A light green color developed and the temperature dropped to 5° during the course of the addition. Water (200 ml) was added, and the solution was extracted several times with ether. Overnight storage of the ether extract in the refrigerator led to precipitation of a white solid, which was recrystallized from chloroform to give 30 g (30%) of white needles, mp 146–148° (lit.[16] mp 135°). This was identified as 3,3′-dinitro-2,2′-azodioxynorbornane from its melting point and infrared spectrum: ir (KBr) 1540, 1355 ($-NO_2$), 1193, 1223, and 1216 cm^{-1} (azodioxy).

Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.31; H, 5.88; N, 16.47. Found: C, 49.50; H, 5.95; N, 16.34.

Addition of Nitrosyl Chloride to Bicyclo[2.2.2]octene-2[22] (16).—Nitrosyl chloride (2.3 ml, 0.05 mol) was added to 5.4 g (0.05 mol) of bicyclo[2.2.2]octene-2 in 25 ml of carbon tetrachloride by the general addition method at 10°. The color of the solution turned from red to blue in 4 hr, and a small amount (0.44 g) of white solid was isolated by filtration. Washing with acetone gave a purer material, mp 94.5–97.5°. This was identified as the dimer of a mixture of *cis*- and *trans*-2,3-dichloro-2-nitrosobicyclo[2.2.2]octane (17). The nmr spectrum is shown in Figure 5.

Anal. Calcd for $C_8H_{11}Cl_2NO$: C, 46.15; H, 5.29; Cl, 34.13; N, 6.73. Found: C, 45.96; H, 6.27; Cl, 33.87; N, 6.62.

The supernatant liquid was evaporated and the residue was shown to be a mixture of starting olefin and product 17.

Registry No.—**1**, 694-91-7; **2**, 32846-86-9; **5**, 16219-75-3; **6**, 32846-87-0; **9**, 32846-82-5; **10**, 32846-83-6; **11**, 32846-84-7; **14**, 4659-42-1; **15**, 32839-07-9; **16**, 931-64-6; **17**, 32839-08-0; nitrosyl chloride, 2696-92-6; 3,3′-dinitro-2,2′-azodioxynorbornane, 32861-60-2.

Acknowledgment.—We wish to thank Mr. William O. Brown and Mr. Russell Turner for assistance with portions of the experimental procedures.

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[22] Chemical Samples Co., Columbus, Ohio.

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trans,trans,cis-2,8,12-*trans*-Bicyclo[8.4.0]tetradecatriene[1,2]

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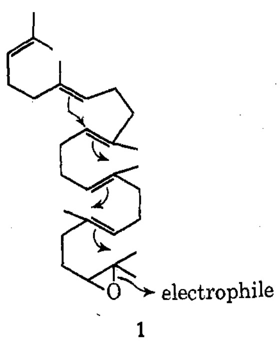
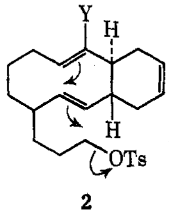
The synthesis is described of a *trans,trans*-1,5-cyclodecadiene **4a** which is thermally stable but not degenerate with respect to the Cope rearrangement.

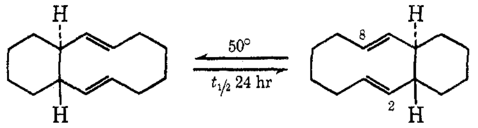
One postulate for the enzymatically controlled cyclization of squalene oxide (**1**) involves epoxide cleavage with conformational holding and nucleophilic participation of remote double bonds, acting through intermediate double bonds. Attractive as such a postulate might appear, it is virtually without experimental test; and appropriate models are not easily conceived or synthesized.[3] Our experience with the *trans,trans*-2,8-*trans*-bicyclo[8.4.0]tetradecadiene system (**3a,b**)[4,5] suggested that a study of compounds like **2** should be informative with respect to the extent of participation of the remote bond in solvolysis of the tosylate, with Y appropriately substituted. This article details preliminary work leading to the synthesis of the corresponding unsubstituted system **4a**, *trans,trans,cis*-2,8,12-*trans*-bicyclo[8.4.0]tetradecatriene; **4a** possesses one more double bond than the system **3a,b**. This additional double bond should have the effect of heavily weighting the Cope-related equilibrium **4a,b** in favor of **4a** (**4b** is highly strained), thus avoiding the problem of constitutional isomers which arises upon substituting the **3b** system at C-4.



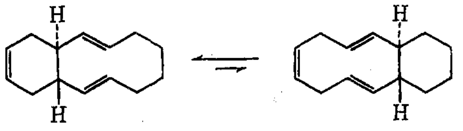
1



2



3a 3b



4a 4b

On the basis of the established synthetic route to **3a,b** (**5** → **6a** → **6c** → **3a,b** in Scheme I),[4] preparation of **4a,b** simply involved making and fragmenting the appropriately substituted *trans,syn,trans*-dodecahydroanthracene **7**. This appeared to be particularly straightforward because the synthesis of **3a,b** proceeded from **5** (formed by isomerizing the bis adduct of butadiene and benzoquinone[6]), a compound already functionalized with two identical double bonds, correctly positioned; and the simplest solution was therefore to reduce one of them. However, no conditions of catalytic hydrogenation could be found which resulted in any selectivity in the absorption of the first and second moles of hydrogen; or in any mixture which could be separated into its unreduced, partially reduced, and fully reduced components.

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[1] The investigation was supported by Public Health Service Research Grant GM 16338 from the Division of General Medical Sciences, U. S. Public Health Service.

[2] The article is abstracted from the Ph.D. Thesis of G. O. S., Wesleyan University, 1971.

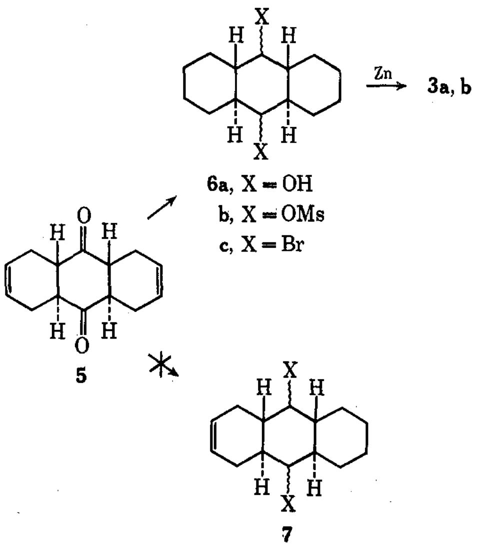
[3] For a review of polyolefin cyclizations see W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968). For comments, additional references, and one example of a double bond participating in an S$_N$2′ displacement see G. D. Sargent, J. A. Hall, M. J. Harrison, W. H. Demisch, and M. D. Schwartz, *J. Amer. Chem. Soc.*, **91**, 2379 (1969).

[4] P. S. Wharton, Y. Sumi, and R. A. Kretchmer, *J. Org. Chem.*, **30**, 234 (1965).

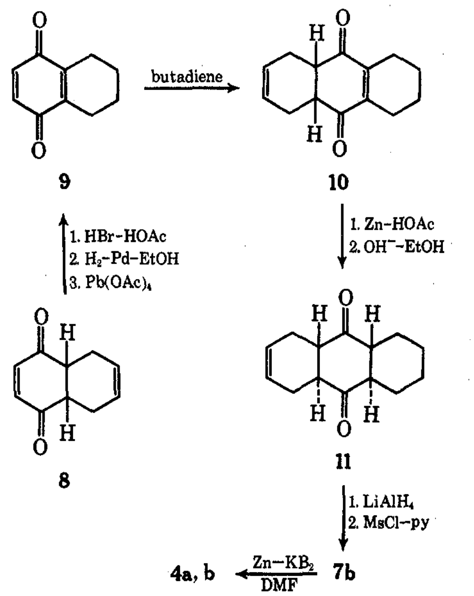
[5] P. S. Wharton and R. A. Kretchmer, *ibid.*, **33**, 4258 (1968).

[6] K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **501**, 247 (1933).

SCHEME I



SCHEME II



A more rational route proceeding *via* quinone **9** was then pursued; see Scheme II. Quinone **9** is conveniently made in three steps from the monoadduct of butadiene and benzoquinone (**8**):[7,8] acid-catalyzed aromatization of enedione **8**, catalytic hydrogenation of the isolated double bond, and oxidation of the hydroquinone. Addition to **9** of excess butadiene in benzene solution at room temperature afforded tricyclic dione **10** in high yield (addition to the less substituted side of the quinone).[9] Reduction of the conjugated double bond of **10** was accomplished with zinc in acetic acid; the product, obtained in 87% yield, consisting of a mixture[10] of isomeric diones, mp 169–208°. This mixture was isomerized in 74% yield to white, platelike crystals, mp 225–231°, by dissolving in a small volume of hot alcohol, adding ethanolic potassium hydroxide solution while hot, and then allowing to crystallize. The crystals obtained in this way consisted principally of trans,syn,trans dione **11**, as shown by catalytic reduction and comparison of the product with authentic 9,10-diketo-*trans,syn,trans*-perhydroanthracene.[6]

Lithium aluminum hydride reduction of dione **11** gave a mixture of isomeric diols **7a** which was subjected to the fragmentation sequence successfully used in the preparation of **3a**,**b**: conversion of diol mixture **6a** to dibromide **6c** with phosphorus tribromide in carbon tetrachloride and then fragmentation of the dibromides with zinc.[4] However, the reported conversion of **6a** to **6c** was never very satisfactory and when it was found that attempted parallel conversion of **7a** to **7c** gave completely saturated compounds, apparently from addition of hydrogen bromide to the double bond, further attempts to effect the conversion were discontinued while alternatives were examined using the more plentiful diol mixture **6a**. A successful method was developed *via* dimesylate mixture **6b** (straightforwardly obtained, although the corresponding ditosylate could not be made) and it was eventually found that **6b** could be fragmented to **3a**,**b** in ~34% yield (based on diol) by treatment with zinc dust in dimethylformamide at 60–70° containing potassium bromide. Preparatively, this is simpler and also approximately five times more efficient than the former procedure.

The occurrence of an interesting set of interactions of the fragmentation reagents can be appreciated from the observations that treatment of dimesylate mixture with zinc alone induced no fragmentation and treatment with potassium bromide alone resulted mainly in elimination, not substitution, of the mesylate functions. Informative fragmentations were carried out on individual dimesylate isomers *trans*-(ee)-**6b** and *cis*-(ea)-**6b**,[11] which were made by mesylating the corresponding diols. Reactions were monitored by observation of characteristic absorptions in the nmr spectra of products obtained from aliquots periodically removed. After 70 hr trans and cis dimesylates afforded products consistent with 47 and 31% fragmentation, respectively, with much elimination apparent from the loss of mesylate hydrogen absorption and the appearance of vinyl hydrogen absorption at δ 5.0 ppm. The effect of an added equivalent amount of potassium hydroxide was striking, the extent of fragmentation of cis dimesylate decreasing only slightly from 31 to 20% and of trans dimesylate dropping sharply from 47 to 6%.

These facts are consistent with the major pathway of fragmentation consisting of (1) initial substitution to form a bromomesylate, with axial mesylate reacting faster than equatorial,[12] cis (ea) dimesylate thereby yielding trans (ee) bromomesylate preferentially and trans (ee) dimesylate giving cis (a) bromo (e) mesylate, with mesylate equatorial in both intermediate bromomesylates; (2) reaction of zinc with both equatorial and axial bromine to give carbon–zinc bonds which are

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(7) O. Diels and K. Alder, *Chem. Ber.*, **62**, 2337 (1929).

(8) In principle it is simpler to reduce the isolated double bond of **8**, thereby saving several steps, but attempted catalytic reductions yielded only phenolic compounds and tars from aromatization (independent experiments of Flesch).

(9) See the following for comments on selectivity in 1,4 cycloadditions to substituted quinones: M. F. Ansell, B. W. Nash, and D. A. Wilson, *J. Chem. Soc.*, 3012 (1963).

(10) Similar zinc reductions have been found to give either cis or trans isomers or mixtures; see C. S. Barries and D. H. R. Barton, *ibid.*, 1419 (1952) and J. Scotney and E. V. Truter, *J. Chem. Soc., C*, 1079 (1969).

(11) The symbols e and a are abbreviations designating equatorial and axial stereochemistry.

(12) See the following for pertinent comments: E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 224–228.

configurationally labile[13] and more stable in the less hindered equatorial position; (3) formation of trans,-trans diene **3a,b** by fragmentation of the configurationally ideal[14] trans (ee) mesyloxyzinc intermediate. Elimination is a hazard starting from either dimesylate, although only axial leaving groups are readily susceptible to E2 elimination:[12] cis dimesylate can directly afford olefin by elimination of an axial mesylate in competition with substitution; trans dimesylate can after formation of cis bromomesylate which can eliminate axial bromine in competition with reaction with zinc or further substitution. The addition of hydroxide has a relatively unfavorable action on trans dimesylate because the axial bromine of the intermediate bromomesylate is relatively more susceptible to hydroxide-induced elimination than is the axial mesylate of cis dimesylate.

Application of the dimesylate fragmentation sequence to the mixture of diols **7a** afforded in 48% yield, after chromatography, an oily triene characterized as **4a** by analytical and spectroscopic data. The oil was examined for the presence of the Cope-related isomer **4b** but none could be detected: ozonolysis, with an oxidative work-up and subsequent esterification, yielded dimethyl adipate, as expected from **4a**, but not a trace of dimethyl *trans*-1,2-cyclohexanedicarboxylate, which would be formed from any **4b** present. Based on this successful preparation of **4a**, syntheses of compounds like **2** are underway.

Experimental Section

Physical Data.—Melting points were determined in capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. The analysis was performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were obtained on Beckman IR-8 and Perkin-Elmer Model 137 Infracord spectrometers. Varian A-60 and A-60A spectrometers were used to record nmr spectra, and chemical shifts are reported in parts per million measured from an internal tetramethylsilane reference. Gas-liquid phase chromatography (glpc) was performed on Varian Aerograph A-90 and A-90-P gas chromatographs. All peak areas were measured with a Disc chart integrator.

Materials.—Activated zinc was prepared by stirring zinc dust in 1 *N* hydrochloric acid for 15 min and washing with distilled water until neutral. The zinc was then washed three times with absolute ethanol and three times with anhydrous ether, and dried at 60 or 100° overnight. Potassium bromide was recrystallized, pulverized, and dried for at least 2 hr at 110° before use. Solvents were dried and/or distilled before use with the exception of ether and alcohol. Purified pentane was prepared from distilled pentane by washing it successively with concentrated sulfuric acid, concentrated potassium permanganate in 10% sulfuric acid, and water. It was then dried and eluted through acid-washed alumina. Silica gel used in column chromatography was Grade 950, mesh size 60–200, obtained from Davison Chemical. Anhydrous magnesium sulfate was used to dry organic extracts.

***trans,trans*-2,8-*trans*-Bicyclo[8.4.0]tetradecadiene (3a,b).**—The following represents an improvement over the previously reported procedure.[4] A mixture of 100.0 g of **5**,[6] mp 235–243°, and 480 ml of absolute ethanol was hydrogenated over *ca.* 18 g of W-2 Raney nickel catalyst at 1500 psi and 150–200° for 18 hr. The resulting slurry was diluted with 5000 ml of tetrahydrofuran, heated to near boiling temperature, and filtered while hot. The liquid was cooled to 5°. Filtration and drying yielded 49.4 g (48%) of **6a** as a white powder, mp 242.5–250.5°.

To a stirred suspension of 1.12 g (5.00 mmol) of this powder in 25 ml of dry pyridine, cooled to ice-bath temperature, was added 3.75 g (32.5 mmol) of methanesulfonyl chloride. Stirring was continued for 15 min and then the mixture was allowed to stand unstirred overnight at 6°. Then after stirring for 30 min the mixture was poured into 100 ml of cold water. The white solid which formed was collected by filtration, washed with cold 5% hydrochloric acid, cold water, and ether, and then dried, yielding 1.73 g (91%) of **6b** as a white powder: mp 127.0–129.5° dec; ir (KBr) 3.47, 7.53, and 8.56 μ; nmr (acetone-d_6) δ 0.8–2.2 (complex, 20), 3.10 and 3.13 (singlets, 3.5 and 2.5, combined $-OSO_2CH_3$), and 4.20 and 4.62 ppm (complex, 1.4 and 0.6, combined methine protons at carbon bearing $-OSO_2CH_3$).

A mixture of 6.84 g (0.0180 mol) of dimesylate **6b**, similar to that obtained above, mp 124.0–127.5° dec, 8.57 g (0.0720 mol) of freshly dried potassium bromide powder, and 3.53 g (0.0540 g-atom) of activated zinc dust in 90 ml of dimethylformamide was heated to 60–70° for 47 hr. During the reaction 10 ml of dimethylformamide was added to rinse the walls of the reaction flask. The resulting mixture was filtered and the remaining zinc was washed repeatedly with pentane. The combined filtrates were diluted with additional pentane (total 500 ml) and then washed six times with 250 ml of water, dried, and concentrated under reduced pressure to give 3.35 g of a white paste (96% based on loss of both mesylate groups). This material was chromatographed on 250 g of silica gel (column length: diameter = 12.8:1), collecting 20 150-ml fractions of pentane as eluent. Fractions 2–4 yielded 0.49 g of a mixture of saturated and unsaturated compounds. Fractions 5–15 yielded 1.25 g (34% based on diol mixture **6a**) of **3a,b** as an oily, white solid whose ir and nmr spectra were identical with those of authentic diene.[4]

Fragmentation of *cis*-9,10-Dimethanesulfonyloxy-*trans,syn,-trans*-perhydroanthracene.—A sample of cis diol **6a** was obtained from catalytic hydrogenation under 2000 psi of hydrogen at 100° for 20 hr of 10.0 g (4.63 mmol) of dione **5**, mp 239.5–245.5°, in 200 ml of ethyl acetate containing 1 ml of 60% perchloric acid and 0.75 g of platinum oxide. The resulting slurry was diluted with 1000 ml of warm ethyl acetate and filtered. A precipitate formed in the filtrate. After cooling, collection and drying yielded 0.86 g (8%) of white, flocculent crystals, mp 260–263°. The mother liquor was concentrated at reduced pressure to give a second crop of 0.42 g (4%) of white powder, mp 255–262°, ir (KBr) identical with that of the first crop. Combined crops 1 and 2 were recrystallized from tetrahydrofuran, yielding 0.78 g of cis diol **6a** as fine, white needles, mp 265.5–266.5°. [Correlation of the stereochemistry of this diol with that of the known diacetates was established by acetylating a mixture of 100 mg (0.446 mmol) of diol with 1.0 ml of acetic anhydride in 5 ml of pyridine at reflux temperature for 1 hr. Work-up gave 136 mg (99%) of white powder, mp 152.0–156.5°, recrystallization of which afforded material with mp 159.0–161.0°, undepressed upon mixing with authentic cis diacetate.[4]] To a mixture of 600 mg (2.68 mmol) of diol **6a**, mp 265.5–266.5°, and 15 ml of pyridine, cooled to ice-bath temperature, was added, with stirring, 1.50 ml of distilled methanesulfonyl chloride. After 18 hr at *ca.* 6° the mixture was poured into 25 ml of cold water. The resulting precipitate was collected, washed, and dried, affording 968 mg (95%) of *cis*-**6b** as a white powder, mp 125.0–125.5° dec.

Fragmentation of 380 mg (1.00 mmol) of *cis*-**6b** was carried out in the presence of 196 mg (3.00 mg-atom) of activated zinc dust and 476 mg (4.00 mmol) of potassium bromide powder in 8 ml of dimethylformamide, heated at 60–65°, with stirring under nitrogen. Periodically, aliquots were removed to monitor the course of the reaction and, after 70 hr, the remaining reaction mixture was worked up. Analysis of the nmr spectrum of the crude product indicated a yield of **3a,b** of 30% (based on absorption at δ 4.8 ppm) with much elimination of methanesulfonic acid (based on absorption at δ 5.0 ppm).

Fragmentation of *cis*-**6b** was also carried out in the presence of base: a mixture of 300 mg (0.790 mmol) of *cis*-**6b**, 150 mg (2.37 mg-atom) of activated zinc dust, 386 mg (3.16 mmol) of potassium bromide powder, and 49 mg (1.2 mmol) of sodium hydroxide in 7 ml of dimethylformamide was heated at 60–70° and aliquots were removed periodically to monitor the course of the reaction. Work-up, after 70 hr, gave a product, the nmr spectrum of which indicated a yield of **3a,b** of 20% with much elimination of methanesulfonic acid.

Fragmentation of *trans*-9,10-Dimethanesulfonyloxy-*trans,syn,-trans*-perhydroanthracene.—A sample of trans diol **6a**, mp 284–

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[13] J. Boersma and J. C. Noltes, *J. Organometal. Chem.*, **8**, 551 (1967).

[14] The stereochemistry of fragmentation reactions is discussed by C. A. Grob, *Angew. Chem., Int. Ed. Engl.*, **8**, 535 (1969), and C. A. Grob and P. W. Schiess, *ibid.*, **6**, 1 (1967).

285°, was obtained by saponification of the corresponding diacetate.[4] The remaining procedures closely followed those described for fragmentation of *cis*-**6b**. Mesylation of a 600-mg sample of *trans*-**6a** afforded 970 mg (95%) of *trans*-**6b** as a white powder, mp 181.0–181.5° dec.

Fragmentation of a 380 mg (1.00 mmol) sample of *trans*-**6b** with 196 mg (3.00 mg-atom) of activated zinc dust and 476 mg (4.00 mmol) of potassium bromide in 8 ml of dimethylformamide at 60–70° for 70 hr yielded a product containing 46% of fragmentation product **3a,b** and much olefin from elimination of methanesulfonic acid. Fragmentation of a 300 mg (0.790 mmol) sample of *trans*-**6b** under similar conditions but with the addition of 47 mg (1.2 mmol) of sodium hydroxide afforded a product in which elimination of methanesulfonic acid had predominated, fragmentation accounting for only 6% (based on nmr absorption at δ 4.8 ppm).

9,10-Diketo-Δ^2-*trans,syn,trans*-dodecahydroanthracene (11).—A solution of 8.47 g (52.2 mmol) of quinone **9**[7] in 15 ml of dry benzene solution containing 11 g (210 mmol) of butadiene was kept in the dark at room temperature for 17 days. During the reaction period an additional 2 g (38 mmol) of butadiene in benzene was added to the mixture. Finally, the reaction mixture was concentrated to dryness under reduced pressure, yielding 10.9 g (96%) of a beige powder: mp 108–111°; nmr (CCl_4) δ 1.65 (complex, 4), 2.27 (complex, 8), 3.03 (complex, 2), and 5.49 ppm (complex, 2). (Absorption at δ 7.56 ppm indicated contamination by starting material to be less than 2%.) The crude solid was crystallized from 10% ethyl acetate–hexane to yield 5.90 g (52%) of beige needles: mp 112–113.5°; ir (KBr) 6.16 μ. Concentration of the mother liquor gave a second crop of 2.60 g (23%), mp 110–112°.

Over a 15-min period, 30 g (0.46 g-atom) of activated zinc was added in portions to a solution of 10.0 g (16.0 mmol) of butadiene adduct, mp 109–112°, in 300 ml of glacial acetic acid maintained at 115°. The mixture was heated at reflux temperature under nitrogen for 85 min and then filtered while hot. Additional warm acetic acid was used to rinse the collected zinc. The combined filtrates were diluted with 1750 ml of ether and subsequently washed five times with 500 ml of water, once with 5% sodium bicarbonate solution, and again with water. Drying and concentration at reduced pressure afforded 8.82 g (87%) of a mixture of stereoisomeric diones as a white, violet-tinged solid: mp 169–208°; ir (KBr) 5.91 μ; nmr ($CDCl_3$) δ 0.7–3.7 (complex, 16), and 5.79 ppm (s, 2). The crude mixture of reduced diones (8.68 g) was dissolved with heating and stirring in 30 ml of ethanol and the solution was treated with 2 ml of a 5% ethanolic potassium hydroxide solution. A reddish-brown coloration developed and was followed by the rapid separation of white crystals. The mixture was cooled at 6° for 2 hr and the precipitate was collected, washed with cold ethanol, and dried, affording 6.41 g (74%) of white plates, mp 225–231°, ir (KBr) 5.92 μ. This substance was characterized as **11** by hydrogenation of a 250-mg sample in 80 ml of tetrahydrofuran for 100 min at room temperature under 300 psi of hydrogen and over 500 mg of 5% palladium on charcoal. The resulting mixture was heated to near reflux temperature and filtered while hot, and the filtrate was concentrated under reduced pressure to yield yellow-white prisms, mp 215–226°, no nmr (CF_3CO_2H) absorption due to vinyl hydrogen. Crystallization from ethanol yielded 180 mg (71%) of white needles, mp 249–252.5°, undepressed upon mixing with a sample of authentic 9,10-diketo-*trans,syn,trans*-perhydroanthracene,[6] ir (KBr) matched that of authentic material.

***trans,trans,cis*-2,8,12-*trans*-Bicyclo[8.4.0]tetradecatriene (4a).**—To a magnetically stirred suspension of 0.50 g (13 mmol) of lithium aluminum hydride in 75 ml of tetrahydrofuran was added 0.50 g (23 mmol) of dione **11**, in portions along with 15 ml of tetrahydrofuran. Stirring under nitrogen at room temperature was continued overnight. Excess lithium aluminum hydride was destroyed by addition of ethanol and water, and 50 ml of 5% hydrochloric acid was then added. Organic solvents were removed under reduced pressure and the remaining solid was filtered and then washed successively with 10% sodium hydroxide solution, water, 5% hydrochloric acid, and ethanol, yielding, after drying, 1.29 g of yellow powder. This material was extracted with chloroform–2% hydrochloric acid, the chloroform extracts yielding 0.32 g (63%) of a mixture of diols **7a** as a pale yellow powder, mp 197–227°, ir (KBr) showing no carbonyl absorption.

In a typical run, 13.8 g (120 mmol) of methanesulfonyl chloride was added to a cooled, stirred suspension of 4.08 g (18.4 mmol) of diol mixture **7a**, obtained as described above, in 100 ml of dry pyridine. The mixture was stored at 5° for 2 days. Addition of 350 ml of cold water produced a white solid which was collected and washed with 5% hydrochloric acid, water, and ether. Drying yielded 6.61 g (95%) of a mixture of dimesylates **7b** as a white powder, mp 129–130° dec.

A mixture of 6.39 g (16.9 mmol) of this dimesylate mixture, 8.05 g (67.6 mmol) of dried potassium bromide powder, and 3.32 g (50.7 mg-atoms) of activated zinc in 90 ml of dry dimethylformamide was stirred under nitrogen at 60–70° for 28 hr. The zinc remaining in the reaction mixture was removed by filtration and washed with pentane. Washing the combined filtrates thoroughly with water and further work-up yielded 3.00 g of a clear, slightly yellow oil: nmr (CCl_4) δ 0.6–3.0 (complex), 4.75 (complex, trans-disubstituted C=C), and 5.15 ppm (broad singlet, cis-disubstituted C=C). The integration ratio for absorbance at δ 5.15 (2 H) and 4.75 ppm (4 H) of 20:23 indicated that triene **4a** formed about 58% of the mixture.

The reaction product was chromatographed on 225 g of silica gel (column length:diameter = 11:1) using eight 175-ml portions of distilled pentane followed by nine 175-ml portions of 5% ether–pentane as eluting solvents. Fractions 2 and 3 yielded 0.095 g of a white solid, probably Δ^2-*trans,syn,trans*-dodecahydroanthracene: mp 49.5–51°; nmr (CCl_4) δ 0.5–2.4 (complex, 20) and 5.60 ppm (c, 2, J = 2 Hz, disubstituted C=C). Fractions 4–7 yielded 0.458 g of a clear, colorless oil, probably a mixture of $\Delta^{2,4a(10)}$- and $\Delta^{2,10}$-*trans,cis*-decahydroanthracenes: nmr (CCl_4) δ 0.6–3.0 (complex, 17), 5.15 (complex, 11, trisubstituted C=C), and 5.68 ppm (complex, 2, disubstituted C=C). Fractions 9–14 yielded 1.530 g (48% based on starting dimesylate mixture) of *trans,trans,cis*-2,8,12-*trans*-bicyclo[8.4.0]tetradecatriene (**4a**) as a clear, very pale yellow oil: ir (CCl_4) 10.34 μ; nmr (CCl_4) δ 0.6–2.9 (complex, 14), 4.75 ppm (complex, 4, trans-disubstituted C=C), and 5.72 ppm (d, 2, J = 11 Hz, cis-disubstituted C=C). A portion of this material was rechromatographed over silica gel using purified pentane as eluting solvent. Evaporation of solvent from the third of five fractions afforded an analytical sample.

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 88.88; H, 10.91.

Ozonolysis of 4a.—An excess of ozone from a Welsbach ozonator, Model T-408, was bubbled into a solution of 48 mg (0.26 mmol) of triene **4a** in 7 ml of dry methylene chloride at −75°. The resulting blue solution and white gelatinous precipitate were allowed to warm to room temperature and 3 ml of 40% peracetic acid (FMC Corp.) was then added. After diluting the mixture with ethyl acetate and heating it to reflux for 28 hr, 150 mg of 30% palladium on charcoal was added. The total mixture was dried, filtered, and concentrated under reduced pressure to give 70 mg of brown residue, ir ($CHCl_3$) 5.78 μ. The residue was dissolved in ether and washed with 10 ml of 10% sodium hydroxide solution. Acidification of the aqueous phase with 15 ml of 10% hydrochloric acid, followed by thorough extraction with ether, yielded, upon further work-up, 10.5 mg of yellow solid which was esterified with diazomethane. The product was subjected to glpc analysis at 150° on a 5 ft × 0.25 in. column packed with 5% Carbowax 20M on Chromasorb T; only one peak was apparent, with a retention time of 3.6 min, identical by coinjection with the retention time of an authentic sample of dimethyl adipate. The peak of an authentic sample of dimethyl *trans*-1,2-cyclohexanedicarboxylate, subjected to the above-described column conditions, appeared at 6.0 min.

Registry No.—**3a,b**, 17510-77-9; **4a**, 32687-22-0; **6a**, 3922-06-3; **6b**, 32675-59-5; **7a** (mixture of diols), 32675-58-4; **10**, 32675-56-2; **11**, 32675-57-3; Δ^2-*trans,syn,trans*-dodecahydroanthracene, 32675-60-8.