J. Org. Chem. **1983**, *48*, 273–276

minor unidentified products (no olefinic carbon was observed by ^{13}C NMR). This was then subjected to column chromatography (silica gel) to give a mixture of **1** and **2** (13.0 g, 35.8 mmol, 77% yield) (10:1 petroleum ether–ethyl acetate as eluant) as a white solid (mp 60–62 °C): IR (KBr disk) 2950, 2880, 1450, 1295, 1260, 1245, 1190, 1160, 1130, 1090, 1060, 1020, 930, 865, 820, 790, 740, 670 cm^{-1}; mass spectrum, *m/e* (relative intensity) 362 (M^+, $C_8H_{12}I_2$, 1), 235 ($M^+ - I$, 99), 107 ($M^+ - I_2 - H$, 100).

A mixture of **1** and **2** was subjected to column chromatography on a silica gel 60 prepacked column (Merck, size A) with petroleum ether as eluant to give each of pure **1** and **2**, the former being eluted at first. **1**: mp 79–80 °C (recrystallized from *n*-hexane); ^1H NMR ($CDCl_3$) δ 1.2–2.4 (m, 8 H), 2.5–3.1 (m, 2 H), 3.75–4.0 (m, 1 H), 4.1–4.35 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 30.6 (t), 31.1 (d, CI), 32.1 (d, CI), 34.3 (t), 36.9 (t), 39.8 (t), 47.8 (d, CH), 54.5 (d, CH). **2**: mp 67–68 °C (recrystallized from *n*-hexane); ^1H NMR ($CDCl_3$) δ 1.80 (t, 4 H), 1.95–2.3 (m, 4 H), 2.5–2.85 (m, 2 H), 4.25–4.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.2 (d, CI), 33.4 (t), 38.1 (t), 47.6 (d, CH).

Anal. Calcd for $C_8H_{12}I_2$: C, 26.55; H, 3.34; I, 70.11. Found for **1**: C, 26.51; H, 3.41; I, 69.85. Found for **2**: C, 26.47; H, 3.38; I, 69.99.

Iodination of COD in Acetonitrile (MeCN). A solution of iodine (7.61 g, 30 mmol) and COD (2.16 g, 20 mmol) in MeCN (50 mL) was stirred at 25 °C for 24 h. The mixture was then added to aqueous NaCl (150 mL) and extracted with chloroform. The extract was treated as described above and the residue was subjected to column chromatography to give a mixture of **1** and **2** (1.45 g, 4.0 mmol, 20% yield; *n*-hexane as eluant) and a mixture of **3** and **4** (2.31 g, 7.88 mmol, 39% yield; ethyl acetate as eluant), both as solids. The HPLC analysis revealed the ratios of **1**/**2** and **3**/**4** to be 46/54 and 50/50, respectively. Mixture of **3** and **4**: mp 65–85 °C; IR (KBr disk) 3400 (s), 3110, 2980 (s), 2900, 1640 (s), 1545 (s), 1450, 1370, 1305, 1185, 1170, 1130, 825, 695 cm^{-1}; mass spectrum, *m/e* (relative intensity) 293 (M^+, $C_{10}H_{16}INO$, 4), 234 (M^+ − NHCOMe − H, 3), 166 ($M^+ - I$, 78), 107 (M^+ − I − NHCOMe − H, 100).

A mixture of **3** and **4** was subjected to column chromatography on a silica gel 60 prepacked column (Merck, size A) with 1:1 benzene–hexane as eluant to give pure **3** and **4** each as a white solid, the latter being eluted at first. **3**: mp 136–137 °C dec; ^1H NMR ($CDCl_3$) δ 1.0–2.30 (m, 9 H), 1.94 (s, 3 H), 2.64 (quintet, 1 H), 3.70–4.25 (m, 2 H), 5.60 (s, br, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.4 (q), 30.7 (d), 30.8 (t), 32.9 (t), 33.4 (t), 36.5 (t), 47.4 (d), 48.6 (d), 58.8 (d), 169.8 (s). **4**: mp 125–126 °C; ^1H NMR ($CDCl_3$) δ 1.25–2.24 (m, 8 H), 1.90 (s, 3 H), 2.36–2.84 (m, 2 H), 4.0–4.40 (m, 2 H), 5.88 (s, br, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.2 (q), 25.7 (t), 31.8 (t), 31.8 (t), 35.9 (d), 39.3 (t), 44.6 (d), 48.0 (d), 53.9 (d), 169.8 (s).

Anal. Calcd for $C_{10}H_{16}INO$: C, 40.97; H, 5.50; N, 4.78; I, 43.29. Found for **3**: C, 40.81; H, 5.58; N, 4.84; I, 43.08. Found for **4**: C, 41.01; H, 5.59; N, 4.60; I, 43.32.

Iodination of COD in *N,N*-Dimethylformamide (DMF). The same scale reaction as in the case of CCl_4 was carried out with DMF as solvent at 25 °C for 24 h. After the usual workup procedure (addition of brine, washing with aqueous $Na_2S_2O_3$, extraction with benzene), evaporation of the solvent left a yellow-brown oil, which was passed through a short column of silica gel to remove resinous products. The eluent contained **5** (X = OCHO) and small amounts of **1** and **2**, the former then being isolated by preparative TLC (10:1 petroleum ether–ethyl acetate; Merck silica gel 60 F-254 plate) as a pale yellow oil (7.84 g, 28 mmol, 60% yield): IR 3040, 2955, 1730 (s), 1485, 1430, 1175 (s), 1070, 1030, 990, 710, 655 cm^{-1}; mass spectrum, *m/e* (relative intensity) 280 (M^+, $C_9H_{13}IO_2$, 16), 251 (M^+ − CHO, 9), 153 ($M^+ - I$, 100); ^1H NMR ($CDCl_3$) δ 1.4–2.8 (m, 8 H), 4.62 (dt, 1 H), 5.40 (dt, 1 H), 5.44–5.88 (m, 2 H), 8.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.6 (t), 27.1 (t), 30.8 (t), 34.6 (d, CI), 36.7 (t), 77.3 (d, COCHO), 127.4 (d), 129.4 (d), 159.3 (d).

Anal. Calcd for $C_9H_{13}IO_2$: C, 38.59; H, 4.68. Found: C, 37.92; H, 4.70.

Acknowledgment. We thank Professor K. B. Wiberg of Yale University for his helpful discussion.

Registry No. **1**, 84064-77-7; **2**, 84064-78-8; **3**, 84064-79-9; **4**, 84107-46-0; **5** (X = OCHO), 84064-80-2; **6**, 29417-22-9; **7**, 24165-06-8; **8**, 3194-57-8; (*Z,Z*)-COD, 1552-12-1.

A Butatriene Cycloaddition Equivalent Approach to the Multiple Linear Homologation of Six-Membered Rings and the Synthesis of Benzocyclobutenes

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The construction of six-membered rings through Diels–Alder reactions is of immense importance in organic synthesis. It clearly would be desirable to have methodology available for the construction of linear polycyclic structures through repetitive [2 + 4] cycloadditions. We describe here a straightforward conceptual and experimental means of achieving this end, as well as its elaboration as a general and convenient route to benzocyclobutenes.

Diethyl Acetylenedicarboxylate (DEAD) as a Butatriene Cycloaddition Equivalent. In the course of work directed toward the synthesis of complex polycyclic hydrocarbons, we had need of a convenient approach to molecules of general structure **1**.[1] Conceptually, at least, these may be obtained through repetitive 1,2,3-butatriene [2 + 4] cycloadditions, as shown in Scheme I. Cycloaddition of butatriene to a 1,3-diene can, in principle, yield a cycloadduct which contains an exocyclic 1,2-dimethylene unit. This can react with a second molecule of butatriene, and the sequence should be repeatable indefinitely. Unfortunately, direct use of butatriene in this reaction is not feasible due to its apparently weak dienophilicity[2] and its propensity toward oligomerization;[3] thus we perforce need some type of butatriene synthetic equivalent. The requirements for such a method are that it involve a good, readily available dienophile and that subsequent chemistry not involve strong acid, base, or high temperature, due to the sensitivity of polydehydro aromatic structures such as **1**. Since this is a linear approach, good to excellent yields are a necessity.

In past years, a variety of reagents which may be considered butatriene synthetic equivalents have been reported, with the purpose of synthesis of the 1,2-dimethylene unit.[4] Most common is maleic anhydride, which usually is elaborated via acetate or amine oxide pyrolysis or via base-induced halide elimination. Such methods often are of moderate to good efficiency, but because of the pyrolytic step or strong base, these did not seem suitable for multiple homologations.

Our approach to this problem has been to use dimethyl or diethyl acetylenedicarboxylate (DMAD or DEAD) as butatriene synthetic equivalents; this is outlined in Scheme II. Several examples of the use of DMAD as a precursor

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(1) Preliminary report: Angus, R. O., Jr.; Johnson, R. P. "Abstracts of Papers", 17th Midwest Regional Meeting of the Americal Chemical Society, Columbia, MO, 1981; American Chemical Society: Washington, DC, 1981.

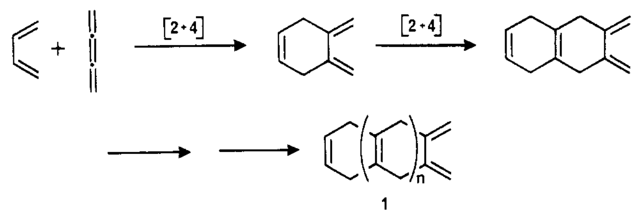
(2) (a) Although the corresponding retro [2 + 4] reaction is well-known,[2b] successful [2 + 4] cycloadditions to the central bond of a butatriene are rare.[2c] (b) Ripoll, J. L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19. (c) Reid, W.; Neidhardt, R. *Justus Liebigs Ann. Chem.* **1970**, *739*, 155.

(3) (a) Schubert, W. M.; Liddicoet, T. H.; Lanke, W. A. *J. Am. Chem. Soc.* **1954**, *76*, 1929. (b) Wille, F.; Dorr, K.; Kerber, H. *Justus Liebigs Ann. Chem.* **1955**, *591*, 177.

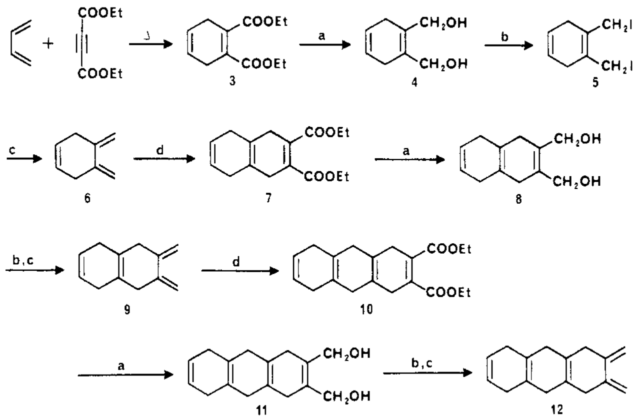
(4) For example: (a) Ottenbrite, R. M.; Alston, P. V. *J. Org. Chem.* **1974**, *39*, 1115. (b) Cope, A. C.; Ciganek, E. *Org. Synth.* **1959**, *39* 40. (c) Bailey, W. J.; Rosenberg, J. *J. Am. Chem. Soc.* **1955**, *77*, 73. (d) Middlemas, E. D.; Quin, L. D. *J. Org. Chem.* **1979**, *44*, 2587. (e) Butler, D. N.; Snow, R. A. *Can. J. Chem.* **1972**, *50*, 795.

0022-3263/83/1948-0273$01.50/0

Scheme I



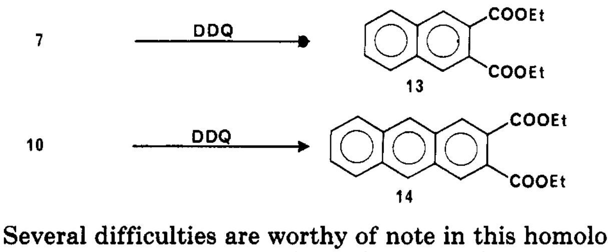
Scheme II[a]



[a] (a) $LiAlH_4$, Et_2O; (b) Me_3SiCl, NaI; (c) Zn/Cu, ether; (d) 2 (1 equiv).

to the 1,2-dimethylene functionality have been reported.[5] Typically, we have found the diethyl ester DEAD to give slightly higher yields in the hydride reduction step (vide infra). Cycloaddition of DEAD (2) with 1,3-butadiene, followed by $LiAlH_4$ reduction, yielded the known diol 4.[6] This was converted to diiodide 5 with Me_3SiI, or Me_3SiCl/NaI, following the procedure of Olah.[7] The diiodide was not isolated but was immediately added to a stirred suspension of zinc–copper couple, maintained at ambient temperature. The workup afforded triene 6 (80% yield), identical with a sample prepared through the amine oxide pyrolysis route.[4b,d]

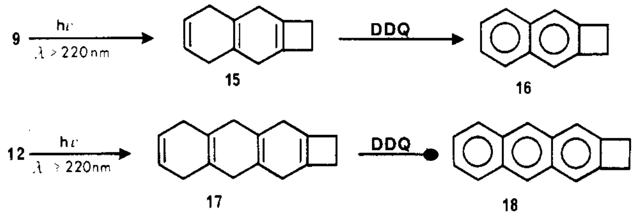
Preparation of higher homologues was accomplished by straightforward repetition of this four-step sequence. Cycloaddition of 6 or its homologue 9 with DEAD proceeded smoothly at 40–50 °C in benzene to afford the dehydro aromatic esters 7 and 10. DDQ oxidation of these led to the expected aromatic structures.



Several difficulties are worthy of note in this homologation sequence. Intermediate diols 8 and 11 proved troublesome because a substantial fraction (10–30%) of product from $LiAlH_4$ reductions was entrained in the inorganic residues, regardless of the workup procedure. Continuous extraction of the residue with refluxing ether improved yields significantly. Second, we found that literature Zn–Cu couple preparations[8] often gave variable yields in the elimination steps. To circumvent this, we developed a new preparation, which invariably yielded a highly reactive couple in a matter of a few minutes. The procedure involves covering a mixture of zinc dust and $CuSO_4 \cdot 5H_2O$ with dry DMF under nitrogen. A rapid and exothermic reaction yields the Zn–Cu couple, ready for use in the elimination step. Details are given in the Experimental Section.

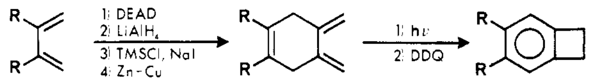
Synthesis of Benzocyclobutenes

This homologation procedure also provides a general and exceptionally simple route to benzocyclobutenes.[9] Photocyclization of 6, followed by oxidation, has been reported by Fonken[10] some years ago. In the present work, cyclization of homologues 9 or or 12 through Vycor-filtered



irradiation of dilute pentane solutions led smoothly to crystalline polydehydro aromatics 15 and 17. Neither has been reported previously. DDQ oxidation yielded the known naphtho[*b*]- and anthro[*b*]cyclobutenes.

This overall sequence thus allows straightforward conversion of a diene moiety into a benzocyclobutene in six steps, with all reactions proceeding in >80% yield. A



similar sequence has been accomplished by Thummel,[9b] using dimethyl cyclobutenedicarboxylate as the dienophile. The present approach avoids the frequently troublesome decarboxylation step.

Experimental Section

General Methods. Melting points are corrected. NMR spectra were obtained on Varian EM-360 or JEOLCO FX-90Q spectrometers, with chemical shifts reported in parts per million downfield from Me_4Si. All new compounds gave satisfactory combustion analysis and/or high-resolution mass spectra.

Dimethyl and diethyl acetylenedicarboxylate (DMAD and DEAD) were prepared from the commercially available monopotassium salt of acetylenedicarboxylic acid.[11]

Diethyl 3,6-Dihydrophthalate (3). Reaction of butadiene (20 g, 0.37 mol) and DEAD (42.5 g, 0.250 mol) at 40–45 °C in a pressure bottle for 5–6 days afforded 57.2 g (98%) of the adduct 3 as a colorless liquid: bp 90–95 °C (0.8 torr); ^1H NMR ($CDCl_3$) δ 5.78 (s, 2 H), 4.27 (q, 4 H), 3.01 (br s, 4 H), 1.27 (t, 6 H); ^{13}C NMR ($CDCl_3$) δ 167.4 (C=O), 132.0, 122.0, 60.5, 27.1, 13.6; IR (neat) 2980, 2900, 2880, 2830, 1720, 1680, 1645, 1255, 1055 cm^{-1}; mass spectrum, m/e 224.10531 ($C_{12}H_{16}O_4$ requires 224.10486).

1,2-Bis(hydroxymethyl)-3,6-dihydrobenzene (4). Diethyl ester 3 was reduced with a twofold molar excess of $LiAlH_4$ in ether at 0 °C. Hydrolysis with 1 M K_2CO_3(aq) and a standard workup

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[5] (a) Talma, A. G.; Goorhuis, J. G. M.; Kellogg, R. M. *J. Org. Chem.* **1980**, *45*, 2544. (b) Beetz, T.; Kellogg, R. M. *J. Am. Chem. Soc.* **1973**, *95*, 7925.

[6] Gaoni, Y.; Schoef, N. *Bull. Soc. Chim. Fr.* **1977**, 485.

[7] Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.

[8] Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* **1973**, *20*, 82–3 and references therein.

[9] Reviews: (a) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471. (b) Thummel, R. P. *Acc. Chem. Res.* **1980**, *13*, 70 and references therein.

[10] Fonken, G. J.; Garrett, J. M. *Tetrahedron Lett.* **1969**, 191.

[11] Huntress, E. H.; Lesslie, T. E.; Bornstein, J. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, pp 329–30.

afforded the diol (92%) as a crystalline solid: mp 46–47 °C (lit.[6] mp 47–48 °C); ^{13}C NMR (acetone-d_6) δ 131.8, 124.9, 61.6, 29.6.

Preparation of Zinc–Copper Couple. Dry DMF was added dropwise quickly under nitrogen to a magnetically stirred intimate mixture of finely powdered $CuSO_4\cdot 5H_2O$ and Zn dust (1:10 molar ratio) until the surface was just covered. An exothermic reaction ensued, and the mixture immediately became black. Slight external cooling was used in the preparation of large quantities.

After cooling, the mixture was diluted with ether and used directly in elimination reactions. Attempted use of anhydrous $CuSO_4$ in this procedure did *not* lead to efficient couple formation.

4,5-Dimethylenecyclohexene (6). A mixture of diol 4 (3.60 g, 25.7 mol) and sodium iodide (11.6 g, 77.0 mmol) in 450 mL of dry ether was stirred under nitrogen at 25 °C and treated dropwise with chlorotrimethylsilane (Me_3SiCl, 16.4 mL, 128.4 mmol). After 1 h, TLC analysis showed no remaining diol, and the mixture was transferred during 45 min via cannula to a stirred suspension of Zn–Cu couple (125 mmol) in 50 mL of ether. After 2 h more, the mixture was filtered, washed with saturated $NaHCO_3$(aq) (4 × 100 mL), dried ($MgSO_4$), and concentrated to afford 2.4 g (82%) of essentially pure **6**, bp 65–71 °C (60 torr) [lit.[4d] bp 73–74 °C (85 torr)].

Diethyl 1,4,5,8-Tetrahydro-2,3-naphthalenedicarboxylate (7). A solution of diene **6** (2.4 g, 23 mmol) and DEAD (4.0 mL, 22 mmol) in benzene (100 mL) was heated at 40–50 °C for 4 h and then concentrated to yield 5.69 g (94%) of adduct **7**, which was recrystallized from hexane: mp 176–178 °C; ^{1}H NMR ($CDCl_3$) δ 5.81 (m, 2 H), 4.27 (q, 4 H), 2.89 (br s, 4 H), 2.58 (br s, 4 H), 1.31 (t, 6 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 167.9 (C=O), 132.5, 124.0, 121.8, 61.0, 32.4, 30.2, 14.1; IR (KBr) 2980, 2880, 2840, 2815, 1725, 1660, 1255, 1065, 1035 cm^{-1}; mass spectrum, *m/e* 276 (M^+), 230 (base), 201, 129, 125, 98; high-resolution mass spectrum, *m/e* 276.136 06 ($C_{16}H_{20}O_4$ requires 276.136 16). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.295. Found: C, 69.34; H, 7.25.

2,3-Bis(hydroxymethyl)-1,4,5,8-tetrahydronaphthalene (8). A solution of diethyl ester **7** (6.09 g, 22.1 mmol) in ether was added dropwise at 0 °C to a stirred mixture of $LiAlH_4$ (1.68 g, 44.1 mmol) in dry ether (450 mL). After 4 h more at ambient temperature, the mixture was hydrolyzed at 0 °C with a large excess of 1 M K_2CO_3(aq). The copius white precipitate was carefully filtered. Concentration of the dried ether layer afforded 2.62 g of diol **8**. Continuous extraction (5 days) of the inorganic residue with refluxing ether gave an additional 0.962 g (total 85% yield) of diol. Data for **8**: mp 147–149 °C; ^{1}H NMR (acetone-d_6) δ 5.75 (br s, 2 H), 4.09 (br s, 2 H), 3.07 (br s, 4 H), 2.66 (br s, 4 H), 2.53 (br s, 4 H); ^{13}C NMR (acetone-d$_6$) δ 131.6, 125.0, 123.6, 60.9, 31.5, 30.8; IR (KBr) 3600–3050, 2864, 2835, 2803, 1665, 1442, 1052, 980 cm^{-1}; mass spectrum, *m/e* 192 (M^+), 174, 143 (base), 131, 91; high-resolution mass spectrum, *m/e* 192.114 97 ($C_{12}H_{16}O_2$ requires 192.115 03). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.69; H, 8.389. Found: C, 75.02; H, 8.48.

2,3-Dimethylene-1,4,5,8-tetrahydronaphthalene (9). Diol **8** (2.35 g, 12.2 mmol) and NaI (3.67 g, 24.4 mmol) in 300 mL of dry ether and 50 mL of dry THF was treated dropwise with Me_3SiCl (77.8 mL, 61.1 mmol). The mixture was added to freshly prepared Zn–Cu couple (60 mmol) in ether. A workup as above afforded the product as a colorless liquid, which was used immediately in the subsequent step. The spectral data were as follows: ^{1}H NMR ($CDCl_3$) δ 5.68 (m, 2 H), 5.06 (br d, 2 H), 4.71 (br d, 2 H), 2.72 (br s, 4 H), 2.48 (br s, 4 H); ^{13}C NMR ($CDCl_3$) δ 145.4, 124.2, 124.1, 108.2, 37.9, 30.8; IR (neat) 2955, 2920, 2890, 2870, 2840, 2805, 1645, 1630, 1425, 880 cm^{-1}; mass spectrum, *m/e* 158 (M^+), 143, 128, 115, 91 (base); high-resolution mass spectrum, *m/e* 158.109 11 ($C_{12}H_{14}$ requires 158.109 55).

Diethyl 1,4,5,8,9,10-Hexahydroanthracene-2,3-dicarboxylate (10). Crude **9**, from above, was treated with DEAD (1.96 mL, 12.2 mmol) in 50 mL of benzene at 40–50 °C during 4 h. Concentration of solvent and recrystallization from ether–hexane yielded 2.21 g (55% overall from diol **8**) of **10** as colorless crystals: mp 99–103 °C; ^{1}H NMR ($CDCl_3$) δ 5.63 (br s, 2 H, C=CH), 4.20 (q, 4 H), 2.85 (br s, 4 H), 2.54 (br s, 4 H), 2.41 (br s, 4 H), 1.25 (t, 6 H); ^{13}C NMR ($CDCl_3$) δ 167.9 (C=O), 132.6, 124.3, 123.1, 121.9, 61.1, 35.2, 32.1, 30.5, 14.1; IR (KBr) 2980, 2875, 2815, 1723, 1244, 1058, 1033 cm^{-1}; mass spectrum, *m/e* 328 (M^+), 282 (base), 252, 210; high-resolution mass spectrum, *m/e* 328.167 32 ($C_{20}H_{24}O_4$ rquires 328.167 47).

2,3-Bis(hydroxymethyl)-1,4,5,8,9,10-hexahydroanthracene (11). Diethyl ester **10** (1.45 g, 440 mmol) was reduced as above with $LiAlH_4$ (344 mg, 8.80 mmol) in ether–THF (to improve solubility). The organic layer yielded 336 mg of product, and continuous extraction (5 days) of the inorganic residue yielded an additional 301 mg of product (total 60%). Data for diol **11**: mp 210–213 °C; ^{1}H NMR (Me_2SO-d_6) δ 5.66 (br s, 2 H), 4.06 (br s, 2 H, OH), 3.23 (br s, 4 H), 2.65 (br s, 4 H), 2.51 (br s, 4 H), 2.39 (br s, 4 H); ^{13}C NMR (Me_2SO-d_6) δ 130.3, 124.2, 122.9, 122.7, 59.8, 34.9, 33.1, 30.0; IR (KBr) 3600–3050, 2860, 2796, 1410, 1040, 998, 978, 958 cm^{-1}; mass spectrum, *m/e* 244 (M^+) 226, 210, 195; high-resolution mass spectrum, *m/e* 244.146 56 ($C_{16}H_{20}O_2$ requires 244.146 33).

2,3-Dimethylene-1,2,3,4,5,8,9,10-octahydroanthracene (12). Diol **11** (182 mg, 0.7449 mmol) was treated with NaI (223 mg, 1.490 mmol) and Me_3SiCl (474 μL, 3.73 mmol) in 40 mL of THF. Elimination was effected by fresh Zn–Cu couple (3.7 mmol) in 15 mL of anhydrous Et_2O. Recrystallization of the product from pentanes afforded 61 mg (39%) of **12** as a colorless solid: mp 88.5–90 °C; ^{1}H NMR ($CDCl_3$) δ 5.68 (s, 2 H, C=CH), 5.07 (d, 2 H, C=CH_2), 4.73 (d, 2 H, C=CH_2), 2.81 (br s, 4 H), 2.51 (br s, 4 H), 2.40 (br s, 4 H); ^{13}C NMR ($CDCl_3$) δ 145.7, 124.4, 123.2, 108.5, 37.5, 36.0, 30.6; IR (CCl_4) 2960, 2868, 2840, 2808, 1655, 1645, 1631, 1427, 884 cm^{-1}; mass spectrum, *m/e* 210 (M^+ and base), 208, 194, 192, 140; high-resolution mass spectrum, *m/e* 210.140 32 ($C_{16}H_{18}$ requires 210.140 85).

Diethyl 2,3-Naphthalenedicarboxylate (13). Compound **7** (86 mg, 0.311 mmol) in benzene was added to DDQ (141 mg, 0.622 mmol) in benzene. After 15 min, the mixture was concentrated and chromatographed over silica gel. Elution with EtOAc–hexane (1:4) gave 78 mg (92%) of **13**: mp 54–55 °C (lit.[12] mp 55 °C); ^{1}H NMR ($CDCl_3$) δ 8.15 (s, 2 H), 7.89–7.33 (m, 4 H), 4.33 (q, 4 H), 1.33 (t, 6 H); ^{13}C NMR δ 167.7 (C=O), 133.4, 130.0, 128.9, 128.6, 128.4, 61.6, 14.2.

Diethyl 2,3-Anthracenedicarboxylate (14). Diester **10** (195 mg, 0.5938 mmole was oxidized with DDQ (404 mg, 1.781 mmol) as above to afford 16 mg (84%) of **14**: mp 99–100 °C; ^{1}H NMR ($CDCl_3$) δ 8.42 (s, 2 H), 8.37 (s, 2 H), 8.02–7.34 (m, 4 H), 4.38 (q, 4 H), 1.38 (t, 6 H); ^{13}C NMR ($CDCl_3$) δ 167.7 (C=O), 133.0, 131.0, 130.4, 128.4, 128.0, 127.8, 126.7, 61.6, 14.2; IR (CCl_4) 2982, 1725, 1540, 1238, 998, 970 cm^{-1}; mass spectrum, *m/e* 322 (M^+) and base) 276, 248, 247; high-resolution mass spectrum, *m/e* 322.119 28 ($C_{20}H_{18}O_4$ requires 322.120 51).

1,4,5,8-Tetrahydronaphtho[*b*]cyclobutene (15). By use of a standard immersion-well apparatus, with a 450-W medium-pressure lamp, a solution of diene **9** (135 mg) in 200 mL of argon-degassed spectrograde pentane was irradiated for 25 min through a Vycor filter. Concentration, and chromatography over silica gel (hexane elution) yielded 130 mg (96%) of **15**: mp 78–81 °C; ^{1}H NMR ($CDCl_3$) δ 5.53 (br s, 2 H), 2.49 (br s, 8 H), 2.34 (br s, 4 H); ^{13}C NMR ($CDCl_3$) δ 139.0, 124.3, 31.8, 31.1, 30.9; IR (CCl_4) 2910, 2875, 2850, 2815, 1678, 1428, 1245 cm^{-1}; mass spectrum, *m/e* 158 (M^+ and base), 143, 129, 115; high-resolution mass spectrum, *m/e* 158.109 34 ($C_{12}H_{12}$ requires 158.109 55).

Naphtho[*b*]cyclobutene (16). Hydrocarbon **15** (99 mg, 0.63 mmol) was oxidized with DDQ (284 mg, 1.25 mmol) in benzene at 25 °C. Silica gel chromatography (hexane elution) yielded 80 mg (81%) of **16**: mp 86–87.5 °C (lit.[13] mp 84.5–86 °C); ^{13}C NMR ($CDCl_3$) δ 144.7, 133.9, 128.0, 124.6, 120.3, 29.4. The ^{1}H NMR spectrum was as reported.[14]

1,4,5,8,9,10-Hexahydroanthro[*b*]cyclobutene (17). Diene **12** (40 mg) in argon-degassed spectrograde pentane was irradiated through Vycor for 20 min. Concentration and chromatography yielded 36 mg (90%) of **17**: mp 143–145 °C; ^{1}H NMR ($CDCl_3$) δ 5.64 (s, 2 H), 2.52 (br s, 8 H) 2.44 (br s, 8 H); IR (CCl_4) 2915, 2865, 2810, 1660, 1430 cm^{-1}; mass spectrum, *m/e* 210 (M^+ and base), 195, 193, 179, 178, 141, 128; high-resolution mass spectrum, *m/e* 210.141 04 ($C_{14}H_9$ requires 210.140 85).

Anthro[*b*]cyclobutene (18). Cyclobutene **17** (23 mg, 0.11 mmol) in 2 mL of CCl_4 was oxidized with DDQ (75 mg, 0.33 mmol). Silica gel chromatography yielded 18 mg (85%) of anthracene **18**: mp >240 °C (lit. mp 245–247); ^{13}C NMR δ 144.7, 122.5, 130.9,

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128.0, 126.0, 124.9, 119.8, 29.8. The ^{1}H NMR was as reported.[14]

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Registry No. 3, 14503-20-9; **4**, 65774-75-6; **5**, 84040-97-1; **6**, 54290-41-4; **7**, 84040-98-2; **8**, 84040-99-3; **9**, 84041-00-9; **10**, 84041-01-0; **11**, 84041-02-1; **12**, 84041-03-2; **13**, 50919-54-5; **14**, 84041-04-3; **15**, 84041-05-4; **16**, 6827-31-2; **17**, 84041-06-5; **18**, 65957-35-9; DEAD, 762-21-0; butadiene, 106-99-0.

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Stereochemistry of the Diels–Alder Reaction of Cyclopentadiene and 3,3,3-Trifluoropropene

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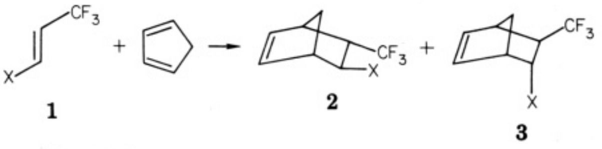
One of the earliest reports of the Diels–Alder reaction notes the preference for endo addition by substituted dienophiles.[1] Alder and Stein first attributed the endo preference to overlap of the π system of unsaturated dienophile substituents with the π system of the diene[1] and later to overlap of the nonbonded electrons of the substituent with the π system of the diene.[2] Since then other investigators have invoked various explanations for the endo preference, including the effect of unsaturated substituents on frontier orbitals,[3-5] steric effects,[6,7] the effect of "strong intermolecular attractive forces",[8] electrostatic effects,[9] or a combination of these effects.[10]

The trifluoromethyl substituent exerts a unique influence on a dienophile since it lacks π electrons, yet it exerts an electron-withdrawing effect on a par with that of the usual dienophile substituents. McBee has made an extensive study of the effect of fluorine and fluorinated substituents on the Diels–Alder reaction of cyclopentadiene with olefins[9,11] (eq 1). The case of 3,3,3-trifluoropropene (**1a**) is of particular interest since it shows the influence of the trifluoromethyl group unperturbed by other substituents, but the stereochemical outcome of this reaction was not determined.[11a] We have repeated this reaction and undertaken a more thorough analysis of the results in order to provide firm data on the influence of the trifluoromethyl group on Diels–Alder stereoselectivity.[12]



(1)

1 **2** **3**

a, X = H; **b**, X = CO$_2$H; **c**, X = CO$_2$Et; **d**, X = CH$_2$OH

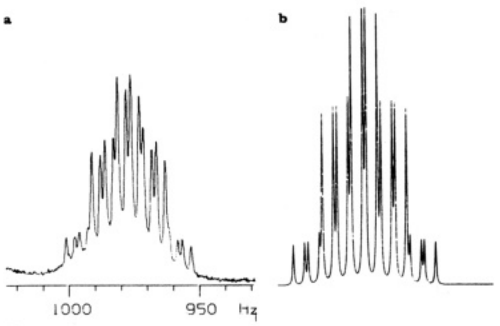


Figure 1. (a) 360-MHz ^{1}H NMR of the CHCF$_3$ signal of major isomer **2a**. (b) Computer simulation of ^4J = 9.6 Hz, ^2J = 9.6 Hz, J = 4.8 Hz, and ^2J = 3.75 Hz.

When an equimolar mixture of **1a** and cyclopentadiene is heated at 135 °C for 84 h, a 4:1 mixture of two products is observed by ^{19}F NMR. After removal of unreacted starting materials the mixture is analyzed by 360-MHz ^{1}H NMR, which resolves the **C**HCF$_3$ signal of the major isomer and allows all coupling constants for this proton to be determined (Figure 1). The values of J = 9.6 Hz (q), J = 9.6 Hz (d), J = 4.8 Hz (d), and J = 3.75 Hz (d) are consistent with the values predicted for the endo isomer **2a** and inconsistent with those predicted for the exo isomer **3a**.[13]

Experiments have been performed to determine if the observed ratio represents a kinetic or a thermodynamic mixture. Small samples of the reactants are heated at 135 °C for 5, 17, and 40 h; in each case the same 4:1 ratio of products is observed. Small samples of pure **2a** and **3a** are obtained by preparative gas chromatography. These are separately heated at 135 °C for 22 h, whereupon analysis by gas chromatography reveals no isomerization of either sample. Thus, the 4:1 ratio in favor of the endo isomer

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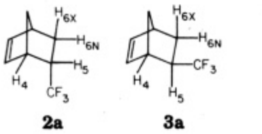
[13] Predicted coupling constants for the endo isomer **2a** are J_{4-5} = 3–4 Hz, J_{5-6X} = 9–10 Hz, and J_{5-6N} = 2.5–5 Hz. For the exo isomer **3a** they are J_{4-5} = 0–2 Hz, J_{5-6X} = 2.5–5 Hz, and J_{5-6N} = 6–7 Hz. In bicyclo[2.2.1]hept-2-enes the exo proton signals appear downfield from the endo proton signals. The signal from the endo H$_5$ of the minor isomer appears to be at δ 2.01, partially obscured by the signal from H$_{6X}$ of the major isomer at δ 1.95, but is indeed upfield of the signal from the exo H$_5$ of the major isomer at δ 2.72. The same argument is used to assign the signals at δ 1.95 (J_{6X-6N} = 12 Hz, J_{6X-5} = 10 Hz, J_{6X-1} = 3.75 Hz) to H$_{6X}$ and at δ 1.13 (J_{6N-6X} = 12 Hz, J_{6N-5} = 5 Hz, J_{6N-1} = 2.5 Hz) to H$_{6N}$ of the major isomer and the signals at δ 1.69 (J_{6X-6N} = 12 Hz, J_{6X-5} = 5 Hz, J_{6X-1} = 3.5 Hz) to H$_{6X}$ and the partly obscured signal at δ 1.38 to H$_{6N}$ of the minor isomer. The coupling constants which are visible are consistent with the assignments. Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; pp 258, 272, 274.



2a **3a**