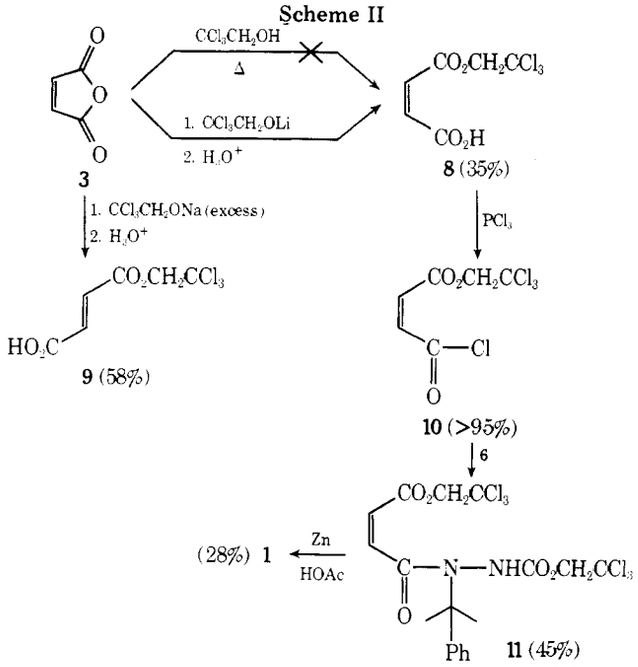
Scheme II



through reversible Michael addition to the double bond. When the reaction was carried out using the lithium alkoxide and excess maleic anhydride, the desired trichloroethyl hydrogen maleate **8** [NMR, J_{vinyl} = 12.4 Hz (cis **HC=H**);[10] ir 722 cm^{-1} (cis C=C)[11]] was obtained. Treatment of maleate **8** with phosphorus trichloride[12] affords maleoyl chloride **10** [NMR, J_{vinyl} = 12.0 Hz (cis **HC=CH**[10]] as a colorless, fuming liquid.

Treatment of trichloroethyl carbazate **6** with maleoyl chloride **10** affords maleamate **11** [NMR, J_{vinyl} = 12.0 Hz (cis **HC=CH**)[10]]. Finally, removal of the two protecting groups with zinc in acetic acid provides the desired α-cumyltetrahydropyridazinedione **1** as a colorless solid. NMR (δ 6.72 and 7.07 ppm, J_{vinyl} = 9.8 Hz) and ir (1665 and 1585 cm^{-1}) spectral data are in accord with that reported for other tetrahydropyridazinediones.[7] When heated in a capillary tube immersed in an oil bath, the amorphous solid changes without melting at ca. 220–230 °C into needles which then melt at 315–316 °C dec. When immersed into hot (250 °C) oil, **1** melts, bubbles, solidifies and does not melt again below 300 °C. Presumably, pyridazinedione **1** loses α-methylstyrene to afford 1,2,3,6-tetrahydropyridazine-3,6-dione (lit. mp >300[13a] and 300–310 °C dec[13b]).

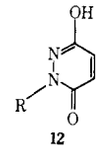
Acknowledgments. This work has been partially supported by the Alfred P. Sloan Research Foundation and by the National Institutes of Health (GM 14518).

Registry No.—**2**, 3178-39-0; **3**, 108-31-6; **4**, 60498-79-5; **5**, 60498-80-8; **6**, 60498-81-9; **8**, 60498-82-0; **9**, 60498-83-1; **10**, 60498-84-2; **11**, 60498-85-3; **12** (R = α-cumyl), 60498-86-4; 2,2,2-trichloroethyl chloroformate, 17341-93-4; sodium trichloroethoxide, 60498-87-5; lithium trichloroethoxide, 60498-88-6.

Supplementary Material Available. Spectral data (NMR, ir, and mass spectra), elemental analyses, and procedures for the preparation of compounds **1**, **4–6**, and **8–11** (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This name and the associated structural formula are used in view of the relationship of **1** to other diacylhydrazines. Numerous studies[2-4] suggest that the structure of **1** would doubtlessly be more accurately portrayed as **12**.



12

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Synthesis of ω-Methoxy-1,2-dihydronaphthalenes. Gas Phase Pyrolysis of 1-(2′-, 3′-, and 4′-Methoxyphenyl)-1,3-butadienes

Michele M. Radcliffe and William P. Weber*

Department of Chemistry, University of Southern California, Los Angeles, California 90007

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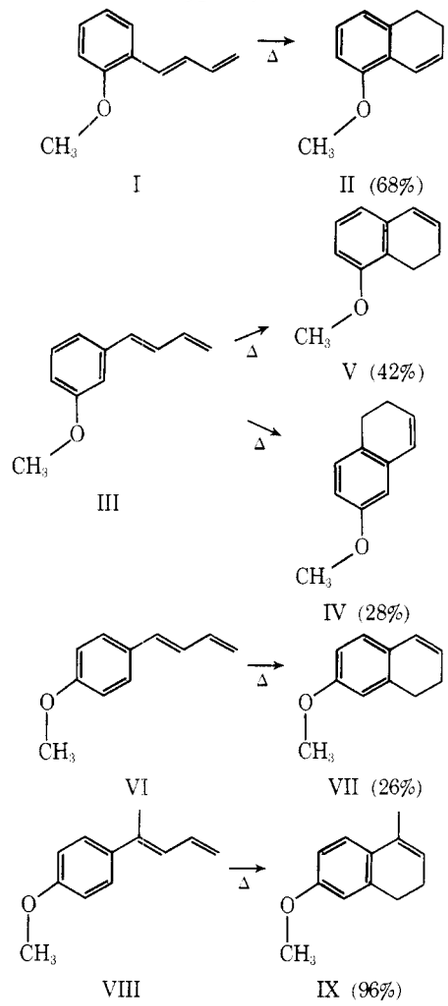
Gas-phase pyrolysis of 1-(2′-methoxyphenyl)-1,3-butadiene yields 5-methoxy-1,2-dihydronaphthalene. Likewise, pyrolysis of 1-(3′-methoxyphenyl)-1,3-butadiene yields a mixture of 6-methoxy- and 8-methoxy-1,2-dihydronaphthalene. Pyrolysis of 1-(4′-methoxyphenyl)-1,3-butadiene yields 7-methoxy-1,2-dihydronaphthalene. Finally, pyrolysis of 2-(4′-methoxyphenyl)-2,4-pentadiene yields 7-methoxy-4-methyl-1,2-dihydronaphthalene. A mechanism for these pyrolysis reactions is discussed.

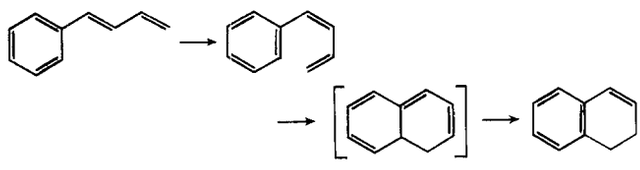
We should like to report the results of the following gas-phase pyrolysis reactions: 1-(2′-methoxyphenyl)-1,3-butadiene (I)[1] yields 5-methoxy-1,2-dihydronaphthalene (II, 68%);[2] 1-(3′-methoxyphenyl)-1,3-butadiene (III)[3] yields a mixture of 6-methoxy-1,2-dihydronaphthalene (IV, 28%)[4] and 8-methoxy-1,2-dihydronaphthalene (V, 42%);[2] 1-(4′-methoxyphenyl)-1,3-butadiene (VI)[1,5] yields 7-methoxy-1,2-dihydronaphthalene (VII, 62%);[6-8] and finally 2-(4′-methoxyphenyl)-2,4-pentadiene (VIII) yields 7-methoxy-4-methyl-1,2-dihydronaphthalene (IX, 96%)[9-13] (Scheme I).

These results are consistent with the three-step mechanism

Scheme I. Thermal Electrocyclic Reactions of 1-(2′-, 3′-, and 4′-Methoxyphenyl)-1,3-butadienes

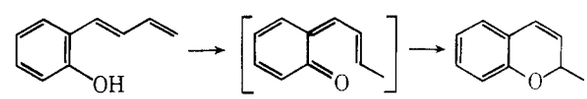


previously proposed to account for the formation of 1,2-dihydronaphthalene on pyrolysis of 1-phenyl-1,3-butadiene in the gas phase.[14] The first step is an isomerization of *trans*-1-phenyl-1,3-butadiene[15] to *cis*-1-phenyl-1,3-butadiene.[16,17] This step is essential since only the cis isomer has the proper geometry to undergo the second step, a thermally allowed disrotatory electrocyclic reaction converting a conjugated triene composed of the two double bonds of the 1,3-butadiene and 2-π electrons from the benzene ring into a 1,3-cyclohexadiene.[18-21] Other examples of participation of 2-π electrons from a benzene ring in thermal electrocyclic reactions have been reported.[22,23] The final step is a 1,5-sigmatropic suprafacial hydrogen migration leading to restoration of the aromatic nucleus.[24]



Previous syntheses of these ω-methoxy-1,2-dihydronaphthalene (ω = 5, 6, 7, or 8) isomers have utilized a variety of reactions since no one reaction was generally applicable.[2,4,8,13,25]

Our interest in the pyrolysis of these 1-(2′-, 3′-, and 4′-methoxyphenyl)-1,3-butadienes came from several sources. We wanted to define the scope and generality of the electrocyclic pyrolysis reaction. The question of whether a methoxy substituent could be tolerated in the phenyl ring did not appear trivial. Thus, previous work had shown that the product of pyrolysis of 1-(*o*-hydroxyphenyl)-1,3-butadiene was not 1,2-dihydro-5-naphthol but rather 2-methylchromene.[26,27] This result was explained by an initial 1,7-sigmatropic hydrogen shift to yield an ω-vinyl-*o*-quinomethide intermediate which undergoes electrocyclic ring closure to yield 2-methylchromene.[27] Thus, the ability of the reaction to tolerate a methoxy substituent, at least in the ortho position, was not clear. In addition, the ω-methoxy-1,2-dihydronaphthalenes are of interest from a synthetic point of view.[6-8,13]



The starting materials for these electrocyclic pyrolysis reactions were readily prepared. Addition of allylidenetriphenylphosphorane to the 2-, 3-, or 4-anisaldehydes in a Wittig reaction[28] yields the corresponding 1-(2′-, 3′-, or 4′-methoxyphenyl)-1,3-butadienes in a single step, albeit in low yield ($\simeq$30%). Large-scale preparation of 1-(2′-, 3′-, or 4′-methoxyphenyl)-1,3-butadienes were carried out by addition of allyl Grignard reagent to the corresponding 2-, 3-, or 4-anisaldehyde.[29] The product alcohol was dehydrated by distillation from freshly fused $KHSO_4$ in $\simeq$50% overall yield.[5] 2-(4′-Methoxyphenyl)-2,4-pentadiene was prepared starting from 4-methoxyacetophenone. Addition of allyl Grignard reagent gave 2-(4′-methoxyphenyl)-4-penten-2-ol, which was dehydrated by distillation from tosyl chloride in pyridine to yield a 2:1 mixture of VIII and 2-(4′-methoxyphenyl)-1,4-pentadiene.[30] Control experiments showed that 2-(4′-methoxyphenyl)-1,4-pentadiene was unreactive on pyrolysis. Pyrolysis was performed on mixtures of these dienes.

Demethylation of 5-methoxy-1,2-dihydronaphthalene[30] using sodium ethyl mercaptide in dimethylformamide yields 1,2-dihydro-5-naphthol ($\simeq$35%).[2,26,27]

The structures of IV and V obtained from the pyrolysis of III were confirmed by use of Eu(fod)$_3$ NMR shift reagent. Eu(fod)$_3$ behaves as a Lewis acid and thus coordinates to the basic oxygen of these aromatic methyl ethers.[31,32] The effect of Eu(fod)$_3$ on the chemical shift of a particular proton in the substrate is related to the distance and geometry of the proton from the Eu^{3+} ion.[32] Those protons which are closest to the Eu^{3+} ion shift the most.[32] On this basis, we expect downfield shifts for the aromatic protons at C-5 and C-7 in IV. On the other hand, we expect downfield shifts of the aromatic proton at C-7 and the benzylic protons at C-1 in V. Results consistent with these expectations were obtained. For supporting data, plots of the chemical shift of each proton vs. the sum of all the chemical shifts of these protons observed,[33] see supplementary material microfilm edition.

Experimental Section

All reactions were performed under an atmosphere of prepurified nitrogen. Apparatus was flamed dry prior to use. Many of the compounds reported are known; however, spectral properties even of those that are known are meager. For this reason, IR and NMR of all compounds are reported here. IR spectra were recorded on a Perkin-Elmer 337 spectrometer and were calibrated against known peaks in a polystyrene film. NMR spectra were taken in $CDCl_3$ solution on a Varian XL-100 or in CCl_4 solution on a Varian T-60 using Me_4Si as an internal standard. Ultraviolet spectra were taken in spectroquality cyclohexane on a Beckman Acta M spectrometer. GLC was carried out on a Hewlett-Packard F & M 700, using either an 8.5 ft × 0.25 in. 20% polyphenyl ether 6 ring, on Chromosorb P at 190–200 °C (A) or 1.5 ft × 0.25 in. 20% Carbowax on Chromosorb P column at 165 °C (B). Melting points were taken on a Thomas-Hoover instrument and are uncorrected. Microanalyses were performed by Cal. Tech. Analytical Services, Pasadena, Calif.

2-(4′-Methoxyphenyl)-4-penten-2-ol. To a 250-ml three-neck round-bottom flask, equipped with a reflux condenser, pressure-equalizing addition funnel, and overhead stirrer, was added allylmagnesium chloride (Alfa), 1.9 M, in THF, 60 ml (0.13 mol). *p*-

Methoxyacetophenone (MCB), 15.0 g (0.1 mol), dissolved in 50 ml of ether was added dropwise. The mixture was stirred overnight, then hydrolyzed by addition of 100 ml of cold saturated aqueous NH_4Cl. The organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, and filtered, and the volatile solvent removed by evaporation under reduced pressure. The crude alcohol was distilled from K_2CO_3 through a 9-cm distillation head to yield 15.8 g (82 mmol), 83%, of 2-(4′-methoxyphenyl)-4-penten-2-ol: bp 118 °C (0.02 mm). IR (neat) -OH, 3630–3300; C=C, 1620 cm^{-1}. NMR δ 7.35 (d, 2 H), J = 9 Hz; 6.85 (d, 2 H), J = 9 Hz; 5.64 (dt, 1 H), J = 14, 8 Hz; 5.16 (m, 2 H); 3.79 (s, 3 H); 2.65 (dd, 1 H), J = 13, 7 Hz; 2.44 (dd, 1 H), J = 14, 8 Hz; 2.22 (s, 1H); addition of D_2O caused the signal at δ 2.22 to disappear; 1.52 (s, 3 H).

1-(2′-Methoxyphenyl)-3-buten-1-ol. As above, 2-anisaldehyde (MCB) was converted to 1-(2′-methoxyphenyl)-3-buten-1-ol in 86% yield: bp 82 °C (0.1 mm) [lit. 96 °C (0.32 mm)].[37] IR (neat) -OH, br, 3750–3250; $-OCH_3$, 2850; C=C, 1600 cm^{-1}. NMR δ 7.07 (m, 4 H); 5.75 (ddt, 1 H), J = 14, 6, 3 Hz; 4.95 (m, 3 H); 3.80 (s, 3 H); 2.45 (m, 3 H). UV λ 2210 Å, ε 3639; λ 2720 Å, ε 2523; λ 2769 Å, ε 2365.

1-(3′-Methoxyphenyl)-3-buten-1-ol. Similarly, 3-anisaldehyde (Aldrich) gave 1-(3′-methoxyphenyl)-3-buten-1-ol in 75% yield: bp 102 °C (0.1 mm) [lit. 96–97 °C (0.30 mm)].[37] IR (neat) -OH, br, 3800–3200; C=C, 1605 cm^{-1}. NMR δ 7.12 (t, 1 H), J = 8 Hz; 6.90–6.70 (br m, 3 H); 5.91–5.37 (br m, 1 H); 5.10 (d, 1 H), J = 18 Hz; 5.7 (d, 1 H), J = 10 Hz; 4.57 (m, 1 H); 3.75 (s, 3 H); 2.71 (br s, 1 H); addition of D_2O caused the signal at δ 2.71 to disappear; 2.44 (t, 2 H), J = 7 Hz.

1-(4′-Methoxyphenyl)-3-buten-1-ol. In the same way, 4-anisaldehyde (Aldrich)led to 1-(4′-methoxyphenyl)-3-buten-1-ol in 76% yield: bp 93–94 °C (0.1 mm) [lit. 102–103 °C (0.35 mm)].[37] IR (neat) -OH, br, 3700–3130; C=C, 1615 cm^{-1}. NMR δ 7.20 (d, 2 H), J = 9 Hz; 6.82 (d, 2 H), J = 9 Hz; 5.93–5.53 (m, 1 H); 5.13 (d, 1 H), J = 12 Hz; 5.08 (d, 1 H), J = 16 Hz; 4.59 (br t, 1 H), J = 6 Hz; 3.74 (s, 3 H); 2.66–2.62 (br s, 1 H); addition of D_2O caused the signal at δ 2.66–2.62 to disappear; 2.44 (t, 2 H), J = 7 Hz.

2-(4′-Methoxyphenyl)-2,4-pentadiene and 2-(4′-Methoxyphenyl)-1,4-pentadiene. Into a 500-ml three-neck round-bottom flask, equipped with reflux condenser and a Teflon-covered magnetic stirring bar, were placed 200 ml of dry pyridine, 10.0 g (52.5 mmol) of p-toluenesulfonyl chloride (Mallinckrodt), and 9.2 g (47.8 mmol) of 2-(4′-methoxyphenyl)-4-penten-2-ol. The mixture was refluxed overnight. Pyridine was removed by evaporation under reduced pressure. The residue was taken up in 250 ml of ether and washed three times with each of the following: 50 ml of 10% H_2SO_4, 50 ml of aqueous K_2CO_3, and 100 ml of H_2O. The organic layer was dried over Na_2SO_4 and filtered, and the volatile solvents removed by evaporation under reduced pressure. The residue was distilled through a 9-cm vacuum-jacketed column to yield a mixture of dienes, 87% yield, bp 77–78 °C (0.05 mm). Analysis by GLC (B) showed the mixture to consist of VIII (65%) and 2-(4′-methoxyphenyl)-1,4-pentadiene (35%).

VIII: IR (neat) C=C, 1665, 1660; CH_3OAr, 1270–1230 cm^{-1}. NMR δ 7.33 (d, 2 H), J = 9 Hz; 6.83 (d, 2 H), J = 9 Hz; 6.8–6.50 (m, 2 H); 5.27 (dd, 1 H), J = 18, 2 Hz; 5.11 (dd, 1 H), J = 10, 2 Hz; 3.79 (d, 3 H), J = 2 Hz; 2.05 (s, 3 H). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.53; H, 8.01.

2-(4′-Methoxyphenyl)-1,4-pentadiene: IR (neat) C=C, 1625; CH_3OAr, 1240 cm^{-1}. NMR δ 7.36 (d, 2 H), J = 9 Hz; 6.84 (d, 2 H), J = 9 Hz; 5.60–5.0 (m, 5 H) 3.80 (s, 3 H); 3.20 (d, 2 H), J = 4 Hz. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.81; H. 7.97.

1-(2′-Methoxyphenyl)-1,3-butadiene (I). Into a 10-ml round-bottom flask equipped with a 9-cm distillation head and a Teflon-covered magnetic stirring bar were placed 4.65 g (26.0 mmol) of 1-(2′-methoxyphenyl)-3-buten-1-ol and 0.7 g (5.26 mmol) of freshly fused $KHSO_4$. The flask was heated under vacuum (0.1 mm). The product was distilled rapidly since polymerization occurs in the flask. I, 2.24 g (14.1 mmol), 54.2%, was obtained: bp 84 °C (0.3 mm) [lit. 140–143 °C (16 mm)].[1] IR (neat) C=C, 1685 cm^{-1}. NMR δ 7.57–6.24 (br m, 7 H), 5.54–5.04 (br m, 2 H), 3.84 (s, 3 H).

1-(3′-Methoxyphenyl)-1,3-butadiene (III). III prepared as above from 1-(3′-methoxyphenyl)-3-buten-1-ol: bp 96 °C (0.4 mm) [lit. 87 °C (2 mm)].[3] IR (neat) C=C, 1601 cm^{-1}. NMR δ 7.26 (s, 1 H); 7.10–6.60 (m, 4 H), 6.43 (d, 1 H), J = 17 Hz; 6.32 (d, 1 H), J = 15 Hz; 5.45 (d, 1 H), J = 15 Hz; 5.28 (d, 1 H), J = 10 Hz; 3.82 (s, 3 H).

1-(4′-Methoxyphenyl)-1,3-butadiene (VI). In the same manner, 1-(4′-methoxyphenyl)-3-buten-1-ol was converted to VI: bp 80 °C (0.2 mm) [lit. 139–140 °C (12 mm)].[1] IR (neat) C=C, 1595 cm^{-1}. NMR δ 7.31 (d, 2 H), J = 9 Hz; 6.83 (d, 2 H), J = 9 Hz; 6.45 (m, 3 H); 5.18 (m, 2 H); 3.79 (s, 3 H).

Wittig Synthesis of 1-(2′-, 3′-, and 4′-Methoxyphenyl)-1,3-butadienes. 1-(2′-, 3′-, and 4′-methoxyphenyl)-1,3-butadienes were synthesized from the corresponding aldehydes via a Wittig reaction. In a 250-ml round-bottom flask, equipped with reflux condenser, pressure-equilizing addition funnel, and a Teflon-covered magnetic stirring bar, were placed 30.0 g (78 mmol) of allyltriphenylphosphonium bromide (Aldrich) and 250 ml of dry ethyl ether. n-Butyllithium in hexane (Alfa), 32 ml, 2.45 M (78.4 mmol), was added dropwise. After 1 h 10.0 g (73.5 mmol) of 3-anisaldehyde (Aldrich) dissolved in 20 ml of ether was added dropwise. The mixture was allowed to stir overnight. The mixture was filtered. The filtrate was dried over anhydrous $MgSO_4$. Solvents were removed by evaporation under reduced pressure. The residue was bulb to bulb distilled at 0.15 mm to yield 3.45 g (21.5 mmol), 29%, of III.

Pyrolysis of the Dienes. Apparatus. A nitrogen inlet was connected to the top of a 10-ml Hershberg constant rate pressure equalizing addition funnel. The bottom of the addition funnel was connected to a 250-cm long (9 mm o.d. by 8 mm i.d.) quartz pyrolysis tube. The pyrolysis tube was wrapped in the form of a 30-turn spiral, 30 cm high. It was heated by a 30 cm long by 2.5 cm diameter tube furnace which had a 10 °C temperature gradient across the oven. The bottom of the pyrolysis column was connected to a 50-ml two-neck pear-shaped flask which was cooled to −78 °C. The second neck was connected to a trap, cooled to −78 °C. N_2 flowed through the system and into a hood. The diene drop rate, 1/10–11 s, N_2 flow rate 1 ml/19 s, and oven temperature were controlled during each pyrolysis. The oven temperature was monitored by a Leeds and Northrup potentiometer using an iron–constantan thermocouple. Upon completion of the pyrolysis, the solvent was distilled from the product mixture through a 13-cm Vigreux column. Yields were calculated based on recovered starting material.

7-Methoxy-4-methyl-1,2-dihydronaphthalene (IX). The diene mixture (1.6 g, 6.6 mmol) from the dehydration of 2-(4′-methoxyphenyl)-4-penten-2-ol dissolved in 9.5 ml of benzene was pyrolyzed at 439 °C. The residue, 1.04 g (6.0 mmol), was shown by GLC (A) to consist of 30% recovered VIII, 7% 2-(4′-methoxyphenyl)-2,4-pentadiene, and 63% IX. IX had the following properties: bp 75 °C (0.1 mm) [lit. 93–94 °C (1 mm)].[13] IR (neat) C=C, 1605; CH_3OAr, 1245 cm^{-1}. NMR δ 7.12 (d, 1 H), J = 9 Hz; 6.69 (m, 2 H); 5.69 (br s, 1 H); 3.79 (s, 3 H); 2.64 (t, 2 H), J = 7 Hz; 2.23 (br m, 2 H); 2.03 (d, 3 H), J = 2 Hz.

5-Methoxy-1,2-dihydronaphthalene (II). I (2.14 g, 13.4 mmol) dissolved in 20 ml of benzene was pyrolyzed at 460–462 °C. The residue was bulb to bulb distilled at 0.08 mm to yield 1.76 g (11.0 mmol). Analysis of GLC (A) showed the product mixture to consist of recovered I (29%), II (62%), and 1-methoxynaphthalene (8%). II had the following properties: bp 66 °C (0.02 mm) [lit. 130–131 °C (0.15 mm)].[3] IR (neat) C=C, 1565; CH_3OAr, 1250 cm^{-1}. NMR δ 7.08 (t, 1 H), J = 8 Hz; 6.72 (m, 3 H); 6.02 (m, 1 H); 3.82 (s, 3 H); 2.76 (t, 2 H), J = 8 Hz; 2.40–2.12 (br m, 2 H).

8-Methoxy-1,2-dihydronaphthalene (V) and 6-Methoxy-1,2-dihydronaphthalene (IV). III (0.86 g, 5.35 mmol) in 9 ml of benzene was pyrolyzed at 469–471 °C. The residue, 0.60 g (3.74 mmol), was separated by preparative GLC (A). V and IV were isolated in a ratio of 1.55:1.

The isomers were distinguished by use of $Eu(fod)_3$ NMR shift reagent. The $Eu(fod)_3$ (Bio-Rad Laboratories) was dried over P_2O_5. A 0.59 M solution of $Eu(fod)_3$ in $CDCl_3$ (10–25 μl) was syringed into a 5-mm NMR tube containing 6.3 mg of V or IV in 0.4 ml of $CDCl_3$/1% Me_4Si. This procedure was continued until 100 μl of shift reagent solution had been added.

V: bp 70 °C (0.04 mm) [lit. 145 °C (23 mm)].[2] IR (CCl_4) C=C, 1570; $ArOCH_3$, 1255 cm^{-1}. NMR δ 7.08 (t, 1 H), J = 7 Hz; 6.75–6.60 (m, 2 H); 6.40 (br d, 1 H), J = 10 Hz; 5.98 (dt, 1 H), J = 10, 4 Hz; 3.82 (s, 3 H); 2.79 (t, 2 H), J = 8 Hz; 2.38–2.12 (m, 2 H).

IV: bp 71 °C (0.1 mm) [lit. 93–95 °C (1 mm)].[4] IR (CCl_4) C=C, 1600; CH_3OAr, 1248 cm^{-1}. NMR δ 7.00 (d, 1 H), J = 7 Hz; 6.64 (m, 2 H); 6.40 (d, 1 H), J = 9 Hz; 6.01 (dt, 1 H), J = 8, 4 Hz; 3.78 (s, 3 H); 2.72 (t, 2 H), J = 8 Hz; 2.39–2.15 (br m, 2 H).

7-Methoxy-1,2-dihydronaphthalene (VII). VI (0.30 g, 1.87 mmol) dissolved in 5 ml of benzene was pyrolyzed at 478–480 °C. The residue was bulb to bulb distilled at 0.05 mm to yield 0.25 g (1.56 mmol) of product mixture. This was shown by GLC (A) to consist of 33% 2-methoxynaphthalene and 67% VII. VII: bp 63 °C (0.1 mm) [lit. 85–95 °C (1 mm)].[6] IR (neat) C=C, 1605; $ArOCH_3$, 1260 cm^{-1}. NMR δ 6.66 (m, 4 H); 5.86 (m, 1 H); 3.73 (s, 3 H); 2.77 (t, 2 H), J = 7 Hz; 2.38–2.03 (br m, 2 H).

1,2-Dihydro-5-naphthol. Dimethylformamide was distilled from BaO and 15 ml was placed into a 50-ml two-neck round-bottom flask equipped with a reflux condenser, septum, and a Teflon-covered magnetic stirring bar. NaH (0.72 g) was added to the flask and the

mixture was allowed to stir for 5 min. Ethanethiol, distilled from CaH_2, was syringed into the cooled (0 °C) reaction mixture. A 1.6:1 mixture of II and I (0.77 g, 3.8 mmol) was syringed into the reaction and heated for 2.5 h at 140–147 °C.

The reaction mixture was cooled, poured into 150 ml of ice water, and extracted with petroleum ether to remove any unreacted II The aqueous layer was acidified with 4 N HCl and extracted with ether (3 × 50 ml). The organic layers were combined, washed with NaCl solution, dried over anhydrous $MgSO_4$, and filtered, and the volatile solvents removed by evaporation under reduced pressure in a hood. Sublimation yielded white needles, mp 69–71 °C (lit. 69.2–70.2 °C).[2] 1,2-Dihydro-5-naphthol: IR (CCl_4) -OH, br, 3600–3400; C=C, 1600 cm^{-1}. NMR δ 7.03–6.55 (br m, 4 H); 6.00 (dt, 1 H), J = 8, 4 Hz; 1.90 (br s, 1 H), 2.75 (t, 2 H), J = 8 Hz; 1.38–1.17 (br m, 2 H).

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Registry No.—I, 60578-56-0; II, 60573-57-1; III, 39677-53-7; IV, 60573-58-2; V, 60573-59-3; VI, 30448-78-3; VII, 52178-91-3; VIII, 60573-60-6; IX, 4242-13-1; *p*-methoxyacetophenone, 100-06-1; 2-(4′-methoxyphenyl)-4-penten-2-ol, 60573-61-7; 2-anisaldehyde, 135-02-4; 1-(2′-methoxyphenyl)-3-buten-1-ol, 24165-67-1; 3-anisaldehyde, 591-31-1; 1-(3′-methoxyphenyl)-3-buten-1-ol, 24165-65-9; 4-anisaldehyde, 123-11-5; 1-(4′-methoxyphenyl)-3-buten-1-ol, 24165-60-4; 2-(4′-methoxyphenyl)-1,4-pentadiene, 60573-62-8; 1,2-dihydro-5-naphthol, 1429-22-7.

Supplementary Material Available. Plots of observed chemical shifts of protons of IV and V (2 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of Small Ring Bis-Annelated Benzenes

Randolph P. Thummel* and Wutichai Nutakul

Department of Chemistry, University of Houston, Houston, Texas 77004

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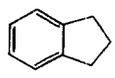
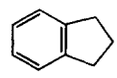
Benzocyclobutene has been prepared by a three-step route involving first the Diels–Alder addition of butadiene to dimethyl cyclobutene-1,2-dicarboxylate. The resulting diester adduct may be hydrolyzed to the corresponding dicarboxylic acid which upon treatment with 2 equiv of lead tetraacetate undergoes bisdecarboxylation and aromatization of the six-membered ring. By substituting different dienes into this scheme, a series of bis-annelated benzene isomers in which the benzene portion was fused to a four- or five-membered ring has been prepared. The ultraviolet and 100-MHz ^1H NMR spectra of these molecules have been reported. In the para-fused series, the chemical shift of the aromatic proton ortho to the fused ring is found to shift upfield with increasing strain. The shift is attributed to a perturbation of the aromatic ring current rather than to inductive effects due to rehybridization at the bridgehead carbon atoms. A shift to longer wavelength absorption in the UV is observed for the para-fused systems as compared to the meta-fused ones. The extinction coefficient is found to increase as the system becomes more symmetrical and more planar.

In 1930 Mills and Nixon proposed that the five-membered ring of indan might sufficiently distort the geometry of the benzene portion of this molecule so that Kekulé resonance form **1a** would be preferred over **1b** and thus partial double



1a



1b

bond fixation might result.[1] Since that time these predictions have been shown to be ambiguous[2] while a theoretical treatment has even been presented which favors structure **1b** over **1a**.[3] Nevertheless, more recent calculations using the CNDO/2 technique[4] as well as an extended Hückel treatment[5] both support a preferred structure in which the bridging bond is lengthened for strained benzocycloalkenes.

There are two fundamental devices whereby one can hope to induce bond localization in an otherwise aromatic molecule: the incorporation of steric strain and the demands of an electronic environment. The latter approach is demonstrated in molecules such as phenanthrene and triphenylene where some bond alteration in the central ring results from the fusion of two or three benzene rings meta to one another. The incorporation of steric strain into an aromatic molecule as a probe of bond localization offers the advantage of not electronically perturbing the cyclic π system. Various structural and spectroscopic studies on the benzocyclopropene[6] and benzocyclobutene system have sought to delineate any bond fixation. X-ray crystallographic data are available for naphthocyclopropene[7] and one derivative of benzocyclopropene.[8] Both studies are inconclusive in that they find the 1,2, the 5,6, and the 1,6 bonds all to be shorter than the C–C bond