δ 1.03 (s, 3 H, CH_3), 1.20–2.65 (m, 14 H), 2.90 (m, 2 H), 3.83 (s, 3 H, OCH_3), 6.73 (m, 2 H), 7.24 (m, 1 H); ^{13}C NMR δ 14.7, 23.7, 26.3, 27.5, 29.7, 32.5, 33.5, 39.3, 43.2, 47.1, 50.4, 55.2, 84.6 (q, $^2J_{C-F}$ = 26.0 Hz), 111.5, 113.8, 126.2, 127.1 (q, $^1J_{C-F}$ = 285.9 Hz, CF_3), 132.3, 137.8, 157.5; ^{19}F NMR δ -76.0; IR (KBr) 3442 (s), 1033–1254 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{25}F_3O_5$: C, 68.27; H, 7.64. Found: C, 67.92; H, 7.26.

Preparation of Pentafluoroethyl- and Heptafluoropropyl-Substituted Alcohols (17–22). General Procedure. The same procedure as that described above to prepare the trifluoromethylated siloxy derivatives was employed here. However, the cleavage of the siloxy derivatives to the corresponding alcohols was effected by tetrabutylammonium fluoride (1 M solution in THF) as follows. To the cooled (0 °C) reaction mixture was added dropwise with stirring 10 mL of 1 M TBAF (10 mmol) in THF. After the addition the ice bath was removed, and the solution was stirred at room temperature for 5 h. Subsequent workup procedure was identical with that described above to isolate the trifluoromethylated alcohols.

2-Phenyl-3,3,4,4,4-pentafluorobutan-2-ol (17): 81% yield; colorless oil; bp 69–70 °C (3.6 mm); ^1H NMR δ 1.77 (s, 3 H, CH_3), 2.66 (s, 1 H, OH), 7.30–7.57 (m, 5 H, Ph); ^{13}C NMR δ 24.3, 75.1 (t, $^2J_{C-F}$ = 24.0 Hz), 108.9–123.0 (m, CF_2CF_3), 126.1, 128.2, 128.5, 138.6; ^{19}F NMR δ -78.4 (s, 3 F, CF_3), -121.7 (d, 1 F, J_{gem} = 277.4 Hz, C*F*(F)), -123.7 (d, 1 F, Jg_{em} = 277.4 Hz, CF(*F*)). Anal. Calcd for $C_{10}H_9FO$: C, 50.00; H, 3.78. Found: C, 50.38; H, 3.42.

1-(Pentafluoroethyl)-1-cyclohexanol (18): 82% yield; colorless oil; bp 63–64 °C (20 mm); ^1H NMR δ 1.66 (m, 10 H), 2.19 (s, 1 H, OH); ^{13}C NMR δ 20.2, 24.9, 29.7, 73.4 (t, $^2J_{C-F}$ = 22.7 Hz), 108.7–129.0 (m, CF_3CF_2); ^{19}F NMR δ -78.9 (3 F, CF_3), -127.7 (2 F, CF_2). Anal. Calcd for $C_8H_{11}F_5O$: C, 44.04; H, 5.08. Found: C, 44.06; H, 5.05.

1-Phenyl-2,2,3,3,3-pentafluoropropanol (19): 86% yield; colorless oil; bp 73–74 °C (4.2 mm); ^1H NMR δ 3.03 (br s, 1 H, OH), 4.97 (dd, 1 *H*, J_{H-F} = 16.4, 7.8 Hz, C*H*OH), 7.36 (br s, 5 H, Ph); ^{13}C NMR δ 72.0 (dd, J_{C-F} = 27.6, 22.9 Hz), 106.9–122.7 (m, CF_3CF_2), 127.9, 128.6, 129.7, 133.8; ^{19}F NMR δ -81.9 (3 F, CF_3), -122.8 (m, 1 F, $CF_3CF(F)$), -129.3 (m, 1 F, $CF_3C(F)F$). Anal. Calcd for $C_9H_7F_5O$: C, 47.80; H, 3.12. Found: C, 47.98; H. 3.14.

2-Phenyl-3,3,4,4,5,5,5-heptafluoropentan-2-ol (20): 78% yield; colorless oil; bp 63–64 °C (1.7 mm); ^1H NMR δ 1.80 (s, 3 H, CH_3), 2.66 (br s, 1 H, OH), 7.34–7.95 (m, 5 H, Ph); ^{13}C NMR δ 24.8, 76.4 (m), 104.0–121.7 (m, $CF_2CF_2CF_3$), 126.2, 128.2, 128.5, 138.7; ^{19}F NMR δ -81.5 (t, 3 F, $^3J_{F-F}$ = 10.7 Hz, CF_3), -117.1 to -120.8 (m, 2 F, CF_2), -121.5 to -125.2 (m, 2 F, CF_2). Anal. Calcd for $C_{11}H_9F_7O$: C, 45.53; H, 3.13. Found: C, 46.05; H, 3.11.

1-(Heptafluoropropyl)-1-cyclohexanol (21): 81% yield; colorless oil; bp 77–78 °C (20 mm); ^1H NMR δ 1.67 (m, 10 H), 2.63 (br s, 1 H, OH); ^{13}C NMR δ 20.3, 25.0, 29.8, 74.9 (t, $^2J_{C-F}$ = 22 Hz), 104.0–132.2 (m, $CF_2CF_2CF_3$); ^{19}F NMR δ -81.7 (t, 3 F, $^3J_{F-F}$ = 10.6 Hz, CF_3), -123.9 to -124.2 (m, 4 F, CF_2CF_2). Anal. Calcd for $C_9H_{11}F_7O$: C, 40.31; H, 4.13. Found: C, 40.36; H, 4.25.

1-Phenyl-2,2,3,3,4,4,4-heptafluorobutan-1-ol (22): 66% yield; colorless oil; bp 75–76 °C (3 mm); ^1H NMR δ 3.37 (br s, 1 H, OH), 5.00–5.12 (m, 1 H, *H*COH), 7.36 (m, 5 H, Ph); ^{13}C NMR δ 72.0 (dd, J_{C-F} = 28.2, 22 Hz), 103.0–121.4 (m, $CF_2CF_2CF_3$), 128.1, 128.6, 129.7, 134.0; ^{19}F NMR δ -81.6 (t, 3 F, $^3J_{F-F}$ = 10.2 Hz), -118.5 to -120.2 (m, 1 F, C*F*(F)CF_2), -126.0 to -128.1 (m, 3 F, CF(*F*)CF_2). Anal. Calcd for $C_{10}H_7F_7O$: C, 43.49; H, 2.55. Found: C, 43.06; H, 2.46.

General Procedure for Reaction of Lactones with 1a. Preparation of Compounds 24b and 24c. The stoichiometry and reaction conditions employed here were the same as that used to prepare the siloxy derivatives of the trifluoromethyl-substituted alcohols (see above). Thus 10 mmol of the lactone **23** and 12 mmol of **1a** in 10 mL of THF were treated with catalytic amount of TBAF (20 mg) at 0 °C. The ice bath was removed, and the reaction mixture was allowed to warm up to room temperature. After 1 h the solvent was removed with a rotary evaporator. Distillation of the residue afforded pure products. In the case of β-propiolactone (**23a**), the adduct **24a** was stable in solution. However, it decomposed extensively during attempted distillation under reduced pressure. ε-Caprolactone (**23d**) gave a mixture of products (see text) which was not separated. The product identities of **24d**, **25**, and **26** were carried out by GC–MS analysis and ^{13}C and ^{19}F NMR spectroscopy (three peaks at δ -80.3, -76.2, and -81.4 for **24d**, **25**, and **26**, respectively).

2-(Trifluoromethyl)-2-((trimethylsilyl)oxy)tetrahydrofuran (24b): 70% yield; colorless oil; bp 78–80 °C (40 mm); ^1H NMR δ 0.13 (s, 9 H, $Si(CH_3)_3$), 1.95–2.30 (m, 4 H), 3.90 (br q, 1 H, J = 7.2 Hz), 4.13 (m, 1 H); ^{13}C NMR δ 1.1, 24.4, 35.4, 70.7, 104.0 (q, $^2J_{C-F}$ = 32.8 Hz, $(CH_3)_3SiO(C)CF_3$), 123.1 (q, $^1J_{C-F}$ = 285.7 Hz, CF_3); ^{19}F NMR δ -84.5. Anal. Calcd for $C_8H_{15}F_3O_2Si$: C, 42.11; H, 6.63. Found: C, 42.50; H. 6.73.

2-(Trifluoromethyl)-2-((trimethylsilyl)oxy)tetrahydropyran (24c): 75% yield; colorless oil; bp 96–98 °C (38 mm); ^1H NMR δ 0.18 (s, 9 H, $Si(CH_3)_3$), 1.69 (m, 6 H), 3.75 (m, 2 H); ^{13}C NMR δ -1.35, 15.8, 22.7, 28.0, 60.1, 92.4 (q, $^2J_{C-F}$ = 31.7 Hz, $(CH_3)_3SiO(C)CF_3$), 121.3 (q, $^1J_{C-F}$ = 286.7 Hz, CR_3); ^{19}F NMR δ -81.2. Anal. Calcd for $C_9H_{17}F_3O_2Si$: C, 44.63; H. 7.07. Found: C, 44.35; H, 7.49.

Acknowledgment. We thank Prof. George A. Olah for his kind support and helpful discussions. Support of this work by the Loker Hydrocarbon Research Institute is gratefully acknowledged.

A Photoannulation Route to Naphthalenes from Cyclic Ketones

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Received July 23, 1990

A three-step naphthalene annulation of cyclic ketones has been developed. Aldol condensation with an aromatic aldehyde followed by Wittig olefination produces a 1,3-diene, which undergoes oxidative photocyclization to produce a naphthalene derivative. Ketone ring sizes of C_5 to C_8 were annulated successfully. The sequence was also applied successfully to three methyl-substituted derivatives and one polycyclic case.

Introduction

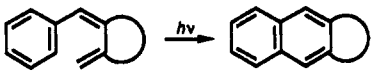
The photochemical electrocyclization of six π electron systems is one of the most general and useful organic photochemical transformations. The oxidative photocyclization of stilbenes to phenanthrenes, for example, has been widely studied and regularly reviewed.[1] A potentially useful example of a six π electron photocyclization is the conversion of a 1-aryl-1,3-butadiene to a naphthalene derivative. This reaction has been reported for several substituted examples[2] but the reaction fails for the parent hydrocarbon, 1-phenyl-1,3-butadiene; a variety of photoaddition and four π electron cyclization reactions are observed instead.[3] We initially felt that the failure of the

(1) See, for example: Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 185. Mallory, F. B.; Mallory, C. W. *Org. React. (N.Y.)* **1984**, *30*, 1.

(2) Leznoff, C. C.; Hayward, R. J. *Can. J. Chem.* **1970**, *48*, 1842.

0022-3263/91/1956-0989$02.50/0

parent to photocyclize may be due in part to the relative inaccessibility of the *Z*-cis structure needed for the reaction to occur.[4] In that case, incorporation of the double bonds into a cyclic framework where they are both exocyclic (eq 1) might give a structure capable of cyclization.



(1)

We report here that we have prepared several such compounds and have found that they do photocyclize with reasonable efficiency (yields of 45–74%). In addition, the sequence Aldol condensation–Wittig olefination–oxidative photocyclization is a convenient and inexpensive route to partially reduced linear polycyclic hydrocarbons.

Results

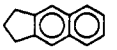
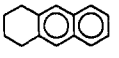
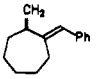
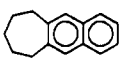
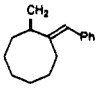
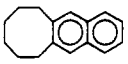
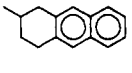
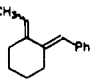
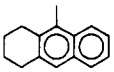
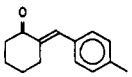
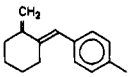
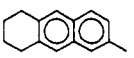
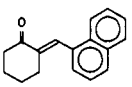
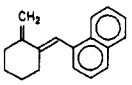
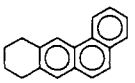
The dienes used for the photochemical experiments were prepared from cycloalkanones in two steps: aldol condensation with an aromatic aldehyde following literature procedures[5] to produce a benzalcycloalkanone was followed by a Wittig olefination. The benzalcycloalkanones and dienes were produced as the *E* isomers in all cases except **6a**, where the *E* ketone produced a nearly equal mixture of *E,E* and *E,Z* isomers.

Initial photochemical experiments were performed on 1-benzal-2-methylenecyclohexane (**2a**). Photolyses were performed in several solvents, using both air and iodine as oxidants and using quartz, Vycor, and Pyrex glassware. Successful photocyclization occurred in acetonitrile, benzene, cyclohexane, and ether. Isomerization to the *Z* isomer but no photocyclization occurred in methanol. The use of iodine as the oxidant resulted in low yields. The best results were obtained when the irradiation was carried out under aerobic conditions (an open beaker) in benzene using quartz glassware. Conversion to photocyclized product occurred significantly faster in benzene than in cyclohexane, suggesting that sensitization of the reaction by benzene may be occurring. The photocyclization could also be sensitized by benzophenone. The reactant concentration in the experiments reported in Table I was 0.005 M. Lowering the concentration to 0.002 M did not significantly increase the yield.

The results of our experiments are presented in Table I and illustrate several features of the reaction. The annulation sequence succeeded with all ring sizes examined (C_5–C_8). The successful result with the cyclopentane derivative is noteworthy since a related nonphotochemical annulation sequence gave a very low yield in this case.[6] The reaction was also successful with methyl substituents present on either ring or on the exocyclic double bond. One polycyclic case was also examined.

The photocyclization appears to be a general reaction that, despite sometimes modest photocyclization yields, should be of wide applicability. The dienes are easily prepared from readily available starting materials, and the photocyclization products can be easily separated from polymeric or polar byproducts. Finally, the annulation sequence is highly convergent. For example, appropriate selection of the cyclohexanone, aromatic aldehyde, and ylide will allow the selective introduction of a substituent at any position of 1,2,3,4-tetrahydroanthracene.

Table I. Naphthalene Annulation of Cyclic Ketones (Yields Are Given in Parentheses)

entry	aldol adduct	Wittig product	photocyclization product
1		 1a (42 %)	 1b (57 %)
2		 2a (78 %)	 2b (57 %)
3		 3a (79 %)	 3b (74 %)
4		 4a (44 %)	 4b (58 %)
5		 5a (73 %)	 5b (45 %)
6		 6a (49 %)	 6b (56 %)
7		 7a (74 %)	 7b (61 %)
8		 8a (66 %)	 8b (48 %)

Experimental Section

^{13}C NMR spectra were recorded at 50 MHz. Tetrahydrofuran (THF) was distilled from sodium/benzophenone before use. Other solvents were fractionally distilled and stored over molecular sieves prior to use. Benzalcycloalkanones were prepared by aldol condensations according to literature procedures.[5] Melting points were determined in capillary tubes and are corrected. Flash column chromatography was performed on silica gel 60 (Aldrich Chemical Co.). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Dienes. General Procedure. To a cold (0 °C) stirred slurry of methyltriphenylphosphonium iodide or bromide (5 mmol) in THF (25 mL) under a nitrogen atmosphere was added an equivalent amount of butyllithium, and the resulting mixture was stirred for 15 min. The ketone, dissolved in 1–2 mL of THF, was then added via cannula, the ice bath was removed, and the reaction was allowed to proceed for 1–3 h. The mixture was poured into an equal volume of water and extracted with ether (3 × 25 mL). The ether extracts were dried (Na_2SO_4) and evaporated, and the product was isolated by flash chromatography (petroleum ether eluent).

1a: 42% yield; colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 1.6–1.8 (m, 2 H), 2.3–2.5 (m, 2 H), 2.5–2.7 (m, 2 H), 4.9–5.0 (m,

(3) (a) Pomerantz, M.; Gruber, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 6615. (b) Baldry, P. J. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1913. (c) Baldry, P. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 805.

(4) Consistent with this is our observation that 3-ethyl-2-methyl-1-phenyl-1,3-butadiene, in which *Z*-cis and *Z*-trans conformations are of comparable energy, does photocyclize. R. J. Olsen and J. M. Sherrick, unpublished results.

(5) (a) House, H. O.; Wasson, R. L. *J. Am. Chem. Soc.* **1956**, *78*, 4394. (b) Walton, H. M. *J. Org. Chem.* **1957**, *22*, 1161.

(6) Tius, M. A.; Gomez-Galeno, J. *Tetrahedron Lett.* **1986**, *27*, 2571.

1 H), 5.4-5.5 (m, 1 H), 6.8-6.9 (m, 1 H), 7.0-7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.5, 32.5, 33.5, 102.5, 119.9, 126.3, 128.2, 128.7, 138.1, 141.8, 150.6; IR (film) 694, 745, 870, 1447, 1493, 1598, 2960, 3035 cm^{-1}. Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.49; H, 8.35.

2a: 78% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.6-1.8 (m, 4 H), 2.2-2.4 (m, 2 H), 2.4-2.6 (m, 2 H), 4.6-4.8 (m, 1 H), 4.9-5.0 (m, 1 H), 6.5-6.6 (m, 1 H), 7.1-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 26.8, 27.3, 30.2, 35.9, 109.2, 123.7, 126.8, 128.5, 129.8, 138.3, 143.2, 151.6; IR (film) 658, 750, 865, 1430, 1480, 1615, 2830, 2920, 3005, 3060 cm^{-1}; UV (cyclohexane) λ_{max} 260 (ε 630); maleic anhydride adduct mp 137-138 °C (lit.[7] mp 139 °C).

3a: 79% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.5-1.7 (m, 6 H), 2.3-2.4 (m, 2 H), 2.5-2.6 (m, 2 H), 4.7-4.8 (m, 1 H), 5.4-5.5 (m, 1 H), 6.6-6.7 (m, 1 H), 7.1-7.4 (m, 5 H); IR (film) 690, 747, 875, 1435, 1590, 2840, 2905, 3010, 3070 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H. 9.15. Found: C, 90.53; H, 8.96.

4a: 44% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.4-1.8 (m, 8 H), 2.3-2.4 (m, 2 H), 2.5-2.6 (m, 2 H), 4.8-4.9 (m, 1 H), 5.1-5.2 (m, 1 H), 6.6-6.7 (m, 1 H), 7.1-7.5 (m, 5 H); IR (film) 696, 749, 894, 1444, 1491, 1597, 2920, 3030, 3085 cm^{-1}. Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.54; H, 9.33.

5a: 73% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92, (d, J = 6.3 Hz, 3 H), 1.24 (dq, J = 4.4, 12.2 Hz, 1 H), 1.5-1.7 (m, 1 H), 1.8-1.9 (m, 2 H), 2.2-2.3 (m, 1 H), 2.46 (dt, J = 3.9, 13.7 Hz, 1 H), 2.8-2.9 (m, 1 H), 4.6-4.7 (m, 1 H), 4.9-5.1 (m, 1 H), 6.5-6.6 (m, 1 H), 7.1-7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 22.0, 32.4, 34.4, 34.9, 37.9, 108.7, 123.2, 126.2, 128.0, 129.3, 137.7, 142.1, 150.6; IR (film) 690, 730, 857, 886, 1151, 1435, 1620, 2910, 2940, 3010, 3070 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.57; H, 9.06.

6a (Wittig reaction using ethyltriphenylphosphonium iodide): 49% yield (as a mixture of isomers); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.5-1.8 (m with doublets at 1.68 and 1.78, total of 7 H), 2.2-2.4 (m, 2 H), 2.4-2.6 (m, 2 H), 5.3-5.7 (quartets, 1 H), 6.2-6.5 (multiplets, 1 H), 7.1-7.4 (m, 5 H); IR (film) 688, 751, 810, 909, 985, 1436, 1590, 2830, 2910, 3010 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.65; H, 9.47.

7a: 74% yield; colorless oil; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.5-1.9 (m, 4 H), 2.2-2.7 (m with s at 2.33, 7 H), 4.6-4.8 (m, 1 H), 4.9-5.0 (m, 1 H), 6.4-6.6 (m, 1 H), 7.0-7.2 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.6, 26.7, 27.3, 30.2, 35.8, 108.9, 123.5, 129.1, 129.7, 135.4, 136.4, 142.5, 151.7; IR (film) 800, 880, 1430, 1500, 1610, 2850, 2920, 3010, 3070 cm^{-1}. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.75; H, 8.91.

8a: 66% yield; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.4-1.8 (m, 4 H), 2.2-2.5 (m, 4 H), 4.8 (m, 1 H), 5.1 (m, 1 H), 7.0 (m, 1 H), 7.2-7.6 (m, 4 H), 7.6-7.9 (m, 2 H), 7.9-8.1 (m, 1 H); IR (film) 770, 880, 1385, 1430, 1620, 2840, 2920, 3045 cm^{-1}. Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 91.81; H, 7.64.

Photocyclization of Dienes. General Procedure. A solution of 1 mmol of diene in 200 mL of benzene in an open quartz beaker was placed approximately 15 cm from a 450-W medium-pressure mercury vapor lamp in a water-cooled quartz immersion apparatus and irradiated for 3-6 h. After the irradiation the solvent was evaporated and the product was purified by flash chromatography (petroleum ether eluent). All photoproducts except **7b** were known compounds and were identified by comparison of melting points and/or spectroscopic data with literature values.

1b: 57% yield; mp 94-95 °C (lit.[8] mp 94 °C).

2b: 57% yield; mp 98-99 °C (lit.[6,9] mp 92-94 °C, 103-105 °C).

3b: 74% yield; mp 103-105 °C (lit.[6] mp 104-105 °C).

4b: 58% yield; colorless oil (lit.[10] mp 54-55 °C).

5b: 45% yield; 70-72 °C (lit.[11] mp 69-74 °C).

6b: 56% yield; colorless oil.[12]

7b: 61% yield; white crystals; mp 72-73 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.8-2.0 (m, 4 H), 2.46 (s, 3 H), 2.9-3.1 (m, 4 H), 7.2-7.3 (m, 1 H), 7.4-7.7 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.6, 21.8, 23.2, 23.5, 29.7, 125.7, 126.2, 126.5, 127.0, 127.3, 130.5, 132.4, 134.3, 135.2, 136.2; IR (Nujol) 797, 876, 922, 1501 cm^{-1}. Anal. Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.68; H, 8.24.

8b: 48% yield; mp 89-90 °C (lit.[13] mp 89-90 °C).

Acknowledgments are made to the Haines Research Fund at Wabash College, the Howard Hughes Medical Institute, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. 1, 1921-90-0; **1a**, 130954-49-3; **1b**, 1624-26-6; **2**, 1467-15-8; **2a**, 130954-50-6; **2a** (maleic anhydride adduct), 130954-57-3; **2b**, 2141-42-6; **3**, 88356-04-1; **3a**, 130954-51-7; **3b**, 7092-91-3; **4**, 69202-72-8; **4a**, 130954-52-8; **4b**, 16271-28-6; **5**, 75910-68-8; **5a**, 130954-53-9; **5b**, 85268-79-7; (*E*)-**6a**, 130954-54-0; (*Z*)-**6a**, 130954-55-1; **6b**, 101111-40-4; **7**, 130954-47-1; **7a**, 130954-56-2; **7b**, 89155-69-1; **8**, 130954-48-2; **8a**, 122214-17-9; **8b**, 67064-62-4; methyltriphenylphosphonium iodide, 2065-66-9; methyltriphenylphosphonium bromide, 1779-49-3; ethyltriphenylphosphonium iodide, 4736-60-1.

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Reduction of DMAD-Anthracene Adducts. Synthesis and Conformations of Substituted Cyclodecadienes

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Received June 21, 1990

A general method for reducing DMAD-anthracene adducts to the corresponding enediols is described. Thus, the ester groups of **1** were reduced without C=C reduction using the DIBAH-*n*BuLi "ate" complex to give previously unknown **2** in high yield. Analogous enediols **5-7** were similarly prepared. Base treatment of dibromide **3** and dithiol **9**, both prepared from **2** by standard methods, gave conformationally rigid dithiacyclodecadiene **10**. With *o*-, *m*-, and *p*-xylylenedithiols, dibromide **3** gave respectively the conformationally labile cyclophanes **12** and **13** and the rigid cyclophane **14**. Tetrabromide **16** and dithiol **9** gave cuppedophane **17**, but tetrabromide **18** and **9** formed bis-*m*-cyclophane **19** instead.

It is surprising that although the dimethyl acetylenedicarboxylate (DMAD) adduct of anthracene (**1**) has been known since 1931,[1] the enediol **2** that might be derived from it by reduction is as yet unreported. Attempts to

0022-3263/91/1956-0991$02.50/0