducing 31 with $LiAlH_4$ as described in the preparation of 2-(5-hexenyl)-3-furylmethanol (44). 46 (yield; 94%): ^1H NMR ($CDCl_3$) δ 7.3 (d, 1 H, J = 2 Hz), 6.2 (d, 1 H, J = 2 Hz), 6.1-5.4 (m, 1 H), 5.1-4.7 (m, 2 H), 4.3 (s, 2 H), 2.4 (t, 2 H, J = 7 Hz), 2.1-0.8 (m, 10 H); IR (neat, NaCl) 3700-3100, 3090, 2940, 2880, 1640, 1630, 1520, 1470, 1440, 1150, 1050, 1000, 910, 730 cm^{-1}.

2-Methyl-3-furoic acid (47)

Compound 47 was prepared by the hydrolysis of ethyl 2-methyl-3-furoate (32)[9] with a 1:1 solution of methanol and 20% NaOH.[37] 47 (yield; 72%): mp 102-103°C (Lit.[38] mp 102-3°C); ^1H NMR ($CDCl_3$) δ 7.2 (d, 1 H, J = 2 Hz), 6.6 (d, 1 H, J = 2 Hz), 2.5 (s, 3 H).

N,N-Dimethyl-2-methyl-3-furamide (33)

To 1.9 g (15.1 mmol) of 47 was added 3.2 g (27 mmol) of thionyl chloride over a 10-min period with stirring. After the reaction mixture was heated to 120°C for 1 h, 5 ml of benzene was added to the reaction mixture. The reaction mixture was distilled until the temperature of the vapors reached 95°C. The mixture was cooled, another 5 ml of benzene was added and the distillation was continued until the

temperature of the vapors again reached 95°C. The cooled residual acid chloride was dissolved into 2 ml of benzene and was added dropwise to 5 g (111 mmol) of anhydrous dimethylamine in 3 ml of benzene at 0°C with vigorous stirring. The mixture was stirred at room temperature for 15 h. After the addition of 5 ml of water, the layers were separated and the aqueous phase was extracted with ether (2 x 5 ml). The organic layers were combined, dried ($MgSO_4$), concentrated, and distilled to give 1.5 g (9.8 mmol, 65%) of 33: bp 80-82°C (0.5 torr) (Lit.[33] mp 28°C); ^1H NMR (CCl_4) δ 7.2 (d, 1 H, J = 2 Hz), 6.3 (d, 1 H, J = 2 Hz), 3.0 (s, 6 H), 2.4 (s, 3 H); IR (neat, NaCl) 3040, 2950, 1620, 1500, 1410, 1390, 1280, 1230, 1140, 1080, 900 cm^{-1}; GC/MS (70eV) m/e (% base peak) 153 (43), 124 (20), 110 (12), 109 (100), 80 (8), 72 (15), 67 (6), 53 (18), 52 (15), 51 (15).

N,N-Dimethyl-2-(6-heptenyl)-3-furamide (34)

To 5.5 ml of n-BuLi in hexane (2.0 N) at -78°C was added dropwise 1.01 g (10 mmol) of diisopropylamine in 10 ml of THF over a 10-min period. The mixture was stirred at -78°C for 30 min and was added dropwise to 1.53 g (10 mmol) of N,N-dimethyl-2-methyl-3-furamide (23) in 10 ml of THF at -78°C. After the mixture was stirred for 1 h at -78°C, 1.6 g (9.8 mmol) of 6-bromo-1-hexene in 10 ml of THF was added dropwise at -78°C. The reaction mixture was stirred at -78°C for 2 h. The mixture was worked up with saturated NH_4Cl,

followed by ether extraction and column chromatography on silica gel (10% ether in hexanes) to give 967 mg (4.1 mmol, 42%) of an oil 34: ^{1}H NMR (CCl_4) δ 7.1 (d, 1 H, J = 2 Hz), 6.2 (d, 1 H, J = 2 Hz), 5.8-5.2 (m, 1 H), 4.8-4.5 (m, 2 H), 2.9 (s, 6 H), 2.6 (t, 2 H, J = 7 Hz), 2.1-0.9 (m, 8 H); IR (neat, NaCl) 3100, 3080, 2900, 2840, 1620, 1500, 1440, 1390, 1380, 1260, 1130, 1000, 890, 720 cm^{-1}; GC/MS (70eV) m/e (% base peak) 236 (1.53), 235 (10), 192 (11), 191 (54), 166 (58), 153 (35), 149 (10), 135 (10), 124 (23), 123 (17), 122 (12), 121 (53), 110 (14), 109 (100), 108 (18), 107 (10), 95 (11), 94 (10), 91 (15), 81 (44), 80 (28), 79 (19), 77 (15), 72 (100), 67 (17), 66 (12), 65 (17), 55 (51), 53 (34), 52 (31), 51 (18), 46 (22); high resolution mass spectrum calculated for $C_{14}H_{21}NO_2$ 235.15723, measured 235.15689.

2-(6-Heptenyl)-3-furoic acid (30)

To 520 mg (2.2 mmol) of 34 was added 4 g of KOH in 26 ml of ethylene glycol and the mixture was heated to reflux for 7 h. After cooling, the reaction mixture was poured into 40 ml of cold water. The mixture was acidified with 9 N hydrochloric acid to pH 3 and was extracted with ether (3 x 30 ml). The ether layers were combined, dried ($MgSO_4$), and concentrated to give 412 mg (1.98 mmol, 90%) of crude acid 30. The ^{1}H NMR spectrum and IR spectrum of 30 were well matched with those of 30 obtained from 27.

2-(5-Hexenyl)-3-furylmethyl benzoate (21)

Compound 21 was prepared by esterifying 150 mg of 2-(5-hexenyl)-3-furylmethanol (44) with benzoyl chloride in the presence of triethylamine.[8] A solution of 126 mg (0.9 mmol) of benzoyl chloride in 3 ml of THF was added dropwise to a stirred solution of 150 mg (0.83 mmol) of 44 and 101 mg (1.0 mmol) of triethylamine in 3 ml of THF. The mixture was stirred at room temperature for 15 h. After the addition of 2 ml of water, the layers were separated and the aqueous phase was extracted with ether (2 x 10 ml). The combined organic layers was washed successively with 1 N HCl (3 x 10 ml), saturated $NaHCO_3$ (3 x 10 ml), and saturated NaCl (3 x 10 ml). The organic layer was dried ($MgSO_4$), concentrated, and purified by column chromatography on silica gel (4% ether in hexanes) to give 189 mg (0.67 mmol, 80%) of an oil 21: ^1H NMR ($CDCl_3$) δ 8.1-7.1 (m, 5 H), 7.1 (d, 1 H, J = 2 Hz), 6.3 (d, 1 H, J = 2 Hz), 5.9-5.2 (m, 1 H), 5.1 (s, 2 H), 5.1-4.7 (m, 2 H), 2.6 (t, 2 H, J = 7 Hz), 2.2-0.8 (m, 6 H); IR (neat, NaCl) 3070, 2950, 2850, 1710, 1250, 1100, 1000, 760 cm^{-1}; GC/MS (20eV) m/e (% base peak) 284 (3), 163 (13), 162 (100), 134 (29), 133 (33), 120 (17), 119 (41), 108 (10), 105 (37), 94 (21), 80 (4); high resolution mass spectrum, calculated for $C_{18}H_{20}O_3$ 284.14125, measured 284.14044; elemental analysis calculated: C, 76.02, H, 7.04, found: C, 75.89, H, 7.12.

2-(6-Heptenyl)-3-furylmethyl benzoate (22)

Compound 22 was prepared by reacting 2-(6-heptenyl)-3-furylmethanol (45) with benzoyl chloride as described in the preparation of 21. 22 (yield; 79%): ^{1}H NMR ($CDCl_3$) δ 8.1-7.8 (m, 2 H), 7.6-7.3 (m, 3 H), 7.2 (d, 1 H, J = 2 Hz), 6.3 (d, 1 H, J = 2 Hz), 6.0-5.3 (m, 1 H), 5.2 (s, 2 H), 5.15-4.7 (m, 2 H), 2.7 (t, 2 H, J = 7 Hz), 2.2-1.0 (m, 8 H); IR (neat, NaCl) 3080, 2940, 2860, 1720, 1260, 1100, 700 cm^{-1}; high resolution mass spectrum calculated for $C_{19}H_{22}O_3$ 298.15690, measured 298.15667.

2-(7-Octenyl)-3-furylmethyl benzoate (23)

Compound 23 was prepared by reacting 2-(7-octenyl)-3-furylmethanol (46) with benzoyl chloride as described in the synthesis of 21. 23 (yield; 79%): ^{1}H NMR ($CDCl_3$) δ 8.1-7.8 (m, 2 H), 7.5-7.2 (m, 3 H), 7.15 (d, 1 H, J = 2 Hz), 6.3 (d, 1 H, J = 2 Hz), 5.9-5.3 (m, 1 H), 5.1 (s, 2 H), 5.1-4.7 (m, 2 H), 2.7 (t, 2 H, J = 7 Hz), 2.1-1.1 (m, 10 H); IR (neat, NaCl) 3090, 2950, 2880, 1720, 1650, 1270, 1100, 710 cm^{-1}; GC/MS (70eV) m/e (% base peak) 191 (3), 190 (26), 175 (3), 162 (6), 161 (5), 148 (5), 147 (15), 135 (4), 134 (10), 133 (30), 122 (10), 121 (18), 108 (32), 105 (100), 95 (37), 94 (36), 81 (9), 79 (11), 77 (39), 167 (9), 66 (5), 65 (7), 55 (19), 51 (11).

2-(5-Hexenyl)-3-furylmethyl-α,α-$\underline{d}_2$ benzoate ($\underset{\sim}{\underset{\sim}{21}}$-$\underline{d}_2$)

To a stirred slurry of 30 mg (0.72 mmol) of $LiAlD_4$ in 3 ml of THF at 0°C was slowly added a solution of 140 mg (0.72 mmol) of 2-(5-hexenyl)-3-furoic acid ($\underset{\sim}{\underset{\sim}{29}}$) in 3 ml of THF. The mixture was stirred at room temperature for 15 h and a standard workup[37] gave 2-(5-hexenyl)-3-furylmethyl-α,α-$\underline{d}_2$ alcohol ($\underset{\sim}{\underset{\sim}{44}}$-$\underline{d}_2$) (122 mg, 93%): ^{1}H NMR ($CDCl_3$) δ 7.2 (d, 1 H, J = 2 Hz), 6.2 (d, 1 H, J = 2 Hz), 5.8-5.2 (m, 1 H), 5.0-4.7 (m, 2 H), 2.5 (t, 2 H, J = 7 Hz), 2.1-0.8 (m, 6 H); IR (neat, NaCl) 3680-3060, 3100, 2950, 2880, 1645, 1630, 1520, 1260, 770 cm^{-1}. Without further purification 118 mg (0.65 mmol) of the alcohol was converted to $\underset{\sim}{\underset{\sim}{21}}$-$\underline{d}_2$ using the procedure described in the synthesis of 2-(5-hexenyl)-3-furylmethyl benzoate ($\underset{\sim}{\underset{\sim}{21}}$). $\underset{\sim}{\underset{\sim}{21}}$-$\underline{d}_2$ (yield; 79%): ^{1}H NMR ($CDCl_3$) δ 8.1-7.1 (m, 5 H), 7.1 (d, 1 H, J = 2 Hz), 6.3 (d, 1 H, J = 2 Hz), 5.9-5.2 (m, 1 H), 5.1-4.7 (m, 2 H), 2.6 (t, 2 H, J = 7 Hz), 2.2-0.8 (m, 6 H); IR (neat NaCl) 3080, 2940, 2880, 1710, 1280, 1110, 780, 750, 700 cm^{-1}; mass spectrum (20eV) m/e (% base peak) 286 (2), 284 (0.12), 164 (100), 162 (0.38), 149 (5), 136 (15), 135 (32), 134 (17), 123 (7), 122 (15), 121 (28), 120 (15), 105 (31), 96 (18), 80 (3); high resolution mass spectrum calculated for $C_{18}D_2H_{18}O_3$ 286.15380, measured 286.15401.

General pyrolysis procedure

General pyrolysis procedure has previously been described.[8]

Pyrolysis of 2-(5-hexenyl)-3-furylmethyl benzoate (21)

A 75 mg (0.26 mmol) quantity of 21 was pyrolyzed at 650°C in the normal manner. The pyrolysate was collected in 5 ml of carbon disulfide, dried ($NaHCO_3$), and concentrated. GC and the ^1H NMR analyses of the product mixture indicated that tricyclic compounds 7c,t were formed as major products along with benzoic acid as a byproduct. The oily product was purified by column chromatography on silica gel (hexanes) to give a mixture of cis- and trans-4,5,5a,6,7,8a-hexahydro-8H-indeno[4,5-b]furans (7c,t) (31 mg, 73%): ^1H NMR ($CDCl_3$) 7.16 (d, J = 1.76 Hz), 7.14 (d, J = 0.84 Hz), 6.13 (d, J = 1.74 Hz), 6.08 (d, J = 1.73 Hz), 2.9 (q, J = 6 Hz), 2.6-0.7 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 152.93, 152.81, 139.31, 139.06, 115.28, 115.00, 109.36, 108.87, 46.04, 42.25, 38.27, 36.73, 29.81, 29.41, 28.77, 28.37, 26.64, 25.82, 25.68, 23.62, 22.36, 21.71, 19.36; elemental analysis calculated: C, 81.43, H, 8.64, found: C, 81.97, H, 8.95. IR (CCl_4) 2920, 2855, 1500, 1440, 1300, 1210, 1120, 970, 710 cm^{-1}; high resolution mass spectrum calculated for $C_{11}H_{14}O$ 162.10447, measured 162.10423. trans-7: GC/MS (70eV) m/e (% base peak) 163 (8), 162 (72), 161 (9), 134 (39), 133 (100), 120 (30), 119 (55), 118 (9), 105 (22), 94 (20), 92 (10), 91 (81), 81 (9), 79 (17), 78 (10), 77 (30), 65 (21), 55 (12), 53 (13), 52 (9), 51 (20). cis-7: GC/MS (70eV) m/e (% base peak) 163 (6), 162 (100), 161 (16), 134 (65), 133 (83), 131 (12), 121 (9), 120 (29), 119 (50), 118

(11), 106 (11), 105 (48), 103 (10), 94 (21), 92 (12), 91 (91), 81 (30), 80 (9), 79 (30), 78 (16), 77 (49), 67 (11), 65 (22), 55 (18), 53 (22), 52 (12), 51 (29).

Pyrolysis of 2-(5-hexenyl)-3-furylmethyl-α,α-$\underline{d}_2$ benzoate ($\underset{\sim\sim}{21}$-$\underline{d}_2$)

A 60 mg (0.21 mmol) quantity of $\underset{\sim\sim}{21}$-$\underline{d}_2$ was pyrolyzed as described in the pyrolysis of $\underset{\sim\sim}{21}$ to give a mixture of cis- and trans-4,5,5a,6,7,8a-hexahydro-4,4-dideutero-8H-indeno[4,5-b]-furans ($\underset{\sim\sim\sim}{35}\underset{\sim}{c,t}$) (24 mg, 70%): ^{1}H NMR ($CDCl_3$) δ 7.29 (d, J = 1.7 Hz), 7.25 (d, J = 1.68 Hz), 6.22 (d, J = 1.67 Hz), 6.17 (d, J = 1.68 Hz), 3.0 (q, J = 6 Hz), 2.4-0.8 (m); ^{2}D NMR ($CHCl_3$) δ 2.40 (broad singlet).

Pyrolysis of 2-(6-heptenyl)-3-furylmethyl benzoate ($\underset{\sim\sim}{22}$)

A 232 mg (0.78 mmol) quantity of $\underset{\sim\sim}{22}$ was pyrolyzed at 640°C in the normal manner. The pyrolysate was collected in carbon disulfide, dried ($NaHCO_3$), and concentrated to give (0.56 mmol, 72%) oily products. GC and the ^{1}H NMR analyses of the crude product indicated that an 82% yield of a 47:53 mixture of cis-$\underset{\sim}{8}$ and trans-$\underset{\sim}{8}$, and an 18% yield of a 4:14 mixture of cis-$\underset{\sim\sim}{36}$ and trans-$\underset{\sim\sim}{36}$ were formed by the pyrolysis of $\underset{\sim\sim}{22}$. The pyrolysate was purified by column chromatography on silica gel (hexanes) to give a mixture of 93% pure tricyclic cis- and trans-4,5,5a,6,7,8,9,9a-octahydronaphtho[1,2-b]furans ($\underset{\sim\sim}{8}\underset{\sim}{c,t}$) (80 mg, 58%) and a mixture of 60% pure 1,5-H shift products,

cis- and trans-2-(1,6-heptadienyl)-3-methylfurans (36c,t) (8 mg, 6%). 8c,t: ^{1}H NMR ($CDCl_3$) δ 7.17 (d, 1 H, J = 2 Hz), 6.09 (d, 1 H, J = 2 Hz), 2.81 (q, J = 6 Hz), 2.6-0.8 (m). ^{13}C NMR ($CDCl_3$) δ 153.42, 140.27, 115.82, 115.50, 110.36, 110.23, 41.67, 41.64, 35.23, 34.91, 33.66, 31.10, 28.95, 28.93, 26.97, 26.79, 26.24, 24.00, 23.94, 22.21, 20.76. IR (neat, NaCl) 2910, 2840, 1500, 1440, 1300, 1220, 1120, 1020, 880, 710 cm^{-1}; high resolution mass spectrum calculated for $C_{12}H_{16}O$ 176.12012, measured 176.11999. trans-8: GC/MS (70eV) m/e (% base peak) 177 (13), 176 (100), 175 (8), 148 (18), 147 (23), 134 (27), 133 (81), 132 (9), 131 (10), 120 (24), 119 (28), 117 (11), 115 (9), 108 (8), 107 (12), 105 (29), 104 (9), 95 (14), 94 (26), 92 (12), 91 (65), 81 (18), 79 (30), 78 (11), 77 (37), 67 (12), 65 (20), 55 (19), 53 (18), 51 (16). cis-8: GC/MS (70eV) m/e (% base peak) 177 (9.01), 176 (73.57), 175 (4.10), 148 (11), 147 (15), 134 (19), 133 (100), 120 (20), 119 (25), 105 (17), 95 (9), 94 (29), 92 (8), 91 (54), 81 (11), 79 (19), 78 (8), 77 (26), 65 (17), 54 (13), 53 (13), 51 (13). 36c,t ^{1}H NMR ($CDCl_3$) δ 7.15 (d, 1 H, J = 1.7), 6.29-5.65 (m, 4 H), 5.15-4.82 (m, 2 H), 2.2-1.0 (m, 9 H). cis-36: GC/MS (70eV) m/e (% base peak) 176 (4.52), 134 (13), 121 (51), 108 (100), 95 (28), 93 (13), 91 (45), 79 (24), 78 (10), 77 (46), 65 (15), 55 (15), 53 (16), 51 (13). trans-36: GC/MS (70eV) m/e (% base peak) 178 (0.82), 177 (12.23), 176 (100), 175 (10), 161 (70), 148 (15), 147 (67), 143 (21), 134 (49), 133 (84), 132 (14),

131 (18), 121 (16), 120 (17), 119 (62), 117 (14), 115 (15), 108 (49), 107 (18), 106 (10), 105 (60), 103 (14), 95 (39), 94 (38), 92 (11), 91 (96), 81 (16), 79 (41), 78 (19), 77 (62), 67 (16), 65 (30), 63 (12), 55 (27), 53 (26), 52 (13), 51 (31).

Pyrolysis of 2-(7-octenyl)-3-furylmethyl benzoate (23)

A 90 mg (0.289 mmol) of 23 was pyrolyzed at 640°C in the normal manner. The pyrolysate was collected in carbon disulfide, dried ($NaHCO_3$), and concentrated to give 36 mg of an oily product. GC and the ^1H NMR spectral analyses of the crude product mixture indicated that a 36% yield of a 1:1 mixture of cis- and trans-4,5,5a,6,7,8,9,10a-octahydrocyclohepta[g]benzofurans (9c,t), and a 64% yield of a 1:3 mixture of cis- and trans-2-(1,7-octadienyl)-3-methylfurans (37c,t) were formed by the pyrolysis of 23. The crude product was purified by column chromatography to give 82% pure 9c,t (10 mg, 18%) and 89% pure 37c,t (18 mg, 33%). 9c,t: ^1H NMR ($CDCl_3$) δ 7.2 (d, 1 H, J = 1.7 Hz), 6.1 (d, 1 H, J = 1.7 Hz), 3.4 (q, 1 H, J = 6 Hz), 2.6-1.0 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 154.80, 154.47, 149.39, 140.57, 140.47, 140.32, 139.09, 129.57, 114.72, 114.18, 113.22, 110.16, 109.93, 42.98, 41.21, 38.72, 38.29, 36.68, 33.79, 32.89, 32.66, 31.60, 29.41, 28.95, 28.87, 28.64, 27.01, 26.69, 26.39, 25.50, 22.20, 21.59; GC/IR 2920, 2840, 1460 cm^{-1}; GC/MS (70eV) m/e (% base peak) 191 (9), 190 (65), 162 (11), 147 (20), 134 (21), 133 (100), 122 (9), 121 (9), 119 (20), 108 (14), 107 (12), 105 (13), 95 (11), 94

(35), 91 (41), 81 (11), 79 (20), 77 (26), 67 (11), 65 (15), 55 (20), 53 (14), 51 (12). 37c,t: ^{1}H NMR ($CDCl_3$) δ 7.15 (d, 1 H, J = 1.7 Hz), 6.17 (d, 1 H, J = 1.7 Hz), 6.15-6.10 (m, 1 H), 6.09-5.95 (m, 1 H), 5.85-5.65 (m, 1 H), 5.05-4.85 (m, 2 H), 2.25-1.95 (m, 7 H), 1.55-0.75 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 140.31, 139.08, 128.41, 116.86, 114.72, 114.67, 114.33, 113.68, 33.68, 33.59, 32.93, 32.71, 28.98, 28.47. cis-37: GC/IR 3100, 3050, 2920, 2840, 1650, 1500, 1460, 1080, 1020, 890, 790 cm^{-1}; GC/MS (70eV) m/e (% base peak) 190 (2.53), 175 (1), 161 (2), 147 (5), 133 (4), 122 (9), 121 (56), 109 (11), 108 (100), 95 (29), 93 (12), 91 (28), 79 (15), 78 (7), 77 (33), 67 (6), 65 (12), 55 (15), 53 (13), 51 (9). trans-37: GC/IR 3100, 3050, 2920, 2840, 1650, 1460, 1510, 1150, 1080, 960, 920, 890, 790 cm^{-1}; GC/MS (70eV) m/e (% base peak) 190 (6), 175 (1), 161 (2), 147 (5), 133 (5), 122 (10), 121 (62), 109 (10), 108 (100), 103 (5), 95 (29), 93 (12), 91 (28), 79 (15), 77 (33), 67 (7), 65 (11), 55 (14), 53 (12), 51 (8).

REFERENCES

1. For leading references see: McCullough, J. J. Acc. Chem. Res. 1980, 13, 270.

2. Cava, M. P.; Napier, D. R. J. Am. Chem. Soc. 1957, 79, 1701.

3. Summes, P. G. Tetrahedron 1976, 32, 405.

4. Schiess, P.; Rutschmann, S.; Toan, V. V. Tetrahedron Lett. 1982, 23, 2518.

5. Spangler, R. J.; Beckmann, B. G.; Kim, J. H. J. Org. Chem. 1971, 42, 2989.

6. Cava, M. P.; Deana, A. A. J. Am. Chem. Soc. 1959, 81, 4266.

7. Cava, M. P.; Mitchell, M. J.; Deana, A. A. J. Org. Chem. 1960, 25, 1481.

8. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. J. Am. Chem. Soc. 1981, 103, 6691.

9. Winberg, H. E.; Fawcett, F. S.; Mochel, W. E.; Theobald, C. W. J. Am. Chem. Soc. 1960, 82, 1428.

10. Ito, Y.; Nakatsuka, M.; Saegusa, T. J. Am. Chem. Soc. 1980, 102, 863.

11. Oppolzer, W.; Bättig, K.; Petrzilka, M. Helv. Chim. Acta 1978, 61, 1945.

12. Kametani, T.; Nemoto, H.; Ishikawa, H.; Shiroyama, K.; Matsumoto, H.; Fukumoto, K. J. Am. Chem. Soc. 1977, 99, 3461.

13. Grieco, P. A.; Takigawa, T.; Schillinger, W. J. J. Org. Chem. 1980, 45, 2247.

14. Oppolzer, W. Synthesis 1978, 793.

15. Kametani, T.; Fukumoto, K. Heterocycles 1977, 8, 519.

16. Nicolaou, K. C.; Barnette, W. E.; Ma, P. J. Org. Chem. 1980, 45, 1463.

17. Oppolzer, W. J. Am. Chem. Soc. 1971, 93, 3833.

18. Kametani, T.; Takemura, M.; Ogasawara, M.; Fukomoto, K. J. Heterocycl. Chem. 1974, 11, 179.

19. Kametani, T.; Kajiwara, M.; Takahashi, T.; Fukomoto, K. J. Chem. Soc. Perkin Trans. 1 1975, 737.

20. Chou, C. H.; Trahanovsky, W. S. J. Am. Chem. Soc. 1986, 108, 1438.

21. Büchi, G.; Wüest, H. J. Org. Chem. 1966, 31, 977.

22. Cimino, G.; Stefano, S. D.; Guerriero, A.; Minale, L. Tetrahedron Lett. 1975, 1417.

23. Cimino, G.; Stefano, S. D.; Guerriero, A.; Minale, L. Tetrahedron Lett. 1975, 3723.

24. Nasipuri, D.; Das, G. J. Chem. Soc. Perkin Trans. 1 1979, 2776.

25. Tanis, S. P.; Herrinton, P. M. J. Org. Chem. 1983, 48, 4572.

26. Matsumoto, T.; Usui, S. Chem. Lett. 1978, 105.

27. Akita, H.; Oishi, T. Chem. Pharm. Bull. 1981, 29, 1580.

28. Smith III, A. B.; Mewshaw, R. J. Org. Chem. 1984, 49, 3685.

29. Meyer, A. I.; Gabel, R.; Mihelich, E. D. J. Org. Chem. 1978, 43, 1372.

30. Puterbaugh, W. H.; Hauser, C. R. J. Org. Chem. 1969, 29, 853.

31. Kametani, T.; Tsubuki, M.; Shiratori, Y.; Kato, Y.; Nemoto, H.; Fukumoto, K.; Satoh, F.; Inoue, H. J. Org. Chem. 1977, 42, 2672.

32. Oppolzer, W. Tetrahedron Lett. 1974, 1001.

33. Gregor, V. E.; Wiseman, J. R. Department of Chemistry, University of Michigan, Ann Arbor. Private communication.

34. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. J. Org. Chem. 1971, 36, 3575.

35. Bohlmann, F.; Grenz, M.; Niedballa, H. Chem. Ber. 1968, 101, 532.

36. Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis Vol. 1", Wiley: New York, 1967; p. 584.

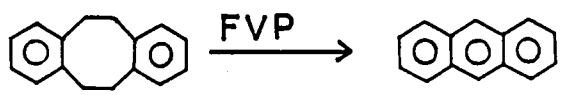
37. Norman, R. "Organic Syntheses Collective Volume IV", John Wiley & Sons, Inc.: New York, 1967; p. 628.

38. Benary, E. Berichte 1911, 44, 496.

PART II. FORMATION OF ANTHRACENE AND OTHER POLYCYCLIC AROMATIC COMPOUNDS IN THE PYROLYSIS OF 1,5-DIBENZOCYCLOOCTADIENES AND RELATED COMPOUNDS

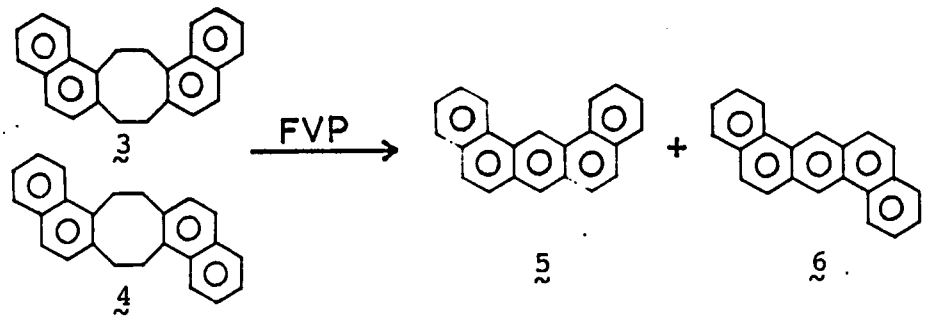
INTRODUCTION

The flash vacuum pyrolysis (FVP) of 1 has been found to give anthracene (2) and other products.[1,2] The generality



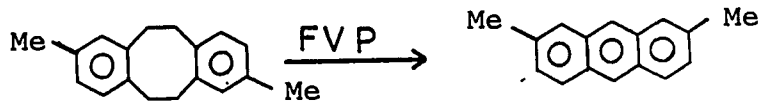
1 2 (1)

of conversion 1 to 2 is indicated by the pyrolysis of the corresponding [4+4] dimers of 1,2-naphthoquinodimethane 3 and 4. A 1:1 molar ratio of 3:4 produced a 1:1 mixture of 5:6.

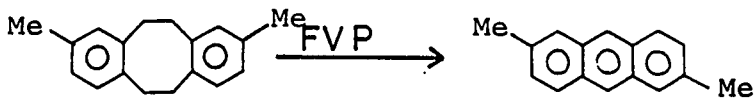


3 4 5 6 (2)

The regiochemistry of this conversion has also been established by the pyrolysis of the appropriately labeled dimethyl derivatives 7 and 8.



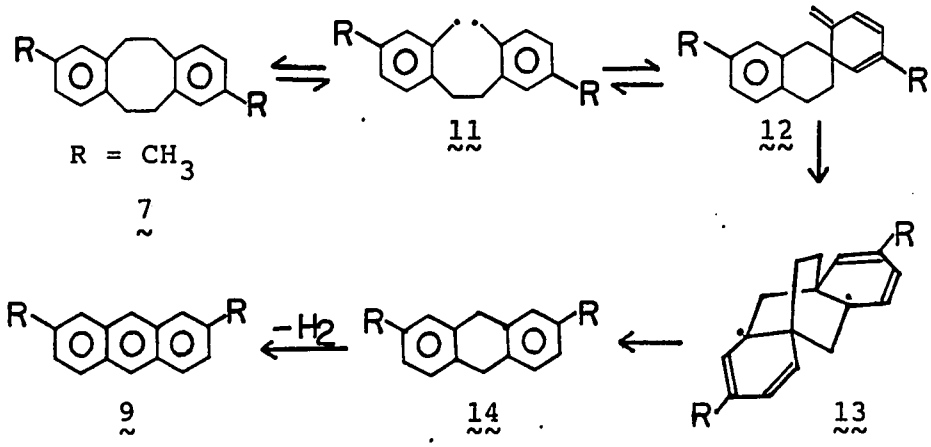
7 9 (3)



8 10 (4)

The "transoid" [4+4] dimer 7 gave the "cisoid" anthracene (9) and the "cisoid" [4+4] dimer 8 gave the "transoid" anthracene (10). This means that the aromatic rings of the starting material are flipped 180° relative to each other. The high regiospecificity of the transformation also rules out the possibility that the [4+4] dimers are reverting back to the respective o-xylylene prior to anthracene formation. A mechanism[1,2] has been proposed for this conversion which accounts for the regiospecificity of the reaction, and is shown in Scheme 1 using the transformation of 7 as an example.

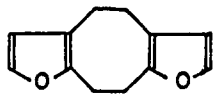
Scheme 1



The [4+2] dimer (12) is an attractive intermediate because half of the ring flip takes place in going from the [4+4] to the [4+2] dimer. The proposed diradical 13 should be relatively stable, having two delocalized radicals and no severely strained bonds, and rationalizes the facile loss of ethylene because the C-C bonds which undergo cleavage are

parallel with the π-orbitals of the radical sites. Also, the elimination of ethylene from 13 would be energetically favorable as two aromatic rings and two closed shell molecules would be generated. The conversion of 14 to 9 has already been described as a facile process.[3,4] Although diradicals 11 and 13 are reasonable intermediates, concerted reactions involving no intermediates cannot be excluded.

In order to extend this transformation both to gain mechanistic insight and to establish the generality of the reaction, flash vacuum pyrolysis (FVP) of 15, 16, and 17 was carried out. The pyrolysis of 15 was expected to give



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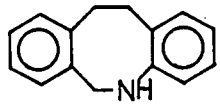

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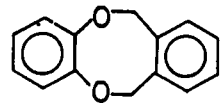

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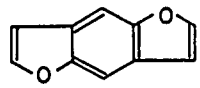
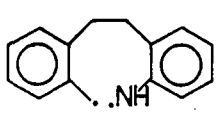
benzo[1,2-b:4,5-b']difuran (18) with one of the furan rings flipped 180° relative to the other. This transformation may



18

also be a convenient way of synthesizing benzodifurans which are made by multistep routes.[5] Compounds 16 and 17 contain one nitrogen atom and two oxygen atoms, respectively. These heteroatoms can be a good probe in determining the mechanism for the conversion of 1 to anthracene (2). It is also

expected that the stable diradicals 19 and 20 can be generated at lower pyrolysis temperatures than that of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1) (900°C). It is possible that



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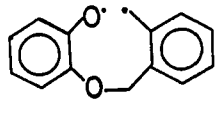
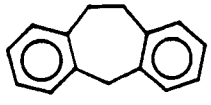


20

the reactive intermediates, which might have been destroyed in the pyrolysis of 1 by high temperature, could be obtained in the pyrolysis of 16 and 17 because of the lower pyrolysis temperature and the stabilizing heteroatom.

FVP of the 7-membered ring compounds including 21, 22, and 23 were also carried out in order to establish the generality of the reaction.



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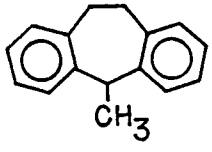

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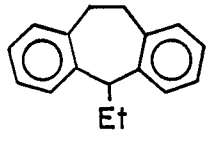

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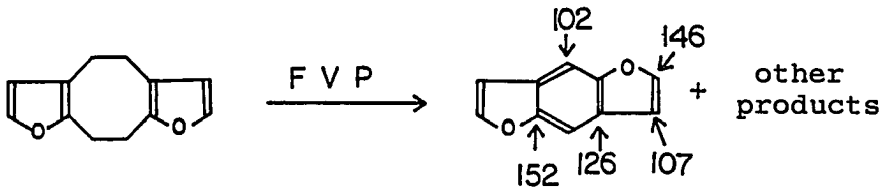
RESULTS

The FVP of 15 at 880-900°C and 10^{-4} torr gave a ca. 8% yield of benzo[1,2-b:4,5-b']difuran (18) along with other products such as benzene, naphthalene, toluene, indene and two unknown products (MW 102 and 132). The structure of 18 was



15 18 (5)

determined by its spectral properties. The ^{1}H NMR spectrum (Fig. 1) exhibited a singlet at δ 7.65, and doublets at δ 7.64 and δ 6.83 (J = 2 Hz). The ^{13}C NMR (Fig. 2) showed five signals as required by the symmetry of 18 at δ 152, 146, 126, 107, and 102. High resolution mass spectral data were consistent with the molecular formula $C_{10}H_6O_2$. The yields of 18 and recovered 15 from the pyrolysis of 15 at various temperatures are presented in Table 1. The maximum yield of 18 was obtained at a pyrolysis temperature of 840-850°C.

The FVP of 16 at 750°C and 10^{-4} torr gave a 75% yield of acridine (24) and an 8% yield of stilbene (25). GC/MS analysis of the crude pyrolysis products indicated that no anthracene (2) was formed in the pyrolysis. The ^{1}H NMR

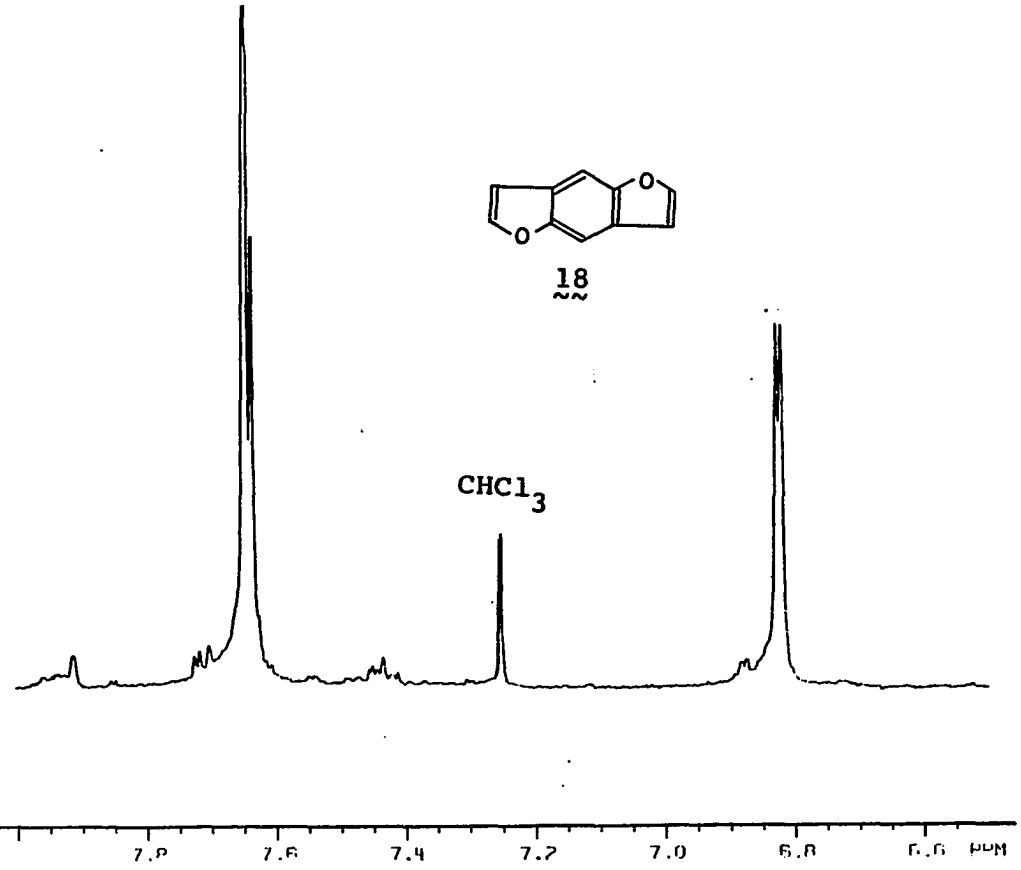


Figure 1. ^{1}H NMR spectrum of benzo[1,2-b:4,5-b']difuran (18)

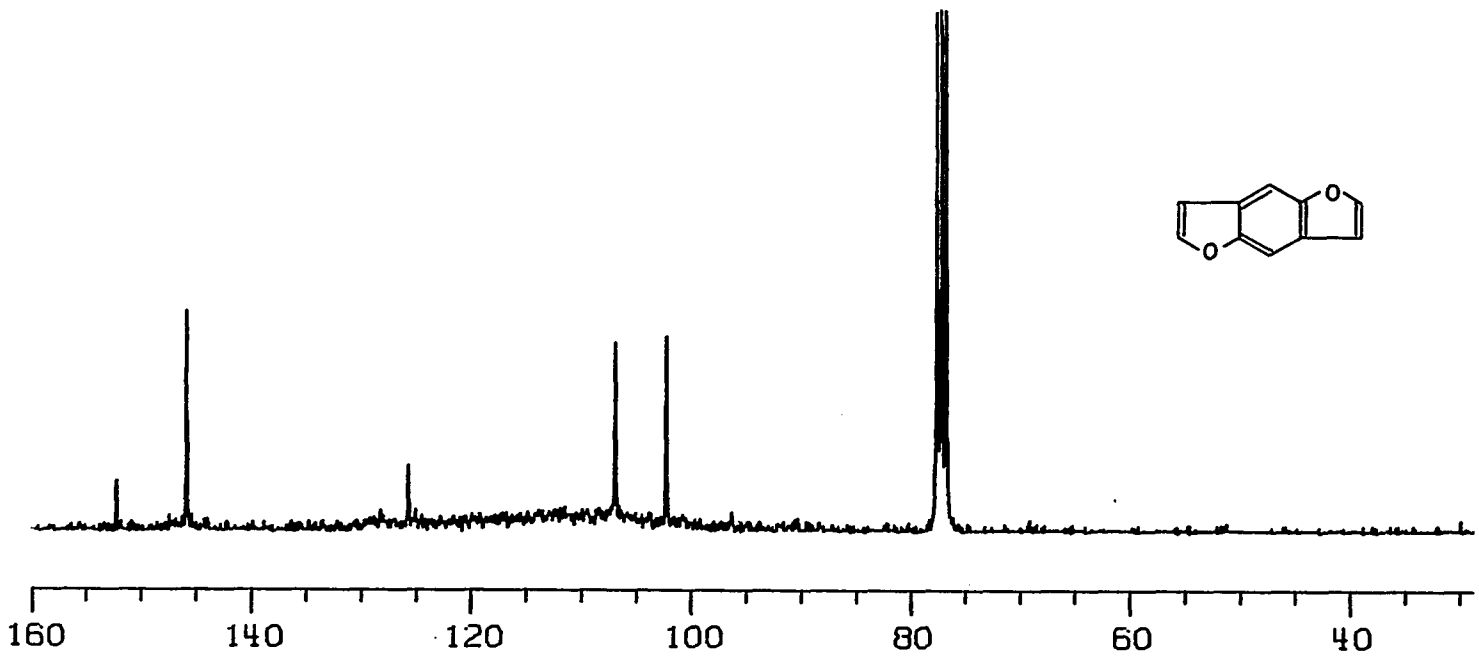
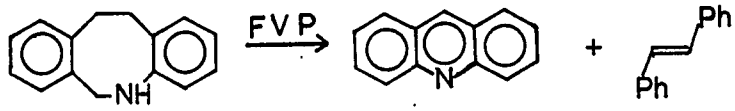


Figure 2. ^{13}C NMR spectrum of benzo[1,2-b:4,5-b']-difuran (18)

Table 1. The yield of benzo[1,2-b:4,5-b']difuran (18) and recovered 4H,5H,9H,10H-cycloocta[1,2-b:6,5-b']-difuran (15) at different pyrolysis temperatures

Temp. °C	Products, %[a]	
	18	15
980-1000	5.4	0
890-905	7.8	2.5
840-850	7.9	5.5
810-817	7.8	12.1
755-767	6.0	44.7
700-710	4.6	75.9

[a]Determined by GC using biphenyl as an internal standard.



16 24 25 (6)

spectrum of 24 (Fig. 3) includes one singlet at δ 8.80, doublets at δ 8.25 and 8.03, and multiplets at δ 7.85-7.74 and 7.60-7.50. The ^{1}H NMR spectrum of 24 is consistent with the reported spectrum[6] of acridine (24).

Compound 17 was prepared from catechol (26) and α,α'-dichloro-o-xylene (27). The gas phase pyrolysis of 17 at

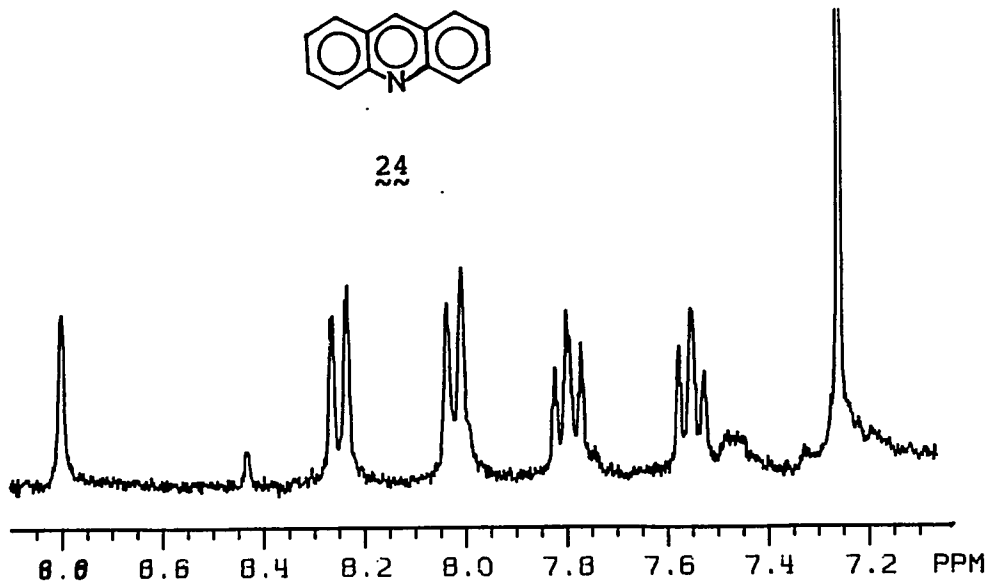
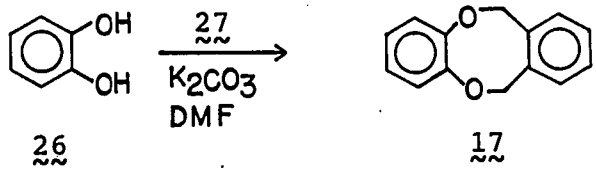
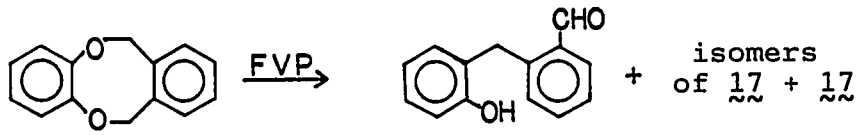


Figure 3. ^{1}H NMR spectrum of acridine (24)



26 17 (7)

580°C and at 10^{-4} torr gave a 60% yield of 28 as a major product along with other isomers of 17 (25%) and recovered 17.



17 28 (8)

The structure of 28 was determined by its spectral properties. The ^1H NMR spectrum (Fig. 4) included a singlet at δ 10.17 for the aldehyde group, a multiplet at δ 7.9-6.75 for the benzene group, a singlet at δ 6.50 for the phenol group and a singlet at δ 4.37 for the benzyl group. The IR spectrum of 28 showed strong absorption at 3300-2800 cm^{-1} for the phenol group and at 1660 cm^{-1} for the aldehyde group. The high resolution mass spectral data were consistent with the molecular formula $C_{14}H_{12}O_2$.

Methyldibenzosuberane (22) was prepared by reacting dibenzosuberone (29) with methyl lithium followed by lithium/ammonium reduction.[7]

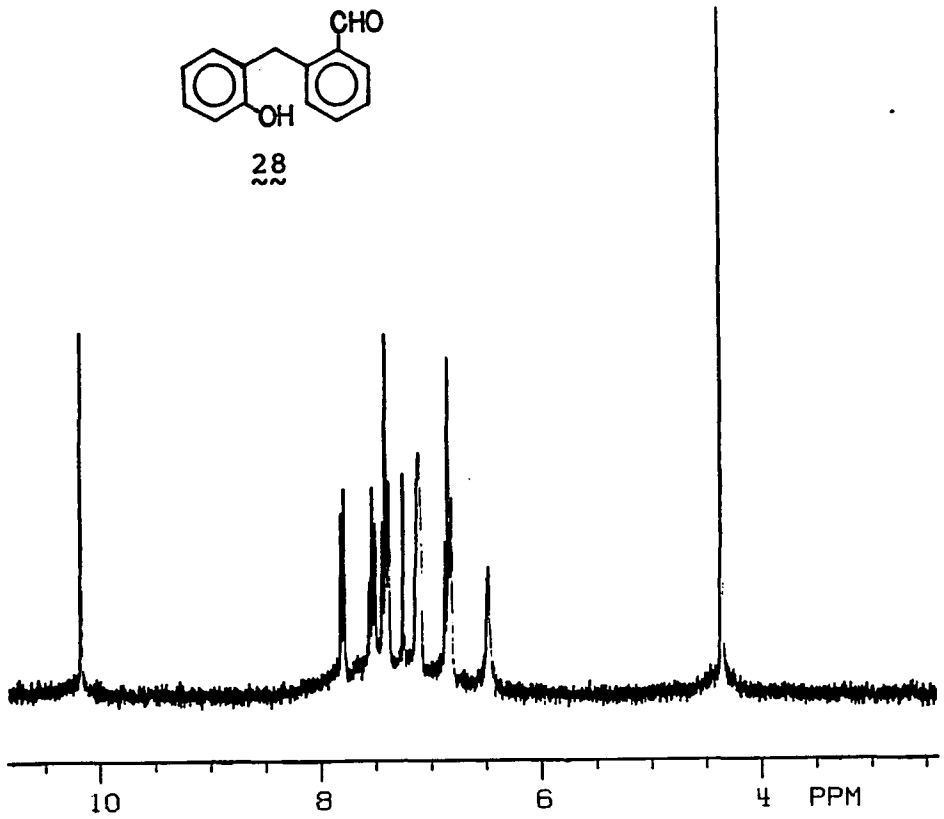
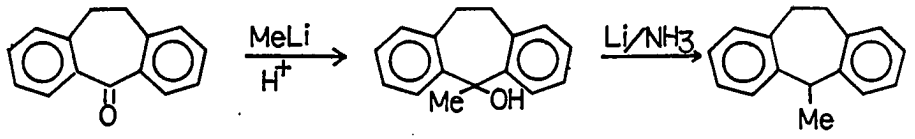
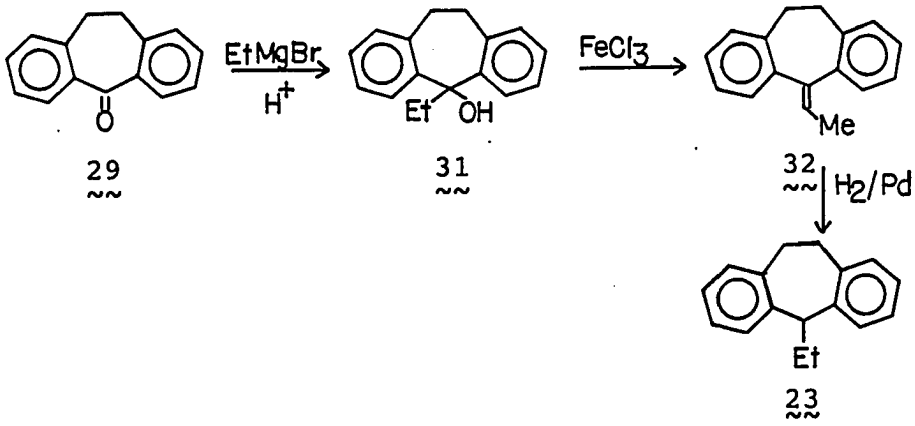


Figure 4. ^{1}H NMR spectrum of (2-hydroxybenzyl)-o-benzaldehyde (28)



29 30 22 (9)

Ethyldibenzosuberane (23) was prepared from dibenzosuberone (29) and this sequence is summarized in equation (10).



29 31 32 23 (10)

FVP of dibenzosuberane (21), 5-methyldibenzosuberane (22), and 5-ethyldibenzosuberane (23) gave anthracene (2) as a major product and 9-methylanthracene (33) as a minor product. Products from the FVP of these dibenzosuberanes are summarized in Table 2.

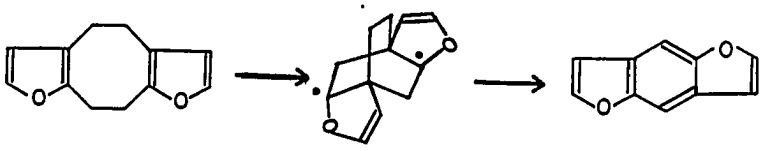
Table 2. FVP of dibenzosuberanes

Reactants	Temperature °C	Products, %[a]		
		Anthracene (2)	9-Methyl-anthracene (33)	Recovered Reactant
21	710	3	-	97
	900	24	5	62
22	700	54	3	30
23	690	72	2	23

[a]Determined by GC using biphenyl as an internal standard.

DISCUSSION

A mechanism has been reported[1,2] for the regiospecific formation of anthracene from the pyrolysis of the [4+4] dimer of o-xylylene (1) and this is presented in Scheme 1. By analogy, the production of 18 from the pyrolysis of 15 could occur by a pathway which involves the analogous biradical 34.

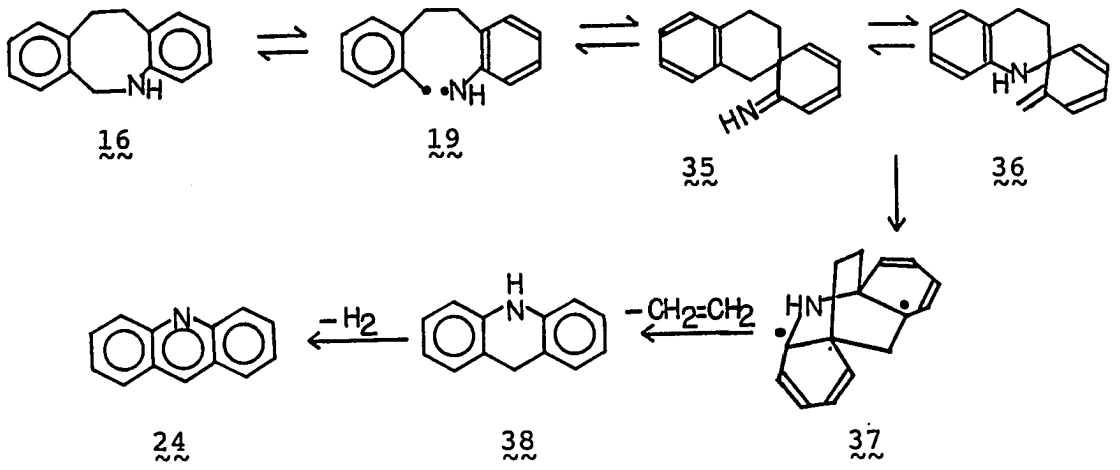


15 34 18

Table 1 shows that the yield of 18 from the pyrolysis of 15 was low at both high and low pyrolysis temperatures. At low pyrolysis temperatures, the yield of recovered 15 was high. We have also observed that as the pyrolysis temperature is raised more benzene, naphthalene and toluene are produced.

The formation of acridine (24) from FVP of 16 can also be explained by an analogous mechanism involving biradical intermediate 37. This pathway is described in Scheme 2. Presumably biradical 19 is initially formed by homolytic cleavage of the C-N bond which is a weaker bond than the C-C bond by ca. 12 kcal/mol.[8] Biradical 19 can rearrange to [4+2] dimers 35 or 36. Both [4+2] dimers 35 and 36 are expected to give biradical 37 by the rearrangement described in the transformation of 1 to anthracene (2) (Scheme 1).

Scheme 2



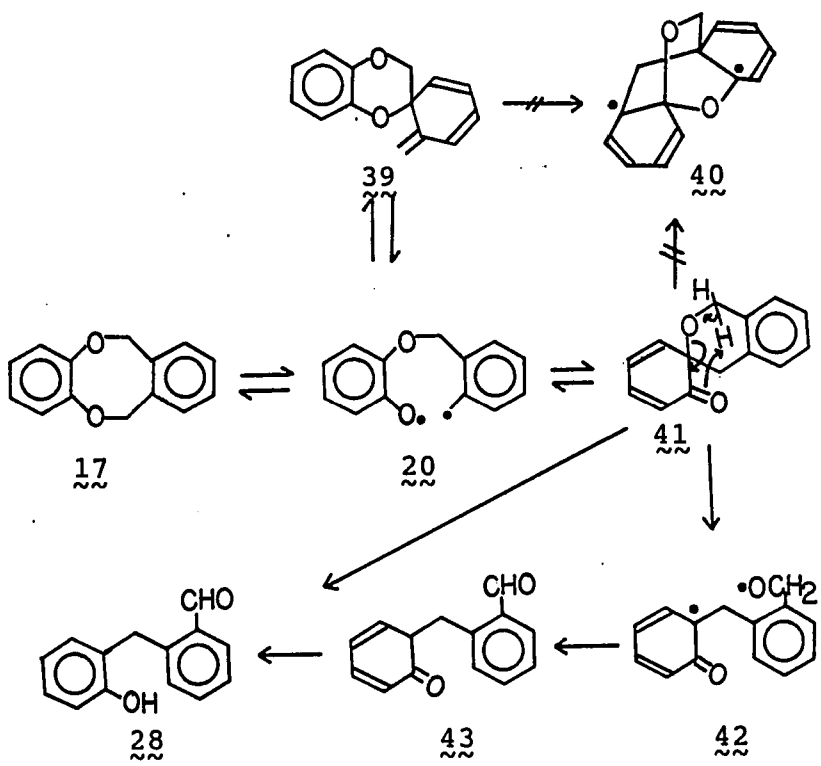
16 19 35 36

24 38 37

Biradical 37 can lose ethylene to give 38 which produces acridine (24) by loss of hydrogen.

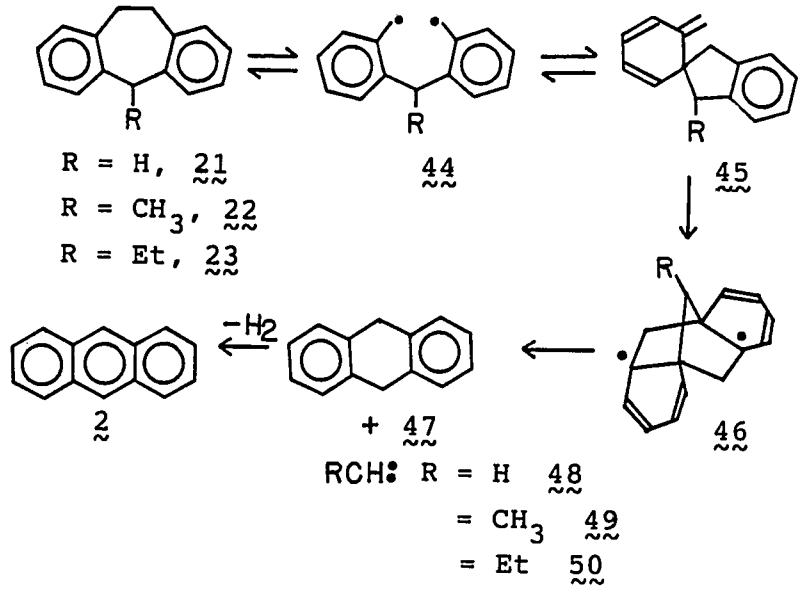
The formation of 28 from 17 by FVP is unusual because no loss of ethylene or formaldehyde occurs by the pyrolysis of 17. In Scheme 3, a pathway which accounts for the formation of 28 from 17 is presented. Formation of 28 can be explained by the conversion of 20 to the [4+2] dimer 41, which rearranges to 28 in a concerted manner, or undergoes homolytic cleavage to give diradical 42. Diradical 42 would undergo 1,5-hydrogen migration[9] to form 43 followed by 1,3-hydrogen shift to give 28. The rearrangement either from the [4+2] dimer 39 or from the [4+2] dimer 41 to diradical 40 would not occur probably because of facile rearrangement from 41 to 28 either in a concerted or stepwise manner.

Scheme 3



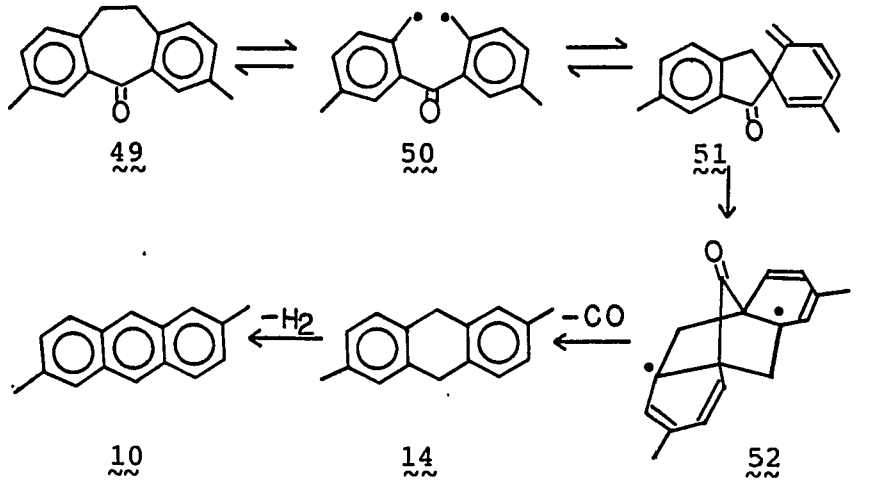
Flash vacuum pyrolysis of dibenzosuberanes gave anthracene as a major product. The formation of anthracene (2) from dibenzosuberanes 21, 22, and 23 by the flash vacuum pyrolyses is believed to take place by the following mechanism in Scheme 4. Homolytic cleavage of bibenzyl would give biradical 44 which undergoes radical insertion into the adjacent aromatic ring to produce spiro compound 45. The novel combination step gives the biradical intermediates 46 which could give carbenes (48-50) and 9,10-dihydroanthracene (47) either by a concerted or stepwise manner.[10] The loss of hydrogen from 9,10-dihydroanthracene (47) gives anthracene (2).

Scheme 4



The formation of biradical intermediates 46 seems to be quite general. In this laboratory,[11] it has also been shown to occur in the FVP of 2,9-dimethyldibenzosuberone (49) (Scheme 5).

Scheme 5



EXPERIMENTAL

Methods and Materials

The pyrolysis apparatus has been previously described.[12] ^{1}H NMR spectra were recorded on a Varian A-60 or a Nicolet 300 spectrometer. ^{13}C NMR spectra were recorded on a Nicolet 300 spectrometer. Chemical shifts are reported in parts per million (δ) from tetramethylsilane (TMS). Gas chromatographic (GC) analysis was performed on a Hewlett-Packard Model 5840-A gas chromatograph (GC) with a fused silica column coated with methyl silicone fluid (J and W scientific DB-1) and a flame ionization detector. Combined gas chromatographic/mass spectral (GC/MS) analysis was performed on a Finnigan 4000 GC/MS with an Incos data system. High resolution mass spectra were measured with either an Associated Electronics Industries MS-902 instrument or an MS 50 mass spectrometer. Infrared spectra (IR) were recorded on either a Beckman Acculab II or a Beckman 4250 spectrophotometer. Melting points were determined on a Hoover Thomas melting point apparatus and are uncorrected. Dibenzosuberane, dibenzosuberone, and 5,6,11,12-tetrahydrodibenzo[b,f]azocin hydrochloride were purchased from Aldrich Chemical Company.

4H,5H,9H,10H-Cycloocta[1,2-b:6,5-b']difuran (15)

Compound 15 was prepared by pyrolyzing 2-methyl-3-furylmethyl benzoate at 640°C as reported by Trahanovsky et al.[13]

15 (yield; 27%): ^{1}H NMR ($CDCl_3$) δ 7.12 (d, 2 H, J = 2 Hz), 6.05 (d, 2 H, J = 2 Hz), 3.00 (s, 4 H), 2.74 (s, 4 H). (^{1}H NMR data were well matched with the reported data.[13])

5,6,11,12-Tetrahydrodibenzo[b,f]azocine (16)

Compound 16 was prepared by washing 5,6,11,12-tetrahydrodibenzo[b,f]azocine hydrochloride with 10% NaOH solution. ^{1}H NMR ($CDCl_3$) δ 7.15-6.65 (m, 7 H), 6.49 (d, 1 H, J = 7.8 Hz), 4.43 (s, 2 H), 3.30 (t, 2 H, J = 6.5 Hz), 3.20 (t, 2 H, J = 6.6 Hz).

6H,11H-Dibenzo[b,f][1,4]-dioxocin (17)

A solution of 1.75 g (10 mmol) of α,α'-dichloro-o-xylene (27) in 35 ml of DMF was added dropwise over 1.0 h to a stirred solution of 1.20 g (10.9 mmol) of catechol (26) and 2.80 g (20.6 mmol) of anhydrous potassium carbonate in 50 ml of DMF at 90°C. The reaction mixture was stirred at 90°C for 12 h. The reaction mixture was cooled to room temperature and this cooled reaction mixture was diluted with 300 ml of cold water. The resulting solution was extracted with ether (3 x 40 ml). The ether layers were combined and washed successively with 10% NaOH (3 x 30 ml) and saturated NaCl (3 x 30 ml). The organic layer was dried ($MgSO_4$) and concentrated to give 1.90 g (9.0 mmol, 90%) of an oil 17: ^{1}H NMR ($CDCl_3$) δ 7.4-6.8 (m, 8 H), 5.40 (s, 4 H), IR (neat, NaCl) 1490, 1240, 1100, 1000, 910, 740 cm^{-1}; GC/MS (70eV) m/e (% base peak) 214

(0.23), 213 (2.46), 212 (17.65), 105 (9), 104 (100), 103 (20), 78 (23), 77 (10), 52 (11); high resolution mass spectrum calculated for $C_{14}H_{12}O_2$ 212.08373, measured 212.08365.

5-Methyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (22)

To 10 ml of 1.5 M methyl lithium in ether 2.10 g (10 mmol) of dibenzosuberone in 10 ml of ether was added dropwise over a 20 min period at room temperature. After the addition was complete, the reaction mixture was heated to reflux for 2 h. The reaction mixture was cooled to room temperature and then the mixture was worked up with saturated NH_4Cl followed by ether extraction to give 2.0 g (8.9 mmol, 89%) of 5-methyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene-5-ol (53): mp 142-143°C (Lit.[14] mp 147-148°C); ^1H NMR ($CDCl_3$) δ 8.2-7.0 (m, 8 H), 3.2 (br s, 4 H), 2.0 (s, 3 H); IR (CCl_4) 3700-3200, 1510 cm^{-1}. Without further purification, 400 mg of 53 was converted to 16 with Li/NH_3[7], followed by thin layer chromatography on silica gel (5% ether in hexanes) to give 230 mg (1.1 mmol, 62%) of an oil, 22: ^1H NMR ($CDCl_3$) δ 7.15-7.05 (m, 8 H), 4.43 (q, 1 H, J = 7.2 Hz), 3.21 (s, 4 H), 1.71 (d, 3 H, J = 7.5 Hz); [Lit.[14] ^1H NMR (CCl_4) δ 6.6 (m, 8 H), 3.9 (q, 1 H), 2.9 (s, 4 H), 1.3 (d, 3 H)]; IR (neat, NaCl) 3040, 2920, 1480, 1450, 1030, 740 cm^{-1}; mass spectrum (70eV) m/e (% base peak) 208 (32), 194 (18), 193 (100), 191 (12), 178 (35), 165 (11), 115 (35), 89 (14); high resolution mass spectrum calculated for $C_{16}H_{16}$ 208.12520, measured 208.12565.

5-Ethylidene-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (54)

To 432 mg (17.8 mmol) of Mg, 2.18 g (14.0 mmol) of EtI in 20 ml of dry ether was added dropwise with vigorous stirring. The solution was stirred at room temperature for 1 h. To this solution 2.1 g (10 mmol) of dibenzosuberone (29) was added dropwise at room temperature. The reaction mixture was heated to reflux for 2 h. The reaction mixture was cooled to room temperature and then the mixture was worked up with saturated NH_4Cl followed by ether extraction to give a crude (80%) 5-ethyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene-5-ol (55). Without further purification, 55 was converted to 54 with 10% $FeCl_3$ in silica gel[15] followed by column chromatography on alumina (Woelm I, hexanes) to give 1.0 g (45%) of 54: ^1H NMR ($CDCl_3$) δ 7.3-7.0 (m, 8 H), 5.96 (q, 1 H, J = 7.0 Hz), 3.6-2.8 (broad s, 4 H), 1.73 (d, 3 H, J = 6.9 Hz); [Lit.[16] ^1H NMR ($CDCl_3$) δ 7.4-6.9 (m, 8 H), 5.95 (q, 1 H, J = 7.0 Hz), 3.06 (broad s, 4 H), 1.72 (d, 3 H, J = 7.0 Hz)]; IR (neat, NaCl) 3040, 3000, 2900, 2840, 1480, 1430, 1350, 760, 740, 730 cm^{-1}; GC/MS (70eV) m/e (% base peak) 222 (1.54), 221 (17.45), 220 (100), 219 (53.33), 206 (11), 205 (64), 204 (23), 203 (24), 202 (22), 191 (27), 190 (11), 189 (16), 179 (11), 178 (27), 165 (13), 129 (18), 128 (18), 115 (18), 107 (14), 105 (12), 102 (24), 101 (43), 96 (34), 95 (26), 91 (29), 89 (27), 88 (13), 83 (15), 77 (13), 76 (14), 63 (15), 51 (14).

5-Ethyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (23)

Compound 23 was prepared by hydrogenating 54 with 5% Pd/C in EtOH at 60 psi hydrogen pressure for 3 h. 23 (yield; 92%): ^{1}H NMR ($CDCl_3$) δ 7.20-7.05 (m, 8 H), 3.87 (t, 1 H, J = 7.8 Hz), 3.40-2.85 (m, 4 H), 2.11 (q, 2 H, J = 7.5 Hz), 0.88 (t, 3 H, J = 7.5 Hz); [Lit.[16] ^{1}H NMR ($CDCl_3$) δ 7.3-6.9 (m, 8 H), 3.85 (t, 1 H, J = 7.8 Hz), 3.14 (m, 4 H), 2.09 (q of d, 2 H), 0.85 (t, 3 H, J = 7.0 Hz)]; IR (neat, NaCl) 3040, 3000, 2940, 2910, 1480, 1445, 1360, 1300, 1100, 740 cm^{-1}; GC/MS (70eV) m/e (% base peak) 224 (0.1), 223 (0.95), 222 (5.24), 194 (16), 193 (100), 178 (25), 115 (39), 91 (13), 89 (10); high resolution mass spectrum calculated for $C_{17}H_{18}$ 222.14085, measured 222.14114.

General FVP procedure

The furnace was maintained at temperatures ranging between 500-900°C. A sample in a pyrex boat was placed into the sample chamber and the system was evacuated to ca. 10^{-4} torr. The sample chamber was heated to ca. 100°C during the pyrolysis. After the pyrolysis, $CDCl_3$ was deposited into the liquid nitrogen trap through a side arm. Upon completion of the pyrolysis, nitrogen was introduced into the system and the trap was slowly warmed to room temperature. The product solution was dried, filtered, and concentrated.

FVP of 4H,5H,9H,10H-cycloocta[1,2-b:6,5-b']difuran (15)

A 640 mg (3.4 mmol) of 15 was pyrolyzed at 870-890°C in the normal manner. GC and ^{1}H NMR analyses of the pyrolysis products indicated benzene and toluene were formed as major products along with an 8% yield of benzo[1,2-b:4,5-b']difuran (18), and other minor products. After removal of the solvent, 18 was separated from the pyrolysis products by column chromatography on silica gel (hexanes) to give 26 mg (0.16 mmol, 4.8%) of white crystalline product 18: mp 100-101.5°C (Lit.[5] 111°C); ^{1}H NMR ($CDCl_3$) δ 7.65 (s, 2 H), 7.64 (d, 2 H, J = 2 Hz), 6.83 (d, 2 H, J = 2 Hz); ^{13}C NMR ($CDCl_3$) δ 152, 146, 126, 107, 102; IR (KBr) 1550, 1420, 1380, 1300, 1150, 1020, 850, 750, 700 cm^{-1}; UV (hexane) λ_{max1} = 222 nm (E_1 = 15000), λ_{max2} = 274 nm (E_2 = 9400); GC/MS (70eV) m/e (% base peak) 160 (0.76), 159 (9.71), 158 (100), 130 (15), 129 (14), 102 (44), 79 (11), 76 (16), 75 (19), 74 (17), 63 (8), 51 (39), 50 (37); high resolution mass spectrum calculated for $C_{10}H_6O_2$ 158.03678, measured 158.03667.

FVP of 5,6,11,12-tetrahydrodibenzo[b,f]azocine (16)

A 200 mg (0.96 mmol) quantity of 16 was pyrolyzed at 750°C in the normal manner. GC and ^{1}H NMR spectral analyses of the crude product mixture indicated acridine (24) was formed as a major product (75%) along with stilbene (25) and an other minor product (MW 168). 24: ^{1}H NMR ($CDCl_3$) δ 8.80 (s, 1 H), 8.25 (d, 1 H, J = 10 Hz), 8.03 (d, 1 H, J = 10 Hz), 7.85-7.74

(m, 1 H), 7.60-7.50 (m, 1 H); [Lit.[6] ^{1}H NMR ($CDCl_3$) δ 8.5-8.1 (m), 7.9-7.2 (m)]; GC/MS (70eV) m/e (% base peak) 181 (0.9), 180 (13.80), 179 (100), 178 (21), 152 (11), 151 (13), 90 (17), 89 (41), 76 (18), 75 (14), 63 (12). 25: GC/MS (70eV) m/e (% base peak) 182 (1.12), 181 (14.04), 180 (100), 179 (74), 178 (46), 176 (14), 165 (35), 152 (14), 90 (19), 89 (60), 88 (23), 83 (13), 76 (45), 75 (11), 63 (11).

FVP of 6H,11H-dibenzo[b,f][1,4]-dioxocin (17)

A 500 mg (2.36 mmol) quantity of 17 was pyrolyzed at 580°C in the normal manner. The pyrolysate in liquid nitrogen trap was collected in $CDCl_3$. The pyrolysate which was deposited in the quartz tube after the hot zone was dissolved in $CDCl_3$. After the organic layer was combined, dried ($MgSO_4$), and concentrated, the crude product was purified by thin layer chromatography on silica gel (50% ether in hexanes) to give 250 mg (1.18 mmol; 50%) of (2-hydroxybenzyl)-o-benzaldehyde (28): mp 138-139°C; ^{1}H NMR ($CDCl_3$) δ 10.17 (s, 1 H), 7.90-6.75 (m, 8 H), 6.50 (s, 1 H), 4.37 (s, 2 H); IR (KBr) 3300-2800, 1660, 1580, 1450, 1250, 1210, 740 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 194.77, 153.89, 142.35, 134.12, 133.57, 133.36, 131.71, 130.63, 127.98, 126.88, 126.15, 120.60, 116.14, 32.18; GC/MS (70eV) m/e (% base peak) 214 (1.95), 213 (10.05), 212 (75.62), 211 (24), 196 (12), 195 (86), 194 (61), 184 (25), 183 (18), 181 (18), 177 (11), 169 (13), 167 (23), 166 (25), 165 (73), 155 (14), 153 (23), 152 (36), 151 (10), 141 (25), 139

(14), 129 (12), 128 (28), 127 (18), 119 (11), 118 (100), 115 (38), 105 (14), 97 (28), 91 (45), 90 (97), 89 (35), 82 (26), 82 (41), 78 (30), 77 (76), 76 (39), 75 (16), 65 (27), 64 (19), 63 (45), 55 (23), 53 (15), 52 (13), 51 (53), 50 (18); high resolution mass spectrum calculated for $C_{14}H_{12}O_2$ 212.08373, measured 212.08382.

FVP of 10,11-dihydro-5H-dibenzo[a,d]cycloheptene (21)

The pyrolysis of 21 was carried out in the normal manner at 710°C and 900°C using 30 mg quantities of 21. GC and ^1H NMR spectral analyses indicated anthracene (2) was formed as a major product along with 9-methylanthracene (33). Products from FVP of 21 at different pyrolysis temperatures are summarized in Table 2. 2: ^1H NMR ($CDCl_3$) δ 8.41 (s, 2 H), 8.05-7.90 (m, 4 H), 7.48-7.39 (m, 4 H); [Lit.[17] ^1H NMR ($CDCl_3$) δ 8.44 (s, 2 H), 8.12-7.85 (m, 4 H), 7.60-7.38 (m, 4 H)]; GC/MS (70eV) m/e (% base peak) 180 (1.02), 179 (14.36), 178 (100), 177 (8), 176 (16), 89 (13), 88 (7), 76 (12). 33: ^1H NMR ($CDCl_3$) δ 8.25-8.35 (m), 8.00 (d, J = 7.8 Hz), 7.53-7.42 (m), 3.09 (s); [Lit.[18] ^1H NMR ($CDCl_3$) δ 8.31, 8.26, 7.97, 7.48, 7.43, 3.07]; GC/MS (70eV) m/e (% base peak) 194 (1.12), 193 (15.53), 192 (100), 191 (58), 190 (10), 189 (26), 165 (7), 96 (17), 95 (16), 83 (12).

FVP of 5-methyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (22)

A 35 mg quantity of 22 was pyrolyzed at 700°C in the normal manner. GC and ^{1}H NMR spectral analyses indicated a 54% yield of anthracene (2), a 3% yield of 9-methylanthracene (33), and a 30% yield of recovered 22 were formed in the pyrolysis.

FVP of 5-ethyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (23)

A 35 mg quantity of 23 was pyrolyzed at 690°C in the normal manner. GC and ^{1}H NMR spectral analyses indicated a 72% yield of anthracene (2), a 2% yield of 9-methylanthracene, and a 23% yield of recovered 23 were formed in the pyrolysis.

REFERENCES

1. Trahanovsky, W. S.; Surber, B. W. J. Am. Chem. Soc. 1985, 107, 4995.

2. Surber, B. W. Ph. D. Dissertation, Iowa State University, 1984.

3. Vornkov, M. G.; Deryagina, E. N.; Shagun, L. G. Zh. Org. Khim. 1982, 18, 902.

4. Gajewski, J. J. "Hydrocarbon Thermal Isomerizations" Vol. 44 of Organic Chemistry, a series of monographs, H. H. Wasserman, ed., Academic Press: New York, 1981; pp. 128-130.

5. Loic, R.; Buisson, J. P.; Royer, R.; Aberbeck, D. Eur. J. Med. Chem. Chim. Ther. 1977, 12, 31.

6. Pouchert, C. J. "The Aldrich Library of NMR spectra, Edition II, Vol. 2," Aldrich Chemical Co.: Milwaukee, 1983; p. 749, spectra C.

7. Small, G. H.; Minella, A. E.; Hall, S. S. J. Org. Chem. 1975, 40, 3151.

8. Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", Harper and Row: New York, 1981; pp. 146-147.

9. Freidlina, R. K.; Terent'ev, A. B. Acc. Chem. Res. 1977, 10, 9.

10. R. W. Hoffmann. Angew. Chem. Int. Ed. Engl. 1971, 10, 529.

11. Tunkel, J. L. Ph. D. Dissertation, Iowa State University, 1985.

12. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, H. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. J. Org. Chem. 1971, 36, 3575.

13. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. J. Am. Chem. Soc. 1981, 103, 6691.

14. Hafelinger, G.; Streitwieser Chem. Ber. 1968, 101, 657.

15. Keinan, E.; Mazur, Y. J. Org. Chem. 1978, 43, 1020.

16. Paquette, L. A.; Meehan, G. V. J. Am. Chem. Soc. 1970, 92, 3039.

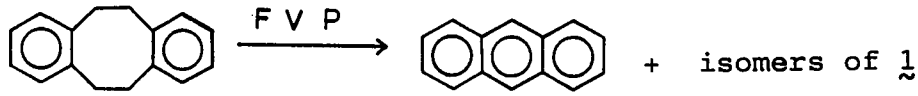
17. Pouchert, C. J. "The Aldrich Library of NMR Spectra, Edition II" Aldrich Chemical Co.: Milwaukee, 1983, p. 763, spectra D, Vol. 1.

18. Caspar, M. L.; Stothers, J. B.; Wilson, N. K. Can. J. Chem. 1975, 53, 1958.

PART III. FORMATION OF 9-METHYLANTHRACENE AND ANTHRACENE IN THE PYROLYSIS OF 5,6,11,12-TETRAHYDRODIBENZO[a,e]CYCLOOCTENE AND RELATED COMPOUNDS

INTRODUCTION

The flash vacuum pyrolysis (FVP) of the [4+4] dimer of o-xylylene (1) has been found to give anthracene (2) and other products.[1,2]



1 2

The regiochemistry of this conversion has also been established by the pyrolysis of the appropriately labeled dimethyl derivatives 3 and 4. The "transoid" [4+4] dimer 3

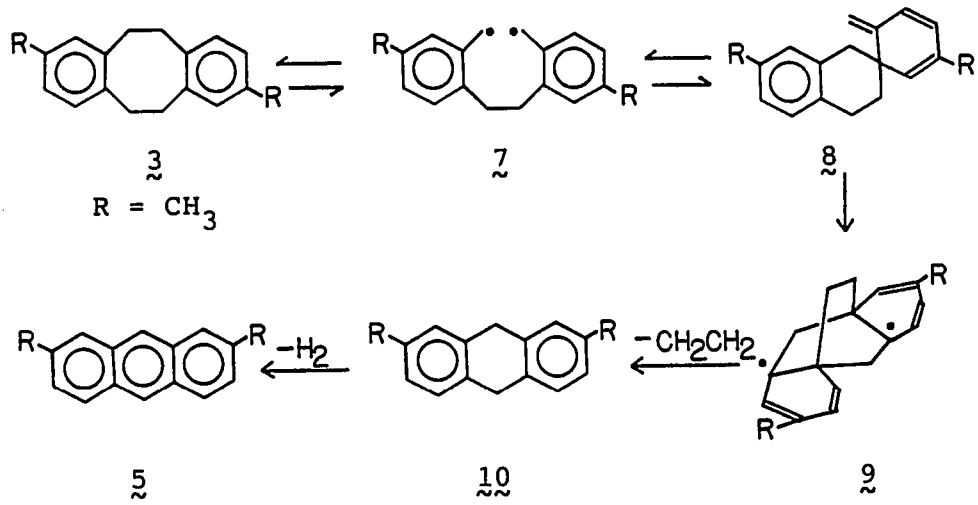
3 5

4 6

gave the "cisoid" anthracene 5 and the "cisoid" [4+4] dimer 4 gave the "transoid" anthracene 6. This means that the aromatic rings of the starting material are flipped 180° relative to each other. A mechanism has been proposed for this conversion which accounts for the regiospecificity of the

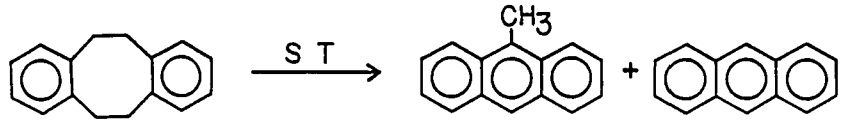
reaction, and is shown in Scheme 1 using the transformation of 3 as an example.

Scheme 1



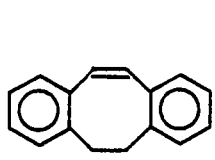
3 (R = CH_3) 7 8 5 10 9

During the course of preparing the [4+4] dimer of o-xylylene (1) by pyrolyzing benzocyclobutene[3] in a sealed tube, we identified as additional products[4] one dimer and two trimers of o-xylylene. In order to achieve a better understanding of the formation of these products, sealed tube pyrolysis (ST) of the [4+4] dimer of o-xylylene (1) was carried out. Unexpectedly sealed tube pyrolysis of 1 gave 9-methylanthracene (11) as a major product and anthracene (2) as a minor product contrary to the formation of 2 from FVP of



1 11 2

1. In order to study the mechanism of the formation of 11 from a sealed tube pyrolysis of 1, several possible precursors for 11, specifically 12, 13, 14, 15, and 16 were prepared and pyrolyzed in sealed tubes. As an extension of the conversion



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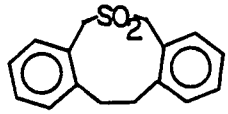

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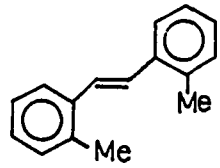

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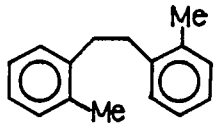

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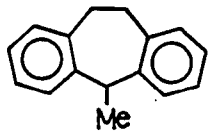

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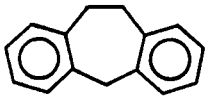
of 1 to 9-methylanthracene (11), sealed tube pyrolysis of 7-membered compounds including 17 to 20 were carried out.



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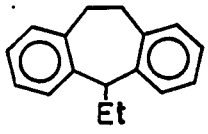

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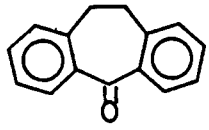

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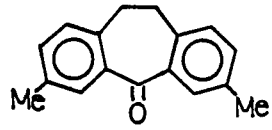

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RESULTS

The pyrolysis of the [4+4] dimer of o-xylylene (1) in a sealed tube gave 9-methylanthracene (11) as a major product and anthracene (2) as a minor product. Products from sealed tube pyrolysis of 1 at different temperatures for 3 h are displayed in Table 1. Products from sealed tube pyrolysis of 1 at 395°C for different periods of time are also displayed in Table 1. The yield of 9-methylanthracene (11) and anthracene (2) increased as the reaction temperature was increased (Table 1) or the reaction time was increased (Table 2). Sealed tube pyrolysis of 1 in the presence of naphthalene, dibenzyl, and eicosane are summarized in Table 3. Yields of anthracene (2) and 9-methylanthracene (11) were increased in the presence of bibenzyl and eicosane. On the other hand yields of 2 and 11 were decreased in the presence of naphthalene. Products from sealed tube pyrolysis of 1 in the presence of naphthalene at 420°C for different periods of time are also summarized in Table 4. These results are also plotted in Fig. 1. These data indicated 1 was converted to 9-methylanthracene (11) by overall loss of one carbon and four hydrogen atoms. 9-Methylanthracene (11) was also slowly converted to anthracene (2). A sealed tube pyrolysis of 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (3) at 420°C for 3 h gave a 51% yield of 2,6,9-trimethylanthracene (21) and a 49% yield of recovered 3. The ^{1}H NMR spectrum (Fig. 2) of the

Table 1. Sealed tube pyrolysis of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1) at different temperatures for 3 h

Reaction Temperature, °C	Products, %[a] 9-methylanthracene (11)	anthracene (2)	1
395	36	-	64
420	71	7	22
440	78	19	3

[a]Relative yield determined by GC.

Table 2. Sealed tube pyrolysis of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1) at 395°C for different periods of time

Reaction time hours	Products, %[a] 9-methylanthracene (11)	anthracene (2)	1
3	35	-	65
6	51	3	45
9	55	4	32
18	65	8	21

[a]Determined by GC using biphenyl as an internal standard.

Table 3. Sealed tube pyrolysis of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1) in the presence of different compounds at 420°C for 1 h

	Reactants	Products, %[a] 9-methylanthracene (11)	anthracene (2)	1
1.	5 mg of 1	37	2	61
2.	52 mg of bibenzyl + 5 mg of 1	64	12	14
3.	53 mg of naphthalene + 5 mg of 1	3	-	97
4.	43 mg of eicosane + 4 mg of 1	37	11	43

[a]Determined by GC using biphenyl as an internal standard.

Table 4. Sealed tube pyrolysis of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1) in the presence of 10-fold excess of naphthalene at 420°C for different periods of time

Reaction time, hours[b]	Products, %[a]		
	9-methylanthracene (11)	anthracene (2)	1
1	7.9	0.5	91.6
3	24.9	3.1	72
5	32.5	5.8	49.7
8	51.5	16.9	31.3
11	44.5	21.7	19.1
13	42.8	36.3	8.6
18	35.6	39.9	3.3
20	25.1	56.7	1.6

[a]Determined by GC using biphenyl as an internal standard.

[b]*Ca.* 5 mg of 1 + *ca.* 50 mg of naphthalene sample.

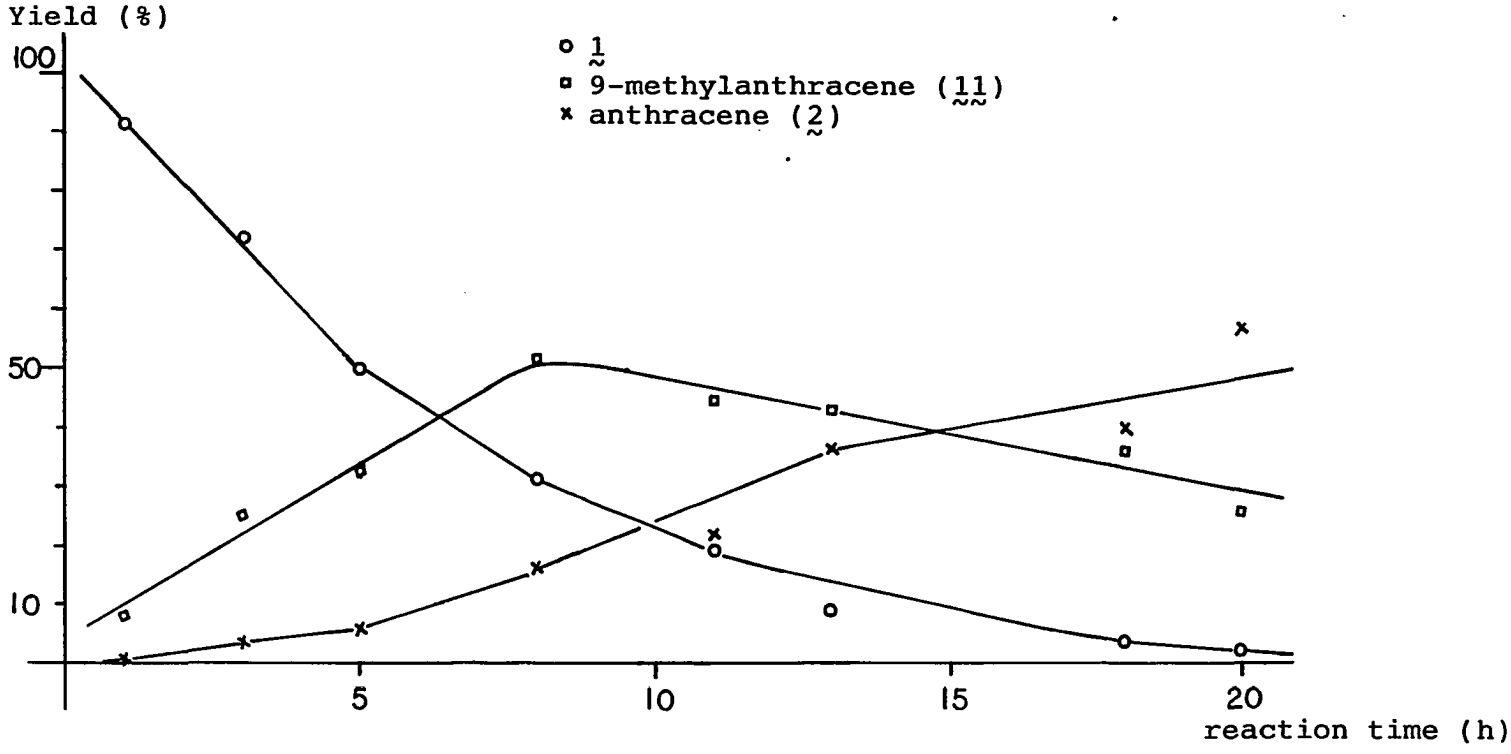


Figure 1. Sealed tube pyrolysis of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1) in the presence of naphthalene at 420°C for different periods of time (from Table 4)

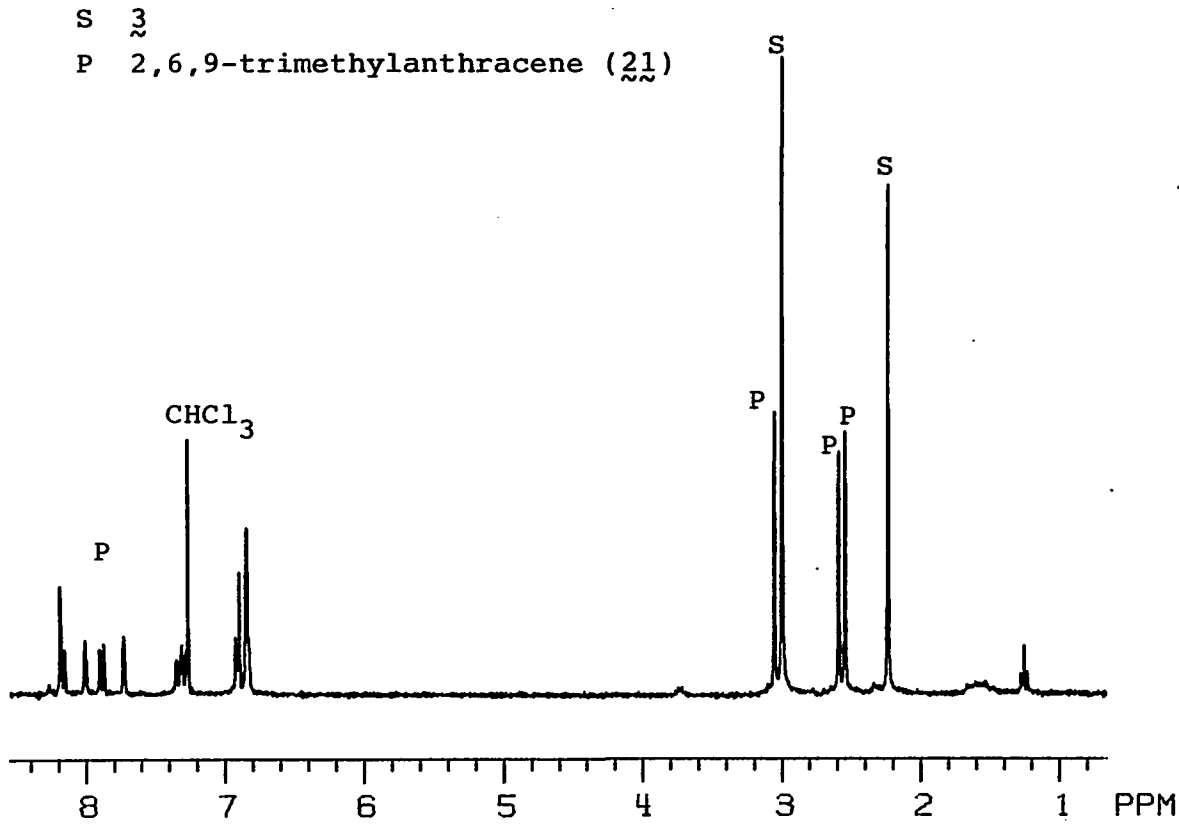
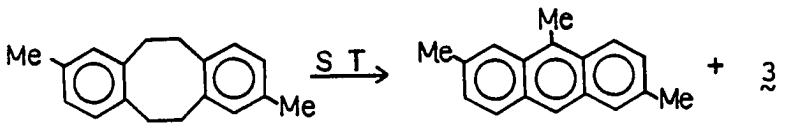


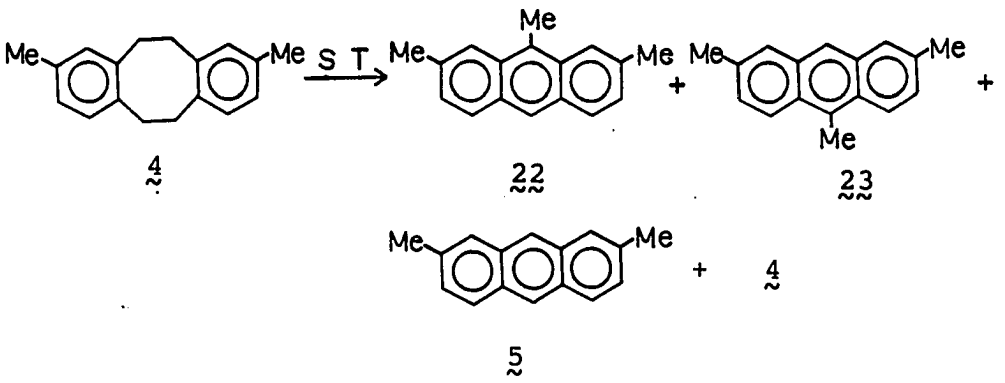
Figure 2. ^{1}H NMR spectrum of a sealed tube pyrolysis product of 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (3)



3 21

reaction mixture indicated new aromatic peaks at δ 8.2-6.8 and singlets at δ 3.045, 2.579, and 2.534 for the methyl groups.

A sealed tube pyrolysis of 4 at 450°C for 4 h gave a total of 69% yield of about a 1:1 mixture of 2,7,9-trimethylanthracene (22) and 2,7,10-trimethylanthracene (23), a 22% yield of 2,7-dimethylanthracene (5), and a 9% yield of recovered 4.



4 22 23

5

The ^{1}H NMR spectrum (Fig. 3) of the sealed tube pyrolysis mixture of 4 shows new singlet peaks at δ 3.038, 3.053, 2.580, and 2.534 for the methyl groups. GC/MS data were also consistent with the molecular formula $C_{17}H_{16}$.

A sealed tube pyrolysis of 1-d_4 at 440°C for 9 h gave a 65% yield of deuterated 9-methylanthracene (11-d_x), a 16%

S: 4
P: 2,7,9-trimethylanthracene (22) and 2,7,10-trimethylanthracene (23)

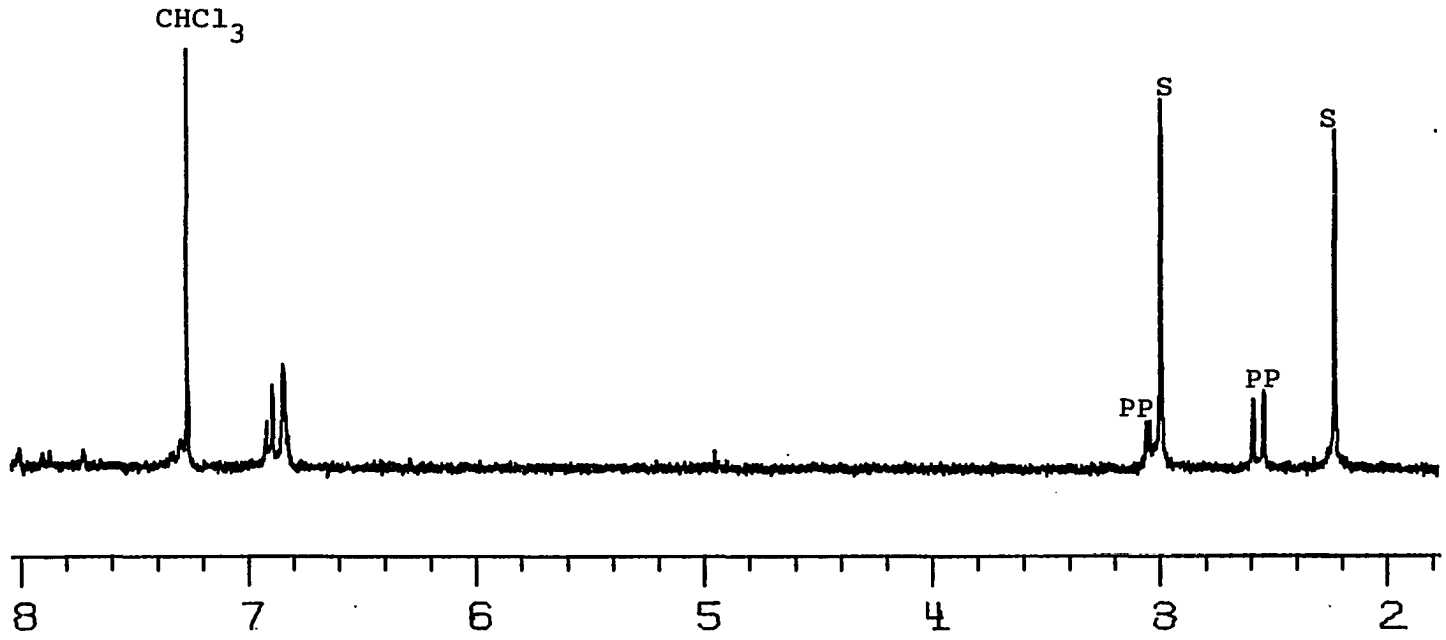
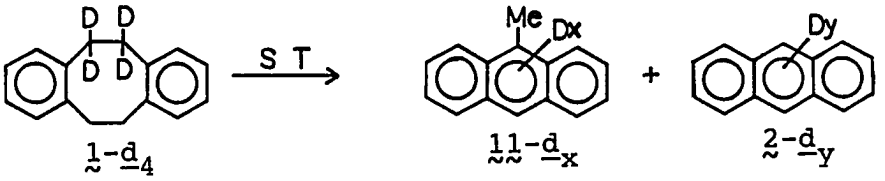


Figure 3. ^{1}H NMR spectrum of a sealed tube pyrolysis product of 2,9-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (4)



$\underset{\sim}{1}$-$\underline{d}_4$ $\underset{\sim\sim}{11}$-$\underline{d}_x$ $\underset{\sim}{2}$-$\underline{d}_y$

yield of deuterated anthracene ($\underset{\sim}{2}$-$\underline{d}_y$), and a 16% yield of recovered $\underset{\sim}{1}$-$\underline{d}_4$. The deuterium content of the products was determined by GC/MS using 16eV and this is summarized in Table 5. The ratio of deuterated anthracene species was 1:1.63:0.48:0.02 for d_0, d_1, d_2, and d_3, respectively. The ratio of deuterated 9-methylanthracene species was 1:4.10:6.53:4.11:0.73 for d_0, d_1, d_2, d_3, and d_4, respectively. Recovered $\underset{\sim}{1}$-$\underline{d}_4$ its maintained d_4 content.

A sealed tube pyrolysis of dibenzo[c,g]thiapindioxide-5,5,7,7-$\underline{d}_4$ ($\underset{\sim\sim}{13}$-$\underline{d}_4$) at 420°C for 3 h also gave a 70% yield of deuterated 9-methylanthracene, a 17% yield of deuterated anthracene and a 5% yield of $\underset{\sim}{1}$-$\underline{d}_4$. The deuterium content of the products was determined by GC/MS using 16eV and this is also summarized in Table 5. The ratio of deuterated anthracene species was 1.6:2.3:1.0:0.04 for d_0, d_1, d_2, and d_3, respectively. The ratio of deuterated 9-methylanthracene species was 1:1.8:2.2:1.4:0.5 for d_0, d_1, d_2, d_3, and d_4, respectively.

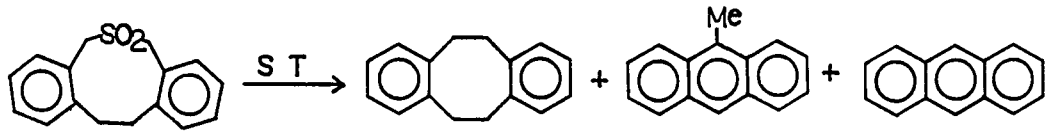
A sealed tube pyrolysis of dibenzothiapindioxide ($\underset{\sim\sim}{13}$) at 420°C for 3.5 h gave a 64% yield of $\underset{\sim\sim}{11}$, a 28% yield of $\underset{\sim}{1}$, and

Table 5. Mass spectral data of anthracene (2) and 9-methylanthracene (11) from the sealed tube pyrolysis of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene-5,5,6,6-d_4 (1-d_4) and dibenzo[c,g]thiapindioxide-5,5,7,7-d_4 (13-d_4)

Products	m/e	Relative intensity of undeuterated compound[a]	Relative intensity of products from 1-d_4[a]	Relative intensity of products from 13-d_4[a]
anthracene (2)	177	10	936	-
	178	126787	131952	2161
	179	18812	216570	3416
	180	1299	96409	1859
	181	64	13566	309
	182	-	1100	-
9-methylanthracene (11)	191	7421	10702	1505
	192	115465	124940	6081
	193	18984	532476	11065
	194	1419	901848	13568
	195	65	654308	8554
	196		185900	3046
	197		24303	
	198		1944	

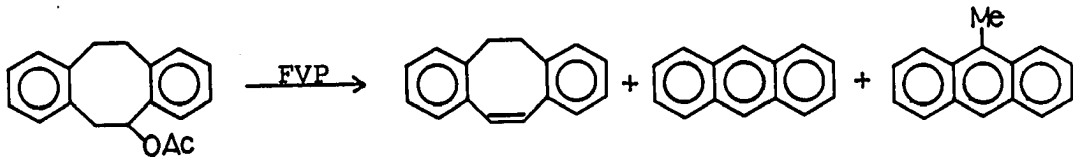
[a]Ionization voltage was 16eV.

a 6% yield of 2. The FVP and sealed tube pyrolysis of



13 1 11 2

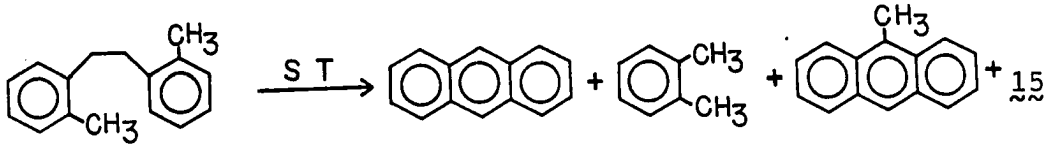
5,6-dihydrodibenzo[a,e]cyclooctene (12) and trans-2,2'-dimethylstilbene (14) did not give appreciable amounts of either 2 or 11 and these results are summarized in Table 6. The FVP of 24 at 780°C gave a 48% yield of 5,6-dihydrodibenzo[a,e]-cyclooctene (12), a 14% yield of anthracene (2), a 7% yield of 9-methylanthracene (11) and other unknown minor products. The



24 12 2 11

FVP of 12 at 900°C gave only a 43% yield of recovered 12 and a total of 45% yield of three unknown isomers of 12.

A sealed tube pyrolysis of di-o-tolylethane (15) at 420°C for 2 h gave a 22% yield of o-xylene, a 28% yield of anthracene (2), an 8% yield of 9-methylanthracene (11), and a 29% yield of recovered 15. In order to achieve a better understanding of the formation of 2 from the sealed tube



15 2 28 11

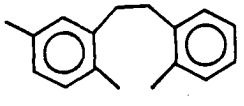
pyrolysis of 15, it was decided to determine the regiochemistry of the reaction by studying a sealed tube pyrolysis of unsymmetrically labeled trimethyl derivative 25,

Table 6. Sealed tube pyrolysis and the FVP of 5,6-dihydrodibenzo[a,e]cyclooctene (12) and trans-2,2'-dimethylstilbene (14)

Reactants	Reaction Conditions	Products, %[a]
12	1. ST 420°C for 1 h	black tar + trace of anthracene (2)
	2. ST 380°C for 25 min	unknown MW 206 (20%) + 2 (5%) + unknown MW 204 (21%) + 12 (35%) + unknown MW 208 (17%)
	3. FVP 900°C, 10^{-4} torr	3 unknown isomers of 12 (45%) + 12 (43%)
14	1. ST 420°C for 3 h	black tar + trace of 2 and 14
	2. ST 400°C for 1 h	an unknown MW 208 (30%) + 14 (70%)
	3. FVP 770°C, 10^{-4} torr	an unknown MW 208 (22%) + 14 (70%)
	4. FVP 950°C, 10^{-4} torr	2 (44%) + an unknown MW 208 (13%) + 14 (22%)

[a]Relative yield determined by GC.

symmetrically labeled tetramethyl derivative 26, and tetradeuterated bibenzyl 15-d_4.



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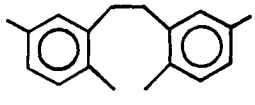

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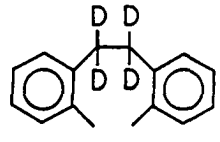
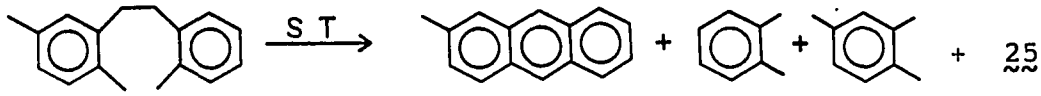


15-d_4

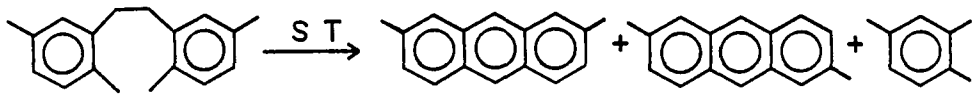
A sealed tube pyrolysis of 25 at 420°C for 2 h gave a 37% yield of 2-methylanthracene (27), a total of 47% yield of o-xylene and 1,2,4-trimethylbenzene (29) and recovered 25 (16%). Neither anthracene nor dimethylanthracene was formed



25 27 28 29

in the sealed tube pyrolysis of 25. The ^{1}H NMR spectrum of the reaction mixture of 25 (Fig. 4) included new singlets at δ 8.35, 8.27, and 7.74 and a multiplet at δ 8.0-7.85 for the aromatic group and a singlet at δ 2.534 for the methyl group. GC/MS data were consistent with the molecular formula $C_{15}H_{12}$.

A sealed tube pyrolysis of 26 at 420°C for 2 h gave a 13% yield of 2,7-dimethylanthracene (5), a 22% yield of 2,6-dimethylanthracene (6), a 40% yield of 29, and recovered 26. The formation of 5 and 6 was confirmed by the comparison



26 5 6 29

between the reported[2,5] ^{1}H NMR spectrum of 5 and 6, and the ^{1}H NMR spectrum of the reaction mixture (Fig. 5).

A sealed tube pyrolysis of 15-d_4 at 420°C for 2 h also gave a 26% yield of deuterated o-xylene (28-d_z), a 36% yield

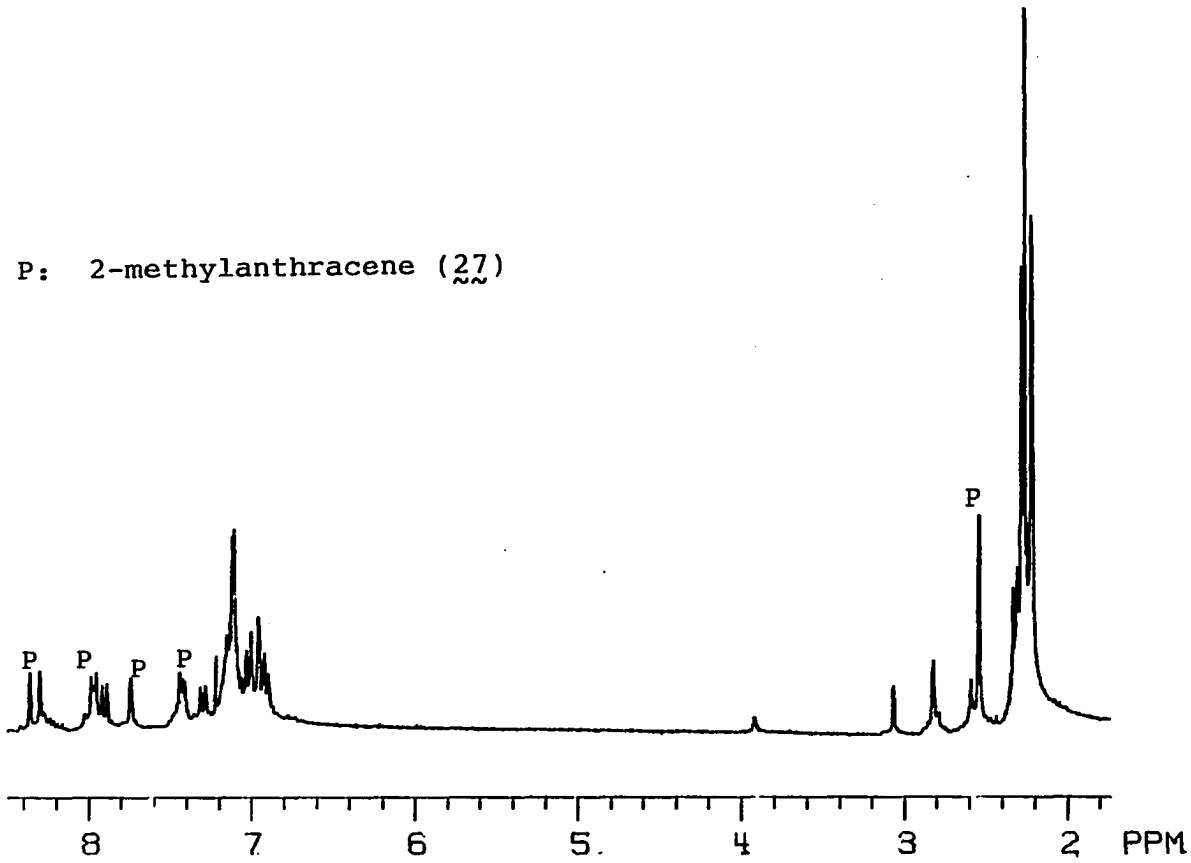


Figure 4. ^{1}H NMR spectrum of a sealed tube pyrolysis product of 2,2',5-trimethylbibenzyl (25) at 420°C for 2 h

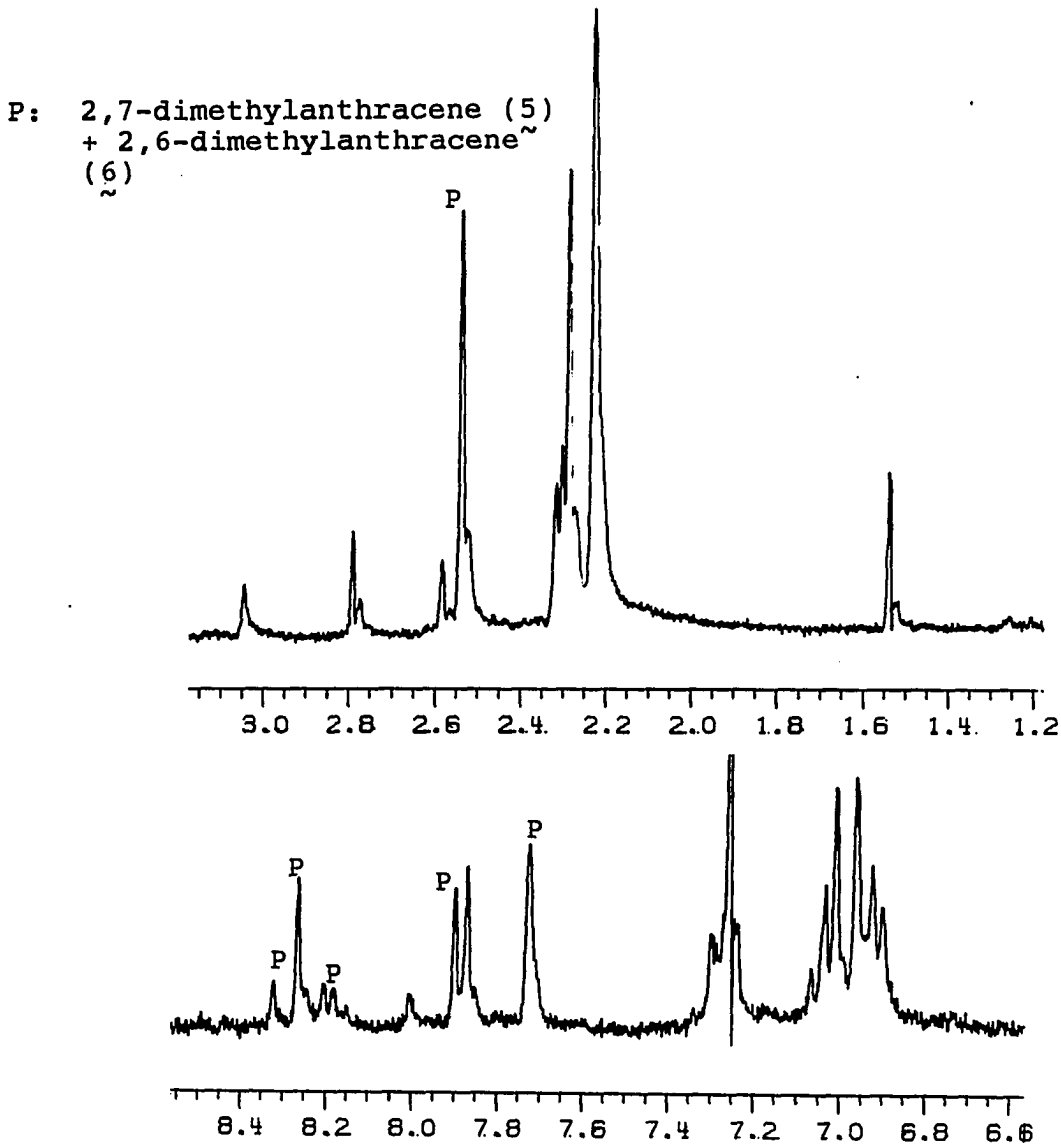
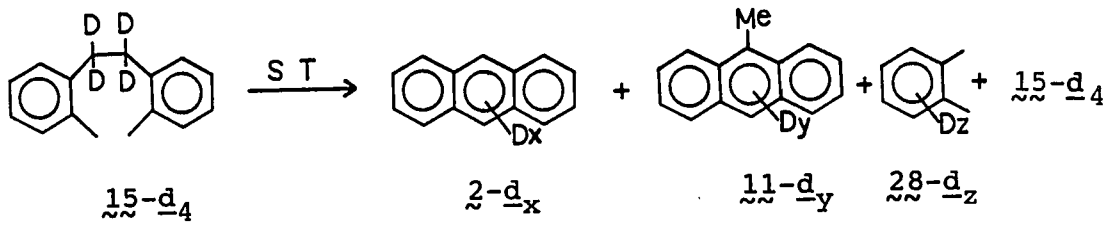


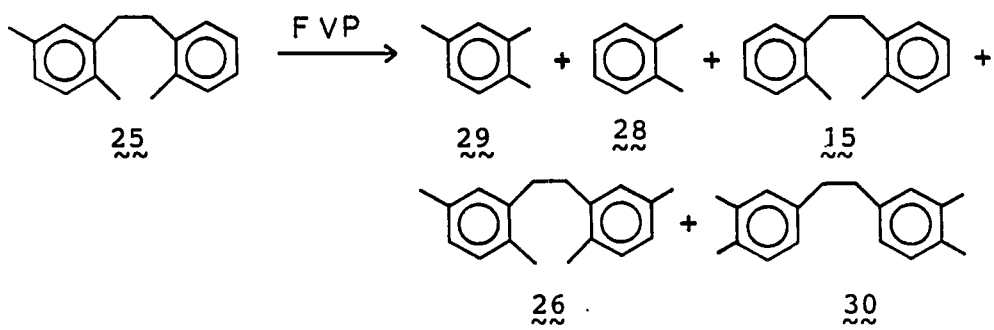
Figure 5. ^{1}H NMR spectrum of a sealed tube reaction of 2,2',5,5'-tetramethylbibenzyl (26) at 420°C for 2 h

of deuterated anthracene (2-d_x), a 9% yield of deuterated 9-methylanthracene (11-d_y), and an 18% yield of recovered 15-d_4. The deuterium content was determined by GC/MS using



16eV and this is summarized in Table 7. The ratio of deuterated anthracene species was 1:2.12:0.98:0.02 for d_0, d_1, d_2, and d_3, respectively. The recovered 15-d_4 maintained its d_4 content.

The FVP of 25 at 840°C and 10^{-4} torr gave a mixture of 18% of 29, 18% of o-xylene (28), 14% of 15, 10% of 25, 11% of 26,



and 4% of 30. Neither anthracene nor 9-methylanthracene was observed in the FVP of 25.

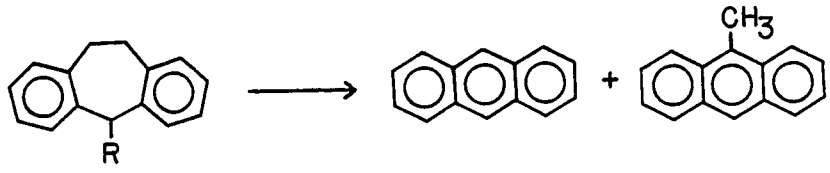
Sealed tube pyrolysis of dibenzosuberane (17), methyldibenzosuberane (16), and ethyldibenzosuberane (18) also

Table 7. Mass spectral data of anthracene (2) and 9-methylanthracene (11) from the sealed tube pyrolysis of di-o-tolylethane (15) and di-o-tolylethane-d_4 (15-d_4)

Products	m/e	Relative intensity of undeuterated compound[a]	Relative intensity of product[a]	Calculated peak intensity
anthracene	178	503098	31648	1 d_0
(2)	179	75745	71936	2.12 d_1
	180	5424	41472	0.98 d_2
	181	-	5640	0.02 d_3
	182	-	433	
9-methyl-	192	29119	3481	0.24 d_0
anthracene	193	4731	15280	1 d_1
(11)	194	367	25091	1.54 d_2
	195	-	15180	0.77 d_3
	196	-	3789	0.11 d_4
	197	-	449	

[a]Ionization voltage was 16eV.

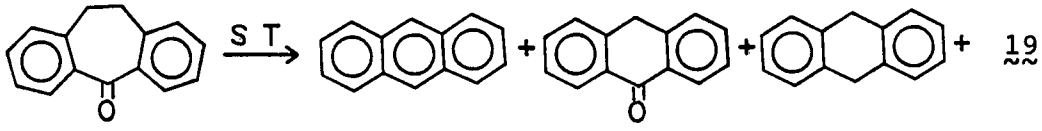
gave anthracene (2) and 9-methylanthracene (11) and these are summarized in Table 8.



R = H 17
CH3 16
Et 18

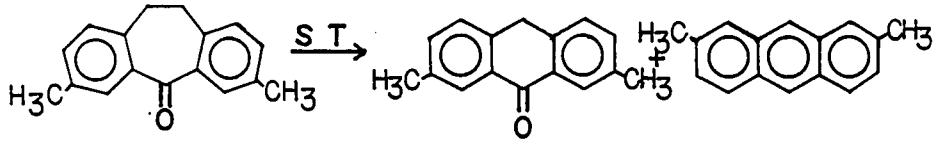
2 11

A sealed tube pyrolysis of dibenzosuberone (19) at 420°C for 2 h gave a 50% yield of anthracene (2) as a major product along with a 17% yield of anthrone (31), a 7% yield of 9,10-dihydroanthracene (32), and a 10% yield of recovered 19.



19 2 31 32

A sealed tube pyrolysis of 2,9-dimethyldibenzosuberone (20) at 420°C for 3 h gave a 77% yield of 2,7-dimethylanthrone (33), a 7% yield of 2,7-dimethylanthracene (5), and an 8% yield of recovered 20. The structure of 33 was determined by



20 33 5

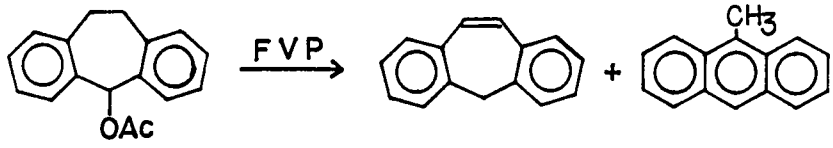
Table 8. Sealed tube pyrolysis of dibenzosuberanes

Reactants	Reaction conditions	Products, %[a] 9-methylanthracene (11)	anthracene (2)	recovered reactant	other products
dibenzosuberane (17)	420°C for 2.5 h	13	52	28	9,10-dihydroanthracene (9%) + 9,10-dihydro-9-methylanthracene (2%)
5-methyldibenzosuberane (16)	420°C for 1 h	67	8	16	
5-ethyldibenzosuberane (18)	420°C for 1 h	33	33	trace	17 (9%) + 9-ethylanthracene (14%)

[a]Relative yield determined by GC.

its spectral properties. The ^{1}H NMR spectrum included singlets at δ 8.18 for the benzene proton adjacent to the carbonyl group, at δ 7.40 for the other benzene protons, at δ 4.25 for the benzyl group, and at δ 2.50 for the methyl groups. GC/MS data were consistent with the molecular formula $C_{16}H_{14}O$. Pure 2,7-dimethylanthracene (5) was obtained from a sealed tube pyrolysis of 20 at 430°C for 6 h. The structure of 5 was determined by comparison of the reported[5] ^{1}H NMR spectrum of 5.

The FVP of 34 at 600°C gave an 85% yield of 35, a 3% yield of anthracene (2), a 1% yield of 11, and a 1% yield of 9,10-dihydroanthracene (32). The FVP of 34 at 780°C gave a

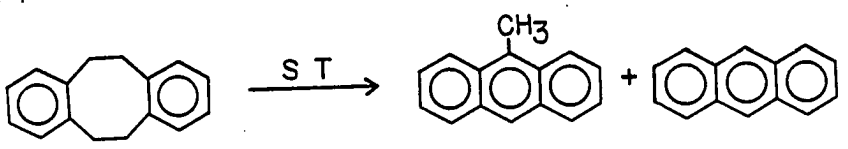


34 35 11

32% yield of 35, a 37% yield of 11, and other minor products. The structure of 35 was determined by its spectral properties. The ^{1}H NMR of 35 included a multiplet at δ 7.31-7.00 for the benzene and olefin groups, and a singlet at δ 3.733 for the benzyl group. GC/MS data were also consistent with the molecular formula $C_{15}H_{12}$.

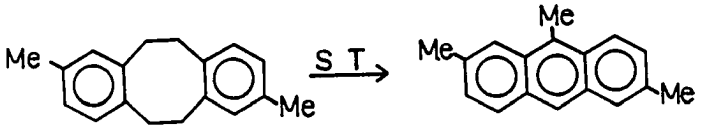
DISCUSSION

A sealed tube pyrolysis of 1 gave 9-methylanthracene (11) as a major product and anthracene (2) as a minor product.

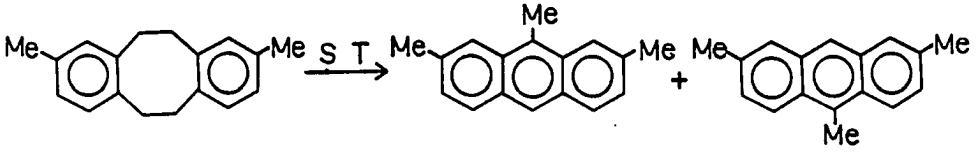


1 11 2

The "transoid" [4+4] dimer 3 gave 21 and the "cisoid" [4+4] dimer 4 gave a 1:1 mixture of 22 and 23. This indicates



3 21

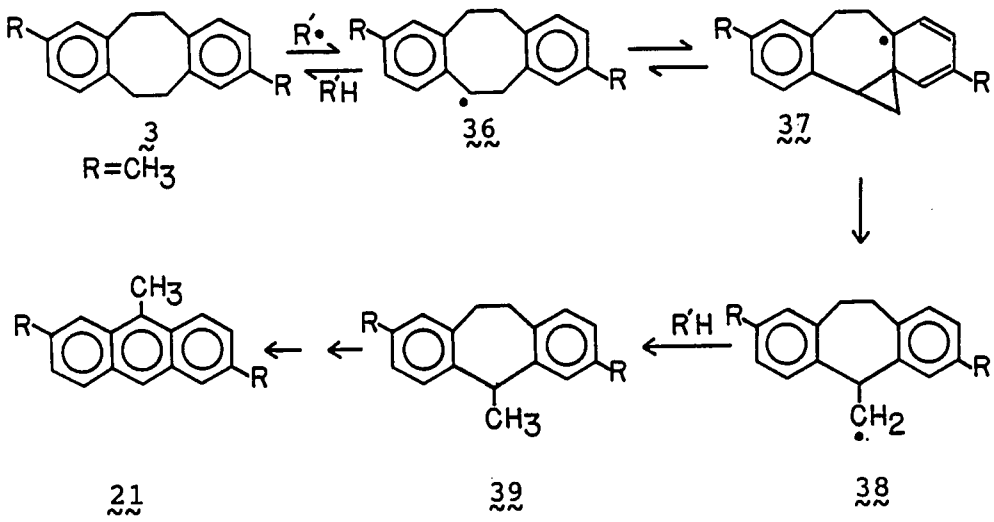


4 22 23

9-methylanthracenes are produced from the [4+4] dimers of o-xylylene with retention of stereochemistry. A mechanism for the conversion of 1 to 11 which accounts for the regio-specificity of the reaction is shown in Scheme 2 using the transformation of 3 as an example. Radical 36 can be in equilibrium with cyclopropylcarbinyl radical 37, which would undergo ring contraction to give radical 38. Radical 38 would abstract a hydrogen from hydrocarbons to give dibenzosuberane

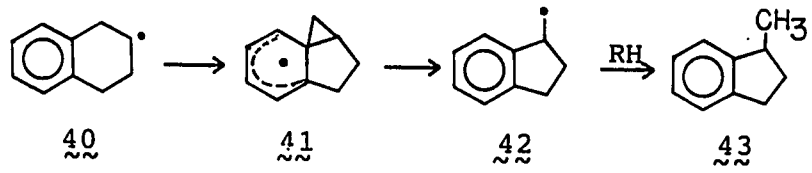
39. Dibenzosuberane 39 is believed to give trimethylanthracene (21) by the same kind of ring contraction as described in the conversion of 36 to 38 because a sealed tube pyrolysis of 5-methyldibenzosuberane (16) gave 9-methylanthracene (11) as a

Scheme 2



major product (see Scheme 7). The transformation of radical 36 to radical 38 is a kind of neophyl radical rearrangement[6,7] and a similar transformation has been proposed[8] for the formation of 1-methylindane (43) from 2-tetralyl radical (40) (Scheme 3). The presence of a radical initiator such as

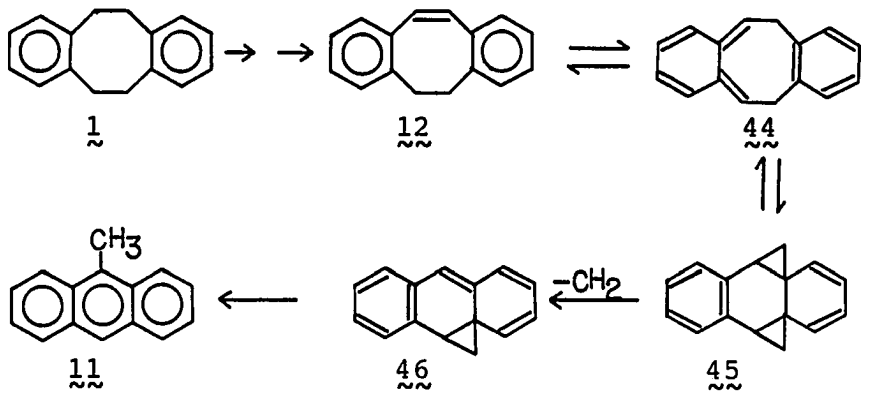
Scheme 3



bibenzyl and eicosane enhanced the yields of the formation of 9-methylanthracene (11) from sealed tube pyrolysis of 1. On the other hand, the presence of a 10-fold excess naphthalene reduced the yields of formation of 9-methylanthracene (11), presumably by collision with radicals to act like a radical inhibitor (Table 3). These results also support the radical chain mechanism for the formation of 11 from the [4+4] dimer of o-xylylene (1) as described in Scheme 2. Unfortunately, sealed tube pyrolysis of 1-d_4 and dibenzo[c,g]thiapindioxide-d_4 (13-d_4) did not give further information useful in elucidating the mechanism of the formation of 9-methylanthracene (11) from the sealed tube pyrolysis of 1, because of complicated chain reactions, as well as the deuterium isotope effect.

We thought that compound 44 may be involved in the transformation of 1 to 11 by the pathway described in Scheme 4.

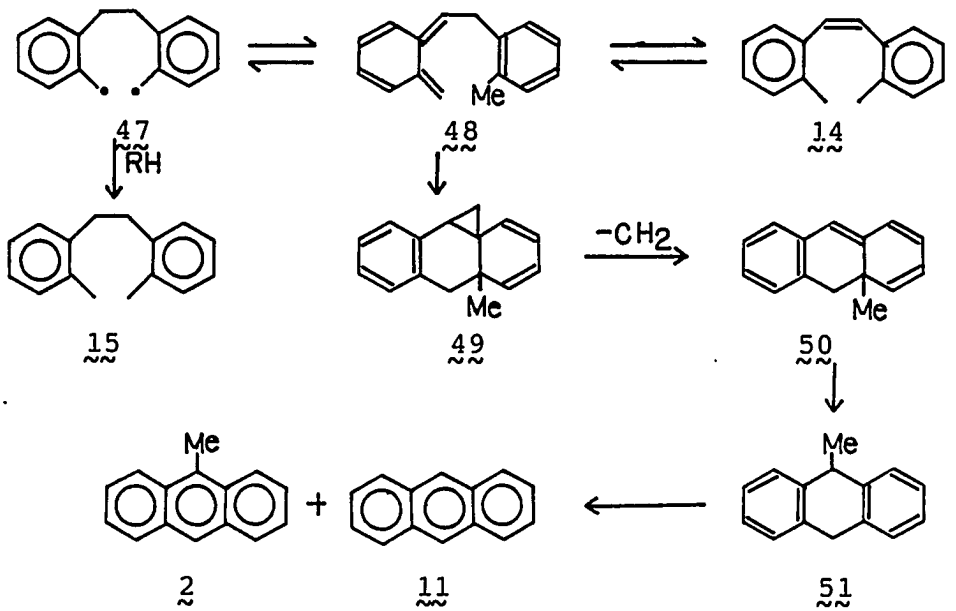
Scheme 4



Compound 44 was generated from 5,6-dihydrodibenzo[a,e]-cyclooctene (12) by sealed tube pyrolysis and by FVP, or from 5,6,11,12-tetrahydrocyclooctenyl acetate (24) by FVP. However, neither FVP nor sealed tube pyrolysis of 12 gave appreciable amounts of 9-methylanthracene (11) (but gave recovered 12 and unknown isomers of 12) (see Table 6). Although the FVP of 5,6,11,12-tetrahydrodibenzo[a,e]cyclo-octenyl acetate (24) at 780°C gave some 11, the contribution of 44 to the formation of 11 is believed to be small under sealed tube pyrolysis conditions.

It was also expected that 47 could be generated by the homolytic cleavage of the [4+4] dimer of o-xylylene (1) which undergoes 1,5-hydrogen migration[9] to give 48 or abstracts hydrogen to give di-o-tolylethane (15). Compound 48 may

Scheme 5



undergo a 1,5-hydrogen shift to give dimethylstilbene (14) or undergo 6π electron cyclization to give compound 49. Loss of methylene would give compound 50, which is thought to undergo a 1,3-methyl shift to give 9-methyl-9,10-dihydroanthracene (51). The loss of hydrogen or methane from 51 would give 9-methylanthracene (11) and anthracene (2), respectively. Compound 48 was generated from the pyrolysis of 2,2'-dimethylstilbene (14). But neither FVP nor sealed tube pyrolysis of 14 gave appreciable amounts of 2 and 11. Sealed tube pyrolyses of 5,6-dihydrodibenzo[a,e]cyclooctene (12) and 14 indicated neither homo [4+2] π cycloaddition (e.g. 45, see Scheme 4) nor homo 6 π electron cyclization (e.g. 49, see Scheme 5) is taking place in a sealed tube pyrolysis. A sealed tube pyrolysis of dibenzo[c,g]thiapindioxide (13) also gave 9-methylanthracene (11) and anthracene (2) at a faster rate than in a sealed tube pyrolysis of the [4+4] dimer of o-xylylene (1). Under sealed tube pyrolysis reaction conditions (420°C), sulfur dioxide would be eliminated from 13 to give 1 by a stepwise manner. It is believed that sulfur dioxide initiates a radical chain reaction from 1 to give 11 by the mechanism described in Scheme 2.

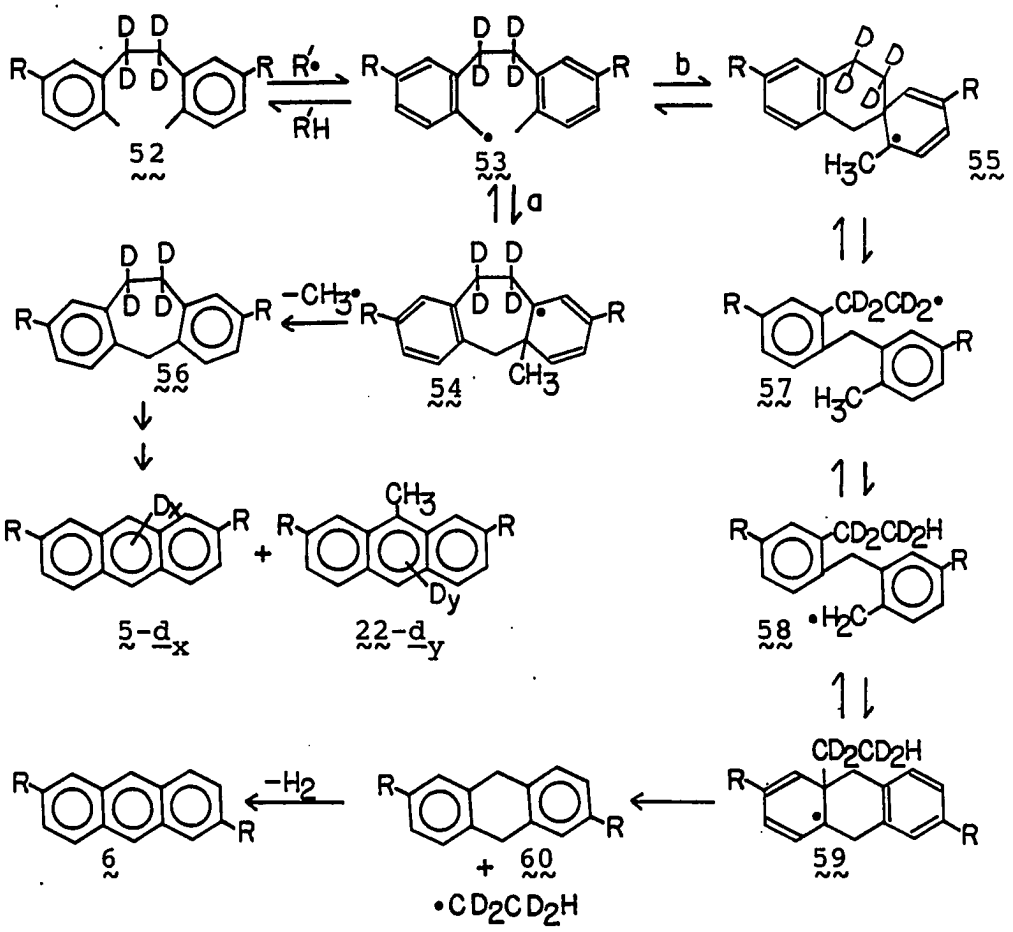
A sealed tube pyrolysis of 1,2-di-o-tolylethane (15) gave anthracene (2) and o-xylene (28) as major products. A sealed tube pyrolysis of 2,2',5-trimethylbibenzyl (25) also gave 2-methylanthracene (27), o-xylene (28), and 1,2,4-trimethyl-

benzene (29), but it did not give anthracene and dimethylanthracene. The FVP of 25 did not give anthracenes but gave scrambled products including o-xylene, 1,2,4-trimethylbenzene (29) and substituted bibenzyls. These results indicate that anthracene (2) is formed from di-o-tolylethane (15) without benzylic bond breaking.

A sealed tube pyrolysis of symmetrically substituted 2,2',5,5'-tetramethylbibenzyl (26) gave 2,7-dimethylanthracene (5), 2,6-dimethylanthracene (6), and 1,2,4-trimethylbenzene (29). This result indicates that anthracene (2) is formed from a sealed tube pyrolysis of 15 with no regiospecificity. Based on the results of the pyrolysis of substituted bibenzyls, a possible mechanism for the formation of anthracene (2) from a sealed tube pyrolysis of di-o-tolylethane (15) is presented in Scheme 6 using the transformation of 52 as an example. Although it is not easy to predict the exact deuterium distribution in a free radical chain reaction, the formation of d_1 and d_2 anthracene species is predicted by the reaction pathway a, and d_0 anthracene by the reaction pathway b assuming no deuterium scrambling. The ratio of deuterated anthracene species, obtained from a sealed tube pyrolysis of di-o-tolylethane-d_4 (15-d_4), was 1:2.12:0.98:0.02 for d_0, d_1, d_2, and d_3, respectively. Retention of regiochemistry is expected by the reaction pathway a, since dibenzosuberane 56 is expected to give 2,7-dimethylanthracene (5) (see Scheme 7).

A 180° ring flip is expected by the reaction pathway b to give 2,6-dimethylanthracene (6).

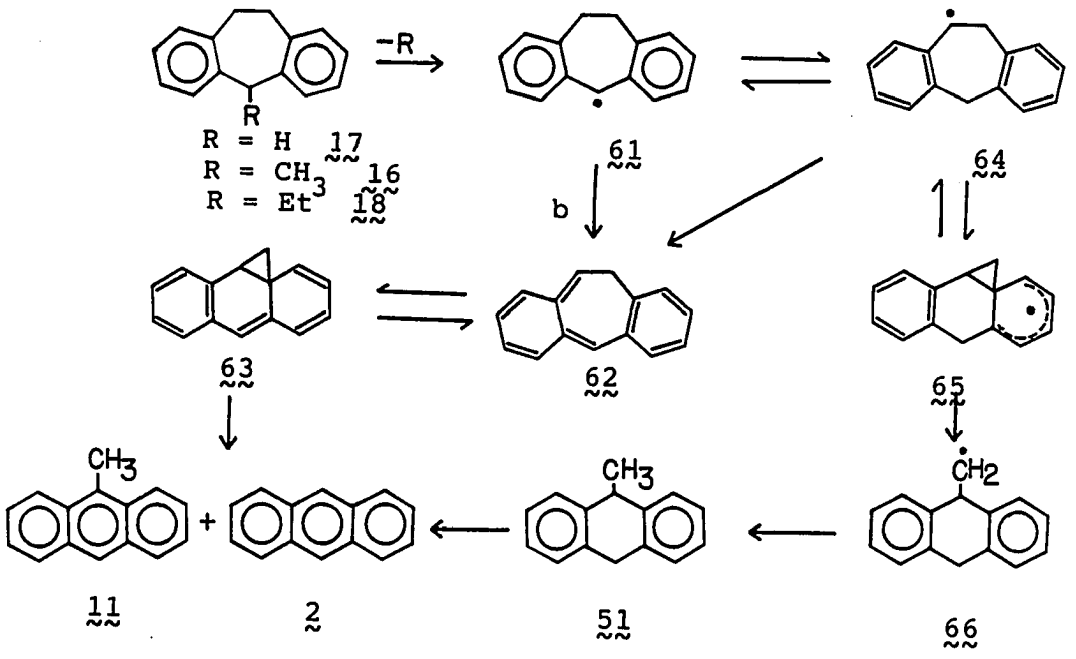
Scheme 6



Sealed tube pyrolysis of dibenzosuberanes 16, 17, and 18 gave anthracene (2) and 9-methylanthracene (11) (see Table 8). In Scheme 7, pathways which account for the formation of 2 and 11 from dibenzosuberanes are presented. Compound 62 may be a reasonable intermediate for the formation of 9-methylanthracene (11) from sealed tube

pyrolysis of dibenzosuberanes because the FVP of dibenzosuberyl acetate (34) at 780°C gave 11 as a major product. Compound 62 can be generated from 34 presumably by an elimination of acetic acid.[10] Compound 62 can undergo cyclization to give 63 which can rearrange to

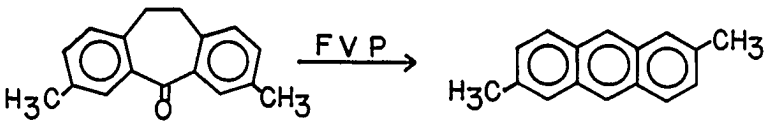
Scheme 7



9-methylanthracene (11) or can lose methylene to give anthracene (2). It has also been reported[11] that compound 62 is responsible for the formation of 9-methylanthracene and anthracene. Cyclopropylcarbinyl radical 65 may also be a reasonable intermediate for the formation of 9-methylanthracene and anthracene from sealed tube pyrolyses of dibenzosuberanes since conversion of 64 to 66 would be a

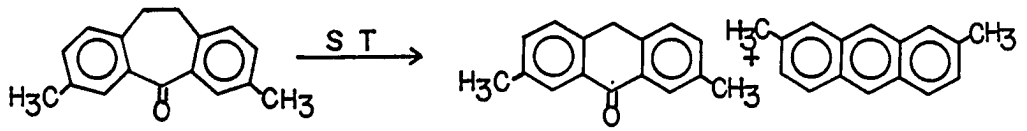
favorable process for reducing the ring strain. Sealed tube pyrolyses of dibenzosuberanes gave different products depending on substituents, e.g., for R = H (17) gave anthracene (2) as a major product, on the other hand, for R = CH_3 (16) gave 9-methylanthracene (11) as a major product (see Table 8). These results can be explained by different degrees of hydrogen abstracting power of the formed radical including hydrogen radical, methyl radical, and ethyl radical. For example, methyl radical would abstract hydrogen while ethyl radical would give hydrogen. It is not certain how these formed radicals affect the radical chain reactions under a sealed tube pyrolysis condition.

It has been reported that the FVP of dibenzosuberones gave anthracenes in quantitative yield.[5,12] A sealed tube pyrolysis of dibenzosuberone (19) also gave anthracene (2) as a major product along with anthrone (31) and other products. The FVP of 2,9-dimethyldibenzosuberone (20) is known to give 2,6-dimethylanthracene (6) as a sole product.[5] On the other



20 6

hand, a sealed tube pyrolysis of 20 gave 2,7-dimethylanthrone (33) as a major product and 2,7-dimethylanthracene (5) as a minor product. The formation of anthrones from sealed tube

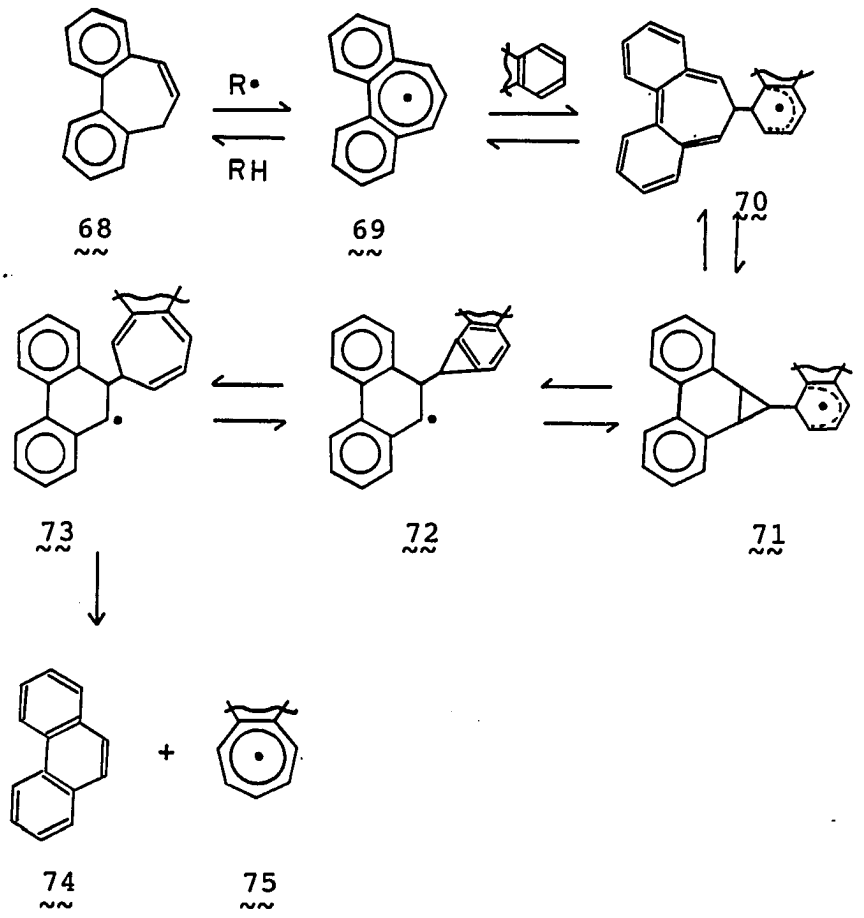


20 33 5

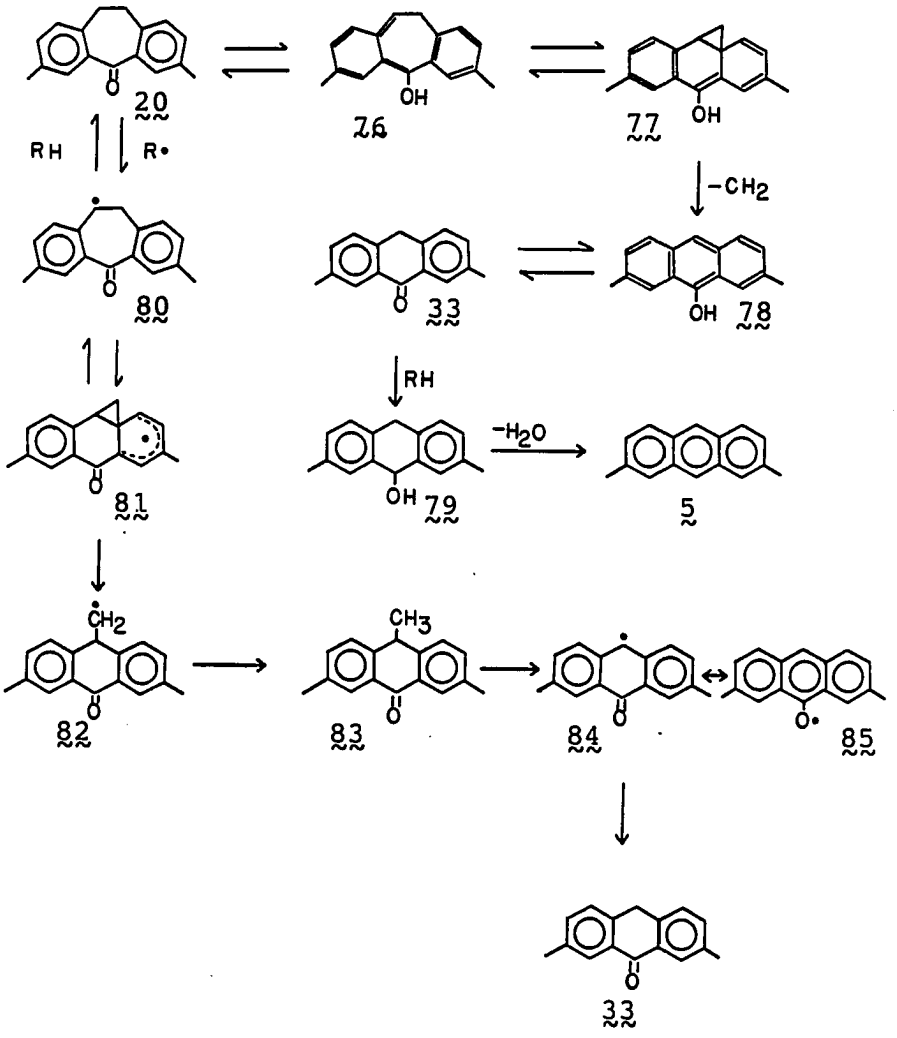
pyrolyses of dibenzosuberones indicated methylene loss is taking place with retention of stereochemistry. There have been examples of methylene loss from 7-membered ring compounds including benzotropilidene[11,13] and dibenzotropilidene.[14] A speculative mechanism[14] has been proposed for the formation of phenanthrene (74) from sealed tube pyrolyses of 68 and this is described in Scheme 8.

It is not easy to explain the formation of anthrones from sealed tube pyrolysis of dibenzosuberones using the mechanism presented in Scheme 8. There may be two alternative mechanisms for the formation of anthrones which account for the regiospecific formation of anthrones and these are presented in Scheme 9. An enolization[15,16] from dimethyldibenzosuberone (20) would give 76 which can undergo 6 π-electron cyclization to give 77. Loss of methylene from 77 would give 9-hydroxyanthracene (78) which is a tautomer of dimethylanthrone (33). This reaction pathway does not require a radical chain reaction and thus makes it a less attractive mechanism, but it cannot be excluded. Radical 80 would be formed by a radical chain process from 20 and is in equilibrium with a cyclopropylcarbinyl radical 81 which would

Scheme 8



Scheme 9



undergo ring contraction to give radical 82. Radical 82 would abstract a hydrogen from hydrocarbons to give methylanthrone (83) and hydrocarbon radicals. Methylanthrone (83) can undergo homolytic cleavage to give dimethylanthryl radical (84) and methyl radical. A hydrogen abstraction of dimethylanthryl radical (84) can give 2,7-dimethylanthrone (33). The

formation of 2,7-dimethylanthracene (5) can be explained by the formation of 2,7-dimethyl-9-hydroxy-9,10-dihydroanthracene (79) from 2,7-dimethylanthrone (33) by a radical process.[17] Compound 79 can undergo dehydration to give 2,7-dimethylanthracene (5) with retention of the dimethyl groups.

In conclusion, the regiospecific formation of 9-methylanthracene (11) from sealed tube pyrolysis of the [4+4] dimer of o-xylylene (1) can be explained by the mechanism in Scheme 2. We also point out that overall loss of one carbon and four hydrogen atoms from 1 or dibenzosuberane (17) and loss of methylene from dibenzosuberones are taking place by the ring contraction through a neophyl radical rearrangement[6,7] under the sealed tube pyrolysis condition. We have also observed the formation of anthracenes from the sealed tube pyrolysis of di-o-tolylethanes.

EXPERIMENTAL

Methods and Materials

The pyrolysis apparatus has been previously described.[18] ^{1}H NMR spectra were recorded on a Varian A-60 or a Nicolet 300 spectrometer. ^{13}C NMR spectra were recorded on a Nicolet 300 spectrometer. Chemical shifts are reported in parts per million (δ) from tetramethylsilane (TMS). Gas chromatographic (GC) analysis was performed on a Hewlett Packard Model 5840-A gas chromatograph (GC) with a fused silica column coated with methyl silicone fluid (J and W scientific DB-1) and a flame ionization detector. Combined gas chromatographic/mass spectra (GC/MS) analysis was performed on a Finnigan 4000 GC/MS with Incos data system. High resolution mass spectra were measured with either an Associated Electronics Industries MS-902 instrument or an MS 50 mass spectrometer. Infrared spectra (IR) were recorded on either a Beckman Acculab II or a Beckman 4250 spectrophotometer. GC/IR analysis was performed on an IBM FT/IR model 98. Melting points were determined on a Hoover Thomas melting point apparatus and are uncorrected. 5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene (1), 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene-5,5,6,6-d_4 (1-d_4), dibenzo-[c,g]thiapindioxide (13), dibenzo[c,g]thiapindioxide-5,5,7,7-d_4 (13-d_4), and 2,9-dimethyldibenzosuberone (20) were obtained from Tunkel.[5] 2,8-Dimethyl-5,6,11,12-tetra-hydrodibenzo[a,e]cyclooctene (3) and 2,9-dimethyl-5,6,11,12-

tetrahydrodibenzo[a,e]cyclooctene (4) were obtained from Surber.[2] α-Bromo-o-xylene, eicosane, dibenzosuberol, dibenzosuberone, 2,5-dimethylbenzyl chloride, and lithium aluminum deuteride were purchased from Aldrich Chemical Company.

Di-o-tolyl sulfone (86)

Compound 86 was prepared by reacting 6.5 g of α-bromo-o-xylene with 9.3 g of $Na_2S,9H_2O$ followed by reaction with 30% H_2O_2/glacial acetic acid using a reported method.[19] 86 (yield; 43%): mp 197°C; ^1H NMR ($CDCl_3$) δ 7.40-7.20 (m, 8 H), 4.28 (s, 4 H), 2.35 (s, 6 H).

trans-2,2'-Dimethylstilbene (14)

Compound 14 was prepared by reacting 411 mg of di-o-tolyl sulfone with 6.0 g of powdered KOH in 30 ml of t-BuOH and 50 ml of CCl_4 at 65°C for 1.5 h using the method of Koenig et al.[20] 14 (yield; 80%): mp 80-81 (Lit.[21] mp 80-81°C); ^1H NMR ($CDCl_3$) δ 7.64 (d, 2 H, J = 6.6 Hz), 7.3-7.2 (m, 8 H), 2.41 (s, 6 H); GC/MS (70eV) m/e (% base peak) 210 (1.20), 209 (15.59), 208 (100), 194 (11), 193 (67), 192 (13), 191 (11), 179 (13), 178 (61), 116 (21), 115 (31), 103 (11), 102 (15), 91 (11), 89 (14).

5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene-5-ol (87)

Compound 87 was prepared by brominating 700 mg of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1) with 600 mg of

N-bromosuccinimide (NBS)[22] followed by hydrolysis with 1:1 20% NaOH/acetone solution at 95°C for 2 h and thin layer chromatography on silica gel (5% ether in hexanes) (see Appendix II). 87 (yield; 37%): ^{1}H NMR ($CDCl_3$) δ 7.10-6.85 (m, 8 H), 5.25 (t, 1 H, J = 8 Hz), 3.60-2.85 (m, 7 H); [Lit.[23] ^{1}H NMR ($CDCl_3$) δ 7.33-7.0 (m, 8 H), 5.26 (t, 1 H, J = 8 Hz), 3.77-3.0 (m, 7 H)]; IR (CCl_4) 3600-3100, 3080, 2920, 2870, 1480, 1440, 1110, 745 cm^{-1}; GC/MS (70eV) m/e (% base peak) 225 (0.40), 224 (3.37), 209 (4), 206 (15), 106 (8), 105 (100), 91 (18), 77 (9).

5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctenyl acetate (24)

A solution of 200 mg (0.89 mmol) of 87 in 3 ml of THF and 7 ml of acetic anhydride was heated to reflux for 15 h. After cooling, the solvent was removed by vacuum followed by thin layer chromatography on silica gel (5% ether in hexanes) to give 185 mg (0.70 mmol, 78%) of an oily liquid, 24: ^{1}H NMR ($CDCl_3$) δ 7.15-6.87 (m, 8 H), 6.26 (t, 1 H, J = 8.4 Hz), 3.61-3.00 (m, 6 H), 2.11 (s, 3 H); IR (neat, NaCl) 3070, 3020, 2930, 2880, 1725, 1480, 1440, 1360, 1230, 1010, 950, 900, 750, 720 cm^{-1}; GC/MS (70eV) m/e (% base peak) 268 (0.01), 267 (0.19), 266 (1.41), 233 (12), 230 (5), 219 (5), 207 (20), 206 (100), 205 (30), 195 (5), 178 (8), 147 (9), 119 (8), 105 (24), 104 (6), 103 (6), 91 (11); high resolution mass spectrum calculated for $C_{18}H_{18}O_2$ 266.13068, measured 266.13081.

5,6-Dihydrodibenzo[a,e]cyclooctene (12)

A 60 mg (0.23 mmol) quantity of 24 was pyrolyzed at 600°C in the normal manner. The pyrolysate was collected in $CDCl_3$ and concentrated to give 35 mg (0.17 mmol; 74%) of 12: mp 52-54°C (Lit.[24] mp 53.6-54.4°C); ^1H NMR ($CDCl_3$) δ 7.2-7.0 (m, 8 H), 6.73 (s, 2 H), 3.18 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 139.66, 136.62, 131.29, 130.03, 129.74, 126.84, 125.34, 35.68; GC/MS (70eV) m/e (% base peak) 208 (1.13), 207 (15.49), 206 (100), 205 (67), 203 (13), 202 (15), 191 (52), 189 (15), 178 (20), 165 (11), 115 (11), 91 (20), 89 (12).

Dibenzosuberyl acetate (34)

Compound 34 was prepared by reacting 210 mg of dibenzosuberol with acetic anhydride as described in the preparation of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctenyl acetate (24). 34 (yield; 91%): ^1H NMR ($CDCl_3$) δ 7.5-6.8 (m, 9 H), 3.9-2.5 (m, 4 H), 2.1 (s, 3 H); IR (neat, NaCl) 3040, 2900, 1730, 1490, 1440, 1360, 1230, 1030, 1010, 950, 760 cm^{-1}; GC/MS (70eV) m/e (% base peak) 254 (0.15), 253 (1.85), 252 (10.34), 210 (21), 209 (37), 193 (57), 192 (100), 191 (54), 189 (14), 178 (26), 165 (21), 115 (22), 89 (9); high resolution mass spectrum calculated for $C_{17}H_{16}O_2$ 252.11503, measured 252.11561.

1,2-Di-o-tolylethane (15)

Compound 15 was prepared by reacting 1.55 g of α-chloro-o-xylene with 288 mg of Mg by the method of Trahanovsky and Brixius.[25] 15 (yield; 38%): mp 66-67°C; ^{1}H NMR ($CDCl_3$) δ 7.15-7.05 (m, 8 H), 2.85 (s, 4 H), 2.34 (s, 6 H); [Lit.[26] ^{1}H NMR ($CDCl_3$) δ 7.03 (s, 8 H), 2.80 (s, 4 H), 2.23 (s, 6 H)]; GC/MS (16eV) m/e (% base peak) 212 (1.44), 211 (17.34), 210 (100), 106 (5), 105 (49).

2-Methyl-α,α-dideuterobenzyl alcohol (88)

Compound 88 was prepared by reacting 2.72 g of o-toluic acid with 840 mg of $LiAlD_4$. 90 (yield; 93%): ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 4 H), 2.5 (s, 1 H), 2.2 (s, 3 H).

α,α-Dideutero-α-bromo-o-xylene (89)

Compound 89 was prepared by reacting 2.3 g of 88 with PBr_3 using a standard procedure.[27] 91 (yield; 78%): ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 4 H), 2.3 (s, 3 H).

1,2-Di-o-tolyltetradeuteroethane (15-d_4)

Compound 15-d_4 was prepared by reacting 89 with Mg as described in the preparation of 1,2-di-o-tolylethane (15). 15-d_4 (yield; 37%): mp 66-67°C; ^{1}H NMR ($CDCl_3$) δ 7.1 (m, 8 H), 2.3 (s, 6 H); GC/MS (16eV) m/e (% base peak) 216 (2.11), 215 (20.63), 214 (100), 213 (16.44), 212 (1.5), 108 (11), 107 (61); high resolution mass spectrum calculated for $C_{16}H_{14}D_4$ 214.16596, measured 214.16560.

5-Methyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (16)

Compound 16 was prepared[28] by reacting dibenzosuberone with CH_3Li followed by Li/NH_3[29] reduction.

5-Ethyl-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (18)

Compound 18 was prepared[28] by reacting dibenzosuberone with ethyl magnesium iodide followed by 10% $FeCl_3$ in silica gel[30] treatment and hydrogenation using 5% Pd/C catalyst.

2,2',5-Trimethylstilbene (91)

Compound 91 was prepared by reacting 2,2',5-trimethyl-β-hydroxybibenzyl (90) with 10% $FeCl_3$ in silica gel.[30] Compound 90 was prepared by reacting 1.2 g (10 mmol) of o-tolualdehyde with 2,5-dimethylbenzyl magnesium chloride using standard procedure.[31] 90 (yield; 78%): mp 76-77°C; ^1H NMR ($CDCl_3$) δ 7.5-6.8 (m, 7 H), 5.2 (t, 1 H, J = 6 Hz), 3.0 (s, 1 H), 2.8 (d, 2 H, J = 6 Hz), 2.3 (s, 9 H); IR (CCl_4) 3700-3100, 1630, 1500, 200, 960 cm^{-1}. 91 (yield; 38%): mp 69-71; ^1H NMR ($CDCl_3$) δ 7.6-6.8 (m, 9 H), 2.3 (s, 3 H), 2.2 (s, 6 H); GC/MS (70eV) m/e (% base peak) 223 (18.69), 222 (100), 208 (17), 207 (92), 193 (23), 192 (96), 191 (34), 190 (14), 189 (21), 178 (17), 165 (17), 130 (14), 129 (15), 128 (12), 119 (14), 116 (23), 115 (36), 91 (16), 89 (13), 77 (23); high resolution mass spectrum calculated for $C_{17}H_{18}$ 222.14085, measured 222.14117.

2,2',5-Trimethylbibenzyl (25)

Compound 25 was prepared by hydrogenating 2,2',5-trimethylstilbene (91) with 5% Pd/C in EtOH at 60 psi hydrogen pressure for 3 h. 25 (yield; 95%): mp 108-109°C; ^{1}H NMR ($CDCl_3$) δ 7.2-6.85 (m, 7 H), 2.82 (s, 4 H), 2.33 (s, 3 H), 2.30 (s, 3 H), 2.28 (s, 3 H); GC/MS (70eV) m/e (% base peak) 226 (0.33), 225 (3.86), 224 (20.81), 120 (10), 119 (100), 105 (29), 91 (11), 77 (10); high resolution mass spectrum calculated for $C_{17}H_{20}$ 224.15650, measured 224.15631.

2,2',5,5'-Tetramethylbibenzyl (26)

Compound 26 was prepared by reacting 2,5-dimethylbenzyl chloride with magnesium as described in the preparation of 1,2-di-o-tolylethane (15). 26 (yield; 36%): mp 102-104°C; ^{1}H NMR ($CDCl_3$) δ 7.07-6.91 (m, 6 H), 2.79 (s, 4 H), 2.30 (s, 6 H), 2.28 (s, 6 H); GC/MS (70eV) 240 (0.30), 239 (3.24), 238 (16.69), 120 (9), 119 (100), 91 (11), 76 (6); high resolution mass spèctrum calculated for $C_{18}H_{22}$ 238.17216, measured 238.17176.

General FVP procedure

General FVP procedure has been previously described.[28]

FVP of 5,6-dihydrodibenzo[a,e]cyclooctene (12)

A 20 mg quantity of 12 was pyrolyzed at 900°C in the normal manner. GC and GC/MS analyses indicated a total of 45%

yield of three isomers of 12 and recovered 12 (43%) were formed in the pyrolysis.

FVP of trans-2,2'-dimethylstilbene (14)

A 30 mg quantity of 14 was pyrolyzed at 950°C in the normal manner. GC and GC/MS analyses indicated a 44% yield of anthracene (2), a 13% yield of an isomer of 14, and a 22% yield of 14 were formed in the pyrolysis. 2: ^{1}H NMR ($CDCl_3$) δ 8.41 (s, 2 H), 8.05-7.90 (m, 4 H), 7.48-7.39 (m, 4 H); [Lit.[32] ^{1}H NMR ($CDCl_3$) δ 8.44 (s, 2 H), 8.20-7.85 (m, 4 H), 7.60-7.38 (m, 4 H)]; GC/MS (70eV) m/e (% base peak) 180 (1.02), 179 (14.36), 178 (100), 177 (8), 176 (16), 89 (13), 88 (7), 76 (12).

FVP of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctenyl acetate (24)

A 20 mg quantity of 24 was pyrolyzed at 780°C in the normal manner. GC and GC/MS analyses indicated a 48% yield of 5,6-dihydrodibenzo[a,e]cyclooctene (12), a 14% yield of anthracene (2), a 7% yield of 9-methylanthracene (11), and other isomers of MW 206 were formed in the pyrolysis.

FVP of 2,2',5-trimethylbibenzyl (25)

A 30 mg quantity of 25 was pyrolyzed at 840°C in the normal manner. GC and GC/MS analyses indicated an 18% yield of o-xylene (28), an 18% yield of 1,2,4-trimethylbenzene (29), a 14% yield of di-o-tolylethane (15), an 11% yield of

2,2',5,5'-tetramethylbibenzyl (26), a 4% yield of 3,3',4,4'-tetramethylbibenzyl (30), and recovered 25 (10%) were formed in the pyrolysis. These products were identified by the GC retention time and GC/MS data. 28: GC/MS (70eV) m/e (% base peak) 107 (8.8), 106 (100), 105 (1.9). 29: GC/MS (70eV) m/e (% base peak) 121 (5.2), 120 (56.1), 119 (12.4), 106 (8), 105 (100), 91 (10), 79 (8), 77 (13). 30: GC/MS (70eV) m/e (% base peak) 238 (16), 119 (100), 91 (10).

FVP of dibenzosuberyl acetate (34)

A 50 mg quantity of 34 was pyrolyzed at 780°C in the normal manner. GC and ^{1}H NMR spectral analyses indicated a 32% yield of dibenzoheptatriene (35), and a 37% yield of 9-methylanthracene (11) were formed in the pyrolysis. 35: mp 124-129°C (Lit.[33] mp 133-4°C); ^{1}H NMR ($CDCl_3$) δ 7.31-7.00 (m, 10 H), 3.733 (s, 2 H); GC/MS (70eV) m/e (% base peak) 194 (1.16), 193 (14.27), 192 (100), 191 (81), 190 (10), 189 (26), 165 (13), 96 (10), 94 (13), 83 (9). 11: ^{1}H NMR ($CDCl_3$) δ 8.25-8.35 (m), 8.00 (d, J = 7.8 Hz), 7.53-7.42 (m), 3.09 (s); [Lit.[34] ^{1}H NMR ($CDCl_3$) δ 8.31, 8.26, 7.97, 7.48, 7.44, 3.07]; GC/MS (70eV) m/e (% base peak) 194 (1.12), 193 (15.53), 192 (100), 191 (58), 190 (10), 189 (26), 165 (7), 96 (17), 95 (16), 83 (12).

General sealed tube pyrolysis procedure

Sealed tube pyrolyses were carried out by using Pyrex tubes of about 2 ml capacity and 5-15 mg of sample. The tubes were previously washed with ammonium hydroxide and distilled water and dried. After addition of the sample the tubes were cooled in an ice bath, evacuated to 10^{-1} torr of pressure and sealed. Sealed tube pyrolyses were carried out in a Varian 2800 GC oven. After heating for the required amount of time, the sealed tubes were removed from the oven, cooled, and opened for the analysis. Some samples, particularly when GC analysis was required, were dissolved in a standard biphenyl solution of acetone.

Sealed tube pyrolysis of 5,6,11,12-tetrahydrodibenzo[a,e] cyclooctene (1)

A 5 mg quantity of 1 was pyrolyzed at 420°C for 3 h in the normal manner. GC and ^{1}H NMR analyses indicated 9-methylanthracene (11) was formed as a major product (71%), along with anthracene (7%) and recovered 1 (22%).

Sealed tube pyrolysis of 2,8-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (3)

A 6 mg quantity of 3 was pyrolyzed at 420°C for 3 h in the normal manner. GC and ^{1}H NMR analyses indicated 2,6,9-trimethylanthracene (21) was formed as a major product (51%), along with recovered 3 (49%). 21[35]: ^{1}H NMR ($CDCl_3$) δ 8.18 (s), 8.15 (s), 8.0 (s), 7.88 (d, 8.7 Hz), 7.72 (s), 7.35-7.25

(m), 6.93-6.8 (m), 3.045 (s), 2.579 (s), 2.534 (s); GC/MS m/e (% base peak) 222 (1.8), 221 (18.1), 220 (100), 219 (24), 205 (30), 203 (13), 202 (15), 189 (10), 110 (6), 102 (6), 101 (6).

Sealed tube pyrolysis of 2,9-dimethyl-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (4)

A 4 mg quantity of 4 was pyrolyzed at 450°C for 4 h in the normal manner. GC and ^{1}H NMR analyses indicated a total of 69% yield of a 1:1 mixture of 2,7,9-trimethylanthracene (22) and 2,7,10-trimethylanthracene (23), a 22% yield of 2,7-dimethylanthracene (5) and a 9% yield of recovered 4 were formed in the pyrolysis. 22 + 23: ^{1}H NMR ($CDCl_3$) δ 7.9-6.8 (m), 3.038 (s), 3.053 (s), 2.580 (s), 2.534 (s); [22: Lit.[34] ^{1}H NMR ($CDCl_3$) δ 7.978, 7.850, 7.252, 2.559, 3.009]; GC/MS (70eV) m/e (% base peak) #1: 222 (6.27), 221 (33.33), 220 (100), 219 (15), 206 (17), 205 (29), 203 (12), 202 (13), 189 (16), 110 (12), 102 (14), 89 (11). #2: 222 (3.24), 221 (22.52), 220 (100), 219 (13), 206 (15), 205 (30), 203 (13), 202 (13), 189 (14), 146 (10), 102 (11). 5: GC/MS (70eV) m/e (% base peak) 208 (1.60), 207 (16.80), 206 (100), 205 (20), 191 (15), 189 (16), 89 (11).

Sealed tube pyrolysis of dibenzo[c,g]thiapindioxide (13)

A 10 mg quantity of 13 was pyrolyzed at 420°C for 3.5 h in the normal manner. GC and GC/MS analyses indicated a 64% yield of 9-methylanthracene (11), a 6% yield of anthracene

(2), and a 28% yield of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene were formed in the pyrolysis.

Sealed tube pyrolysis of 5,6-dihydrodibenzo[a,e]cyclooctene (12)

A 5 mg quantity of 12 was pyrolyzed at 380°C for 25 min in the normal manner. GC and GC/MS indicated a 22% yield of an unknown compound (MW 206), a 25% yield of an unknown compound (MW 204), a 16% yield of an unknown compound (MW 208), and a 37% yield of recovered 12 were formed in the pyrolysis. Unknowns, GC/MS (70eV) m/e (% base peak) #1: 208 (1.03), 207 (15.25), 206 (100), 205 (92), 203 (12), 202 (12), 191 (22), 189 (12), 178 (21), 101 (13), 95 (11), 91 (16), 89 (21). #2: 205 (1.14), 204 (7.55), 203 (8), 192 (13), 191 (11), 179 (15), 178 (100), 176 (16), 89 (14), 76 (11). #3: 210 (1.24), 209 (15.07), 208 (100), 207 (24), 193 (10), 192 (47), 191 (25), 189 (11), 180 (61), 179 (25), 178 (20), 165 (15), 152 (25), 151 (13), 89 (13), 76 (11).

Sealed tube pyrolysis of trans-2,2'-dimethylstilbene (14)

A 10 mg quantity of 14 was pyrolyzed at 400°C for 1 h in the normal manner. GC analysis indicated a 22% yield of unknown compound (MW 208) and a 78% yield of unreacted 14 were formed in the pyrolysis.

Sealed tube pyrolysis of 1,2-di-o-tolylethane (15)

A 7 mg quantity of 15 was pyrolyzed at 420°C for 2 h in the normal manner. GC and GC/MS analyses indicated a 28% yield of anthracene (2), a 22% yield of o-xylene, an 8% yield of 9-methylanthracene (11) and a 29% yield of recovered 15 were formed in the pyrolysis.

Sealed tube pyrolysis of 2,2',5-trimethylbibenzyl (25)

A 7 mg quantity of 25 was pyrolyzed at 420°C for 2 h in the normal manner. GC and ^{1}H NMR analyses indicated a 37% yield of 2-methylanthracene (27), a total of 47% yield of o-xylene and 1,2,4-trimethylbenzene and a 16% yield of 25 were formed in the pyrolysis. 27: ^{1}H NMR ($CDCl_3$) δ 8.35 (s), 8.27 (s), 8.0-7.85 (m), 7.74 (s), 7.5-6.85 (m), 2.534 (s) [Lit.[34] ^{1}H NMR ($CDCl_3$) δ 8.334, 8.269, 7.945, 7.938, 7.874, 7.407, 7.399, 7.271, 2.512]; GC/MS (70eV) m/e (% base peak) 194 (1.18), 193 (16.03), 192 (100), 191 (35), 189 (19), 165 (10), 96 (14), 83 (11).

Sealed tube pyrolysis of 2,2',5,5'-tetramethylbibenzyl (26)

A 7 mg quantity of 26 was pyrolyzed at 420°C for 2 h in the normal manner. GC and ^{1}H NMR analyses indicated a 13% yield of 2,7-dimethylanthracene (5), a 22% yield of 2,6-dimethylanthracene (6) and a 40% yield of 1,2,4-trimethylbenzene (29) were formed in the pyrolysis. Compounds 5 and 6 were not able to separate by GC and the relative yield of 5

and 6 was determined by the ^{1}H NMR spectrum of the pyrolysis products. 5 + 6[5]: GC/MS (70eV) m/e (% base peak) 208 (1.65), 207 (17.77), 206 (100), 205 (21), 191 (15), 189 (16), 89 (11); ^{1}H NMR ($CDCl_3$) δ 8.31 (s), 8.26 (s), 8.20 (s), 7.88 (d, J = 9.6 Hz), 7.71 (s), 7.30-7.21 (m), 2.534 (s). 5: [Lit.[2] ^{1}H NMR ($CDCl_3$) δ 8.31 (s, 1 H), 8.20 (s, 1 H), 7.88 (d, 2 H, J = 9.7 Hz), 7.71 (s, 2 H), 7.26 (d, 2 H), 2.53 (s, 6 H)]. 6: [Lit.[2] ^{1}H NMR ($CDCl_3$) δ 8.25 (s, 2 H), 7.87 (d, 2 H), 7.71 (br, s, 2 H), 7.27 (d of d, 2 H), 2.53 (s, 6 H)].

Sealed tube pyrolysis of o-tolyl-α,α,β,β-d_4-ethane (15-d_4)

A 7 mg quantity of 15-d_4 was pyrolyzed at 420°C for 2 h in the normal manner. GC analysis indicated a 26% yield of o-xylene, a 36% yield of anthracene, a 9% yield of 9-methylanthracene (11) and an 18% yield of recovered 15-d_4 were formed in the pyrolysis.

Sealed tube pyrolysis of dibenzosuberane (17)

A 10 mg quantity of 17 was pyrolyzed at 420°C for 2.5 h in the normal manner. GC and GC/MS analyses indicated a 52% yield of anthracene, a 13% yield of 9-methylanthracene (11), a 9% yield of 9,10-dihydroanthracene (32), a 2% yield of 9-methyl-9,10-dihydroanthracene (51), and a 21% yield of 17 were formed in the pyrolysis. 32[36]: GC/MS (70eV) m/e (% base peak) 182 (1.00), 181 (13.86), 180 (100), 179 (98), 178 (58), 176 (15), 165 (24), 152 (11), 89 (47), 88 (12), 76 (24), 63

(9). 51[37]: GC/MS (70eV) m/e (% base peak) 196 (0.20), 195 (2.70), 194 (16.61), 180 (14), 179 (100), 178 (36), 176 (11), 89 (23), 82 (9), 76 (9).

Sealed tube pyrolysis of methyldibenzosuberane (16)

A 10 mg quantity of 16 was pyrolyzed at 420°C for 1 h in the normal manner. GC and ^{1}H NMR spectral analyses indicated a 67% yield of 9-methylanthracene (11), an 8% yield of anthracene (2), and a 16% yield of 16 were formed in the pyrolysis.

Sealed tube pyrolysis of ethyldibenzosuberane (18)

A 10 mg quantity of 18 was pyrolyzed at 420°C for 1 h in the normal manner. GC and ^{1}H NMR spectral analyses indicated a 33% yield of anthracene (2), a 33% yield of 9-methylanthracene (11), a 14% yield of 9-ethylanthracene, and a 9% yield of dibenzosuberane (17) were formed in the pyrolysis. 9-Ethylanthracene[35]: GC/MS (70eV) m/e (% base peak) 208 (0.97), 207 (8.62), 206 (48.19), 192 (17), 191 (100), 189 (22), 165 (8), 103 (11), 101 (16), 96 (17), 94 (26), 89 (25), 88 (11), 83 (15), 76 (10).

Sealed tube pyrolysis of dibenzosuberone (19)

A 10 mg quantity of 19 was pyrolyzed at 420°C for 2 h in the normal manner. GC and ^{1}H NMR spectral analyses indicated a 50% yield of anthracene, a 17% yield of anthrone, a 7% yield

of 9,10-dihydroanthracene (32) and a 10% yield of 19 were formed in the pyrolysis.

Sealed tube pyrolysis of 2,9-dimethyldibenzosuberone (20)

A 10 mg quantity of 20 was pyrolyzed at 420°C for 3 h in the normal manner. GC and ^{1}H NMR spectral analyses indicated a 77% yield of 2,7-dimethylanthrone (33), a 7% yield of 2,7-dimethylanthracene (5), and an 8% yield of 20 were formed in the pyrolysis. 33: mp 152-153°C (Lit.[34] mp 153-154°C); ^{1}H NMR ($CDCl_3$) δ 8.18 (s, 2 H), 7.40 (s, 4 H), 4.25 (s, 2 H), 2.50 (6 H); IR (CCl_4) 1640, 1600, 1280, 1170, 750 cm^{-1}; GC/MS (70eV) m/e (% base peak) 238 (0.91), 237 (10.68), 236 (59.01), 222 (18), 221 (100), 191 (9), 189 (9), 178 (19), 89 (9).

REFERENCES

1. Trahanovsky, W. S.; Surber, B. W. J. Am. Chem. Soc. 1985, 107, 4995.
2. Surber, B. W. Ph. D. Dissertation, Iowa State University, 1984.
3. Jensen, F. R.; Coleman, W. E.; Berlin, A. J. Tetrahedron Lett. 1962, 15.
4. See Appendix I.
5. Tunkel, J. L. Ph. D. Dissertation, Iowa State University, 1985.
6. Zimmerman, H. E., "Molecular Rearrangements" Vol. I, P. de Mayo Ed., Wiley-Interscience: New York, 1973; pp. 416-423.
7. Shevlin, P. B.; Hansen, J. H. J. Org. Chem. 1977, 42, 3011.
8. Franz, A. J.; Camaioni, D. M. J. Org. Chem. 1980, 45, 5247.
9. Freidlina, R. K.; Terent'ev, A. B. Acc. Chem. Res. 1977, 10, 9.
10. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. J. Am. Chem. Soc. 1981, 103, 6691.
11. Pomerantz, M.; Ross, A. S.; Gruber, G. W. J. Am. Chem. Soc. 1972, 94, 1403.
12. Wiersum, U. E. Rec. Trav. Chim. Pay-Bas 1982, 101, 317.
13. Pomerantz, M.; Ross, A. S. J. Am. Chem. Soc. 1975, 97, 5850.
14. Pomerantz, M.; Dassanayake, N. L.; McManus, T. R.; Reynolds, C. J. J. Org. Chem. 1984, 49, 4029.
15. Cook, J. W. J. Chem. Soc. 1931, 487.
16. Fieser, L. F. "Organic Reactions" John Wiley and Sons, Inc.: New York, 1942; Vol. 1, p. 129.

17. Double bond is readily reduced to single bond under sealed tube pyrolyses conditions; see ref. 11, 13, 14.

18. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. J. Org. Chem. 1971, 36, 3575.

19. Ollis, W. D.; Stoddart, J. H. J. Chem. Soc. Perkin I 1976, 926.

20. Koenig, K. E.; Felix, R. A.; Weber, W. P. J. Org. Chem. 1974, 39, 1539.

21. Coops, J.; Hoijtink, G. J.; Kramer, T. J. E. Recueil, 1953, 72, 765.

22. Norman, R. "Organic Syntheses Collective Volume IV", John Wiley & Sons, Inc.: New York, 1967; p. 108.

23. Jung, M. E.; Mossman, A. B.; Lyster, M. A. J. Org. Chem. 1978, 43, 3698.

24. Cope, A. C.; Smith, R. D. J. Am. Chem. Soc. 1955, 77, 4596.

25. Trahanovsky, W. S.; Brixius, D. W. J. Am. Chem. Soc. 1973, 95, 6778.

26. Sargent, M. V.; Smith, D. J. Chem. Soc. 1970, 329.

27. Bergmann, E. D.; Pelchowicz, Z. J. Am. Chem. Soc. 1953, 75, 4281.

28. Lee, S. K. Ph. D. Dissertation Part II, Iowa State University, 1987.

29. Small, G. H.; Minella, A. E.; Hall, S. S. J. Org. Chem. 1975, 40, 3151.

30. Keinan, E.; Mazur, Y. J. Org. Chem. 1978, 43, 1020.

31. Blatt, A. H. "Organic Syntheses Collective Volume II", John Wiley & Sons, Inc.: New York, 1944; p. 406.

32. Pouchert, C. J. "The Aldrich Library of NMR Spectra, Edition II, Vol. 1", Aldrich Chemical Co.: Milwaukee, 1983; p. 763, spectra D.

33. Campbell, T. W. Helv. Chim. Acta 1953, 36, 1489.

34. Caspar, M. L.; Stothers, J. B.; Wilson, N. K. Can. J. Chem. 1975, 53, 1958.

35. Klemm, L. H.; Kohlik, A. J.; Desai, K. B. J. Org. Chem. 1963, 28, 625.

36. Douris, J.; Mathieu, A. Bull. Soc. Chim. Fr. 1971, 3365.

37. Fouche, J. L. Bull. Soc. Chim. Fr. 1970 (4), 1376.

38. Tuschka, T.; Naito, K.; Rickborn, B. J. Org. Chem. 1983, 48, 70.

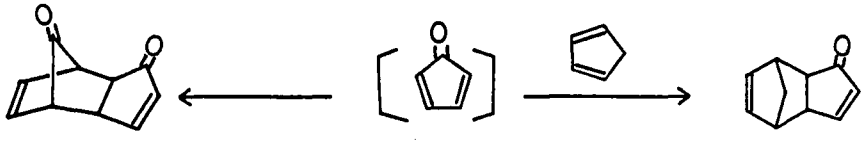
39. Chapman, O. L.; Tsou, U. E. J. Am. Chem. Soc. 1984, 106, 7974.

40. Trahanovsky, W. S.; Scribner, M. E. J. Am. Chem. Soc. 1984, 106, 7976.

PART IV. PREPARATION OF CYCLOPENTADIENONES BY FLASH VACUUM PYROLYSIS AND THEIR DIMERIZATION AND INTRAMOLECULAR REACTIONS

INTRODUCTION

Cyclopentadienone (1) is a very reactive molecule that has been generated by various methods such as the pyrolysis of 4,7,8,9-tetrahydro-4,7-endo-methylene-inden-1-one,[1] o-phenylenesulfite,[2a,2b] o-phenylenecarbonate,[3] or 2,3-dihydro-1,4-benzodioxine,[4] the elimination of hydrogen bromide from 4-bromocyclopentenone,[5] and the photolysis of o-benzoquinone.[6] The existence of cyclopentadienone (1) is based on isolation of its dimer (2), isolation of the cyclopentadiene-cyclopentadienone Diels-Alder reaction product (3) and detection by "The three phase test".[7]

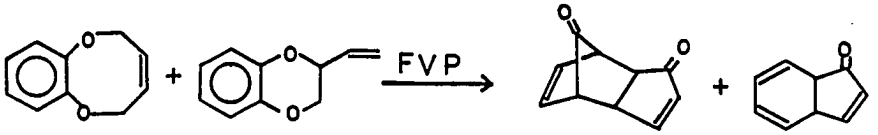


2 1 3

The existence of cyclopentadienone (1) is also supported by its low-temperature IR spectrum[6] and photoelectron spectrum.[8] Recently, cyclopentadienone (1) has been generated by the photolysis or pyrolysis of several precursors and isolated in an argon matrix and the IR and UV spectra of 1 have been determined and discussed.[9]

During the course of studying the chemistry of the [4+4] dimer of o-xylylene and related compounds,[10] we observed that flash vacuum pyrolysis (FVP) of a 2:1 mixture of 4a and 4b gave the cyclopentadienone dimer (2) and dihydroindenone (5).

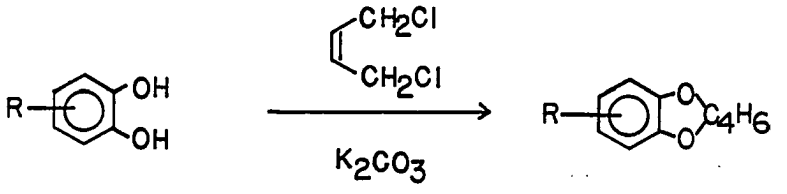
Using this method, we have generated a number of substituted cyclopentadienones including inden-2-one and cyclopentadienones that have an internal dienophile. This work is the subject of this paper.



4a 4b 2 5

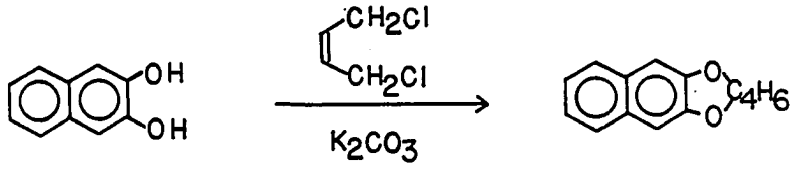
RESULTS

Each of the mixtures of cyclic diethers [a mixture of 6-membered diethers (b and c) and 8-membered diether (a)][11] including 4a,b, 8a,b,c, 9a,b,c, 10a,b,c, 11a,b,c and 12a,b were prepared from the corresponding diol and cis-1,4-dichloro-2-butene.



R = H 6a
3-CHO 6b
4-CHO 6c
3-t-butyl 6d
3,5-di-t-butyl 6e

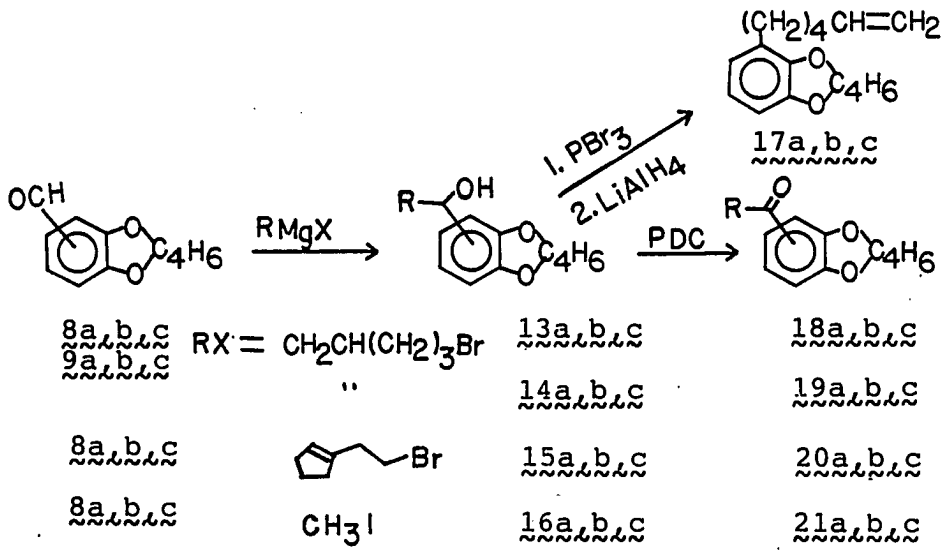
R = H 4a,b
3-CHO 8a,b,c
4-CHO 9a,b,c
3-t-butyl 10a,b,c
3,5-di-t-butyl 11a,b,c



7 12a,b

The syntheses of other substituted cyclic diethers including 17a,b,c[11] to 21a,b,c[11] are summarized in Scheme 1. Each of the corresponding aldehydes 8a,b,c and 9a,b,c were allowed to react with the corresponding Grignard reagents to give alcohols 13a,b,c-16a,b,c, which were converted to the corresponding ketones 18a,b,c, 19a,b,c, 20a,b,c, and 21a,b,c using pyridinium dichromate (PDC). Compounds 17a,b,c were

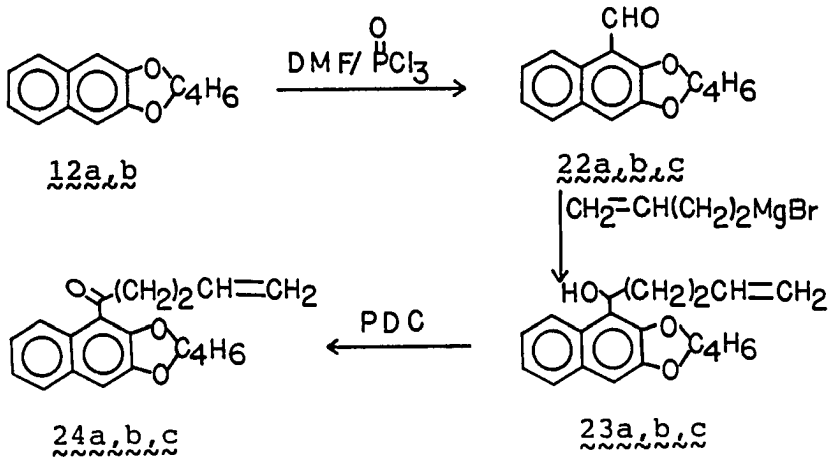
Scheme 1



prepared from alcohol 13a,b,c by reaction with tribromophosphine followed by lithium aluminum hydride.

The synthesis of the mixture of three isomeric compounds represented as 24a,b,c is outlined in Scheme 2. An aldehyde

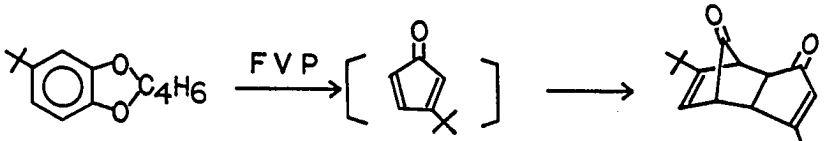
Scheme 2



group was introduced by formylation[12] of 12a,b to give a 1:1:0.8 mixture (unassigned) of 22a,b,c, which was reacted with 3-butenylmagnesium bromide to give 23a,b,c. The mixture of alcohols 23a,b,c was oxidized to 24a,b,c with pyridinium dichromate (PDC).

The pyrolysis of a ca., 2:1 mixture of 2,5-dihydro-1,6-benzodioxocin (4a) and 2-vinyl-2,3-dihydro-1,4-benzodioxine (4b) at 680°C gave an 80% yield of the cyclopentadienone dimer (2) and a 10% yield of dihydroindenone (5). The pure 4b was obtained by heating the mixture of 4a and 4b in an evacuated (10^{-1} torr) sealed tube at 220°C for 2 h. The pyrolysis of 4b at 680°C also gave the cyclopentadienone dimer (2), dihydroindenone (5), and recovered 4b (15%).

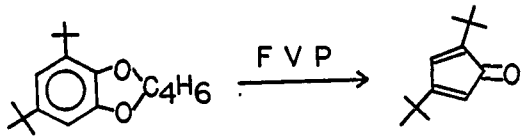
Likewise the pyrolysis of 10a,b,c at 680°C gave a 70% yield of 3-t-butylcyclopentadienone dimer (26) and a small amount of recovered 10a,b,c. The structure of 26 has been



10a,b,c 25 26

proposed by Garbish and Sprecher.[13] The ^{1}H NMR spectrum of the pyrolysis products is consistent with theirs. The low temperature (-60°C) ^{1}H NMR spectrum of the pyrolysis products showed the presence of dimer 26 and 1,3-butadiene.

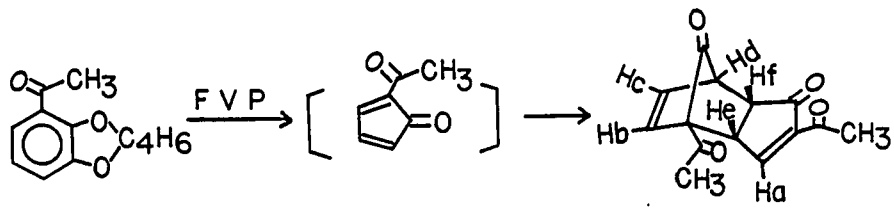
The pyrolysis of 11a,b,c at 680°C gave a 50% relative yield of 2,4-di-t-butylcyclopentadienone (27) along with unknown products. The ^{1}H NMR spectrum of the pyrolysis



11a,b,c 27

products included signals at δ 6.50, 4.96, 1.09, and 1.05. These values are consistent with the reported values.[13]

The pyrolysis of 21a,b,c gave a 73% yield of the 2-acetylcyclopentadienone dimer (29). The structure of 29 was



21a,b,c 28 29

indicated by its spectral properties. The ^{1}H NMR spectrum of the pyrolysis products of 21a,b,c (Fig. 1) included a doublet at δ 8.00 (J = 3 Hz) for H_a, a doublet of doublet at δ 6.60-6.48 for H_c, a doublet at δ 6.30 (J = 6.3 Hz) for H_b, a doublet of doublet at δ 4.0-3.9 for H_f, a triplet at δ 3.7-3.6 (J = 4.2 Hz) for H_e, a multiplet for H_d, and two singlets at δ 2.40 and 2.34 for the two acetyl groups. The IR spectrum showed a broad and strong absorption from 1800 cm^{-1} to 1530

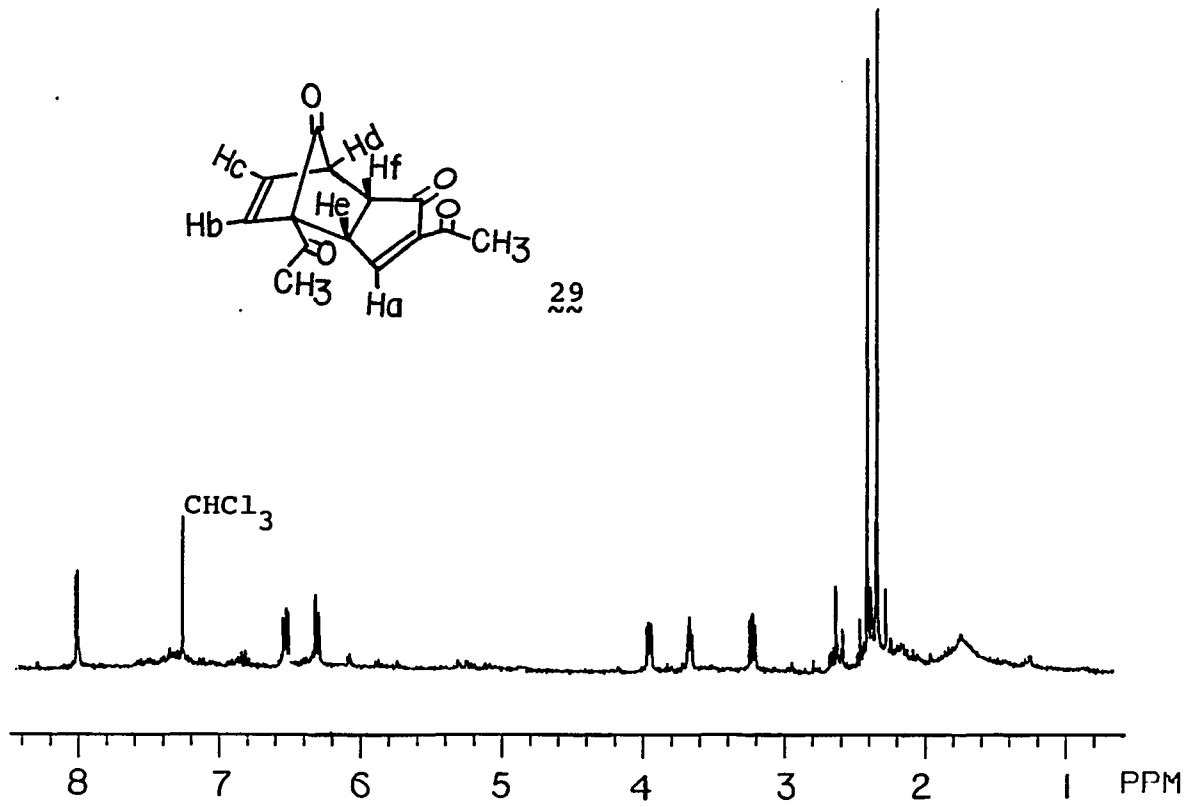
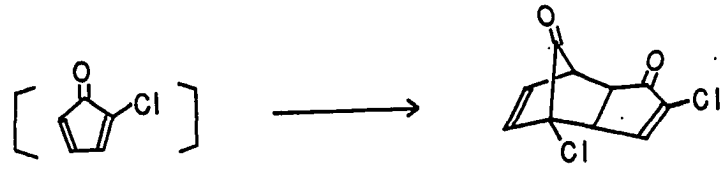


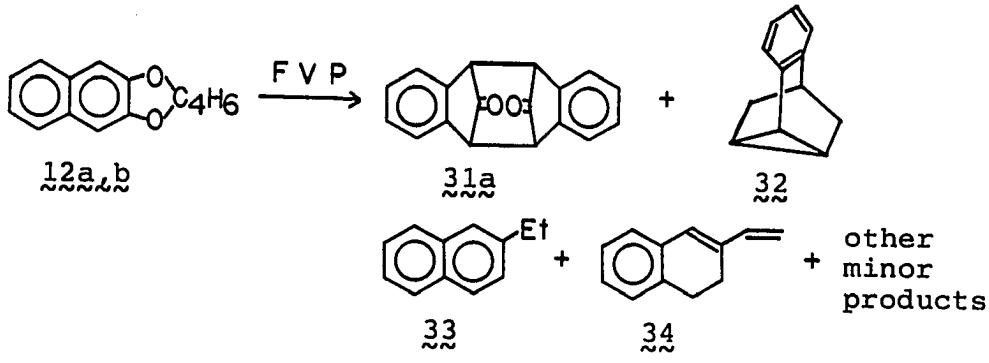
Figure 1. ^{1}H NMR spectrum of the pyrolysis products of a mixture of 7-acetyl-2,5-dihydro-1,6-benzodioxocin (21a), 2-vinyl-5-acetyl-2,3-dihydro-1,4-benzodioxine (21b), and 2-vinyl-8-acetyl-2,3-dihydro-1,4-benzodioxine (21c) (21a,b,c)

cm^{-1}. The assignment of the structure 29 is consistent with that of 2-chlorocyclopentadienone dimer (30).[5]



30

The pyrolysis of 12a,b at 680°C gave up to a 50% yield of the [4+4] dimer of inden-2-one (31a) as a major product along with 3,4-benzotricyclo[3,2,1,$0^{2,7}$]octene (32), 2-ethylnaphthalene (33), 3-vinyl-1,2-dihydronaphthalene (34) and other minor products such as naphthalene, 2-vinylnaphthalene, and dibenzo[a,e]cyclooctene. The distribution of the pyrolysis



12a,b 31a 32 33 34

products was dependent on the rate of the pyrolysis. With a rapid heating rate of the sample chamber and using a large quantity (1.2 g) of 12a,b, the [4+4] dimer of inden-2-one (31a) was a major product. However, with a slow heating rate of the sample chamber and using a small quantity (20 mg) of

12a,b, 3,4-benzotricyclo[3,2,1,$0^{2,7}$]octene (32), 2-ethylnaphthalene (33), and 3-vinyl-1,2-dihydronaphthalene (34) were major products along with small amounts of the [4+4] dimer of inden-2-one (31a). These results are summarized in Table 1.

The structure of the dimer of inden-2-one (31a) was determined by its spectral properties. The ^{1}H NMR spectrum (Fig. 2) included an AA'BB' signal at δ 7.47-7.30 for the benzene protons and a singlet at δ 3.74 for the benzylic proton. The ^{13}C NMR spectrum of 31a showed five different peaks, at δ 201.97 for the carbonyl carbon, at δ 138.72, 128.78, and 124.17 for the benzene ring carbons and at δ 56.62 for the benzylic carbon as required by the symmetry of 31a. The IR spectrum of 31a showed strong absorption at 1777 cm^{-1}. This carbonyl band is well matched with the reported value of the carbonyl band (1768 cm^{-1})[14] of the dimer of 1,3-diphenyl-inden-2-one (31b). High resolution mass spectrum was consistent with the molecular formula $C_{18}H_{12}O_2$.

The structure of 32 was determined by its spectral properties. The ^{1}H NMR spectrum (Fig. 3) indicated a multiplet at δ 7.34-6.95 for the protons in the benzene ring, a triplet at δ 3.03 (J = 4.6 Hz) for H_a, a triplet at δ 2.13 (J = 7.2 Hz) for H_b, a doublet of doublet at δ 1.84-1.78 for H_c, a doublet at δ 1.65 (J = 6.9 Hz) for H_d, and a doublet at δ 0.97 (J = 11.4 Hz) for H_e. The COSY ^{1}H NMR spectrum (Fig.

Table 1. The pyrolysis products of a 2:1 mixture of 2,5-dihydro-1,6-napthodioxocin (12a) and 2-vinyl-2,3-dihydro-1,4-naphthodioxine (12b) at 680°C

Pyrolysis Condition	Products, %[a]			
	The dimer of inden-2-one (31a)	3,4-benzo-tricyclo-[3,2,1,$0^{2,7}$] octene (32)	2-ethyl-naphthalene (33)	3-vinyl-1,2-dihydro-naphthalene (34)
1. fast heating, 1.2 g sample	50	7	16	6
2. slow heating, 20 mg sample	3	18	44	12

[a]Relative yield determined by GC.

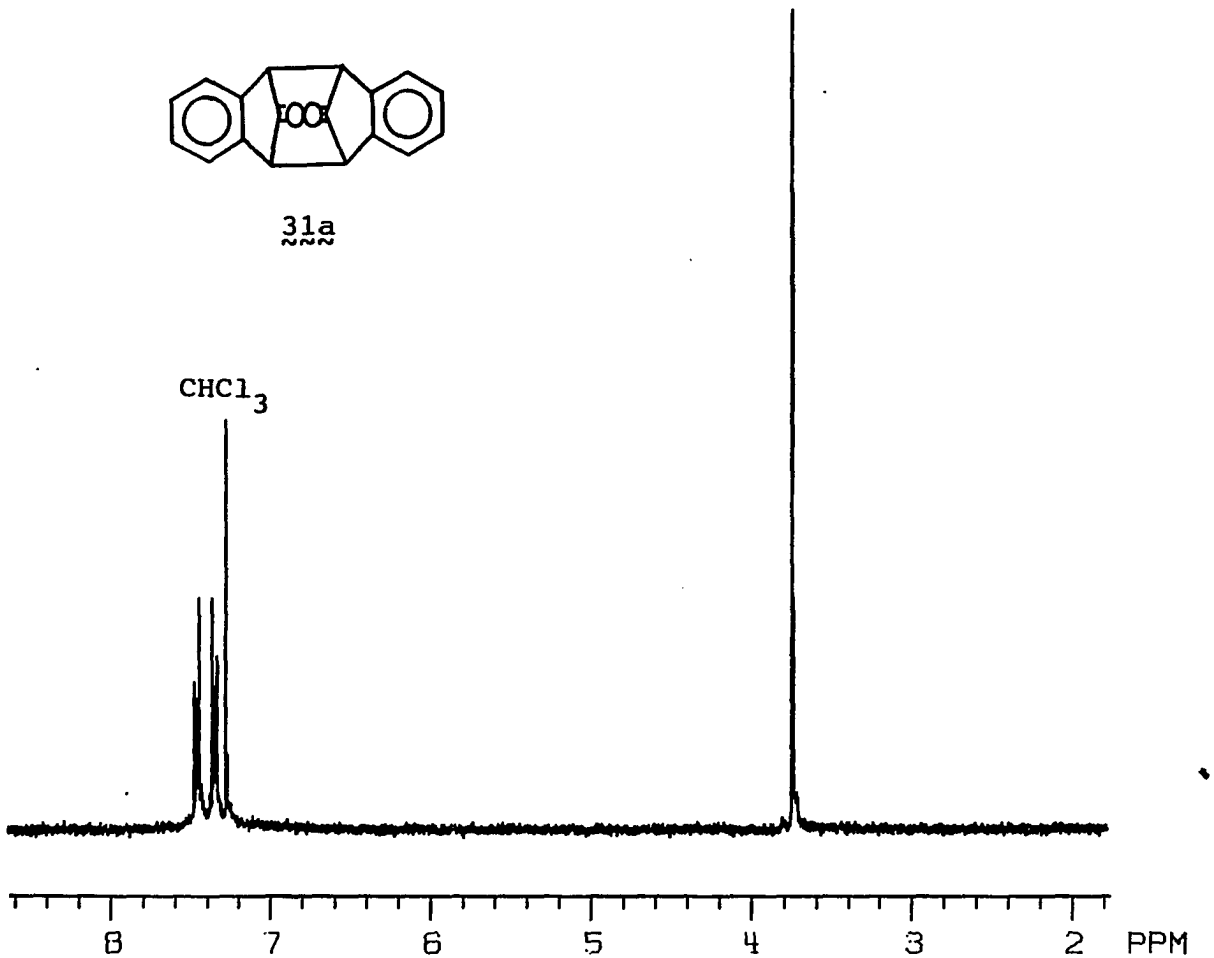


Figure 2. ^{1}H NMR spectrum of the [4+4] dimer of inden-2-one (31a)

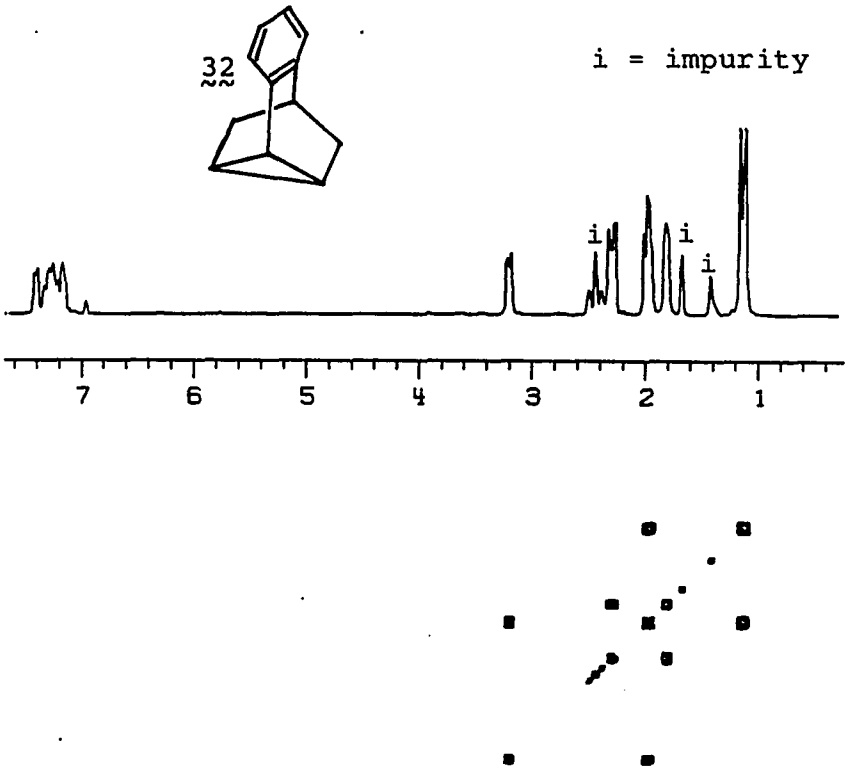
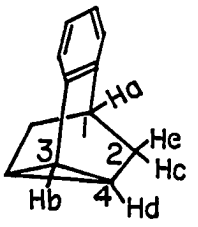


Figure 3. COSY ^{1}H NMR spectrum of 3,4-benzotricyclo-[3,2,1,$0^{2,7}$]octene (32)



32

3) also showed three correlations including H_a and H_c, H_c and H_e, and H_b and H_d. The ^{13}C NMR spectrum (Fig. 4) of 32 included peaks at δ 140.80, 134.76, 126.08, 125.72, 124.06 and 122.94 of six different benzene ring carbon at δ 36.36 (d, J_{CH} = 142 Hz) for the carbon 1, 28.66 (t, J_{CH} = 133 Hz) for the carbon 2, 18.67 (d, J_{CH} = 161 Hz) for the carbon 3 and 15.88 (d, J_{CH} = 171 Hz) for the carbon 4. The methane chemical ionization mass spectrum showed a strong M+1 peak at m/e 157. High resolution mass spectral data were also consistent with the molecular formula $C_{12}H_{12}$. These spectral data matched very well the reported spectral data[15,16] of 32. The structure of 3-vinyl-1,2-dihydronaphthalene (34) was determined by its spectral properties. The ^1H NMR spectrum (Fig. 5) included a multiplet at δ 7.20-7.00 of the benzene protons, a doublet of doublet splitting pattern at δ 6.59-6.48 for the vinyl C-H proton, doublets at δ 5.33 (J = 17.4 Hz) and δ 5.13 (J = 10.8 Hz) for the vinyl CH_2 proton and triplets at δ 2.85 (J = 8.1 Hz), and δ 2.46 (J = 8.1 Hz) for the methylene

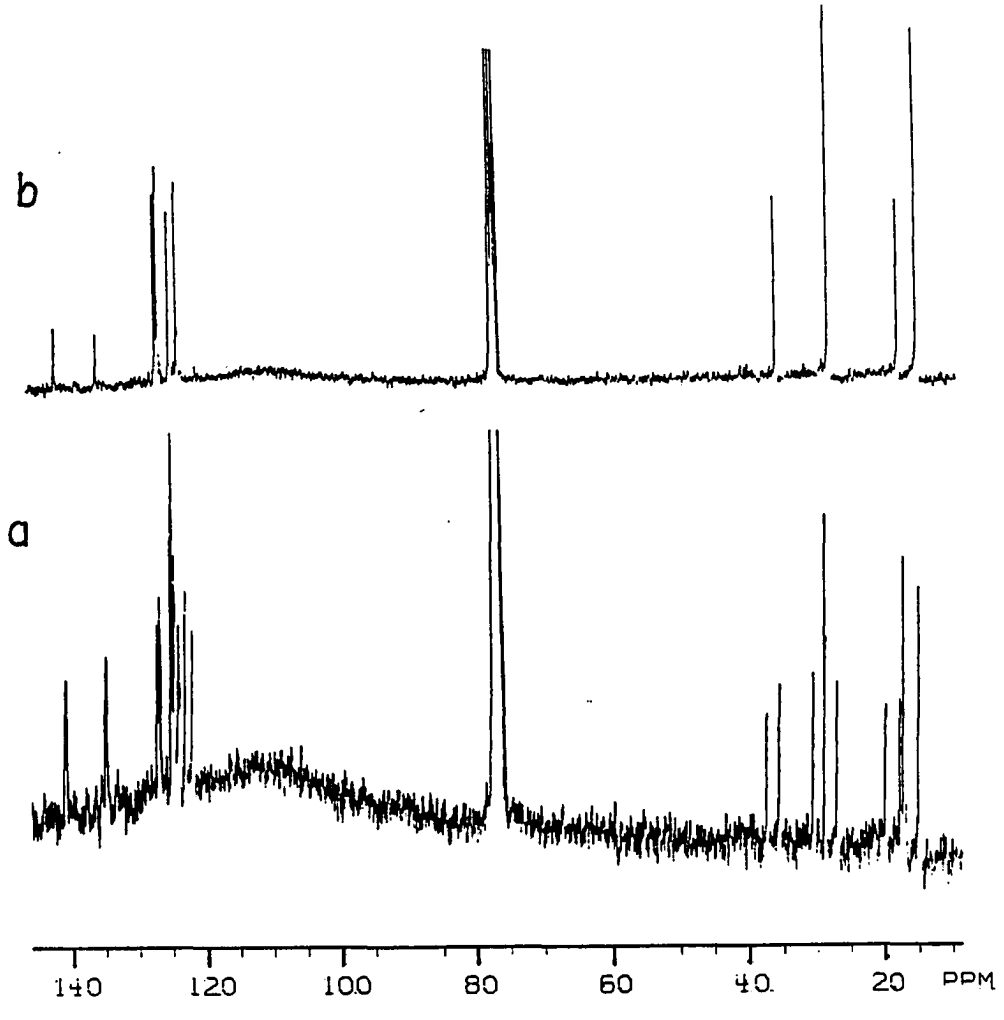


Figure 4. ^{13}C NMR spectrum of 3,4-benzotricyclo-[3,2,1,$0^{2,7}$]octene (32); a = CH coupled spectrum; b = proton decoupled spectrum

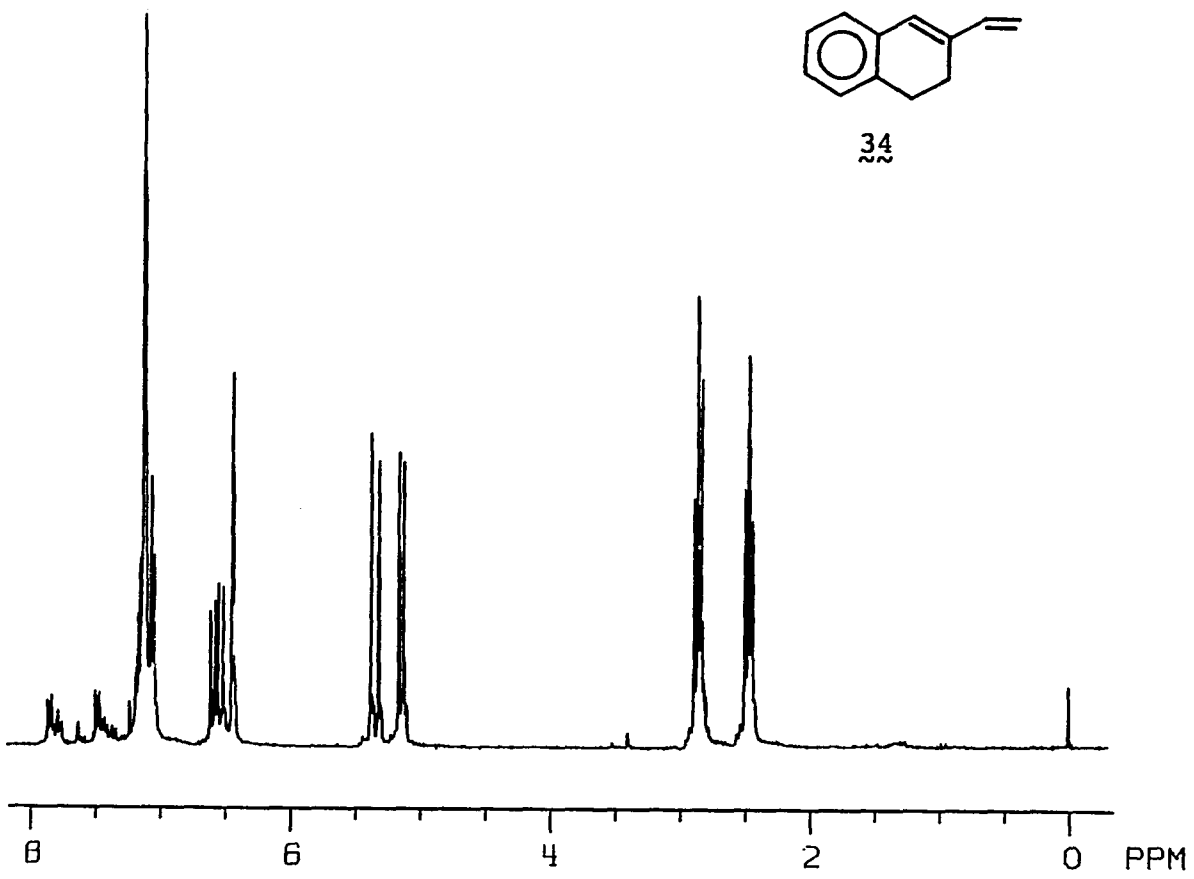
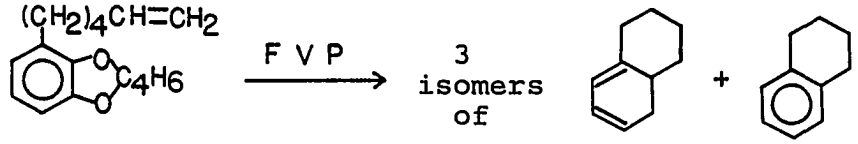


Figure 5. ^{1}H NMR spectrum of 3-vinyl-1,2-dihydronaphthalene (34)

protons of the 6-membered ring. GC/MS data were consistent with the molecular formula $C_{12}H_{12}$.

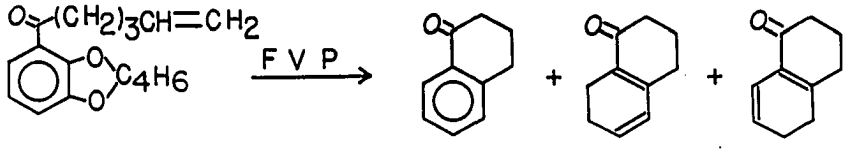
The pyrolysis of 17a,b,c at 680°C gave a total of 81% yield of a mixture of three isomers of hexahydronaphthalene (such as 35) and a 7% yield of tetralin (36). The formation



17a,b,c 35 36

of hexahydronaphthalenes was confirmed by GC/MS data and by the isolation of the tetralin (36) which was obtained by treating the pyrolysis products with 5% palladium on carbon. About a 92% yield of tetralin (36) was obtained by stirring the pyrolysis products of 17a,b,c with palladium on carbon for 15 h at room temperature. The hydrogenation of the pyrolysis products with 5% palladium on carbon at 60 psi hydrogen for 3 h gave a 38% yield of cis-decalin, a 13% yield of trans-decalin, a 33% yield of 1,2,3,4,5,6,7,8-octahydronaphthalene and a 13% yield of tetralin (36).

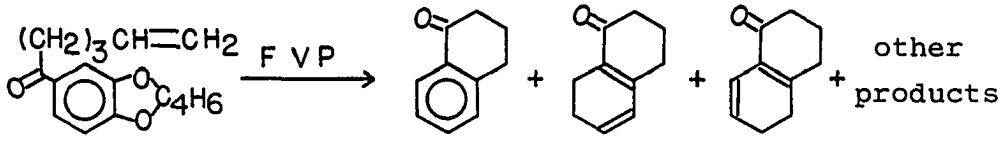
The pyrolysis of 18a,b,c gave a 10% yield of α-tetralone (37), a 46% yield of 38, and a 34% yield of 39. α-Tetralone



18a,b,c 37 38 39

(37) and a mixture of 38 and 39 were separated from the pyrolysate by thin layer chromatography on silica gel (10% ether in hexanes). The structures of 38 and 39 were determined by the spectral properties of their mixture. The ^{1}H NMR spectrum of a mixture of 38 and 39 included a doublet at δ 6.51 (J = 9.9 Hz) and doublet of triplets at δ 6.3-6.2, 6.0-5.9, and 5.83-5.77. The COSY ^{1}H NMR (Fig. 6) showed a correlation between the peak at δ 6.51 and the peak at δ 5.83-5.77 and a correlation between the peak at δ 6.3-6.2 and the peak at δ 6.0-5.9. The GC/IR showed conjugated carbonyl absorption bands at 1682 cm^{-1} for 38 and at 1697 cm^{-1} for 39. From these data the structures of 38 and 39 were assigned out of six possible conjugated tetrahydronaphthalenones.

The pyrolysis of 19a,b,c at 680°C gave an 11% yield of α-tetralone (37), a 9% yield of 38, a 13% yield of 39, a total of a 23% yield of four unknown isomers of MW 148, and a total of a 6% yield of a mixture of four isomers of MW 176. The



19a,b,c 37 38 39

mixture of 38, 39, and two unknown isomers of MW 148 was separated from the pyrolysis products by thin layer chromatography. This separated mixture was analyzed by ^{1}H NMR (Fig. 7) and GC/IR. The pyrolysis products were also

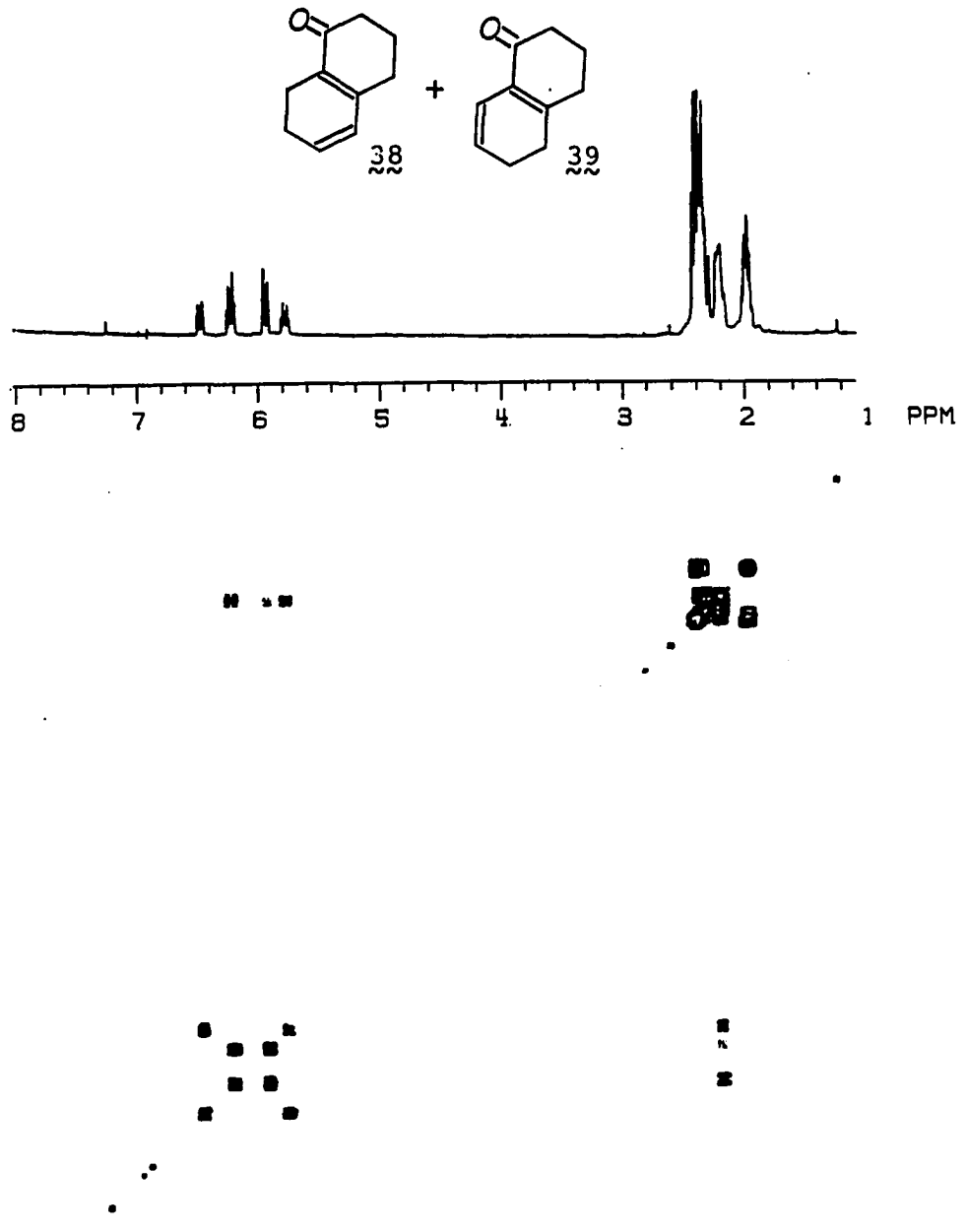


Figure 6. COSY ^{1}H NMR spectrum of a mixture of 3,4,5,6-tetrahydro-1-(2H)-naphthalenone (38) and 3,4,7,8-tetrahydro-1-(2H)-naphthalenone (39)

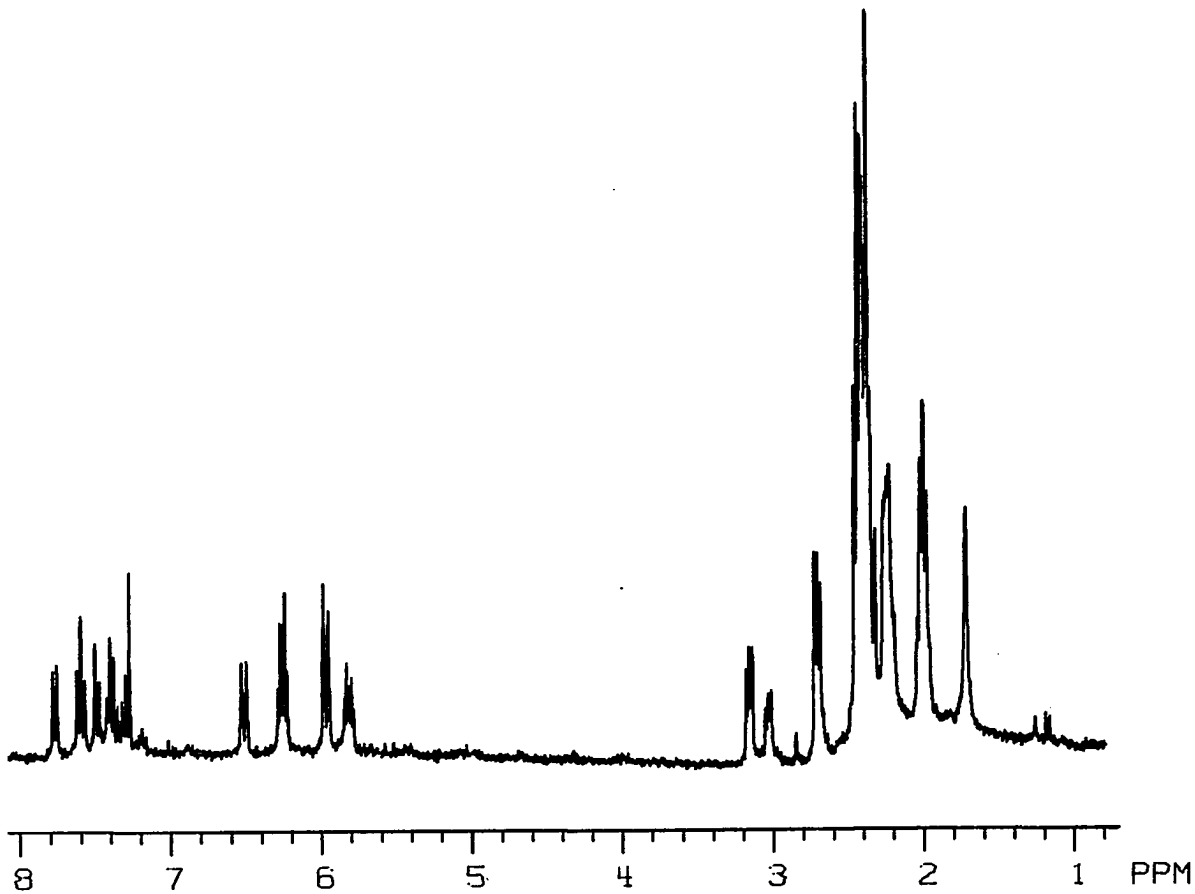
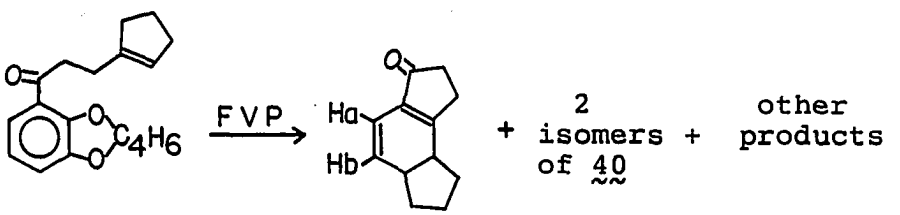


Figure 7. ^{1}H NMR spectrum of the pyrolysis products of a mixture of 8-(5-hexenoyl)-2,5-dihydro-1,6-benzodioxocin (19a), 2-vinyl-6-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (19b), and 2-vinyl-7-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (19c)

converted to α-tetralone (37) by reacting the pyrolysis products with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).

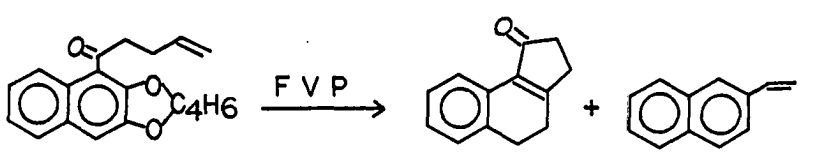
The pyrolysis of 20a,b,c at 660°C gave about a 40% yield of tricyclic compound 40, a total of 10% yield of a mixture of two isomers of 40, and small amounts of unidentified products.



20a,b,c 40

The structure of 40 was tentatively determined by the ^1H NMR spectrum (Fig. 8) and GC/MS data of the pyrolysis products of 20a,b,c. The ^1H NMR spectrum in the olefinic region included a doublet at δ 6.09 (J = 9.6 Hz) for H_a and a doublet of doublet at δ 5.82-5.71 for H_b.

The pyrolysis of 24a,b,c gave a 60% yield of tricyclic 41, a 20% yield of 2-vinylnaphthalene (42), and other minor products such as naphthalene and three isomers of MW 238.



24a,b,c 41 42

The structure of 41 was indicated by its spectral properties. The ^1H NMR spectrum (Fig. 9) included a doublet at δ 8.24 (J =

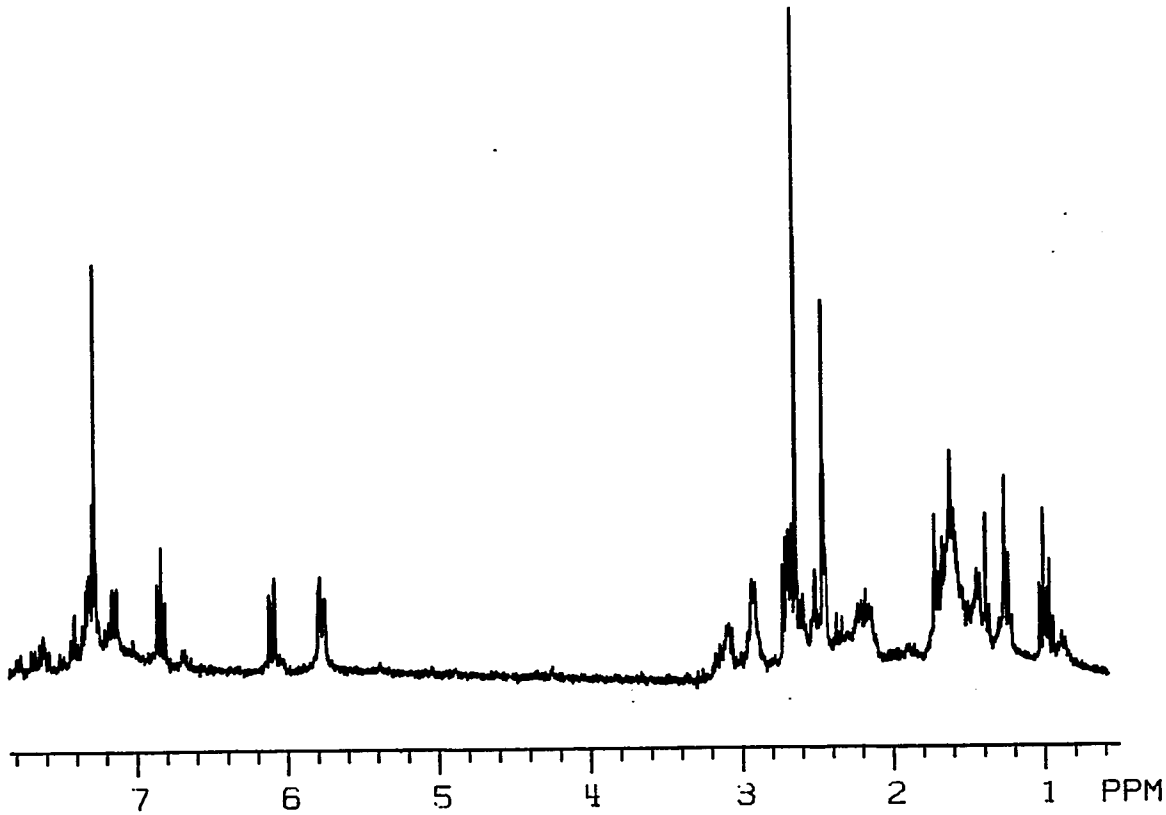
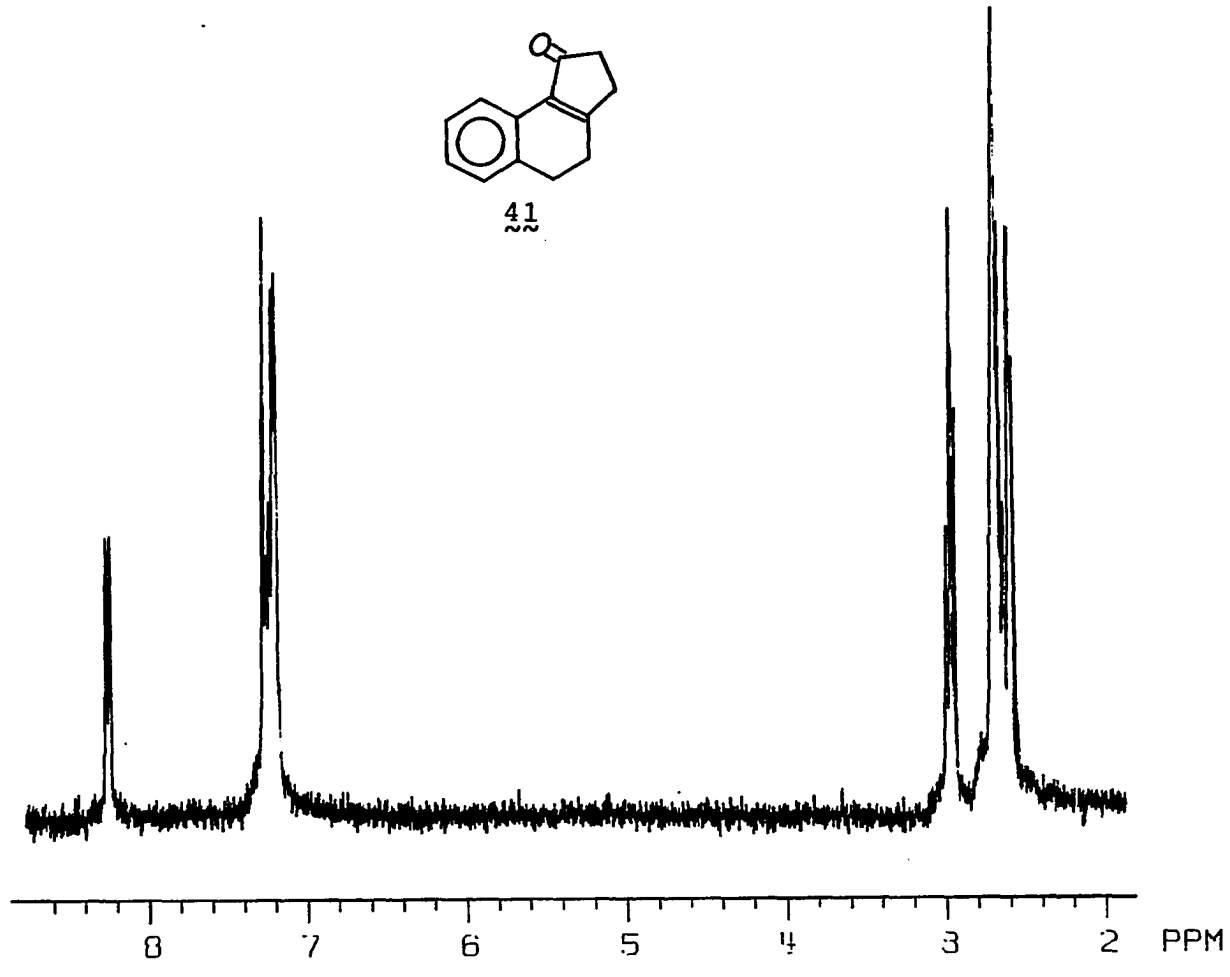


Figure 8. ^{1}H NMR spectrum of the pyrolysis products of a mixture of 7-[3-(1-cyclopentenyl)-propanoyl-2,5-dihydro-1,6-benzodioxocin (20a), 2-vinyl-5-[3-(1-cyclopentenyl)-propanoyl]-2,3-dihydro-1,4-benzodioxine (20b), and 2-vinyl-8[3-(1-cyclopentenyl)-propanoyl]-2,3-dihydro-1,4-benzodioxine (20c)



41

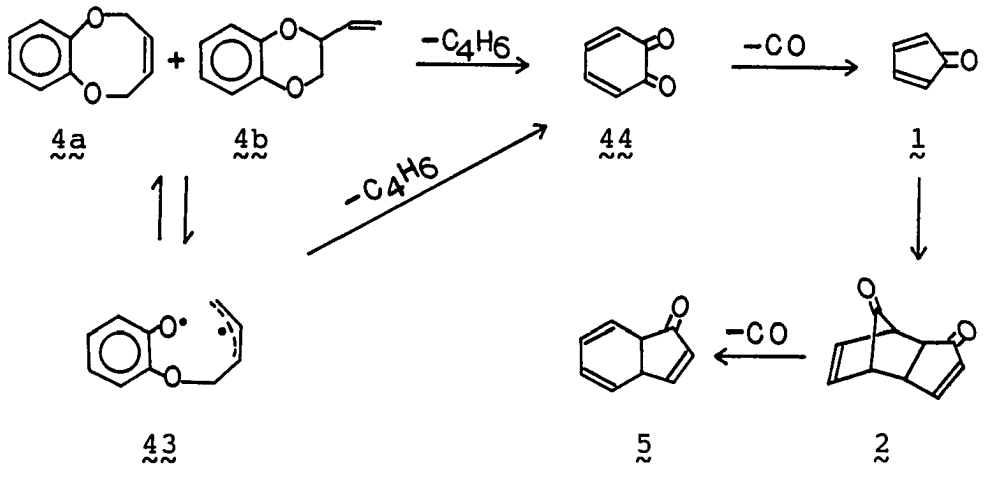
Figure 9. ^{1}H NMR spectrum of 2,3,4,5-tetrahydro-1H-benzo[e]inden-1-one (41)

7.5 Hz) for the benzene proton adjacent to double bond and carbonyl group, multiplets at δ 7.3-7.1 for the other benzene protons, and at δ 2.8-2.5 for three methylenes of the 5- and 6-membered rings. The ^{13}C NMR spectrum included peaks at δ 205.93 for the carbonyl group, at δ 174.64, 134.94, 134.37, 129.12, 127.80, 127.47, 126.73, and 123.99 for the benzene carbons and double bond carbons, and at δ 35.89, 29.24, 27.67, and 27.10 for the carbons of the 5- and 6-membered rings. The IR spectrum showed a strong absorption at 1705 cm^{-1}. High resolution mass spectral data were consistent with the molecular formula $C_{13}H_{12}O$.

DISCUSSION

The formation of cyclopentadienone dimer 2 by the pyrolysis of a mixture of 4a and 4b can be explained by an elimination of butadiene either from biradical 43 or from 4a and 4b to give o-benzoquinone (44) which loses CO to give cyclopentadienone (1). Reactive cyclopentadienone (1) would dimerize to give its dimer (2) (Scheme 3). Cyclopentadienone

Scheme 3

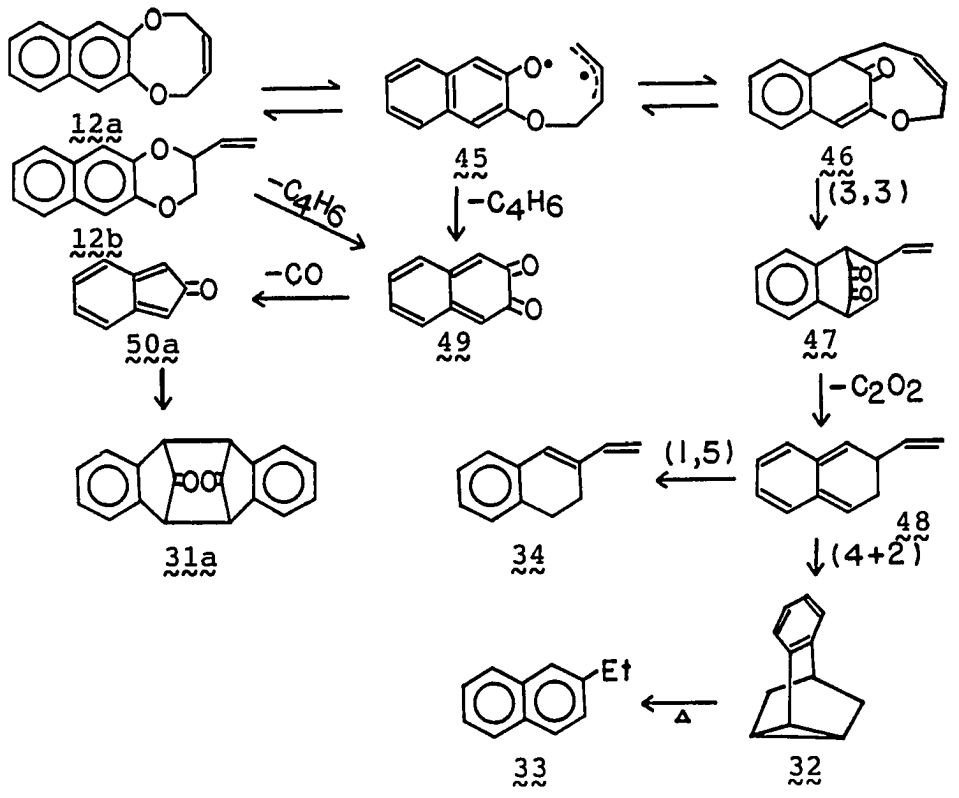


(1) and o-benzoquinone (44) were not obtained, but the formation of cyclopentadienone (1) was confirmed by the isolation of dimer 2 and dihydroindenone (5).

Likewise the pyrolysis of other substituted cyclic diethers including 10a,b,c, 11a,b,c, and 21a,b,c gave the corresponding substituted cyclopentadienone and its dimer in good yields.

The pyrolysis of a mixture of 12a and 12b gave the [4+4] dimer of inden-2-one (31a), 3,4-benzotricyclo[3,2,1,$0^{2,7}$]-octene (32), 2-ethylnaphthalene (33), 3-vinyl-1,2-dihydronaphthalene (34), and other minor products. Pathways which account for the formation of these products are presented in Scheme 4.

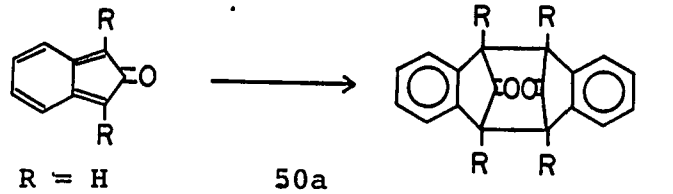
Scheme 4



The formation of 31a can be explained by an elimination of butadiene from 12a, 12b, 45, or 47 to give 49 which would lose CO to give inden-2-one (50a). The reactive 50a would rapidly

dimerize in the hot zone to give 31a probably by a stepwise diradical mechanism.

Substituted inden-2-ones (50b and 50c) have been generated by dehydration of 1-hydroxyindan-2-ones using acetic anhydride[17] or by reductive elimination of monobromo or dibromoindan-2-ones using base.[14,18] The transient existence



R = H 50a
R = Ph 50b
R = C_6H_4-CH_3 50c

R = H 31a
R = Ph 31b

of substituted inden-2-ones (50b and 50c) was proven by the isolation of rapidly formed dimers (such as 31b) as well as Diels-Alder reaction products.[13,14] Up to the present the preparation of the parent compound, inden-2-one (50a), has not been reported.

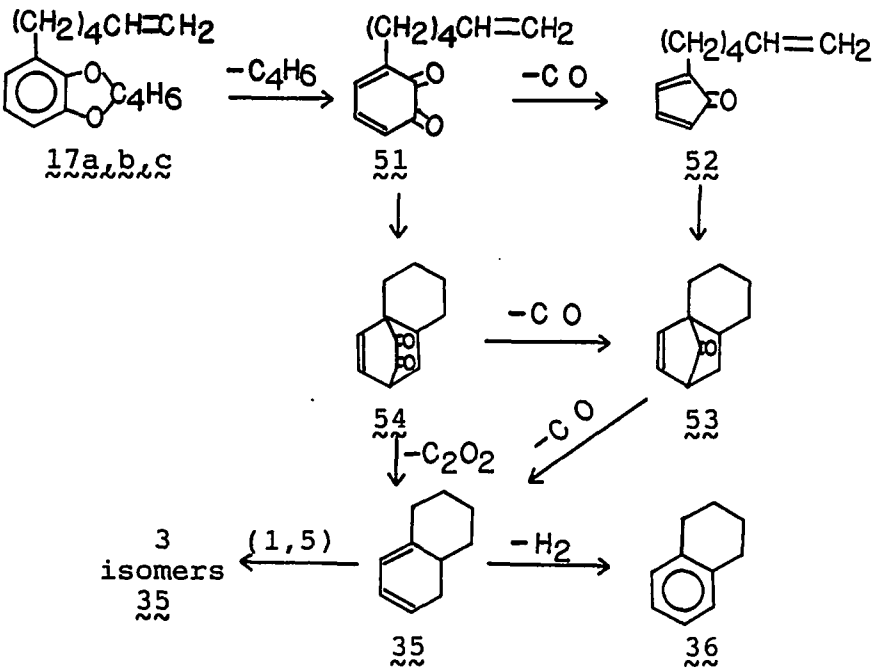
The formation of 3,4-benzotricyclo[3,2,1,$0^{2,7}$]octene (32), 2-ethylnaphthalene (33), and 3-vinyl-1,2-dihydronaphthalene (34) can be explained by the formation of 46 from diradical 45 (see Scheme 4). Compound 46 may undergo a Cope rearrangement to give 47 which can lose C_2O_2 to give o-quinodimethane 48. Compound 48 can undergo an intramolecular [4+2] cycloaddition, or can undergo a 1,5-hydrogen shift to give 3,4-benzotricyclo-[3,2,1,$0^{2,7}$]octene (32) and 3-vinyl-1,2-dihydronaphthalene

(34), respectively. 2-Ethylnaphthalene (33) is believed to be derived from 32 because the pyrolysis of 32 at 690°C gave a 52% yield of 33 and a 28% yield of recovered 32. The pyrolysis of 34 at 680°C did not give any 33 but small amounts of 2-vinylnaphthalene (42) and 34 were recovered. At this time, we have no good mechanism for the formation of 2-ethylnaphthalene (33) from 32.

Recently cyclopentadienone (1) has been used in a synthesis of (±)-sarkomycin by trapping cyclopentadienone (1) with ethyl acrylate.[19] To our knowledge, this is the first example in which cyclopentadienone (1) functions as a diene in trapping with a dienophile. If cyclopentadienones are generated with internal dienophiles such as olefins, the reactive cyclopentadienones could be trapped by the olefins through intramolecular Diels-Alder reactions. This would give good evidence for the existence of transient cyclopentadienone (1). This intramolecular reaction could also be utilized in the synthesis of polycyclic compounds. The feasibility of this postulate was tested by the pyrolysis of substituted cyclic diethers bearing various olefinic groups.

The pyrolysis of 17a,b,c at 680°C gave a mixture of three isomers of hexahydronaphthalenes and tetralin (36). A pathway which accounts for the formation of these products are presented in Scheme 5. An elimination of butadiene from 17a,b,c would give 51 which can lose CO to give

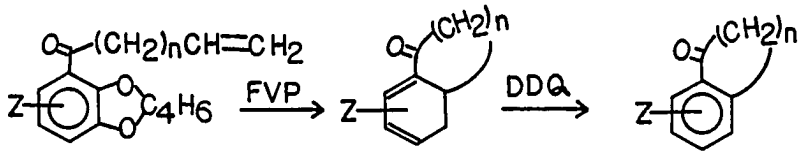
Scheme 5



cyclopentadienone 52. Either 51 or 52 can undergo an intramolecular Diels-Alder reaction to give 54 and 53, respectively. Loss of C_2O_2 from 54 or loss of CO from 53 could give hexahydronaphthalene 35 which can undergo a series of a 1,5-hydrogen shift to give three isomers of hexahydronaphthalenes. It is difficult to tell where the actual intramolecular Diels-Alder reaction is taking place since the intramolecular Diels-Alder reaction products (53 or 54) were not obtained. It is thought that the rate of losing CO from 51 is faster than that of intramolecular Diels-Alder reaction in 51. Therefore, the intramolecular Diels-Alder reaction of 52 would be a more important reaction than that of 51 for the

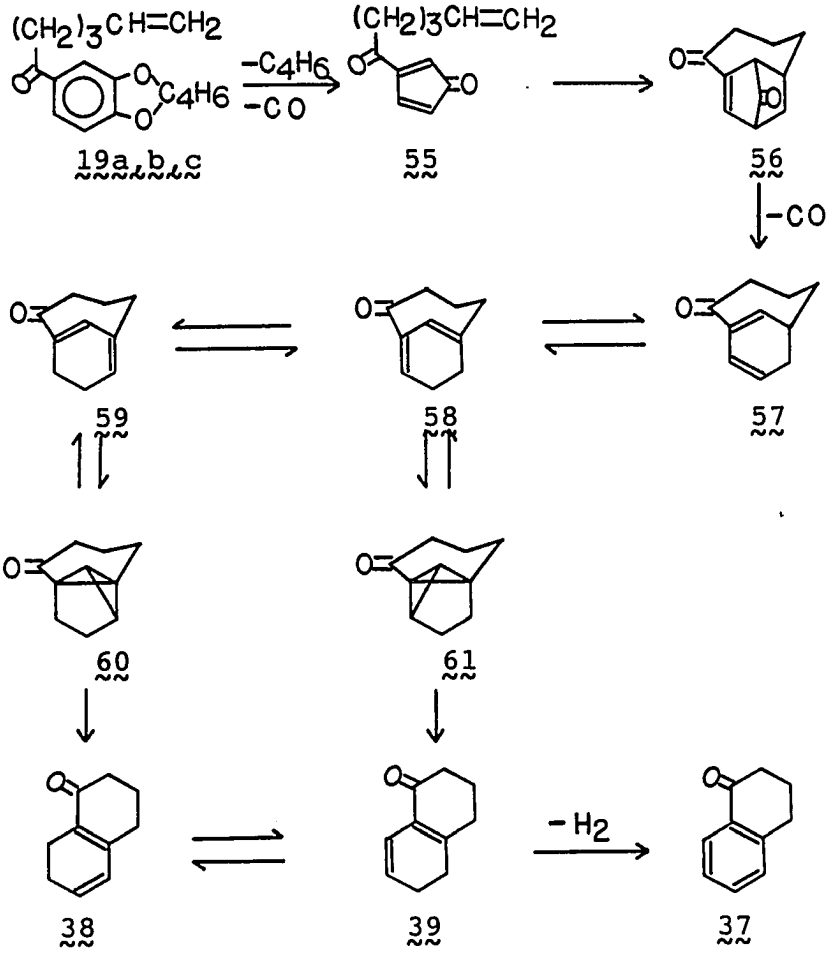
formation of hexahydronaphthalene (35). Hexahydronaphthalenes could undergo dehydrogenation to give tetralin (36).

The pyrolysis of a mixture of 7-(5-hexenoyl)-2,5-dihydro-1,6-benzodioxocin (18a), 2-vinyl-5-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18b), and 2-vinyl-8-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18c) (18a,b,c) gave α-tetralone (37), 3,4,5,6-tetrahydro-1-(2H)-naphthalenone (38), and 3,4,7,8-tetrahydro-1-(2H)-naphthalenone (39). The formation of these products from 18a,b,c can be explained in the same way as described in Scheme 5. This transformation could be utilized in the synthesis of terpenoid natural products which have fused six-membered rings. This transformation could also be utilized in the synthesis of indanones, tetralones, and other larger-ring bicyclic compounds since the pyrolysis products of 18a,b,c gave α-tetralone (37) by the reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).



The pyrolysis of 19a,b,c at 680°C gave α-tetralone (37), 38, and 39, and four unknown isomers of 38 along with other minor products. In Scheme 6, pathways which account for the formation of these products are presented. Successive

Scheme 6



19a,b,c 55 56 59 58 57 60 61 38 39 37

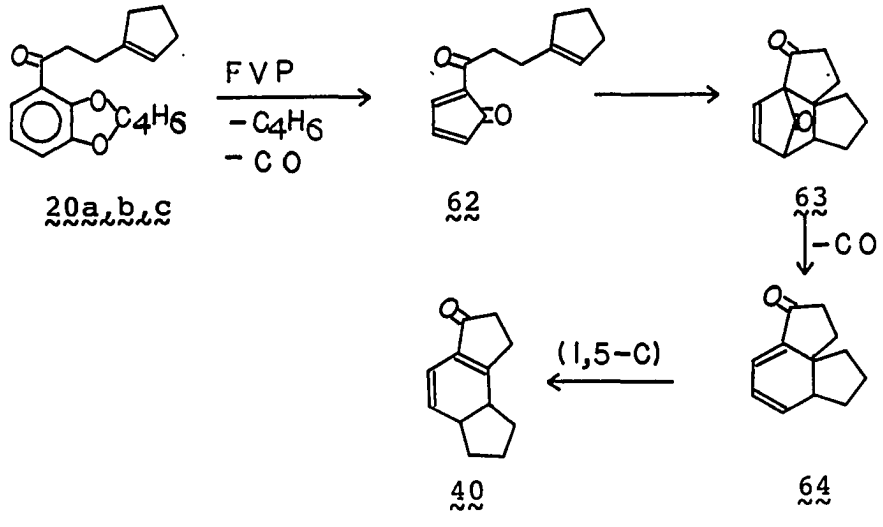
elimination of butadiene and CO from 19a,b,c would give cyclopentadienone 55, which can undergo an intramolecular Diels-Alder reaction to give 56. Loss of CO from 56 can give 57, which would undergo a series of 1,5-hydrogen shifts to give 58 and 59. Either 58 or 59 can undergo [$2\pi_s + 2\pi_a$] cycloaddition to give a bicyclobutene 61 or 60, respectively. Each of 55 and 61 can give the corresponding 38 and 39

probably in a stepwise manner. Dehydrogenation from 38 or 39 can give α-tetralone (37).

Compounds 57, 58, and 59 are thought to be the four unknown isomers of 38. The reaction of the pyrolysis products of 19a,b,c with DDQ gave no 4-metacyclophane[20] but gave α-tetralone (37). This may mean that compounds 57, 58, and 59 readily rearrange to 38 or 39 which then lose hydrogen to give α-tetralone (37), or formed 4-metacyclophane may rearrange[21] to α-tetralone (37) because of the strain in 4-metacyclophane.

The pyrolysis of 20a,b,c gave 40 and isomers of 40. A pathway which accounts for the formation of these products is described in Scheme 7. The production of 40 instead of 64

Scheme 7

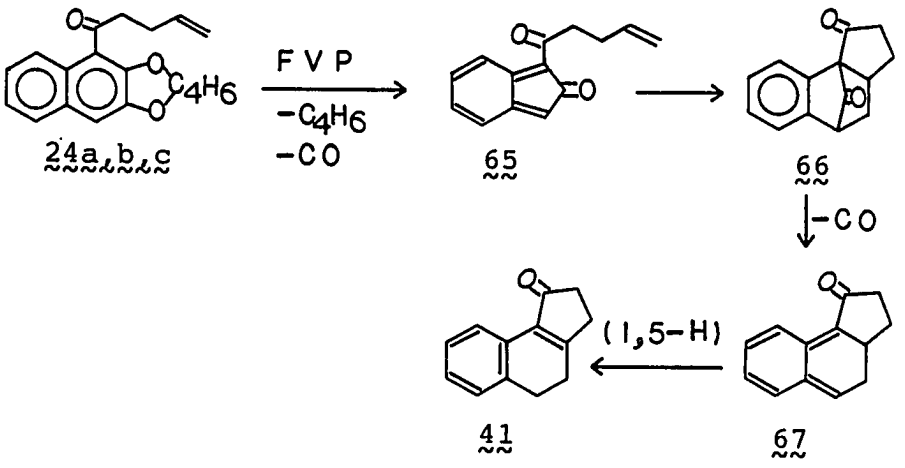


20a,b,c 62 63 40 64

indicated the 1,5-carbon shift is facile under the pyrolysis conditions.

The pyrolysis of 24a,b,c gave 41, 2-vinylnaphthalene (42) and other minor products. A pathway which accounts for the formation of 41 is described in Scheme 8. Successive

Scheme 8



24a,b,c 65 66 67 41

elimination of butadiene and CO from 24a,b,c can give inden-2-one 65, which undergoes Diels-Alder reaction to give 66. A loss of CO from 66 would give o-quinodimethane 67, which could rearrange to 41 by a 1,5-hydrogen shift. 2-Vinylnaphthalene (42) could be derived from 41 or 67 by successive elimination of hydrogen and CO either by a stepwise or concerted manner.

The isolation of 41 from the pyrolysis products of 24a,b,c gave good evidence for the existence of inden-2-one (50a) intermediate. This transformation could be extended to the preparation of polycyclic compounds such as terpenoids and steroids.

As a conclusion cyclopentadienones have been generated by the pyrolysis of cyclic diethers. Using this method inden-2-one (50a) was generated and its [4+4] dimer (31a) was obtained. Cyclopentadienones and inden-2-one have been utilized in the synthesis of polycyclic compounds. The transient existence of these intermediates has also been proven by the isolation of intramolecular Diels-Alder reaction products.

EXPERIMENTAL

Methods and Materials

The pyrolysis apparatus has been previously described[22] and a commercially-available version can be obtained from Kontes Scientific Glassware. ^{1}H NMR spectra were recorded on a Nicolet 300 spectrometer. Chemical shifts are reported in parts per million (δ) from tetramethylsilane (TMS). Gas chromatographic (GC) analysis was performed on a Hewlett Packard Model 5840-A gas chromatograph (GC) with a fused silica column (DB-1) and a flame ionization detector. Combined gas chromatographic/mass spectra (GC/MS) analysis was performed on a Finnigan 4000 GC/MS with an Incos data system. High resolution mass spectra were measured with either an Associated Electronics Industries MS-902 instrument or MS 50 mass spectrometer. Infrared spectra (IR) were recorded on either a Beckman Acculab II or a Beckman 4250 spectrometer. GC/IR analysis was performed on an IBM FT/IR model 98. Melting points were determined on a Hoover Thomas melting point apparatus and are uncorrected. 4-Bromo-1-butene, 5-bromo-1-pentene, 4-t-butylcatechol, 1-cyclopentene acetonitrile, 3,5-di-t-butylcatechol, cis-1,4-dichloro-2-butene, 2,3-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, and 2,3-dihydroxynaphthalene were purchased from Aldrich Chemical Company.

The mixture of 2,5-dihydro-1,6-benzodioxocin (4a) and 2-vinyl-2,3-dihydro-1,4-benzodioxine (4b)

To a solution of 2.2 g (20 mmol) of catechol (6a) and 5.5 g (40 mmol) of anhydrous potassium carbonate in 160 ml of dimethylformamide, 2.5 g (20 mmol) of cis-1,4-dichloro-2-butene in 30 ml of dimethylformamide was added dropwise at 90°C with stirring. The reaction mixture was stirred at 90°C for 9 h. The reaction mixture was cooled to room temperature and this cooled reaction mixture was diluted with 600 ml of cold water followed by ether extraction (3 x 100 ml). The ether layers were combined and washed successively with 10% NaOH (3 x 60 ml) and saturated NaCl (3 x 60 ml). After the organic layer was dried ($MgSO_4$) and concentrated, the crude product was purified by vacuum distillation (60-75°C, 2 torr) to give 2.9 g (17.9 mmol, 90%) of a mixture of colorless liquid 4a and 4b (ca. 2:1 by GC). 4a: ^{1}H NMR ($CDCl_3$) δ 6.95 (s, 4 H), 5.88 (t, 2 H, J = 3.3 Hz), 4.91 (d, 4 H, J = 3.6 Hz); IR (neat, NaCl), 3080, 3040, 2980, 2930, 2870, 1600, 1590, 1500, 1460, 1400, 1370, 1300, 1270, 1250, 1240, 1190, 1110, 1050, 1020, 1000, 980, 960, 780 cm^{-1}; GC/MS (70eV) m/e (% base peaks) 164 (0.4), 163 (5.18), 162 (47), 145 (11), 133 (26), 121 (41), 108 (11), 81 (9), 80 (100), 65 (8), 63 (8), 54 (46), 53 (20), 52 (55), 51 (17). 4b: ^{1}H NMR ($CDCl_3$) δ 6.93-6.80 (m, 4 H), 6.0-5.8 (m, 1 H), 5.64-5.46 (d, 1 H, J = 17.4 Hz), 5.46-5.36 (d, 1 H, J = 10.7 Hz), 4.70-4.55 (m, 1 H),

4.36-4.14 (d of d, 1 H), 4.01-3.81 (d of d, 1 H); GC/MS (70eV) m/e (% base peak) 164 (0.40), 163 (4.89), 162 (46.17), 145 (8), 133 (21), 121 (33), 108 (13), 81 (10), 80 (100), 63 (8), 54 (52), 53 (21), 52 (52), 51 (18), 50 (12). 4a + 4b; high resolution mass spectrum calculated for $C_{10}H_{10}O_2$ 162.06808, measured 162.06782.

The mixture of 8-t-butyl-2,5-dihydro-1,6-benzodioxocin (10a), 2-vinyl-6-t-butyl-2,3-dihydro-1,4-benzodioxine (10b), and 2-vinyl-7-t-butyl-2,3-dihydro-1,4-benzodioxine (10c) (10a,b,c)

Compounds 10a,b,c were prepared by reacting 3-t-butylcatechol (6d) with cis-1,4-dichloro-2-butene as described in the synthesis of 2,5-dihydro-1,6-benzodioxocin (4a) and 2-vinyl-2,3-dihydro-1,4-benzodioxine (4b). 10a,b,c (yield; 88%): ^{1}H NMR ($CDCl_3$) δ 7.1-6.8 (m, 3 H), 5.95-5.8 (m), 5.0-4.85 (d of d), 4.2-3.8 (m), 1.27 (s, 9 H); IR (neat, NaCl) 3040, 2960, 1575, 1500, 1410, 1360, 1300, 1270, 1240, 1130, 1010, 820, 720 cm^{-1}.

The mixture of 7,9-di-t-butyl-2,5-dihydro-1,6-benzodioxocin (11a), 2-vinyl-5,7-di-t-butyl-2,3-dihydro-1,4-benzodioxine (11b), and 2-vinyl-6,8-di-t-butyl-2,3-dihydro-1,4-benzodioxine (11c) (11a,b,c)

Compounds 11a,b,c were prepared by reacting 3,5-di-t-butylcatechol with cis-1,4-dichloro-2-butene as described in the synthesis of 4a and 4b. 11a,b,c (yield; 86%): ^{1}H NMR ($CDCl_3$) δ 7.1-6.75 (m), 6.1-5.8 (m), 5.7-5.3 (m), 5.0-4.6 (m),

4.2-4.35 (m), 3.95-3.80 (m), 1.41 (s), 1.37 (s), 1.29 (s), 1.28 (s); IR (neat, NaCl) 2960, 1600, 1490, 1420, 1360, 1310, 1240, 1050 cm^{-1}.

The mixture of 7-carbaldehyde-2,5-dihydro-1,6-benzodioxocin (8a), 2-vinyl-5-carbaldehyde-2,3-dihydrobenzodioxine (8b), and 2-vinyl-8-carbaldehyde-2,3-dihydrobenzodioxine (8c) (8a,b,c)

Compounds 8a,b,c were prepared by reacting 2,3-dihydroxybenzaldehyde (6b) with cis-1,4-dichloro-2-butene as described in the synthesis of 2,5-dihydro-1,6-benzodioxocin (4a) and 2-vinyl-2,3-dihydro-1,4-benzodioxine (4b). 8a,b,c (yield; 84%): ^1H NMR ($CDCl_3$) δ 10.39 (s), 10.37 (s), 7.60-6.90 (m), 6.00-5.85 (m), 5.60-5.40 (d of d), 5.13 (d, J = 5.7 Hz), 4.86 (d, J = 1.8 Hz), 4.40 (d of d), 4.05 (d of d); IR (neat, NaCl) 3060, 3020, 2960, 2900, 2850, 2700, 1680, 1590, 1580, 1470, 1440, 1390, 1360, 1250, 1200, 1150, 1070, 1000, 950, 910, 860, 780, 755, 710 cm^{-1}; mass spectrum (70eV) m/e (% base peak) 190 (100), 161 (9), 143 (13), 136 (45), 108 (41), 107 (23), 54 (44), 53 (18), 52 (32); high resolution mass spectrum calculated for $C_{11}H_{10}O_3$ 190.06300, measured 190.06290.

The mixture of 8-carbaldehyde-2,5-dihydro-1,6-benzodioxocin (9a), 2-vinyl-6-carbaldehyde-2,3-dihydro-1,4-benzodioxine (9b), and 2-vinyl-7-carbaldehyde-2,3-dihydro-1,4-benzodioxine (9c) (9a,b,c)

Compounds 9a,b,c were prepared by reacting 3,4-dihydroxybenzaldehyde (6c) with cis-1,4-dichloro-2-butene as described

in the synthesis of 2,5-dihydro-1,6-benzodioxocin (4a) and 2-vinyl-2,3-dihydro-1,4-benzodioxine (4b). 9a,b,c (yield; 83%): ^{1}H NMR ($CDCl_3$) δ 9.83 (s), 7.58-7.0 (m), 6.2-6.05 (m), 5.96-5.88 (m), 4.9-4.7 (m); IR (CCl_4) 1695, 1550, 1260, 1120, 1000, 800 cm^{-1}; mass spectrum (70eV) m/e (% base peak) 192 (1.4), 191 (11.9), 190 (100), 161 (14), 149 (59), 137 (7), 133 (25), 108 (20), 84 (8), 80 (28), 79 (24), 77 (8), 70 (7), 54 (91), 53 (20), 52 (15), 51 (22); high resolution mass spectrum calculated for $C_{11}H_{10}O_3$ 190.06300, measured 190.06341.

The mixture of 7-(1-hydroxy-5-hexenyl)-2,5-dihydro-1,6-benzodioxocin (13a), 2-vinyl-5-(1-hydroxy-5-hexenyl)-2,3-dihydro-1,4-benzodioxine (13b), and 2-vinyl-8-(1-hydroxy-5-hexenyl)-2,3-dihydro-1,4-benzodioxine (13c) (13a,b,c)

Compounds 13a,b,c were prepared by reacting 1.0 g (5.3 mmol) of aldehydes 8a,b,c with 4-pentenyl magnesium bromide using a standard procedure.[23] 13a,b,c (yield; 95%): ^{1}H NMR ($CDCl_3$) δ 7.1-6.8 (m, 4 H), 6.0-5.7 (m), 5.60-5.35 (d of d), 5.2-4.7 (m), 4.35-4.25 (d of d), 4.0-3.85 (d of d), 2.5-1.3 (m); IR (neat, NaCl) 3660-3220, 3100, 3040, 2990, 2940, 2880, 1685, 1650, 1600, 1480, 1460, 1273, 1250, 1200, 1100, 1075, 1035, 1005, 915, 790, 735 cm^{-1}.

The mixture of 7-(5-hexenoyl)-2,5-dihydro-1,6-benzodioxocin (18a), 2-vinyl-5-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18b), and 2-vinyl-8-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18c) (18a,b,c)

Compounds 18a,b,c were prepared by treating 1.0 g (3.8 mmol) of alcohols 13a,b,c with 1.9 g (5.0 mmol) of pyridinium dichromate (PDC)[24] followed by column chromatography on silica gel (30% ether in hexanes). 18a,b,c (yield; 93%): ^{1}H NMR ($CDCl_3$) δ 7.3-6.8 (m, 3 H), 6.0-5.73 (m), 5.6-5.4 (m), 5.1-4.8 (m), 4.4-4.3 (m), 4.0-3.9 (m), 2.92 (t, 2 H, J = 7.5 Hz), 2.15-2.05 (m, 2 H), 1.85-1.70 (m, 2 H); IR (neat, NaCl), 3080, 3040, 2980, 2930, 1680, 1645, 1580, 1460, 1370, 1256, 1215, 1080, 990, 950, 910, 790, 740 cm^{-1}; mass spectrum (70eV) m/e (% base peak) 258 (20), 205 (14), 204 (100), 190 (14), 189 (75), 161 (10), 137 (20), 108 (14), 107 (41), 69 (18), 54 (19), 53 (19); high resolution mass spectrum calculated for $C_{16}H_{18}O_3$ 258.1256, measured 258.1257.

The mixture of 7-(5-hexenyl)-2,5-dihydro-1,6-benzodioxocin (17a), 2-vinyl-5-(5-hexenyl)-2,3-dihydro-1,4-benzodioxine (17b), and 2-vinyl-8-(5-hexenyl)-2,3-dihydro-1,4-benzodioxine (17c) (17a,b,c)

Compounds 17a,b,c were prepared by reducing 520 mg of a mixture of 7-(1-bromo-5-hexenyl)-2,5-dihydro-1,6-benzodioxocin (68a), 2-vinyl-5-(1-bromo-5-hexenyl)-2,3-dihydro-1,4-benzodioxine (68b), and 2-vinyl-8-(1-bromo-5-hexenyl)-2,3-dihydro-1,4-benzodioxine (68c) (68a,b,c) with 62 mg of $LiAlH_4$. The

bromo compound 68a,b,c was prepared by reacting 540 mg of a mixture of 7-(1-hydroxy-5-hexenyl)-2,5-dihydro-1,6-benzodioxocin (13a), 2-vinyl-5-(1-hydroxy-5-hexenyl)-2,3-dihydro-1,4-benzodioxine (13b), and 2-vinyl-8-(1-hydroxy-5-hexenyl)-2,3-dihydro-1,4-benzodioxine (13c) (13a,b,c) with 0.65 ml of PBr_3 using a standard procedure.[25] 68a,b,c (yield; 78%): ^1H NMR ($CDCl_3$) δ 7.25-6.75 (m, 3 H), 6.0-5.65 (m), 5.55-5.30 (m), 5.10-4.50 (m), 4.4-4.2 (m), 4.0-3.85 (m), 2.35-1.3 (m); IR (neat, NaCl) 3080, 3040, 2980, 2940, 1640, 1590, 1470, 1270, 1075, 995, 910, 730 cm^{-1}. 17a,b,c (yield; 72%): ^1H NMR ($CDCl_3$) δ 7.0-6.65 (m), 6.0-5.7 (m), 5.6-5.3 (m), 5.1-4.5 (m), 4.4-4.2 (m), 4.0-3.8 (m), 2.59 (t, J = 7.6 Hz), 2.3-1.3 (m); IR (neat, NaCl) 3070, 2920, 2840, 1630, 1580, 1260, 1290, 1080, 1020, 920, 900, 770 cm^{-1}; GC/MS (70eV) m/e (% base peak) 245 (15), 244 (84), 242 (10), 188 (28), 177 (12), 176 (100), 147 (18), 147 (12), 123 (11), 122 (23), 120 (11), 107 (23), 105 (11), 94 (21), 92 (12), 91 (21), 79 (25), 78 (15), 77 (19); high resolution mass spectrum calculated for $C_{16}H_{20}O_2$ 244.1463, measured 244.1465.

The mixture of 8-(5-hexenoyl)-2,5-dihydro-1,6-benzodioxocin (19a), 2-vinyl-6-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (19b), and 2-vinyl-7-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (19c) (19a,b,c)

Compounds 19a,b,c were prepared by reacting a mixture of 8-carbaldehyde-2,5-dihydro-1,6-benzodioxocin, 2-vinyl-6-

carbaldehyde-2,3-dihydro-1,4-benzodioxine, and 2-vinyl-7-carbaldehyde-2,3-dihydro-1,4-benzodioxine (9a,b,c) with 4-pentenylmagnesium bromide followed by PDC oxidation[24] as described in the synthesis of 7-(5-hexenoyl)-2,5-dihydro-1,6-benzodioxocin, 2-vinyl-5-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine and 2-vinyl-8-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18a,b,c). 19a,b,c (yield; 81%): ^{1}H NMR ($CDCl_3$) δ 7.7-7.45 (m), 7.25-7.32 (m), 7.0-6.9 (m), 6.0-5.75 (m), 5.6-5.37 (m), 5.1-4.6 (m), 4.35-4.25 (m), 4.02-3.9 (m), 2.89 (t, J = 7.5 Hz), 2.13 (q, J = 7.6 Hz), 1.9-1.75 (m); IR (CCl_4) 3060, 2960, 2900, 1670, 1590, 1560, 1490, 1405, 1250, 1110, 1005 cm^{-1}; high resolution mass spectrum calculated for $C_{16}H_{18}O_3$ 258.1256, measured 258.1258.

1-Cyclopentene ethylalcohol (69)

Compound 69 was prepared by hydrolyzing 5 g of 1-cyclopentene acetonitrile with 100 ml of 1:1 mixture of methanol and 30% NaOH at 95°C for 24 h followed by $LiAlH_4$ reduction. 69 (yield; 65%): ^{1}H NMR ($CDCl_3$) δ 5.48 (s, 1 H), 3.72 (t, 2 H, J = 6.3 Hz), 2.40-2.20 (m, 6 H), 2.0-1.8 (m, 2 H), 1.57 (s, 1 H); IR (neat, NaCl) 3600-3080 (broad), 3030, 2910, 1660, 1430, 1030, 930, 800 cm^{-1}; [Lit.[26] IR (neat) 3450, 3050, 1645, 1030, 800 cm^{-1}].

2-(1-Cyclopentenyl)ethyl bromide (70)

Compound 70 was prepared by reacting 3 g of 69 with 8.3 ml of PBr_3 using a standard procedure.[25] 70 (yield; 70%): ^1H NMR ($CDCl_3$) δ 5.46 (s, 1 H), 3.61 (t, 2 H, J = 7.2 Hz), 2.56 (t, 2 H, J = 7.2 Hz), 2.4-2.3 (m, 4 H), 2.0-1.8 (m, 2 H); IR (neat, NaCl) 2960, 2870, 1445, 1185, 1060, 975 cm^{-1}; [Lit.[26] IR (neat) 3050, 1645 cm^{-1}].

The mixture of 7-acetyl-2,5-dihydro-1,6-benzodioxocin (21a), 2-vinyl-5-acetyl-2,3-dihydro-1,4-benzodioxine (21b), and 2-vinyl-8-acetyl-2,3-dihydro-1,4-benzodioxine (21c) (21a,b,c) and the mixture of 7-[3-(1-cyclopentenyl)-propanoyl]-2,5-dihydro-1,6-benzodioxocin (20a), 2-vinyl-5[3-(1-cyclopentenyl)-propanoyl]-2,3-dihydro-1,4-benzodioxine (20b), and 2-vinyl-8-[3-(1-cyclopentenyl)-propanoyl]-2,3-dihydro-1,4-benzodioxine (20c) (20a,b,c)

Compounds 21a,b,c and 20a,b,c were prepared by reacting 950 mg of aldehyde 8a,b,c with 500 mg of CH_3I and 457 mg of 2-(1-cyclopentenyl)ethyl bromide (70) followed by PDC oxidation as described in the preparation of the mixture of 7-(5-hexenoyl)-2,5-dihydro-1,6-benzodioxocin (18a), 2-vinyl-5-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18b), and 2-vinyl-8-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18c) (18a,b,c). The mixture of 20a,b,c and the mixture of 21a,b,c were separated by column chromatography on silica gel (5% ether in hexanes) to give 400 mg (2.0 mmol, 56%) of 21a,b,c and 450 mg (1.58 mmol, 45%) of 20a,b,c. 21a,b,c: ^1H NMR

($CDCl_3$) δ 7.4-7.25 (m), 7.16-7.03 (m), 6.97-6.83 (m), 6.0-5.85 (m), 5.6-5.35 (d of d), 5.05 (d, J = 5.7 Hz), 4.84 (d, J = 3 Hz), 4.45-4.35 (m), 4.05-3.90 (m), 2.60 (s), 2.58 (s); IR (NaCl, neat) 2960, 1670, 1580, 1460, 1435, 1260, 1205, 1070, 1000, 780, 720 cm^{-1}; mass spectrum (70eV) m/e (% base peak) 205 (12.3), 204 (89.1), 190 (9), 189 (57), 175 (9), 163 (42), 161 (17), 137 (10), 135 (12), 108 (100), 107 (26), 80 (10), 79 (9), 77 (9), 54 (33), 53 (16); high resolution mass spectrum calculated for $C_{12}H_{12}O_3$ 204.0786, measured 204.0781. 20a,b,c: ^1H NMR ($CDCl_3$) δ 7.43-6.75 (m), 6.0-5.8 (m), 5.6-5.25 (m), 5.1-5.0 (d, J = 5.8 Hz), 4.85-4.8 (d, J = 3 Hz), 4.8-4.6 (m), 4.4-4.25 (m), 4.0-3.9 (m), 3.2-3.0 (m), 2.65-1.7 (m); IR (NaCl, neat) 3080, 3040, 2920, 2840, 1675, 1640, 1590, 1460, 1270, 1090, 990, 930, 780, 730 cm^{-1}; mass spectrum (70eV) m/e (% base peak) 285 (3.3), 284 (15.7), 190 (18), 189 (100), 136 (7), 137 (12), 107 (14), 79 (11), 54 (7), 53 (9); high resolution mass spectrum calculated for $C_{18}H_{20}O_3$ 284.14125, measured 284.14089.

The mixture of 2,5-dihydro-1,6-naphthodioxocin (12a) and 2-vinyl-2,3-dihydro-1,4-naphthodioxine (12b) (12a,b)

Compounds 12a,b were prepared by reacting 2,3-dihydroxy-naphthalene with cis-1,4-dichloro-2-butene as described in the synthesis of 4a and 4b (yield; 91%). 12a: ^1H NMR ($CDCl_3$) δ 7.7-7.6 (m, 2 H), 7.5 (s, 2 H), 7.35-7.25 (m, 2 H), 5.8-5.9 (t, 2 H, J = 3 Hz), 4.95 (d, 4 H, J = 0.9 Hz); GC/MS (70eV)

m/e (% base peak) 214 (0.36), 213 (9.22), 212 (61.87), 183 (18), 172 (12), 171 (100), 131 (8), 130 (24), 127 (17), 115 (16), 114 (13), 103 (9), 102 (82), 77 (8), 76 (17), 75 (9), 63 (10), 53 (12), 52 (7), 51 (10), 50 (7), 39 (16). 12b: ^{1}H NMR ($CDCl_3$) δ 7.7-7.6 (m, 2 H), 7.35-7.25 (m, 4 H), 6.1-5.9 (m, 1 H), 5.6-5.5 (d, 1 H, J = 18.6 Hz), 5.45-5.38 (d, 1 H, J = 10.5 Hz), 4.8-4.7 (m, 1 H), 4.4-4.3 (d of d, 1 H), 4.1-4.0 (d of d, 1 H); IR (CCl_4) 3040, 2970, 2910, 2860, 1640, 1600, 1500, 1465, 1420, 1380, 1360, 1255, 1235, 1217, 1163, 1055, 1020, 980, 920, 880, 855, 810, 735 cm^{-1}; GC/MS (70eV) m/e (% base peak) 214 (1.08), 213 (11.58), 212 (80.70), 183 (16), 172 (11), 171 (100), 131 (9), 130 (27), 127 (17), 115 (14), 114 (13), 102 (78), 77 (9), 76 (18), 75 (9), 63 (10), 53 (14), 51 (11), 50 (8), 40 (8), 39 (14). 12a,b: high resolution mass spectrum calculated for $C_{14}H_{12}O_2$ 212.08373, measured 212.08371.

The mixture of 7-carbaldehyde-2,5-dihydro-1,6-naphthodioxocin (22a), 2-vinyl-5-carbaldehyde-2,3-dihydro-1,4-naphthodioxine (22b), and 2-vinyl-10-carbaldehyde-2,3-dihydro-1,4-naphthodioxine (22c) (22a,b,c)

Compounds 22a,b,c were prepared by reacting 1.9 g of a mixture of 2,5-dihydro-1,6-naphthodioxocin (12a) and 2-vinyl-2,3-dihydro-1,4-naphthodioxine (12b) with the solution of 1.5 ml of DMF and 2.5 ml of phosphorous oxychloride using a literature procedure.[12] 22a,b,c (1:0.8:1 by GC: yield; 69%):

^{1}H NMR ($CDCl_3$) δ 10.88 (s), 10.81 (s), 10.80 (s), 9.14 (d, J = 8.7 Hz), 7.7-7.2 (m), 6.1-5.9 (m), 5.6-5.4 (m), 5.28-5.18 (m), 4.9-4.7 (m), 4.5-4.0 (m); IR (neat, NaCl) 3050, 2980, 2930, 1680, 1510, 1460, 1360, 1250, 1210, 1180, 1160, 1120, 1060, 1020, 935, 910, 860, 750 cm^{-1}; mass spectrum (70eV) m/e (% base peak) 241 (10), 240 (65), 199 (60), 186 (15), 165 (11), 158 (22), 130 (17), 129 (11), 115 (26), 114 (14), 113 (13), 103 (13), 102 (100), 101 (22), 77 (13), 76 (27), 75 (28), 74 (12), 63 (18), 53 (24); high resolution mass spectrum calculated for $C_{15}H_{12}O_3$ 240.07865, measured 240.07873.

The mixture of 7-(4-pentenoyl)-2,5-dihydro-1,6-naphthodioxocin (24a), 2-vinyl-5-(4-pentenoyl)-2,3-dihydro-1,4-naphthodioxine (24b), and 2-vinyl-10-(4-pentenoyl)-2,3-dihydro-1,4-naphthodioxine (24c) (24a,b,c)

Compounds 24a,b,c were prepared by reacting 1.2 g of a mixture of 7-carbaldehyde-2,5-dihydro-1,6-naphthodioxocin (22a), 2-vinyl-5-carbaldehyde-2,3-dihydro-1,4-benzodioxine (22b), and 2-vinyl-10-carbaldehyde-2,3-dihydro-1,4-benzodioxine (22c) (22a,b,c) with 3-butenyl magnesium bromide followed by PDC oxidation as described in the preparation of the mixture of 7-(5-hexenoyl)-2,5-dihydro-1,6-benzodioxocin (18a), 2-vinyl-5-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18b), and 2-vinyl-8-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18c) (18a,b,c). 24a,b,c (yield; 57%): ^{1}H NMR ($CDCl_3$) δ 7.7-7.6 (m), 7.4-7.2 (m), 6.1-5.8 (m), 5.64-5.34 (m), 5.2-4.9

(m), 4.9-4.7 (m), 4.4-4.3 (m), 4.1-3.9 (m), 3.05 (t, J = 7 Hz), 2.52 (q, J = 7 Hz); IR (neat, NaCl) 3080, 2924, 1693, 1504, 1464, 1445, 1394, 1364, 1288, 1258, 1240, 1205, 1084, 1067, 1024, 937, 914, 872 cm^{-1}; mass spectrum (70eV) m/e (% base peak) 295 (6), 294 (28), 240 (18), 239 (100), 212 (34), 186 (11), 158 (19), 157 (97), 129 (25), 115 (13), 102 (16), 101 (28), 81 (15), 75 (14), 55 (37); high resolution mass spectrum calculated for $C_{19}H_{18}O_3$ 294.12560, measured 294.12577.

General pyrolysis procedure

General pyrolysis procedure has been previously described.[10]

Pyrolysis of the mixture of 2,5-dihydro-1,6-benzodioxocin (4a) and 2-vinyl-2,3-dihydro-1,4-benzodioxine (4b)

A 200 mg (1.2 mmol) quantity of a mixture of 4a and 4b was pyrolyzed at 680°C in the normal manner. GC and ^1H NMR analyses of the crude product mixture indicated that the dimer of cyclopentadienone (2) was formed as a major product along with dihydroindenone (5). Cyclopentadienone dimer (2) was crystallized from CCl_4. Cyclopentadienone dimer 2:[5] ^1H NMR δ 7.45-7.35 (d of d, 1 H, J = 2.4, J = 3.3 Hz), 6.45-6.15 (m, 3 H), 3.48-3.38 (m, 1 H), 3.42 (d of d, 1 H, J = 4.2 Hz), 3.22 (d of d, 1 H, J = 3.6 Hz, J = 4.2 Hz), 2.92 (d of d, 1 H, J = 5.4 Hz; J = 5.7 Hz); [Lit.[26] ^1H NMR ($CDCl_3$) δ 7.4 (m, 1 H),

6.3 (m, 3 H), 3.45 (m, 2 H), 3.2 (m, 1 H), 2.9 (t, 1 H)]; IR (CCl_4) 3020, 2920, 1800, 1720, 1340, 1290, 1180, 1090, 880 cm^{-1}; ^{13}C NMR δ 206.39, 199.45, 161.08, 141.62, 130.26, 128.18, 50.03, 49.18, 43.25, 41.51; GC/MS (70eV) m/e (% base peak) 134 (0.38), 133 (5.42), 132 (59.22), 131 (100), 104 (55), 103 (70), 102 (8), 91 (11), 78 (82), 77 (41), 76 (9), 74 (7), 63 (11), 54 (17), 52 (29), 51 (67), 50 (25). Dihydroindenone (5):[5] GC/MS (70eV) 134 (0.44), 133 (6.02), 132 (66.28), 131 (100), 104 (57), 103 (65), 102 (7), 91 (10), 78 (77), 77 (38), 76 (7), 63 (11), 54 (16), 52 (32), 51 (68), 50 (25).

Pyrolysis of the mixture of 8-t-butyl-2,5-dihydro-1,6-benzodioxocin (10a), 2-vinyl-6-t-butyl-2,3-dihydro-1,4-benzodioxine (10b), and 2-vinyl-7-t-butyl-2,3-dihydro-1,4-benzodioxine (10c) (10a,b,c)

A 60 mg (0.3 mmol) sample of the mixture of 10a,b,c was pyrolyzed at 690°C in the normal manner. During the pyrolysis, 2 ml of 1:1 $CS_2/CDCl_3$ was deposited into the product trap. After the pyrolysis was completed, the trap was warmed to -78°C. After transferring some of the product solution to NMR tubes at -78°C, the ^1H NMR spectrum was recorded (-60°C), indicating the presence of 1,3-butadiene and the 3-t-butylcyclopentadienone dimer (26). 1,3-butadiene: ^1H NMR (1:1 $CS_2/CDCl_3$, -60°C) δ 6.36-6.20 (m, 1 H), 5.24-5.00 (m, 2 H). 26: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 6.03 (s, 1 H), 5.77 (s, 1

H), 3.6-2.8 (m, 4 H), 1.20 (s, 9 H), 0.99 (s, 9 H); [Lit.[13] ^{1}H NMR (CCl_4) δ 6.0, 5.76, 3.62-3.08, 1.22, 1.0]; IR (neat, NaCl) 2980, 2880, 1790, 1695, 1600, 1470, 1370, 1295, 1215, 1120, 940 cm^{-1}; GC/MS (70eV) m/e (% base peak) 245 (0.6), 244 (5), 188 (17), 187 (14), 173 (15), 145 (6), 132 (39), 131 (28), 109 (6), 95 (16), 91 (13), 77 (7), 67 (20), 57 (100), 44 (9), 43 (12), 41 (38), 40 (12).

Pyrolysis of the mixture of 7,9-di-t-butyl-2,5-dihydro-1,6-benzodioxocin (11a), 2-vinyl-5,7-di-t-butyl-2,3-dihydro-1,4-benzodioxine (11b), and 2-vinyl-6,8-di-t-butyl-2,3-dihydro-1,4-benzodioxine (11c) (11a,b,c)

A 100 mg (0.4 mmol) quantity of the mixture of 11a,b,c was pyrolyzed at 690°C in the normal manner. GC and ^{1}H NMR spectral analyses of the crude product mixture indicated 2,4-di-t-butylcyclopentadienone (27) was formed as a major product (51% by GC). 27: ^{1}H NMR ($CDCl_3$) δ 6.50 (d, 1 H, J = 1.7 Hz), 4.96 (d, 1 H, J = 1.7 Hz), 1.09 (s, 9 H), 1.05 (s, 9 H); [Lit.[13] ^{1}H NMR (CCl_4) δ 6.50 (J = 1.7 Hz), 4.97 (J = 1.7 Hz), 1.18, 1.17]; IR (neat, NaCl) 2980, 1700, 1630, 1455, 1375, 1240 cm^{-1}.

Pyrolysis of the mixture of 7-acetyl-2,5-dihydro-1,6-benzodioxocin (21a), 2-vinyl-5-acetyl-2,3-dihydro-1,4-benzodioxine (21b), and 2-vinyl-8-acetyl-2,3-dihydro-1,4-benzodioxine (21c) (21a,b,c)

A 100 mg (0.5 mmol) quantity of the mixture of 21a,b,c was pyrolyzed at 680°C in the normal manner. GC and ^{1}H NMR

spectral analyses of the crude product mixture indicated the 2-acetylcyclopentadienone dimer (29) was formed as a major product (73%) along with other minor products (MW 204 and 216). 29: ^{1}H NMR ($CDCl_3$) δ 8.00 (d, 1 H, J = 3 Hz), 6.6-6.48 (d of d, 1 H), 6.30 (d, 1 H, J = 6.3 Hz), 4.0-3.9 (d of d, 1 H), 3.7-3.6 (t, 1 H, J = 4.2 Hz), 3.26-3.18 (m, 1 H), 2.40 (s, 3 H), 2.34 (s, 3 H); IR (neat, NaCl) 2920, 1800-1530 (br), 1450, 1430, 1370, 1240, 910, 730 cm^{-1}; GC/MS (70eV) m/e (% base peak) 216 (20), 201 (9), 174 (33), 173 (19), 132 (10), 131 (63), 130 (10), 115 (11), 102 (11), 76 (7), 75 (8), 63 (7), 51 (9), 43 (100).

Pyrolysis of the mixture of 2,5-dihydro-1,6-naphthodioxocin (12a) and 2-vinyl-2,3-dihydro-1,4-naphthodioxine (12b)

A 1.2 g (5.6 mmol) quantity of a mixture of 12a and 12b was pyrolyzed at 680°C in the normal manner. The low boiling pyrolysate was collected in $CHCl_3$ and concentrated. The ^{1}H NMR spectrum and GC analyses of the low boiling pyrolysate indicated that 2-ethylnaphthalene (33), 3,4-benzotricyclo-[3.2.1.$0^{2,7}$]octene (32), and 3-vinyl-1,2-dihydronaphthalene (34) were major products along with minor products such as naphthalene, dibenzo[a,e]cyclooctene, and 2-vinyl-naphthalene (42). The crude low boiling pyrolysate was purified by column chromatography on alumina (Woelm Activity I, hexanes). The high boiling pyrolysate was deposited on the pyrolysis quartz tube after the hot zone. The GC and GC/MS analyses showed

that the [4+4] dimer of inden-2-one (31a) was the major product. The compound 31a was purified by washing successively with hexanes and CCl_4. The white material in the pyrolysis tube was collected in $CHCl_3$ and the solvent was removed by vacuum to give the [4+4] dimer of inden-2-one (31a). 31a: ^{1}H NMR ($CDCl_3$) δ 7.47-7.30 (8 H, AA'BB' signal), 3.74 (4 H, s); IR ($CDCl_3$) 1777, 1455, 1370, 860 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 201.97, 138.72, 128.78, 124.17, 56.62; GC/MS (70eV) m/e (% base peak) 262 (0.28), 261 (2.49), 260 (14.52), 232 (21), 231 (16), 205 (13), 204 (84), 203 (84), 202 (53), 201 (8), 200 (9), 102 (52), 101 (100), 100 (17), 94 (11), 89 (37), 88 (26), 87 (7), 76 (32), 75 (14), 74 (8), 63 (20), 51 (13), 50 (11) high resolution mass spectrum calculated for $C_{18}H_{12}O_2$ 260.08373, measured 260.08400. 3,4-Benzotricyclo[3.2.1.$0^{2,7}$]-octene (32):[15,16] ^{1}H NMR ($CDCl_3$) δ 7.34-6.95 (m, 4 H), 3.03 (t, 1 H, J = 4.6 Hz), 2,13 (t, 1 H, J = 7.2 Hz), 1.84-1.78 (d of d, 2 H), 1.65 (d, 2 H, J = 6.9 Hz), 0.97 (d, 2 H, J = 11.4 Hz); [Lit.[16] ^{1}H NMR ($CDCl_3$) δ 7.13 (m, 4 H), 3.03 (t, 1 H, J = 4.9 Hz), 2.13 (t, 1 H, J = 7 Hz), 1.81 (m, 2 H), 1.65 (d, 2 H, J = 7 Hz), 0.98 (d, 2 H, J = 11.6 Hz)]; ^{13}C NMR ($CDCl_3$) δ 140.80, 134.76, 126.08, 125.72, 124.06, 122.94, 36.36, 28.66, 18.67, 15.88; IR (neat, NaCl) 3020, 2915, 2840, 1480, 1450, 1367, 1303, 1250, 1180, 1080, 1015, 980, 925, 847, 740 cm^{-1}; GC/MS (70eV) m/e (% base peak) 157 (9.56), 156 (76.39), 155 (28.39), 153 (16), 152 (12), 142 (9), 141 (73), 129 (37), 128

(100), 127 (19), 115 (50), 78 (8), 77 (14), 76 (12), 71 (11), 63 (10), 51 (12), 44 (19); high resolution mass spectrum calculated for $C_{12}H_{12}$ 156.09390, measured 156.09376; methane chemical ionization mass spectrum (70eV, 0.13 torr), 197 (0.6), 185 (6.3), 158 (11.43), 157 (100), 156 (99), 155 (19), 141 (19), 129 (35), 128 (38), 115 (13). 2-Ethylnaphthalene (33): ^{1}H NMR ($CDCl_3$) δ 7.90-7.71 (m, 3 H), 7.61 (s, 1 H), 7.50-7.37 (m, 3 H), 2.80 (q, 2 H, J = 7.5 Hz), 1.32 (t, 3 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 141.71, 133.69, 131.90, 127.76, 127.55, 127.37, 127.03, 125.77, 125.50, 124.95, 29.05, 15.50; [Lit.[27] ^{13}C NMR ($CDCl_3$) for ethyl group; δ 29.08, 15.54]; GC/MS (70eV) m/e (% base peak) 158 (0.70), 157 (12.48), 156 (100), 155 (30), 153 (13), 152 (11), 142 (8), 141 (72), 129 (29), 128 (88), 127 (15), 115 (53), 78 (7), 77 (15), 76 (12), 70 (12), 63 (9), 51 (11). 3-Vinyl-1,2-dihydronaphthalene (34): ^{1}H NMR ($CDCl_3$) δ 7.2-7.0 (m, 4 H), 6.59-6.48 (d of d, 1 H), 6.43 (s, 1 H), 5.33 (d, 1 H, J = 17.4 Hz), 5.13 (d, 1 H, J = 10.8 Hz), 2.85 (t, 2 H, J = 8.1 Hz), 2.46 (t, 2 H, J = 8.1 Hz); IR (CCl_4) 3080, 3050, 3010, 2920, 2870, 2820, 1617, 1600, 1590, 1480, 1445, 1430, 1265, 1190, 1150, 1100, 1020, 980, 930, 875, 850, 770, 745, 710 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 138.49, 137.63, 135.63, 134.49, 128.11, 127.20, 126.98, 126.48, 125.76, 112.65, 27.73, 22.35; GC/MS (70eV) m/e (% base peak) 158 (1.0), 157 (12.81), 156 (100), 155 (30.88), 154 (9), 153 (17), 152 (15), 141 (58), 129 (24), 128 (52), 127 (12), 115

(46), 78 (9), 77 (15), 76 (13), 63 (9), 51 (10), 44 (11); high resolution mass spectrum calculated for $C_{12}H_{12}$ 156.09390, measured 156.09382. Dibenzo[a,e]cyclooctene: ^{1}H NMR ($CDCl_3$) δ 7.17-6.97 (AA'BB', 8 H), 6.74 (s, 4 H); [Lit.[28] ^{1}H NMR ($CDCl_3$) δ 7.04, 6.74]; GC/MS (70eV) m/e (% base peak) 205 (15.35), 204 (100), 203 (100), 202 (44), 201 (8), 200 (6), 176 (7), 102 (11), 101 (33), 89 (8), 88 (7), 76 (11). 2-Vinylnaphthalene (42): ^{1}H NMR ($CDCl_3$) δ 7.90-7.40 (m, 7 H), 6.98-6.80 (d of d, 1 H), 5.88 (d, 1 H, J = 17.4 Hz), 5.34 (d, 1 H, J = 11.1 Hz); [Lit.[29] ^{1}H NMR δ 7.9-7.0 (m), 6.9-6.6 (m), 5.8 (d), 5.3 (d)]; GC/MS (70eV) m/e (% base peak) 156 (1.35), 155 (12.65), 154 (100), 153 (49), 152 (33), 151 (11), 128 (10), 77 (20), 76 (40), 75 (10), 64 (13), 63 (14), 51 (10), 50 (6).

Pyrolysis of the mixture of 7-(5-hexenyl)-2,5-dihydro-1,6-benzodioxocin (17a), 2-vinyl-5-(5-hexenyl)-2,3-dihydro-1,4-benzodioxine (17b), and 2-vinyl-8-(5-hexenyl)-2,3-dihydro-1,4-benzodioxine (17c) (17a,b,c)

A 150 mg (0.6 mmol) quantity of the mixture of 17a,b,c was pyrolyzed at 680°C in the normal manner. ^{1}H NMR, GC, and GC/MS analyses of the crude product mixture indicated three hexahydronaphthalenes (42:10:29 by GC) were formed as major products (81%) along with tetralin (7% by GC). Hexahydronaphthalenes: GC/MS (70eV) m/e (% base peak) #1: 136 (0.21), 135 (5.62), 134 (45.44), 119 (30), 106 (20), 105 (25), 93

(15), 92 (48), 91 (100), 79 (14), 78 (17), 77 (15), 65 (11), 57 (8), 44 (16). #2: 136 (0.33), 135 (4.80), 134 (52.83), 119 (36), 106 (24), 105 (26), 93 (31), 92 (60), 91 (100), 79 (21), 78 (22), 77 (27), 65 (14), 51 (11), 41 (16). #3: 136 (0.27), 135 (5.88), 134 (60), 133 (9), 119 (46), 106 (21), 105 (29), 93 (15), 92 (44), 91 (100), 79 (16), 78 (15), 77 (21), 65 (13), 51 (10), 41 (17).

Preparation of tetralin (36) from the pyrolysis products of 17a,b,c

The pyrolysis products of 17a,b,c (150 mg) in 2 ml of EtOH in the presence of 30 mg of 5% Pd/C was stirred at room temperature for 15 h. GC and GC/MS analyses indicated a 92% yield of tetralin (36) was formed by the reaction. 36: ^{1}H NMR ($CDCl_3$) δ 7.06 (s, 4 H), 2.76 (t, 4 H, J = 6 Hz), 1.79 (t, 4 H, J = 6 Hz); [Lit.[30] ^{1}H NMR δ 7.0 (s), 2.70 (m), 1.9-1.6 (m)]; GC/MS (70eV) m/e (% base peak) 134 (0.44), 133 (5.50), 132 (57), 131 (13), 117 (14), 115 (13), 104 (100), 91 (54), 78 (10), 77 (9), 65 (15), 64 (11), 51 (11).

Hydrogenation of the pyrolysis products of 17a,b,c

This was carried out using 5% Pd/C in ethanol solution at 60 psi hydrogen for 3 h. GC and GC/MS analyses indicated a 38% yield of cis-decalin, a 13% yield of trans-decalin, a 33% yield of 1,2,3,4,5,6,7,8-octahydronaphthalene, and a 13% yield of tetralin was formed by the hydrogenation. cis-Decalin:[31]

GC/MS (70eV) m/e (% base peak) 140 (0.52), 139 (10.77), 138 (97.58), 110 (9), 109 (17), 97 (10), 96 (82), 95 (61), 83 (18), 82 (85), 81 (66), 79 (12), 69 (42), 68 (95), 67 (100), 66 (11), 55 (34), 54 (17), 53 (12), 41 (58). trans-Decalin:[31] GC/MS (70eV) m/e (% base peak) 140 (0.21), 139 (7.29), 138 (65.38), 110 (9), 109 (27), 97 (10), 96 (93), 95 (43), 83 (11), 82 (78), 81 (97), 79 (12), 69 (18), 68 (37), 67 (100), 55 (38), 54 (21), 53 (14), 44 (13), 41 (62). 1,2,3,4,5,6,7,8-Octahydronaphthalene:[32] GC/MS (70eV) m/e (% base peak) 138 (0.59), 137 (10.79), 136 (100), 121 (42), 108 (30), 107 (53), 95 (76), 94 (84), 93 (68), 91 (34), 81 (17), 80 (35), 79 (95), 78 (13), 77 (26), 68 (11), 67 (47), 66 (10), 65 (13), 55 (11), 53 (14), 41 (34).

Pyrolysis of the mixture of 7-(5-hexenoyl)-2,5-dihydro-1,6-benzodioxocin (18a), 2-vinyl-5-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18b), and 2-vinyl-8-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (18c) (18a,b,c)

A 300 mg (1.2 mmol) quantity of a mixture of 18a,b,c was pyrolyzed at 680°C in the normal manner. GC and GC/MS analyses of the crude product mixture indicated a total of 83% yield of tetrahydronaphthalenones (46:34:3 by GC) and α-tetralone (10%) were formed in the pyrolysis. The mixture of 3,4,5,6-tetrahydro-1-(2H)-naphthalenone (38) and 3,4,7,8-tetrahydro-1-(2H)-naphthalenone (39) was separated from α-tetralone (37) and one unknown tetrahydronaphthalenone

by thin layer chromatography on silica gel (10% ether in hexanes). 38: ^{1}H NMR ($CDCl_3$) δ 6.2-6.3 (d of t, 1 H), 5.9-6.0 (d of t, 1 H), 2.5-1.9 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 198.27, 149.79, 128.70, 127.80, 124.86, 37.71, 29.27, 23.23, 22.42, 18.09; GC/MS (70eV) m/e (% base peak) 150 (0.44), 149 (5.66), 148 (51.88), 147 (29), 130 (8), 129 (9), 121 (7), 120 (84), 105 (38), 92 (31), 91 (100), 78 (16), 77 (15), 65 (16), 52 (7), 51 (16), 41 (12); GC/IR 3047, 2947, 2889, 2843, 1682, 1574, 1427, 1404, 1369, 1346, 1319, 1285, 1258, 1234, 1188, 1134, 1115, 1011, 949, 876, 860, 845, 829, 798, 771, 756, 729 cm^{-1}. 39: ^{1}H NMR ($CDCl_3$) δ 6.51 (d, 1 H, J = 9.9 Hz), 5.83-5.77 (d of t, 1 H), 2.5-1.9 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 195.92, 155.45, 135.57, 129.63, 119.85, 37.67, 31.06, 29.06, 22.36, 21.71; GC/MS (70eV) m/e (% base peak) 150 (0.48), 149 (6.94), 148 (65.2), 147 (19), 120 (69), 106 (9), 105 (35), 104 (13), 92 (40), 91 (100), 79 (10), 78 (16), 77 (18), 65 (17), 52 (8), 51 (17), 41 (12), 39 (26); GC/IR 3047, 2947, 2889, 2847, 1697, 1443, 1427, 1400, 1281, 1053, 1011 cm^{-1}. 38 + 39: high resolution mass spectrum calculated for $C_{10}H_{12}O$ 148.0888, measured 148.0886. α-Tetralone (37): ^{1}H NMR ($CDCl_3$) δ 8.03 (d, 1 H, J = 7.8 Hz), 7.47-7.2 (m, 3 H), 2.97 (t, 2 H, J = 6 Hz), 2.66 (t, 2 H, J = 6.5 Hz), 2.14 (m, 2 H); [Lit.[33] ^{1}H NMR ($CDCl_3$) δ 8.0 (d), 7.6-7.0 (m), 3.0-1.8 (m)]; GC/MS (70eV) m/e (% base peak) 148 (0.8), 147 (7), 146 (63), 131 (13), 118

(100), 117 (9), 115 (14), 91 (13), 90 (72), 89 (25), 77 (7), 65 (8), 63 (16), 58 (15), 51 (14), 39 (17).

Pyrolysis of the mixture of 8-(5-hexenoyl)-2,5-dihydro-1,6-benzodioxocin (19a), 2-vinyl-6-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (19b), and 2-vinyl-7-(5-hexenoyl)-2,3-dihydro-1,4-benzodioxine (19c) (19a,b,c)

A 300 mg (1.2 mmol) quantity of a mixture of 19a,b,c was pyrolyzed at 680°C in the normal manner. GC and GC/MS analyses indicated an 11% yield of α-tetralone. A total of 45% yield of a mixture of six isomers of MW 148 and a total of 6% yield of a mixture of four isomers of MW 176 were formed in the pyrolysis. α-Tetralone and a mixture of four isomers of MW 148 were separated from the crude pyrolysis products by thin layer chromatography on silica gel (10% ether in hexanes). A mixture of four isomers of MW 148: ^{1}H NMR ($CDCl_3$) (Fig. 7) δ 7.76 (d, J = 7.5 Hz), 7.59 (t, J = 7.5 Hz), 7.50-7.25 (m), 6.51 (d, J = 9.9 Hz), 6.2-6.3 (d of t), 5.9-6.0 (d of t), 5.83-5.77 (d of t), 3.20-1.95 (m); GC/MS (70eV) m/e (% base peak) #1: 150 (0.04), 149 (0.61), 148 (5.64), 105 (13), 104 (100), 92 (6), 91 (41), 78 (7), 77 (7), 65 (13), 51 (6). #2 (38): 150 (0.33), 149 (4.86), 148 (44.44), 133 (7), 119 (7), 106 (38), 105 (56), 103 (9), 92 (50), 91 (100), 79 (14), 78 (10), 77 (22), 65 (15), 51 (17). #3: 150 (0.32), 149 (4.20), 148 (40.33), 147 (24), 129 (9), 120 (77), 105 (39), 92 (30), 91 (100), 78 (17), 77 (16), 65 (18), 57 (10),

51 (16). #4 (39): 150 (0.36), 149 (5.76), 148 (54.98), 133 (11), 106 (63), 105 (67), 92 (57), 91 (100), 79 (16), 78 (10), 77 (24), 65 (15), 59 (9), 51 (17). GC/IR #1: 1744, 1612, 1319, 1273, 1015, 818, 806, 748, 717 cm^{-1}. #2 (38): 3047, 2947, 2889, 2843, 1682, 1574, 1404, 1369, 1319, 1285, 1188, 1134, 729 cm^{-1}. #3: 2935, 1740, 1601, 1288, 1265, 1045, 1003, 891, 802, 779, 733 cm^{-1}. #4 (39): 3047, 2947, 1697, 1443, 1427, 1400, 1281, 1053, 1011 cm^{-1}.

Preparation of α-tetralone (37) from the pyrolysis products of the mixture of 19a,b,c

A 300 mg (1.2 mmol) quantity of a mixture of 19a,b,c was pyrolyzed at 680°C in the normal manner. The pyrolysate was taken up in 15 ml of benzene. To this solution 272 mg (1.2 mmol) of DDQ was added in one portion at room temperature. The reaction mixture was heated to reflux for 2 h. After cooling, the solution was filtered through silica gel. The filtrate was concentrated and purified by thin layer chromatography on silica gel (10% ether in hexanes) to give 45 mg (0.31 mmol; 26%) of α-tetralone (37).

Pyrolysis of the mixture of 7-[3-(1-cyclopentenyl)-propanoyl]-2,5-dihydro-1,6-benzodioxocin (20a), 2-vinyl-5-[3-(1-cyclopentenyl)-propanoyl]-2,3-dihydro-1,4-benzodioxine (20b), and 2-vinyl-8-[3-(1-cyclopentenyl)-propanoyl]-2,3-dihydro-1,4-benzodioxine (20c) (20a,b,c)

A 50 mg (0.18 mmol) quantity of a mixture of 20a,b,c was pyrolyzed at 660°C in the normal manner. The ^{1}H NMR spectrum, GC and GC/MS analyses of the crude product mixture indicated a 40% yield of 2H-3,5a,6,7,8,8a-hexahydro-as-indacen-1-one (40) and a total of 10% yield of two isomers of MW 174 were formed in the pyrolysis. GC/MS (70eV) m/e (% base peak) #1: 176 (0.20), 175 (4.63), 174 (40.94), 146 (21), 145 (66), 132 (40), 131 (32), 130 (16), 119 (10), 118 (65), 117 (81), 116 (10), 115 (38), 105 (14), 104 (100), 103 (21), 91 (40), 90 (11), 89 (13), 78 (23), 77 (27), 65 (16), 63 (15), 58 (13), 56 (34), 51 (21). #2: 175 (3.99), 174 (33.08), 146 (16), 145 (100), 132 (11), 131 (11), 117 (20), 116 (10), 115 (38), 91 (22), 77 (9), 65 (7), 51 (8). #3 (40): 176 (0.41), 175 (7.30), 174 (56.19), 146 (28), 145 (64), 132 (42), 131 (33), 130 (15), 118 (59), 117 (82), 116 (11), 115 (33), 105 (15), 104 (100), 103 (21), 91 (34), 79 (9), 78 (21), 77 (27), 65 (15), 63 (14), 58 (10), 51 (19); ^{1}H NMR ($CDCl_3$) δ 6.09 (d, J = 9.6 Hz), 5.82-5.71 (d of d), 3.0-2.1 (m) (see Fig. 8).

Pyrolysis of the mixture of 7-(4-pentenoyl)-2,5-dihydro-1,6-naphthodioxocin (24a), 2-vinyl-5-(4-pentenoyl)-2,3-dihydro-1,4-naphthodioxine (24b), and 2-vinyl-10-(4-pentenoyl)-2,3-dihydro-1,4-naphthodioxine (24c) (24a,b,c)

A 50 mg (0.17 mmol) quantity of a mixture of 24a,b,c was pyrolyzed at 660-670°C in the normal manner. The ^{1}H NMR and GC analyses of the crude product mixture indicated 2,3,4,5-tetrahydro-1H-benz[e]inden-1-one (41) (60%) and 2-vinylnaphthalene (42) (20%) were formed as major products along with other minor products (naphthalene and three isomers of MW 238). The crude product mixture was purified by thin layer chromatography on silica gel (10% ether in hexanes) to give 41 and 42. 41: mp 94-96°C; ^{1}H NMR ($CDCl_3$) δ 8.24 (d, 1 H, J = 7.5 Hz), 7.3-7.1 (m, 3 H), 2.96 (t, 2 H, J = 7.8 Hz), 2.8-2.5 (m, 6 H); IR (CCl_4) 2920, 1705, 1510, 1220 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 205.93, 174.64, 134.94, 134.37, 129.12, 127.80, 127.47, 126.73, 123.99, 35.89, 29.24, 27.67, 27.10; GC/MS (70eV) m/e (% base peak) 186 (0.77), 185 (10.23), 184 (100), 156 (25), 155 (22), 153 (12), 152 (13), 142 (27), 140 (82), 129 (27), 128 (75), 127 (22), 126 (10), 115 (40), 78 (14), 77 (18), 76 (16), 75 (11), 64 (13), 63 (18), 51 (17); high resolution mass spectrum calculated for $C_{13}H_{12}O$ 184.08882, measured 184.08861.

REFERENCES

1. Alder, K.; Flock, F. H. Chem. Ber. 1954, 87, 1916.

2. a. DeJongh, D. C.; Van Fossen, R. Y.; Bourgeois, C. F. Tetrahedron Lett. 1967, 271.

   b. DeJongh, D. C.; Fossen, R. Y. V. J. Org. Chem. 1972, 37, 1129.

3. DeJongh, D. C.; Brent, D. A. J. Org. Chem. 1970, 35, 4204.

4. Hageman, H. J.; Wiersum, U. E. Chem. Ber. 1973, 9, 206.

5. Depuy, C. H.; Jsaks, M.; Eilers, K. L.; Morris, G. J. Org. Chem. 1964, 29, 3503.

6. Chapman, O. L.; McIntosh, C. L. J. Chem. Soc. 1971, 770.

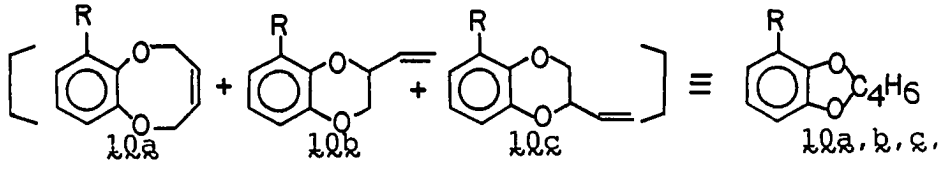
7. Gavinã, H.; Costero, A. M.; Cil, P.; Palozón, B.; Luis, S. V. J. Am. Chem. Soc. 1981, 103, 1797.

8. Koenig, T.; Smith, M.; Snell, W. J. Am. Chem. Soc. 1977, 99, 6663.

9. Maier, G.; Frany, L. H.; Hartan, H. G.; Lary, K.; Reisenauer, H. P. Chem. Ber. 1985, 118, 3196.

10. Lee, S. K. Ph. D. Dissertation, Part II, Iowa State University, 1987.

11. There are three isomers.



12. Chatterjea, J. N.; Prasad, N. Chem. Ber. 1964, 1252.

13. Garbish, E. W.; Sprecher, R. F. J. Am. Chem. Soc. 1969, 91, 6785.

14. Jones, D. W.; Pomfret, A.; Wife, R. L. J. Chem. Soc. Perkin Trans I, 1983, 459.

15. Hahn, R. C.; Rothman, L. J. J. Am. Chem. Soc. 1969, 91, 2409.

16. Morrison, H.; Muthuramu, K.; Pandey, G.; Severance, D.; Bigot, B. J. Org. Chem. 1986, 51, 3358.

17. Holland, J. M.; Jones, D. W. J. Chem. Soc. (C) 1971, 608.

18. Jones, D. W.; Pomfret, A. J. Chem. Soc. Chem. Commun. 1983, 703.

19. Baraldi, P. G.; Barco, A.; Benetti, S.; Pollini, G. P.; Polo, E.; Simoni, D. J. Chem. Soc. Chem. Commun. 1984, 1049.

20. If it obtained, this would be the smallest metacyclophane known. For 5-metacyclophane see; Turkenburg, L. A. M.; Wolf, W. H.; Bickelhaupt, F. Tetrahedron Lett. 1983, 24, 1817 and references therein.

21. Straten, J. W.; Wolf, W. H.; Bickelhaupt, F. Tetrahedron Lett. 1977, 4667.

22. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. J. Org. Chem. 1971, 36, 3575.

23. Blatt, A. H. "Organic Syntheses Collective Volume II", John Wiley & Sons, Inc.: New York, 1944; p. 406.

24. Corey, E. J.; Schmidt, G. Tetrahedron Lett. 1979, 399.

25. Bergmann, E. D.; Pelchowicz, Z. J. Am. Chem. Soc. 1953, 75, 4281.

26. Kato, H.; Miyamoto, N.; Kawanisi, M. Tetrahedron 1970, 26, 2975.

27. Adcock, W.; Kiching, W.; Alberts, V.; Wickham, G.; Doddrell, D. Org. Mag. Reson. 1977, 10, 47.

28. Buchan, G. W.; McCarville, A. R. Can. J. Chem. 1973, 51, 177.

29. Pouchert, C. J. "The Aldrich Library of NMR Spectra, Edition II, Vol. 1", Aldrich Chemical Co.: Milwaukee, 1983; p. 758, spectra D.

30. Pouchert, C. J. "The Aldrich Library of NMR Spectra, Edition II, Vol. 1", Aldrich Chemical Co.: Milwaukee, 1983; p. 738, spectra D.

31. Whitesides, G. M.; Gutowski, F. D. J. Org. Chem. 1976, 41, 2882.

32. Becker, K. B. Helv. Chim. Acta 1977, 60, 68.

33. Pouchert, C. J. "The Aldrich Library of NMR Spectra, Edition II, Vol. 2", Aldrich Chemical Co.: Milwaukee, 1983; p. 14, spectra B.

GENERAL SUMMARY

In Part I, the intramolecular Diels-Alder reactions of 2,3-dimethylene-2,3-dihydrofurans have been investigated through the pyrolysis of 2-alkenyl-3-furylmethyl benzoates. Under FVP conditions each of the 2,3-dimethylene-2,3-dihydrofurans can undergo an intramolecular Diels-Alder reaction or a 1,5-hydrogen shift to give the corresponding tricyclics 4c,t, 5c,t, and 6c,t and 1,5-hydrogen shift products 36c,t and 37c,t.

In Part II, FVP of 1,5-dibenzocyclooctadienes containing heteroatoms and dibenzosuberanes were carried out. The FVP of 1,5-dibenzocyclooctadienes and dibenzosuberanes gave the corresponding tricyclic aromatic compounds [benzodifuran (18), acridine (24), and anthracene] with the exception of 6H,11H-dibenzo[b,f][1,4]-dioxocin (17). The FVP of 17 gave (2-hydroxybenzyl)-o-benzaldehyde (28) as a major product.

In Part III, the formation of 9-methylanthracene from the sealed tube pyrolysis of the [4+4] dimer of o-xylylene (1) was investigated. The sealed tube pyrolysis of the "transoid" [4+4] dimer 3 gave 2,6,9-trimethylanthracene (21) and the "cisoid" [4+4] dimer 4 gave a 1:1 mixture of 2,7,9-trimethylanthracene (22) and 2,7,10-trimethylanthracene (23). These results are different from those obtained in the gas-phase pyrolysis. Pyrolysis of 5-methyldibenzosuberane gave 9-methylanthracene. From the results of the study, a

mechanism for the regiospecific formation of 9-methyl-anthracene from 1 is proposed.

In Part IV, a new method of preparing cyclopentadienones is presented. Cyclopentadienones including inden-2-one were utilized in the synthesis of polycyclic compounds. The transient existence of these intermediates has also been proven by the isolation of polycyclic compounds.

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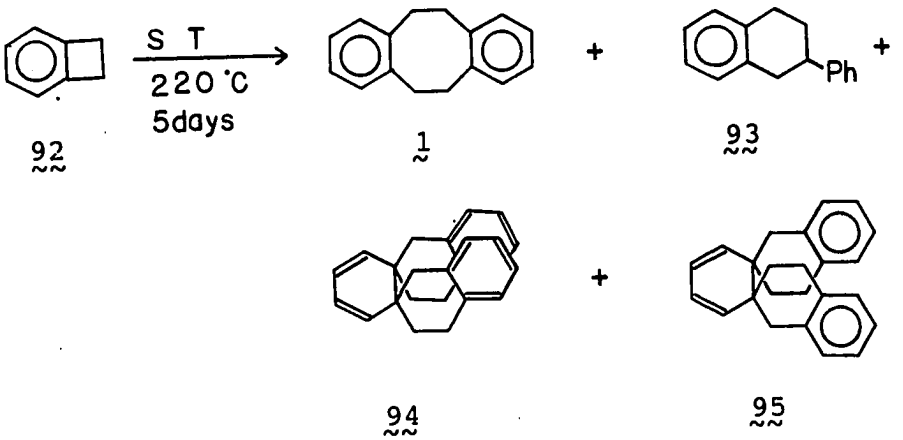
Above all, I would like to thank my parents.

APPENDIX I

Characterization of the Pyrolysis Products of Benzocyclobutene (92)

The [4+4] dimer of o-xylylene (1) is prepared by the pyrolysis of benzocyclobutene (2) in a sealed tube.[3] We observed one isomer of 1 and two trimers of o-xylylene as additional products in a sealed tube pyrolysis of benzocyclobutene (92).

We set out to identify these products because it was believed that the identification of these products could give a better understanding of the formation of anthracene (2) from FVP of 1 and FVP of 92.[1,2] The [4+4] dimer of o-xylylene (1)



92 → 1 + 93 + 94 + 95

and 94 were separated by fractional crystallization from hexanes. 2-Phenyltetralin (93) and a 4:6 mixture of 1 and 95 were separated from the remaining solution by column chromatography on alumina (Woelm, Activity 1, hexanes). 93: ^{1}H NMR ($CDCl_3$) (Fig. 1) δ 7.33-6.92 (m, 9 H), 3.05-2.80 (m, 5

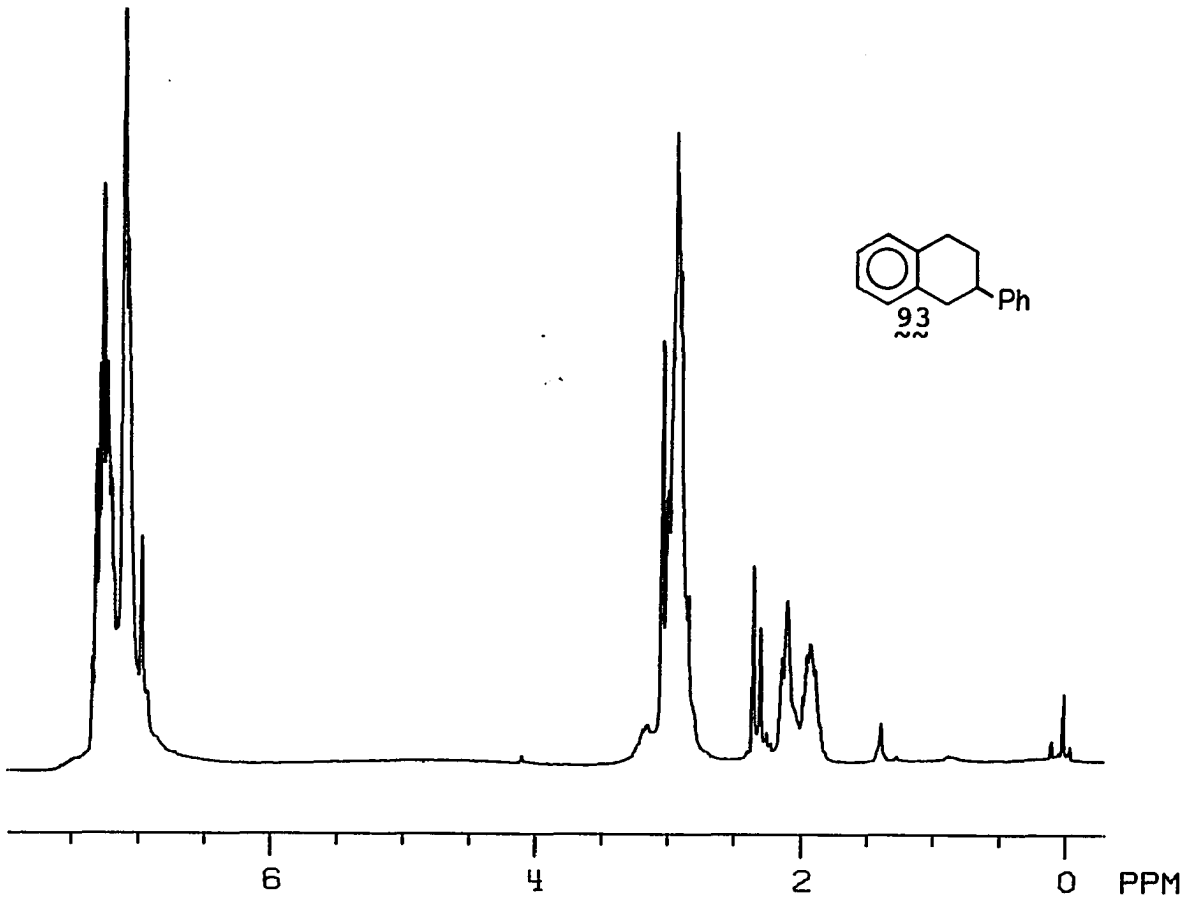


Figure 1. ^{1}H NMR spectrum of 2-phenyltetralin (93)

H), 2.4-1.8 (m, 2 H); [Lit.[38] ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 5 H), 6.9 (br s, 4 H), 3.0 (m, 5 H), 2.1 (m, 2 H)]; ^{13}C NMR ($CDCl_3$) δ 146.59, 136.60, 136.10, 128.97, 128.86, 128.80, 128.44, 126.83, 126.15, 126.06, 125.70, 125.60, 40.74, 37.73, 30.38, 29.75; IR (neat) 3060, 3020, 2910, 2830, 1600, 1570, 1490, 1440, 740, 690 cm^{-1}; GC/MS (70eV) m/e (% base peak) 210 (0.25), 209 (3.20), 208 (19.24), 130 (19), 115 (9), 105 (8), 104 (100), 103 (11), 91 (12), 78 (11). 94: mp 116-117°C; ^{1}H NMR ($CDCl_3$) (Fig. 2) δ 7.2-6.9 (m, 8 H), 5.92-5.82 (d of d, 2 H), 5.68-5.60 (d of d, 2 H), 3.05-2.95 (m, 8 H), 2.2-2.05 (m, 2 H), 1.75-1.60 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 136.23, 136.12, 133.46, 129.98, 128.44, 125.72, 125.66, 122.91, 39.21, 33.98, 28.59, 25.28; IR (CCl_4) 3050, 3010, 2910, 2830, 1570, 1480, 1440, 1330, 1290, 1230, 1170, 1100, 950, 900, 820, 730, 700 cm^{-1}; GC/MS (70eV) m/e (% base peak) 314 (1.61), 313 (13.22), 312 (53.77), 208 (18), 207 (100), 193 (25), 192 (11), 179 (13), 178 (16), 165 (9), 141 (9), 192 (15), 128 (15), 118 (14), 117 (23), 115 (25), 105 (19), 104 (12), 91 (14); high resolution mass spectrum calculated for $C_{24}H_{24}$ 312.18781, measured 312.18769. 95: ^{1}H NMR ($CDCl_3$) (Fig. 3) δ 7.2-7.05 (m, 8 H), 5.92-5.86 (d of d, 2 H), 5.55-5.48 (d of d, 2 H), 2.93-2.63 (m, 8 H), 2.30-2.20 (m, 2 H), 1.65-1.50 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 136.60, 135.20, 133.04, 130.56, 128.67, 125.62, 125.57, 122.82, 38.93, 33.74, 26.82, 25.27; IR (neat) 3060, 3020, 2920, 1590, 1570, 1480, 1440, 1420, 730, 690 cm^{-1};

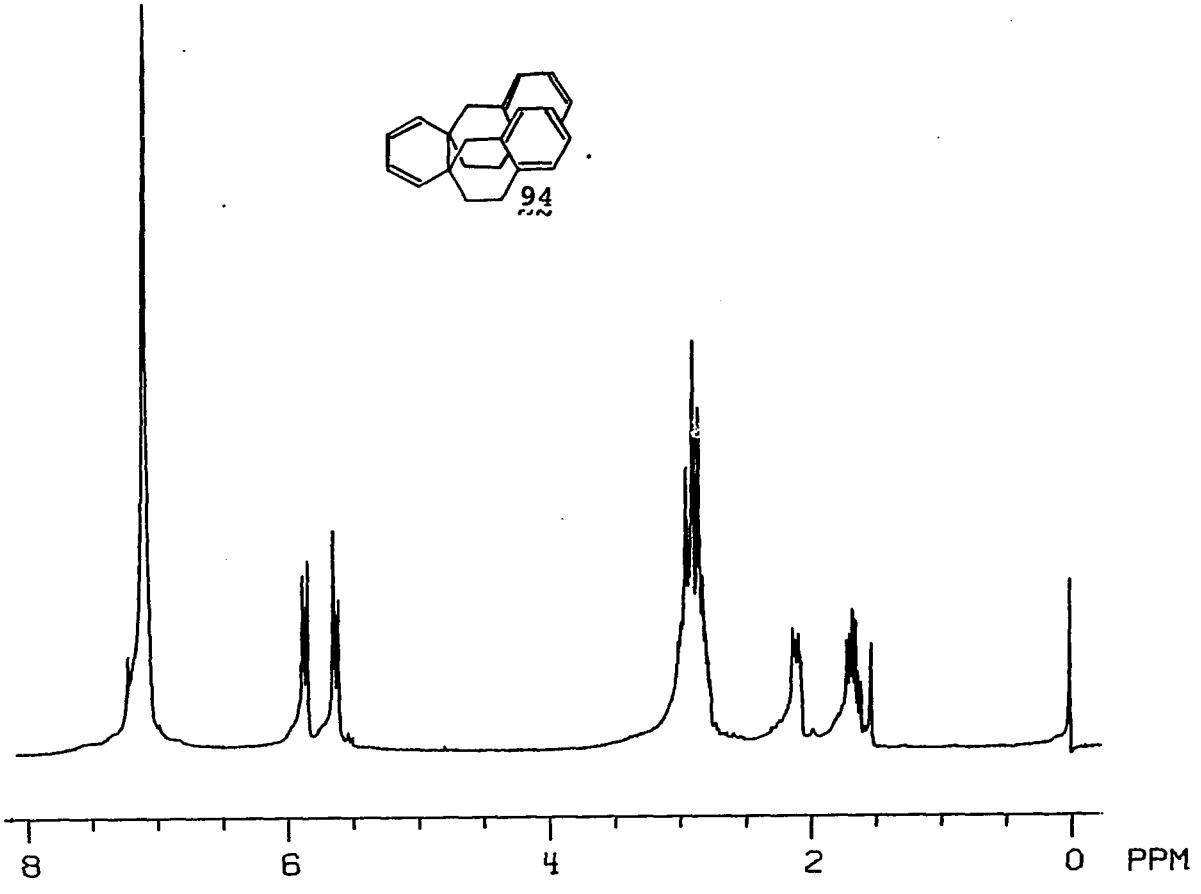


Figure 2. ^{1}H NMR spectrum of trimer 94

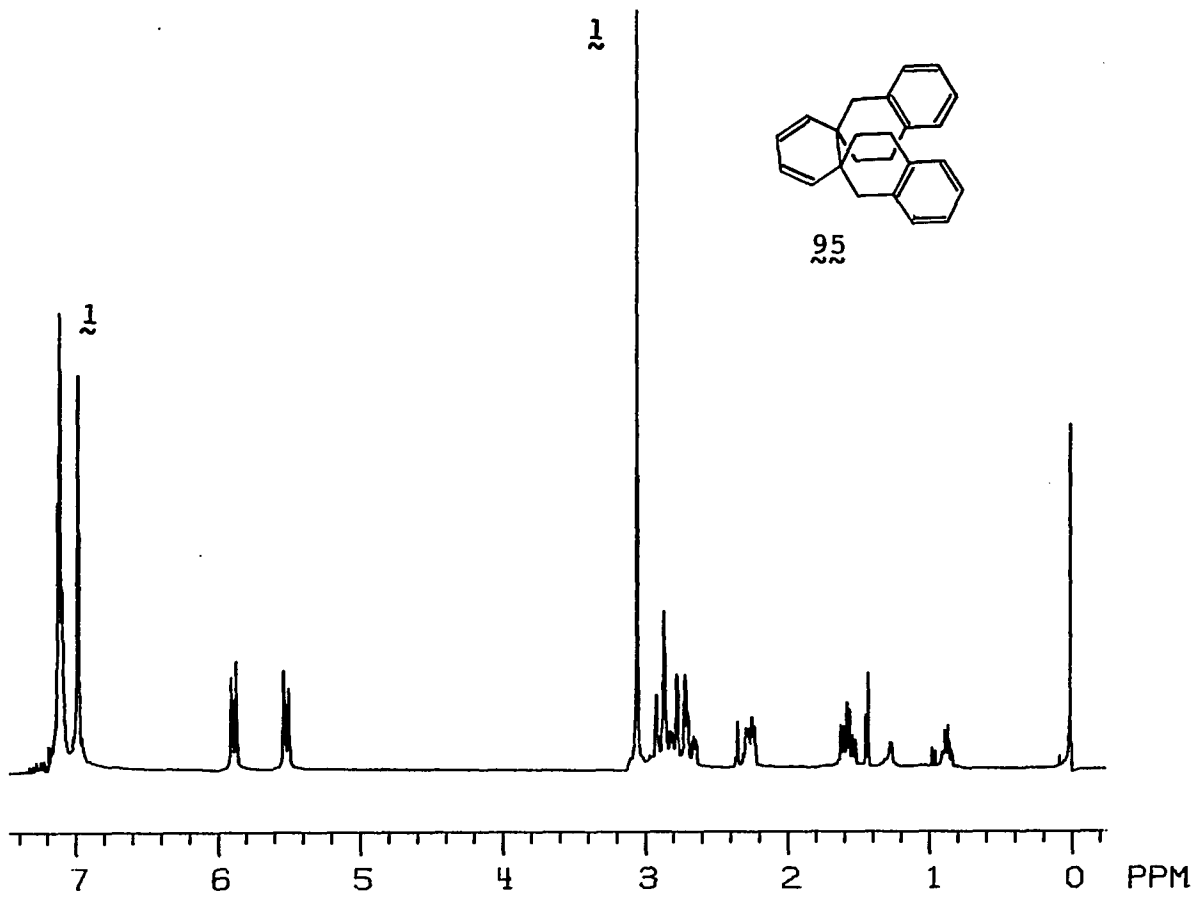
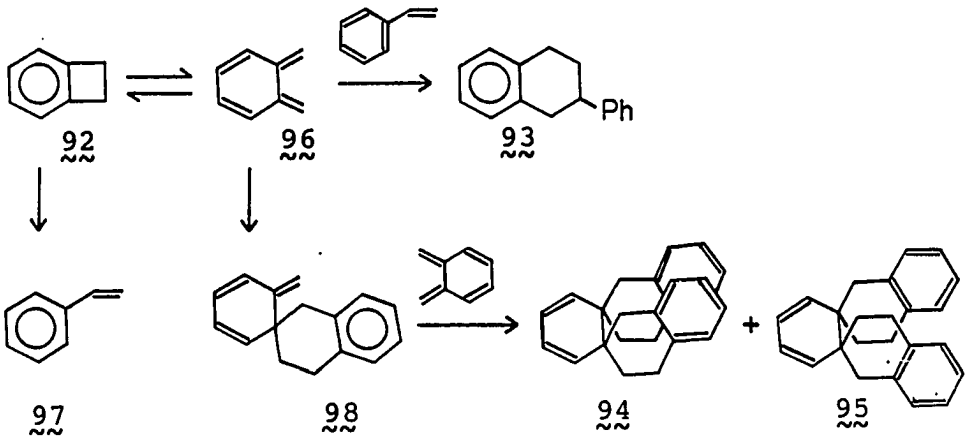


Figure 3. ^{1}H NMR spectrum of a 4:6 mixture of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1) and trimer 95

GC/MS (70eV) m/e (% base peak) 314 (1.22), 313 (10.19), 312 (41.58), 208 (17), 207 (100), 193 (25), 192 (9), 179 (12), 178 (15), 165 (9), 141 (10), 129 (13), 128 (13), 118 (10), 117 (16), 115 (18), 105 (12), 91 (10).

The formation of 2-phenyltetralin (93) and two trimers (94 and 95) from sealed tube pyrolysis of benzocyclobutene (92) is described in Scheme 1.

Scheme 1



The formation of 2-phenyltetralin (93) can be explained by a Diels-Alder reaction of o-xylylene (96) and styrene (97). Styrene (97) can be derived from benzocyclobutene (92) and this has been reported.[39,40] The formation of cis- and trans trimers of o-xylylene (94 and 95) can be explained by a Diels-Alder reaction of the [4+2] dimer (98) and o-xylylene (96).

APPENDIX II

Preparation of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene-5-ol (87)

A solution of 705 mg (3.4 mmol) of 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (1) and 3 mg of benzoyl peroxide in 15 ml of CCl_4 was heated to reflux, and to this was added slowly 603 mg (3.4 mmol) of NBS. After the addition was complete, the mixture was refluxed for an additional 20 min and then cooled in an ice bath. The succinimide was removed by filtration. The filtrate was washed with saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated to give a mixture of 50% of 5-bromo-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (BTDC), 30% of 1, and 20% of dibromo-5,6,11,12-tetrahydrodibenzo[a,e]-cyclooctene. BTDC: GC/MS (70eV) m/e (% base peak) 288 (1.13), 287 (0.06), 286 (1.04), 208 (18), 207 (100), 205 (17), 129 (17), 115 (13), 91 (22). The reaction mixture was hydrolyzed with base without further purification: about 700 mg of the reaction mixture in 10 ml of 1:1 20% NaOH/acetone solution was heated to reflux for 2 h. After the reaction mixture was cooled to room temperature, the reaction mixture was acidified with concentrated HCl and extracted with ether. The organic layer was dried ($MgSO_4$), concentrated, and purified by thin layer chromatography on silica gel (5% ether in hexanes) to give 280 mg (1.25 mmol, 37%) of 87.

APPENDIX III

Determination of Yields in Hydrocarbon Pyrolysis

The yields of products and recovered starting material in the pyrolyses of hydrocarbons were determined by GC by adding a weighed internal standard (biphenyl) to a solution of the pyrolysate. The amount of each product (mg P) was then calculated from the weight of the internal standard (mg IS), the area of the peak of the internal standard (AIS), and the area of the product peak (AP) in the GC trace response factor

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

(res. f.) was included to correct for the differences in the response of the detector to compounds being compared. The response factor for anthracene, 9-methylanthracene, 5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene, benzo[1,2-b:-4,5-b']difuran, and biphenyl were 0.98, 0.99, 1.02, 0.96, and 1.0, respectively.