through a Celite pad, and the filtrate was evaporated. The residue was purified by preparative thin-layer chromatography on silica gel (elution with 15% ethyl acetate in petroleum ether) to afford 10 mg (20%) of a colorless solid, mp 153–155 °C (from ether). The ^1H and ^{13}C NMR spectra of this product were identical with those of adduct **26**.

Acknowledgment. Financial support for the research conducted at The Ohio State University was provided by the National Cancer Institute (Grant CA-12115). The work in Heidelberg was supported by the Fonds der Chemischen Industrie and BASF Aktiengesellschaft, Ludwigshafen.

Registry No. **1**, 6675-72-5; **2**, 6675-71-4; **9**, 84988-39-6; **10**, 84988-40-9; **11**, 84988-41-0; **12**, 84988-42-1; **19**, 84988-43-2; **20**, 84988-44-3; **21**, 84988-45-4; **22**, 84988-46-5; **23**, 84988-47-6; **24**, 85027-44-7; **25**, 85027-45-8; **26**, 84988-48-7; **27**, 84988-49-8; **28**, 84988-50-1; **29**, 84988-52-3; **30**, 84988-51-2; acetone, 67-64-1; dimethyl acetylenedicarboxylate, 762-42-5; methyl propiolate, 922-67-8; *N*-phenylmaleimide, 941-69-5; maleic anhydride, 108-31-6.

[4 + 2] Cycloadditions to Norbornyl- and Norbornenyl-Fused Anthracene Systems[1]

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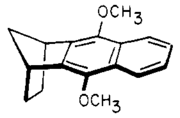
Received July 14, 1982

The preparation and Diels–Alder cycloadditions of 2,3-norbornadienoanthracene (**4**) and 2,3-norborneno-anthracene (**5**) are described. The purpose of this study was to determine if the fused bicyclic frameworks could exert long-range effects on π-facial stereoselectivity. In the several examples which were examined, approximate 1:1 ratios of top- and bottom-face bonding were observed, indicating that remote stereoelectronic effects were inoperative. In most cases, the stereochemical outcome of the particular cycloaddition was ascertained subsequent to chemical degration to the isomer pairs **13**/**14** or **21**/**22**.

The last several years have witnessed an upsurge of interest in π-facial stereoselectivity.[1,3-8] The factors which cause the two faces of a π bond to be nonequivalent such as to favor preferential attack from one side have commanded particular attention.[3-5,9-12] Of especial interest to us have been the discoveries that norbornyl-fused dienes such as **1** (X = CH_2, O, $C{=}C(CH_3)_2$, etc.) enter into highly stereoselective Diels–Alder cycloadditions. Similarly striking stereoelectronic control is exhibited by **2** and its congeners during their capture of singlet oxygen, despite the aromatic character of the π network in these substrates.[13] The impressive ability of norbornyl frameworks to control the stereochemical outcome of chemical reactions at rather long range persists in carbanion **3** where methylation occurs regiospecifically (see arrow) and with exceptional endo stereoselectivity.[14]

1



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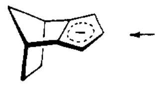

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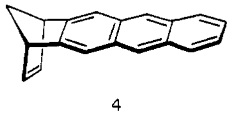
Presently, we have sought to delineate the approximate limits of this phenomenon by subjecting the previously



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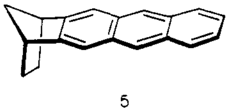

5

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(1) Electronic Control of Stereoselectivity. 17. Part 16: Paquette, L. A.; Hayes, P. C.; Charumilind, P. C.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *J. Am. Chem. Soc.*, in press.

(2) Graduate School Postdoctoral Fellow, 1981–1982.

(3) (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Bohm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *Ibid.* **1980**, *102*, 7218. (c) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1980**, *45*, 4907. (d) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *Ibid.* **1980**, *45*, 4922. (e) Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *Ibid.*, preceding paper in this issue. (f) Paquette, L. A.; Schaefer, A. G.; Blount, J. F.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.*, in press. (g) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *Ibid.*, in press. (h) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *Ibid.*, in press.

(4) (a) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, M. C. *J. Am. Chem. Soc.* **1978**, *100*, 6510. (b) Hertel, L. W.; Paquette, L. A. *Ibid.* **1979**, *101*, 7620. (c) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Böhm, M. C.; Beno, M. A.; Christoph, G. G. *Ibid.* **1981**, *103*, 7106. (d) Paquette, L. A.; Bellamy, F.; Wells, G. J.; Böhm, M. C.; Gleiter, R. *Ibid.* **1981**, *103*, 7122. (e) Paquette, L. A.; Klinger, F.; Hertel, L. W. *J. Org. Chem.* **1981**, *46*, 4403. (f) Paquette, L. A.; Klinger, F. *Ibid.* **1982**, *47*, 272.

(5) (a) Sugimoto, T.; Kobuke, Y.; Furukawa, J. *J. Org. Chem.* **1976**, *41*, 1457. (b) Avenati, M.; Hagenbuch, J.-P.; Mahaim, C.; Vogel, P. *Tetrahedron Lett.* **1980**, 3167. (c) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1819. (d) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

(6) (a) Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1978**, *100*, 6509. (b) Okada, K.; Mukai, T. *Tetrahedron Lett.* **1970**, 3429.

(7) (a) Hoffmann, R. W.; Becherer, J. *Tetrahedron* **1978**, *34*, 1187. (b) Becherer, J.; Hoffmann, R. W. *Ibid.* **1978**, *34*, 1193. (c) Hoffmann, R. W.; Hauel, N. *Tetrahedron Lett.* **1979**, 4959.

(8) Malpass, J. R.; Walker, M. P. *J. Chem. Soc., Chem. Commun.* **1979**, 585.

(9) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4056.

(10) Wipff, G.; Morokuma, K. *Tetrahedron Lett.* **1980**, *21*, 4445.

(11) (a) Mazzocchi, P. H.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozenboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6482. (b) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *Ibid.* **1981**, *103*, 2436. (c) Caramella, P.; Rondan, N. G.; Paddon-Row, M. G.; Houk, K. N. *Ibid.* **1981**, *103*, 2438.

(12) Burgess, E. M.; Liotta, C. L. *J. Org. Chem.* **1981**, *46*, 1703 and relevant references cited therein.

(13) Paquette, L. A.; Bellamy, F.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.* **1980**, *45*, 4913.

(14) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.*, in press.

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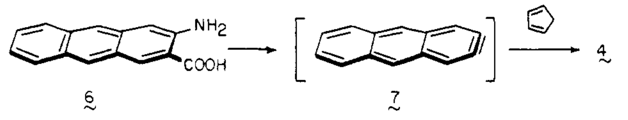
unknown 4 and 5 to cycloaddition reactions with dienophiles. The anthracene subunits in these hydrocarbons necessitate that $[4 + 2]$ π bonding involve only the central aromatic ring. These reaction centers are more distal to the fused bicyclic rings than any heretofore examined. At issue, therefore, is whether product formation will continue to come under the differing influences of the methano and ethano bridges or become totally indiscriminate.

Results

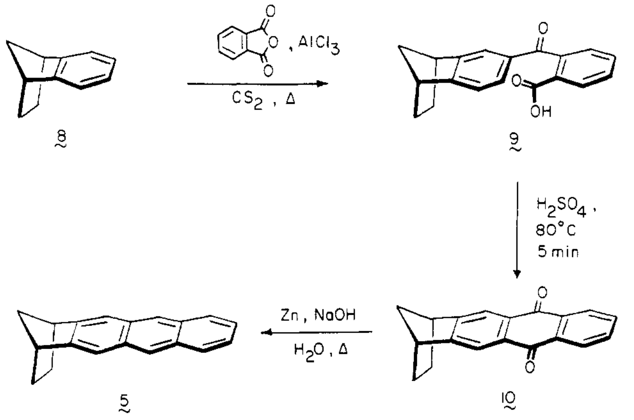
Substrate Synthesis. The structural features of 4 appeared suited to construction by reaction of 2-anthracyne (7) with cyclopentadiene. Consequently, appropriate methods for the diazotization of 2-amino-3-anthracenecarboxylic acid (6)[15] were initially examined. In situ aprotic methods[16a] involving isoamyl nitrite in such solvents as tetrahydrofuran, 1,2-dichloroethane, 1,2-dimethoxyethane, and dichloromethane/acetone afforded 4 in 0–1% yield. When recourse was made instead to preliminary isolation of the diazonium hydrochloride,[16b] followed by thermal decomposition in 1,2-dichloroethane solutions containing no more than 3 equiv of cyclopentadiene, 4 was isolated in 12% yield. Although 4 underwent ready hydrogenation to give 5, the lengthy preparation of 6 and the ensuing poor yields necessitated development of an alternative, more efficient route to 5.



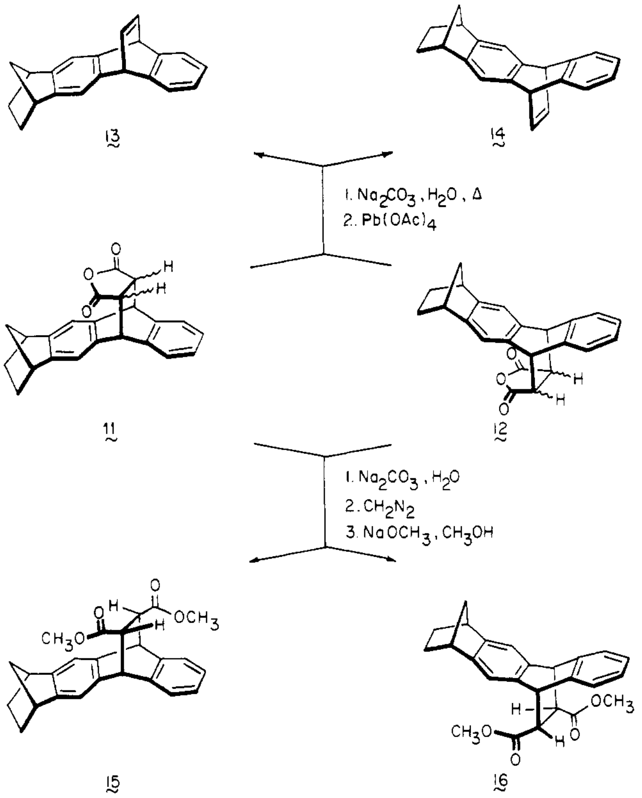
As shown in Scheme I, the Friedel–Crafts acylation of benzonorbornene (8) with phthalic anhydride and the ensuing sulfuric acid catalyzed ring closure proceeded regiospecifically to deliver only the linear anthraquinone 10. As expected from the C_s symmetry of this intermediate, its ^{13}C NMR spectrum consists of only 10 lines. Ultimately, the reduction of 10 with zinc under alkaline conditions afforded 5 in very reasonable quantities.

Cycloaddition Behavior of 5. When 5 was heated with maleic anhydride in xylene solution at the reflux temperature, there was isolated in 96.5% yield a colorless crystalline solid that exhibited a ^{13}C NMR spectrum consisting of 24 lines. Two interpretations would be consistent with these data. The first possibility is that dienophile capture had occurred from a single surface, but with formation of a syn/anti mixture of anhydrides. Alternatively, cycloaddition could have taken place from above and below the anthracene plane to give at least two adducts (due allowance is made for the possible fortuitous overlap of carbon signals in isomer pairs 11 and 12).

Scheme I



Scheme II



Two protocols were developed to resolve this question (Scheme II). In the first, the product mixture was hydrolyzed and subjected to oxidative decarboxylation with lead tetraacetate.[17] If high π-facial stereoselectivity had materialized, then either 13 or 14 would be produced from this reaction sequence, and an 11-line proton-decoupled ^{13}C NMR spectrum would be observed. In the absence of stereoelectronic control, a mixture of 13 and 14 would materialize and give rise to spectral complexities. As matters turned out, paired ^{13}C signals of equal intensity within experimental error were seen for the methano, ethano, and etheno bridge carbons in the two dibenzobarrelenes.

In a second series of experiments, the anhydride mixture was hydrolyzed, treated with diazomethane, and isomerized in alkaline solution. Exclusive above- or below-plane cycloaddition would thereby lead to 15 or 16 but not both, whereas indiscriminate stereoselection would ultimately produce both isomers. In the event, paired aliphatic carbon signals were clearly seen in ca. 1:1 ratios. Two trans diesters were consequently in hand, and maleic anhydride must therefore have added to both π faces of 5 at approximately equal rates.

Due to the unusually rapid hydrolysis of 11 and 12 on attempted chromatography (silica gel, Florisil, etc.), their separation was not pursued further. However, the ratio of 11 to 12 was not altered upon prolonged heating in refluxing xylene.

Similar heating of 5 with dimethyl acetylenedicarboxylate afforded a sharp-melting, crystalline adduct

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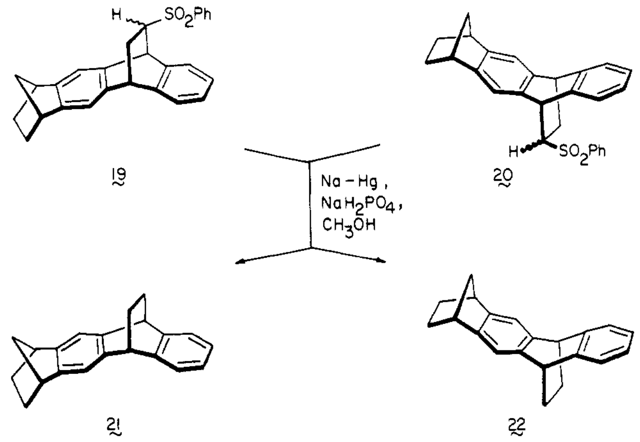
(15) Zimmerman, H. E.; Amick, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3977.

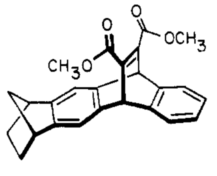
(16) (a) Friedman, L.; Logullo, F. M. *J. Org. Chem.* **1969**, *34*, 3089. (b) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3723.

(17) Cimarusti, C. M.; Wolinsky, J. *J. Am. Chem. Soc.* **1968**, *90*, 113.

Scheme III



(90.5%), the ^{13}C NMR spectrum of which suggested that it was a single isomer. However, 17 and 18 are actually produced in approximately equimolar amounts, and the simplified spectrum is the result of their close structural similarity and similar, but not identical, chemical shift profile. Proof that both stereoisomers were present was obtained by sequential reduction of the inseparable mixture with chromous sulfate,[18] saponification to the dicarboxylic acid stage, and oxidative decarboxylation as before. The resulting dibenzobarrelene product consisted of a 1:1 mixture of 13 and 14 precisely as witnessed earlier.



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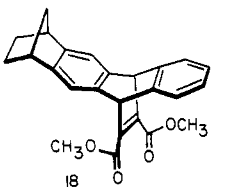
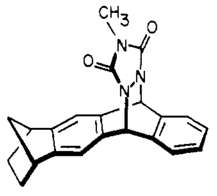


18

Phenyl vinyl sulfone[19] reacted with 5 in a sealed tube at 155 °C for 5 days (benzene as solvent) to produce a mixture of adducts (19 and 20) in 86% yield. Further insight into the nature of these compounds was gained by reductive cleavage of the phenylsulfonyl substituent with sodium amalgam[20] (Scheme III). Once 21 and 22 were in hand, ^{13}C NMR analysis clearly showed their presence in comparable amounts.

In an effort to enhance stereoselectivity, the reaction of 5 with the highly reactive *N*-methyltriazolinedione reagent was examined. A reasonable rate of cycloaddition was seen in refluxing benzene (complete in 24 h). By ^{13}C NMR spectroscopy, it could be readily ascertained that 23 and 24 had been produced in approximately equimolar quantities. Clearly, these lowered conditions of temperature do not lead to enhanced stereoselectivity in this instance.



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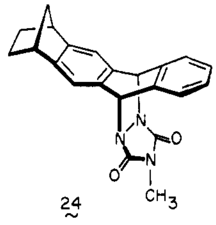
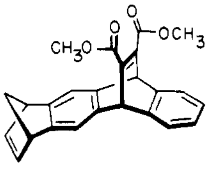


24

Cycloaddition Behavior of 4. Due to the limited amounts of 4 available, our studies were restricted to its response toward dimethyl acetylenedicarboxylate. Under the predescribed conditions, 4 was transformed into an adduct mixture which was directly hydrogenated over platinum at atmospheric pressure. Since this reduction gave rise to a product mixture having NMR spectral characteristics identical with those of 17/18 (1:1), it was clear that the original distribution of 25 and 26 must have been approximately statistical.



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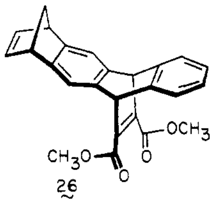

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Discussion

The definitive experimental results which have been compiled to demonstrate that systems such as 1–3 exhibit high π-facial stereoselectivity have been variously interpreted. While Kobuke[5a] and Houk[11] favor π-orbital pyramidalization (for different reasons), Vogel favors product stability control.[5b,6] Our view, which has been gleaned from molecular orbital theory and photoelectron spectroscopic correlations, calls attention to the existence of strong mixing between σ orbitals in the bicyclic moiety and the subjacent diene π_s orbital.[1,3] A pronounced disrotatory tilt of the π orbitals located at C_1 and C_4 of the diene unit occurs. Because of antibonding interactions between this filled orbital and the HOMO of the dienophile, preferential attack occurs from one surface or the other.

In 4 and 5, there is evidently no discrimination which operates during dienophile addition to the central anthracene ring. This can be taken as an indication that the electronic effects which are contained within the norbornyl and norbornenyl σ networks are not well transmitted *through* the intervening benzenoid ring. This insulation is not unexpected and signals the existence of an operational upper limit to long-range stereoselectivity effects of this sort. A counterargument based upon Vogel's reasoning is that the pair of isomeric adducts which are produced in these examples differ so insignificantly in their relative stabilities that the exothermicities of the two cycloaddition pathways become essentially equal.

Although 4 and 5 react with dienophiles in stereochemically random fashion, there remain additional structural variations of diverse type which require examination before the phenomenon in question is fully understood. We hope to report on these developments in the near future.

Experimental Section

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with a Varian EM-390 instrument, and apparent splittings are given in all cases. The ^{13}C NMR spectra were obtained with a Bruker WP-80 spectrometer. Mass spectra were measured on an AEI MS9 spectrometer at an ionization energy of 70 eV. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

6-(2-Carboxybenzoyl)benzonorbornene (9). A stirred mixture of benzonorbornene (1.17 g, 8.1 mmol), phthalic anhydride (1.0 g, 6.76 mmol), anhydrous aluminum chloride (2.28 g, 17.1 mmol), and carbon disulfide (15 mL) was heated at the reflux

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(18) (a) Castro, C. E. *J. Am. Chem. Soc.* **1961**, *83*, 3262. (b) Castro, C. E.; Stephens, R. D.; Mojé, S. *Ibid.* **1966**, *88*, 4964.

(19) (a) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853. (b) Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *Ibid.* **1978**, *100*, 1597.

(20) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477.

temperature for 3 h under a nitrogen atmosphere. The cooled mixture was hydrolyzed with 5 N hydrochloric acid (10 mL), and the organic layer was separated. The organic phase was washed with 10% sodium hydroxide solution (2 × 50 mL). The aqueous washes were acidified to pH 1 and extracted with dichloromethane. The combined organic solutions were dried and evaporated to give **9** as a viscous oil (2.0 g, 100%) which was not readily purifiable and consequently was directly cyclized: IR ($CHCl_3$) 2970, 2950, 2870, 1700, 1665, 1575, 1485, 1445, 1405, 1340, 1305, 1275, 1060, 940, 925, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.8 (br s, 1 H), 8.1 (m, 1 H), 7.7–6.9 (series of m, 6 H), 3.4 (m, 2 H), 2.0–1.1 (series of m, 6 H); MS, *m/e* (M^+) calcd 292.1099, obsd 292.1091.

Cyclization of 9. A mixture of keto acid **9** (40.4 g, 0.138 mol) and fuming sulfuric acid (120 mL) was heated to 80 °C with stirring and held at that temperature for 5 min. The dark mixture was poured onto ice, and the product was extracted into dichloromethane (2 × 200 mL). The combined organic layers were washed with saturated sodium bicarbonate solution and water prior to drying. Evaporation of solvent gave **10** as a tan solid (9.2 g, 25%). Final purification was achieved by column chromatography on silica gel (elution with 10% ether in petroleum ether). Pure **10** was obtained as pale yellow needles: mp 164.0–164.5 °C (from absolute ethanol); IR ($CHCl_3$) 2960, 2870, 1672, 1595, 1365, 1322, 1305, 1290, 1265, 945, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.25 (A_2B_2, 2 H), 8.05 (s, 2 H), 7.7 (A_2B_2, 2 H), 3.5 (br s, 2 H), 2.2–1.55 (series of m, 4 H), 1.22 (d, J = 6.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 183.64, 155.17, 133.75, 132.66, 127.08, 118.94, 48.79, 44.00, 26.34 ppm; MS, *m/e* (M^+) calcd 274.0994, obsd 274.0983. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 82.93; H, 5.17.

2,3-Norbornenoanthracene (5). Zinc dust (20 g) was activated by washing with 10% hydrochloric acid (4 × 50 mL) and then water (5 × 50 mL). Finally, water (165 mL) was added, and the stirred suspension was treated with Fehling's I solution (3.3 mL). Following the addition of **10** (3.3 g, 12.1 mmol), sodium hydroxide (24.8 g), and water (56 mL), the reaction mixture was heated at 100 °C for 24 h, cooled, and filtered through Celite following addition of some dichloromethane. The filtrate was extracted with dichloromethane (3 × 100 mL), and the combined organic layers were dried and evaporated. The residue was adsorbed onto silica gel and purified by flash chromatography. Hexane elution afforded 1.14 g (68% based on recovered starting material) of **5** while elution with 5% ether in hexane returned 1.4 g of **10**. The anthracene was obtained as colorless crystals: mp 223 °C (from absolute ethanol); IR (Nujol) 3020, 1450, 1440, 1420, 1365, 1280, 1100, 935, 890, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.3 (s, 2 H), 7.95 (A_2B_2, 2 H), 7.65 (s, 2 H), 7.4 (A_2B_2, 2 H), 3.55 (br s, 2 H), 2.15–1.67 (series of m, 4 H), 1.6–1.3 (m, 2 H); ^{13}C NMR ($CDCl_3$) 147.30, 131.71, 131.23, 127.93, 125.55, 124.67, 117.44, 47.33, 43.45, 27.96 ppm; MS, *m/e* (M^+) calcd 244.1258, obsd 244.1252. Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.21; H, 6.60.

2,3-Norbornadienoanthracene (4). A suspension of 2-amino-3-anthracenecarboxylic acid (**6**, 850 mg, 3.6 mmol) in absolute methanol (40 mL) was treated at 0 °C with concentrated hydrochloric acid (0.5 mL) and isoamyl nitrite (1.05 mL, 8.5 mmol). The slurry was stirred at 0 °C for 30 min and at room temperature for 3 h. The dark reaction mixture was diluted with dry ether (100 mL), and the insoluble pale brown diazonium hydrochloride was separated by filtration and washed with dry ether. The air-dried salt (510 mg, 1.8 mmol) was added to dichloroethane (15 mL), propylene oxide (250 mg, 4.3 mmol), and freshly cracked cyclopentadiene (310 mg, 4.7 mmol). The stirred mixture was heated at the reflux temperature under nitrogen for 2 h, cooled, and evaporated. The very tarry residue was adsorbed and chromatographed on alumina. With hexane as the eluant, 50 mg of dicyclopentadiene was recovered. Continued elution with 30% dichloromethane in hexane afforded **5** (54 mg, 12%) as colorless plates: mp 233.5–234 °C (from ethanol); IR (Nujol) 3040, 1455, 1420, 1375, 1305, 940, 895, 870, 800, 730, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2 (s, 2 H), 7.95 (m, 2 H), 7.65 (s, 2 H), 7.4 (m, 2 H), 6.75 (br s, 2 H), 4.0 (br s, 2 H), 2.35 (m, 2 H); ^{13}C NMR ($CDCl_3$) 147.44, 141.33, 131.62, 131.13, 127.93, 125.60, 124.77, 118.85, 64.28, 49.28 ppm; MS, *m/e* (M^+) calcd 242.1095, obsd 242.1103. Anal. Calcd for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 93.71; H, 5.84.

Hydrogenation of 4. A solution of **4** (10 mg, 0.041 mmol) in ethyl acetate (5 mL) was treated with platinum oxide (2 mg) and hydrogenated at atmospheric pressure for 15 min. Filtration through Celite and solvent evaporation gave **5** (10 mg, 99%) as a colorless solid, mp 223 °C (from ethanol), identical in all respects with the material obtained earlier.

Reaction of 5 with Maleic Anhydride. A solution of **5** (200 mg, 0.820 mmol) and maleic anhydride (80 mg, 0.820 mmol) in xylene (3 mL) was heated at the reflux temperature for 7.5 h and cooled. Filtration of the precipitated adduct afforded 270 mg (96.5%) of **11**/**12** as a colorless solid: mp 274.5–275.5 °C (from xylene); IR (Nujol) 1865, 1785, 1460, 1375, 1290, 1215, 1210, 1070, 930, 920, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5–7.05 (m, 6 H), 4.75 (m, 2 H), 3.65 (m, 2 H), 3.3 (m, 2 H), 2.0–1.0 (m, 6 H); ^{13}C NMR ($CDCl_3$) 170.70, 148.02, 147.88, 141.47, 137.88, 135.55, 127.54, 126.96, 125.06, 124.19, 117.92, 117.24, 80.83, 76.51, 49.62, 49.32, 48.35, 45.88, 43.60, 26.94, 26.80 ppm; MS, *m/e* (M^+) calcd 342.1256, obsd 342.1265. Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.75; H, 5.36.

Hydrolysis–Decarboxylation of 11/12. A mixture of **11**/**12** (170 mg, 0.50 mmol), sodium carbonate (0.5 g), and water (5 mL) was boiled for 3 h. The hot solution was filtered through a glass wool plug and cooled. Following acidification to pH 6, the precipitated diacid was filtered, washed with water, and dried. There was isolated 180 mg (100%) of product as a colorless powder: mp 165–170 °C dec; IR (Nujol) 1750 cm^{-1}.

A solution of the diacid (1.90 g, 5.28 mmol) in dry pyridine (15 mL) was purged with oxygen for 15 min with stirring. Freshly recrystallized lead tetraacetate (3.45 g, 7.92 mmol) was added in one portion, and the mixture was stirred under oxygen for 10 min at 67 ± 2 °C. The cooled reaction mixture was added to dilute nitric acid (60 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with saturated sodium bicarbonate solution (2 × 50 mL), dried, and evaporated to leave 2 g of a dark oil. Filtration through a column of silica gel (60 g, ether elution) gave a yellowish oil (840 mg) which solidified. MPLC purification on silica gel (hexane elution) afforded 40 mg of recovered diacid and 150 mg (11%) of the olefins **13** and **14** as a colorless solid: mp 194–195 °C (from ethanol); IR ($CHCl_3$) 3060, 2990, 2960, 2860, 1462, 1450, 1325, 1315, 1285, 1100, 672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.1 (m, 2 H), 7.08 (s, 2 H), 7.05–6.8 (m, 4 H), 5.0 (m, 2 H), 3.2 (br s, 2 H), 1.90–0.9 (series of m, 6 H); ^{13}C NMR ($CDCl_3$) 147.05, 144.38, 143.75, 139.96, 139.82, 124.13, 122.73, 116.27, 51.60, 49.81, 49.71, 43.54, 27.18, 27.04 ppm; MS, *m/e* calcd (M^+) calcd 270.1408, obsd 270.1417.

These olefinic isomers were prone to retro-Diels–Alder fragmentation upon standing at room temperature.

Esterification–Isomerization of 11/12. A suspension of the above diacid (330 mg, 0.917 mmol) in benzene (10 mL) was treated at 0 °C with excess ethereal diazomethane until the yellow color persisted. The excess reagent was destroyed by the addition of acetic acid. The reaction mixture was diluted with dichloromethane (50 mL), washed with saturated sodium bicarbonate solution (25 mL), dried, and evaporated to leave the cis diesters as a colorless oil: IR ($CHCl_3$) 3020, 2960, 2870, 1750, 1470, 1450, 1435, 1340, 1280, 1180, 1160, 1050, 1030, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–7.0 (m, 6 H), 4.55 (br s, 2 H), 3.52 (s, 3 H), 3.50 (s, 3 H), 3.3 (br s, 2 H), 3.25 (s, 2 H), 2.0–1.0 (series of m, 6 H); MS, *m/e* (M^+) calcd 388.1674, obsd 388.1666.

A solution of the cis diesters (180 mg, 0.464 mmol) in anhydrous methanol (5 mL) containing a small piece of sodium metal was heated at the reflux temperature for 21 h under nitrogen. The cooled solution was evaporated, dichloromethane (25 mL) was added, and the organic solution was washed with water (2 × 20 mL), dried, and evaporated. There was isolated 110 mg (61%) of a 1:1 mixture of **15** and **16** as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.3–7.0 (m, 6 H), 4.65 (br s, 2 H), 3.55 (s, 6 H), 3.35 (br s, 2 H), 3.25 (br s, 2 H), 2.0–1.0 (series of m, 6 H); ^{13}C NMR ($CDCl_3$) 173.07, 172.93, 146.52, 146.32, 139.28, 126.22, 124.43, 123.55, 117.43, 117.29, 116.56, 52.14, 49.42, 48.20, 47.09, 43.59, 27.28, 27.04 ppm; MS, *m/e* (M^+) calcd 388.1674, obsd 388.1682.

Reaction of 5 with Dimethyl Acetylenedicarboxylate. A solution of **5** (200 mg, 0.82 mmol) and freshly distilled dimethyl acetylenedicarboxylate (116 mg, 0.82 mmol) in xylene (2 mL) was heated at reflux for 10 h under nitrogen. The cooled solution was evaporated, and the residue was chromatographed on silica gel. Hexane elution returned 60 mg of unreacted **5**. Elution with ether furnished 200 mg (90.5% based on recovered starting material) of adduct as colorless fluffy needles: mp 230–231 °C (from hexane); IR ($CHCl_3$) 3020, 2950, 2860, 1740, 1630, 1465, 1450, 1430, 1260, 1100, 1050, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 2 H), 7.18 (s, 2 H), 6.95 (m, 2 H), 5.4 (br s, 2 H), 3.75 (s, 6 H), 3.25 (br s, 2 H), 2.0–1.0 (series of m, 6 H); ^{13}C NMR ($CDCl_3$) 166.13, 147.63, 147.44, 145.50, 144.62, 141.32, 125.15, 123.55, 116.95, 52.86, 52.23, 49.76, 43.49, 26.84 ppm; MS, *m/e* (M^+) calcd 386.1518, obsd 386.1527. Anal. Calcd fof $C_{25}H_{22}O_4$: C, 77.70; H, 5.74. Found: C, 77.55; H, 5.80.

Chromous Ion Reduction of 17/18. A solution of adduct mixture **17**/**18** (1.06 g, 2.75 mmol) in distilled dimethylformamide (15 mL) was added dropwise under nitrogen to a freshly prepared 0.62 N chromous sulfate solution (17 mL, 9.79 mmol) at room temperature. The resultant green reaction mixture was stirred at room temperature for 30 min, treated with water (100 mL), and extracted with ether (5 × 50 mL). The combined ethereal layers were washed with water (4 × 100 mL) and brine (2 × 100 mL), dried, and evaporated. MPLC purification on silica gel (elution with 20% ether in hexane) gave 310 mg (30%) of dihydro diesters **15**/**16** as a colorless viscous oil: IR ($CHCl_3$) 2950, 2870, 1735, 1470, 1460, 1435, 1290, 1260, 1180, 1105, 1015, 880, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.3–6.95 (m, 6 H), 4.6 (br s, 2 H), 3.55 (s, 6 H), 3.35 (br s, 2 H), 3.2 (br s, 2 H), 2.0–0.8 (series of m, 6 H); MS, *m/e* (M^+) calcd 388.1675, obsd 388.1680.

Hydrolysis and Oxidative Decarboxylation of 15/16. A solution of **15**/**16** (310 mg, 0.80 mmol) in methanol (8 mL) was stirred under nitrogen while a solution of potassium hydroxide (470 mg, 8.3 mmol) in water (2 mL) was added. The reaction mixture was stirred at room temperature for 14 h, evaporated under reduced pressure, treated with water (10 mL), and acidified with 30% sulfuric acid. The solid product was separated by filtration, washed twice with water, and dried: 290 mg (100%); mp 165–170 °C; identical with the material previously isolated.

A solution of the diacid mixture (290 mg, 0.81 mmol) in dry pyridine (3 mL) was oxygenated and treated with freshly recrystallized lead tetraacetate (540 mg, 1.21 mmol) as before. There was obtained 50 mg (23%) of **13**/**14**: mp 194 °C dec (from ethanol); identical in all respects with the olefin mixture isolated earlier.

Reaction of 5 with Phenyl Vinyl Sulfone. A solution of **5** (300 mg, 1.23 mmol) and phenyl vinyl sulfone (207 mg, 1.23 mmol) in benzene (5 mL) was heated in a sealed tube at 155 °C for 5 days. The reaction mixture was evaporated, and the residue was chromatographed on silica gel (60 g). There was isolated 60 mg of recovered **5** (hexane elution) and 350 mg (86%) of a mixture of **19** and **20** as a pale yellow solid: mp 209–211 °C; IR ($CHCl_3$) 3070, 2950, 2870, 1445, 1305, 1280, 1240, 1145, 1080, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.75–6.85 (series of m, 11 H), 4.70 (br s, 1 H), 4.20 (br s, 1 H), 3.55–3.15 (m, 3 H), 2.20–0.80 (series of m, 8 H); MS, *m/e* (M^+) calcd 412.1497, obsd 412.1501.

Sodium Amalgam Reduction of 19/20. A solution of the sulfone isomers (310 mg, 0.75 mmol) in dry tetrahydrofuran (4 mL) was introduced via syringe to a mixture of 6% sodium amalgam (1.54 g), sodium dihydrogen phosphate (0.5 g), and dry methanol (3 mL) under a nitrogen atmosphere. The reaction mixture was stirred for 4.5 h, the solution was decanted, and the residual amalgam was washed with tetrahydrofuran. The combined organic layers were diluted with dichloromethane (100 mL), washed with water (2 × 50 mL), dried, and evaporated. Hydrocarbons **21** and **22** (190 mg, 93%) were obtained as colorless needles: mp 220–222 °C dec (from hexanes); IR ($CHCl_3$) 2950, 2865, 1470, 1455, 1335, 1325, 1285, 1130, 1100, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.25–6.70 (series of m, 6 H), 4.15 (br s, 2 H), 3.15 (br s, 2 H), 2.0–0.8 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) 145.35. 144.63, 144.53, 140.89, 125.30, 123.02, 116.13, 116.03, 49.57, 44.42, 43.64, 27.23, 27.14, 26.99 ppm; MS, *m/e* (M^+) calcd 272.1565, obsd 272.1572. Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.65; H, 7.47.

Reaction of 5 with *N*-Methyltriazolinedione. A solution of **5** (200 mg, 0.82 mmol) in benzene (3 mL) containing *N*-methyltriazolinedione (92 mg, 0.082 mmol) was heated at reflux for 24 h (no observable reaction occurred at room temperature over the same time period). Solvent evaporation left 290 mg of a pale pink solid which was chromatographed on silica gel (elution with 30% ethyl acetate in hexane) to give an approximately 1:1 ratio of **23** and **24** as a colorless solid: 276 mg (95%); IR ($CHCl_3$) 3040, 3020, 2980, 2880, 1770, 1725, 1465, 1390, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45–7.0 (m, 6 H), 6.1 (s, 2 H), 3.25 (br s, 2 H), 2.72 (s, 3 H), 2.0–0.8 (series of m, 6 H); ^{13}C NMR ($CDCl_3$) 157.62, 148.38, 137.39, 137.06, 134.43, 134.00, 127.98, 123.66, 116.99, 116.88, 60.85, 60.63, 49.58, 43.68, 26.57, 25.42 ppm; MS, M^+ observed at *m/e* 357, but too transient for high-resolution measurement.

Reaction of 4 with Dimethyl Acetylenedicarboxylate. A solution of **4** (100 mg, 0.413 mmol) and distilled DMAD (50 mg, 0.413 mmol) in xylene (2 mL) was heated to reflux for 10 h. The solvent was evaporated, and the residue was chromatographed on silica gel. Hexane elution returned 20 mg of unreacted **4**. Elution with 50% ether in hexane afforded 100 mg (79%) of adduct mixture **25**/**26** which was directly hydrogenated: IR ($CHCl_3$) 3070, 3030, 2980, 2950, 1750, 1660, 1435, 1325, 1300, 1260, 1150, 1100, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4–7.15 (m, 4 H), 7.0–6.8 (m, 2 H), 6.75–6.55 (m, 2 H), 5.25 (s, 2 H), 3.72 (br s, 8 H), 2.15 (br d, 2 H); ^{13}C NMR ($CDCl_3$) 166.18, 149.72, 147.73 (double peak), 144.72, 144.58, 143.17, 140.79, 125.16, 123.56, 118.22, 70.88, 70.74, 52.87, 52.29, 50.20 ppm; MS, *m/e* (M^+) calcd 384.1361, obsd 384.1369.

Hydrogenation of 23/24. A solution of the adduct mixture (100 mg, 0.26 mmol) in ethyl acetate (10 mL) was hydrogenated over platinum oxide (20 mg) at atmospheric pressure for 20 min. Filtration and evaporation gave 100 mg of an oil which was purified by MPLC on silica gel. Elution with 30% ether in hexane gave 80 mg (80%) of **17**/**18** which was identical in every respect with previously isolated material.

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Registry No. **4**, 85082-69-5; **5**, 85082-70-8; **6**, 85082-81-1; **6** (diazonium chloride), 85082-82-2; **8**, 4486-29-7; **9**, 85082-71-9; **10**, 85082-72-0; **11**, 85082-73-1; **13**, 85082-74-2; **14**, 85115-14-6; **15**, 85082-75-3; **16**, 85115-15-7; **17**, 85082-76-4; **18**, 85115-16-8; **19**, 85082-77-5; **21**, 85082-78-6; **22**, 85115-17-9; **23**, 85082-79-7; **24**, 85115-18-0; **25**, 85082-80-0; **26**, 85115-19-1; phthalic anhydride, 85-44-9; 1,3-cyclopentadiene, 542-92-7; maleic anhyride, 108-31-6; dimethyl acetylenedicarboxylate, 762-42-5; phenyl vinyl sulfone, 5535-48-8; *N*-methyltriazolinedione, 13274-43-6; dimethyl 6,11-ethano-1,4-methanonaphthacene-13,14-dicarboxylate, 85115-20-4; 6,11-ethano-1,4-methanonaphthacene-13,14-dicarboxylic acid, 85082-83-3.