Novel Dimeric Products from 10-Methyleneanthrone

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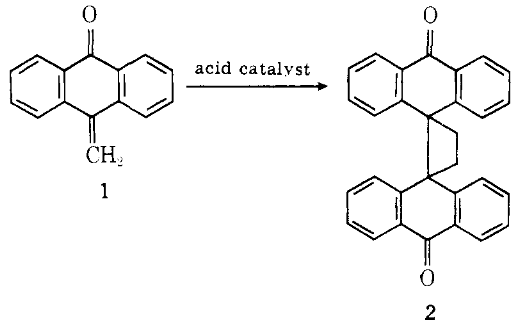
Received September 13, 1977

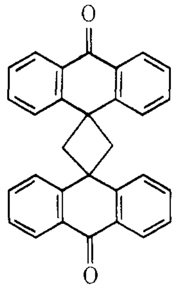
The reaction of 10-methyleneanthrone (1) with acid catalysts in alcohols, benzene, or acetic acid gives anthrone-10-spiro-1′-cyclobutane-2′-spiro-10″-anthrone (2). Acetylation of 2 yields 7-acetoxy-1,2-dihydro-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (8). 7-Alkoxy-1,2-dihydro-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrones (10) are formed by the reaction of 1 with dialkyl sulfates. Mechanistic studies suggest that 2 is formed via a path involving 1,2-cycloaddition (head-to-head linkage) of 1 and that 2 rearranges with ring expansion to 1,2,3,11b-tetrahydrobenz[*de*]anthrone-3-spiro-10′-anthrone (11). The thermal reaction of 2 in usual organic solvents leads to 11, 2,3-dihydrobenz[*de*]anthrone-3-spiro-10′-anthrone (12), and hydroperoxide 13. Acetylation of 12 involves enolization, yielding 7-acetoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (15). 7-Alkoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrones (17) are formed from the reaction of 12 with an excess of alkyl iodides in alcoholic sodium alkoxide. Oxidations of 2, 8, 10, and 12 by chromium trioxide give 10-(1-anthraquinonyl)-10-carboxymethylanthrone (18).

The reaction of 10-methyleneanthrone (1) with acid catalysts, such as alcoholic hydrochloric acid, alcoholic sulfuric acid, or formic acid, is known to give a dimeric product. Its structure has been considered to be either 4 or 5.[1] However, in our reinvestigation of the product, it has been identified as a dimeric product whose structure is of dispiro compound. This dimeric product is expected to be highly reactive because of its high degree of strain. Quinone methides belong to an exceedingly reactive group of substances. Although the dimeric and trimeric forms of the quinone methides have been isolated, the unsubstituted monomeric materials could not be obtained due to their extreme reactivity. Several highly substituted quinone methides are, however, stable and can be isolated. Methyleneanthrone is the sole example of a stable quinone methide having an unsubstituted methylene group.[2] In the literature it has been stated that the phosphite-catalyzed, autoxidative, and reductive dimerizations of 1 give a Diels–Alder dimeric product, a dimeric peroxide, and a reductive dimeric product, respectively.[3] The present paper is concerned with the identification and mechanism of formation of the dimeric product derived from 1 and with its rearrangement.

Results and Discussion

The dimerization reaction of 10-methyleneanthrone (1) in alcohols, benzene, or acetic acid was carried out by refluxing the solution in the presence of various acid catalysts, such as hydrochloric acid, sulfuric acid, aluminum chloride, ferric chloride, boron trifluoride etherate, *p*-toluene sulfonic acid, or polyphosphoric acid. In all these cases, the major product was anthrone-10-spiro-1′-cyclobutane-2′-spiro-10″-anthrone (2), which was a 1,2-cycloaddition product (head-to-head linkage) of 1. The results are summarized in Table I. The reaction of 1 with weak acids, such as phosphoric acid or zinc chloride as an acid catalyst, was carried out in alcohols. In this case, however, 2 was not formed. Moreover, 1 was not converted to 2 by the reflux with an amount of catalyst less than that shown in Table I. The yield of 2 was independent of the reaction temperature (>ca. 50 °C), reaction time (>ca. 15 min), and amount of catalyst (>that shown in Table I). Therefore, it appears that the yield is dependent upon the nature of catalyst and the solubility of 2 in the solvent. Although no experimental test was made, 2 may be formed by the reaction of 1 with strong acids in any organic solvents other than basic ones. The pure spiroanthrone 2 melts at 248–250 °C and is slightly soluble in usual organic solvents. In the solid state, 2 is stable to air and prolonged heating but decomposes rapidly in solution. Although another structural isomer (3, head-to-tail linkage) would be possible as 1,2-cycloaddition product from these reactions, 3 was not isolated in each case.

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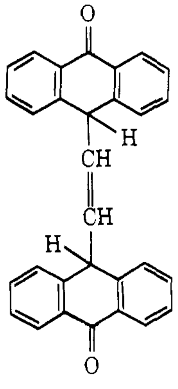
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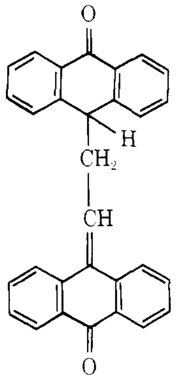
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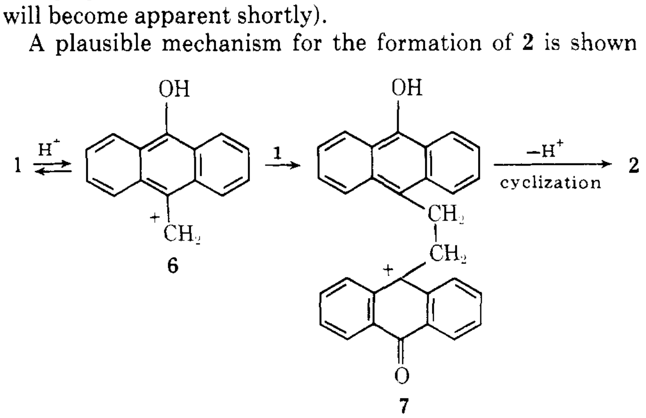
These reactions would also be expected to yield a Diels–Alder dimeric product (11), but 11 was not obtained. The only other product identified under these conditions was 2,3-dihydrobenz[*de*]anthrone-3-spiro-10′-anthrone (12) (for reasons that will become apparent shortly).

A plausible mechanism for the formation of 2 is shown below. It might be supposed that the reaction is actually catalyzed by acid in a process involving three steps: protonation of the carbonyl group in the quinone methide, addition of the



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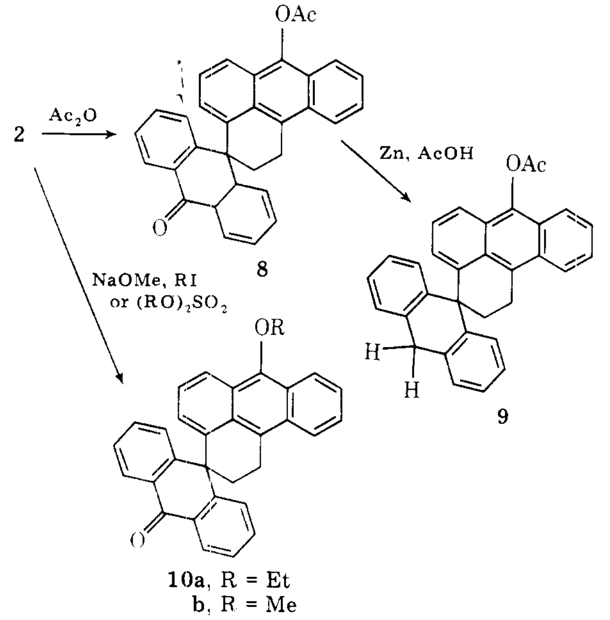
carbocation moiety of 6 to the methylene group of a second quinone methide molecule, and internal cyclization of 7 to form 2 and regenerate the proton. Methyleneanthrone is known to form solid colored complexes with metal halides such as chlorides and bromides of boron and aluminum, in which the carbonyl group of 1 coordinates with metal halides.[4] Many quinones also form hydroxy carbocations in strong acids while undergoing protonation of the carbonyl group in the quinones. These facts support the mechanism for the formation of 2 in the reactions of 1 with acid catalysts as discussed above. The reaction of quinone methides has not been known to form cyclobutane derivatives.

In acetic anhydride, 2 rearranged with simultaneous ring expansion to yield acetylated product 7-acetoxy-1,2-dihydro-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**8**, 64%). The structure of **8** was evident from the fact that it formed 10-(1-anthraquinonyl)-10-carboxymethylanthrone (**19**) on oxidation with chromium trioxide. Reduction of **8** with zinc powder in acetic acid gave 7-acetoxy-1,2-dihydro-3*H*-benz[*de*]anthracene-3-spiro-10′-(9′,10′-dihydroanthracene) (**9**), carbonyl group being reduced. The product **9** could also be formed from **2** with zinc powder and acetic anhydride. The reaction of **2** with ethyl iodide and methyl iodide in boiling methanolic sodium methoxide gave 7-ethoxy-1,2-dihydro-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**10a**, 45%) and 7-methoxy compound (**10b**, 42%), respectively, as the major products. Spiroanthrones **10a** and **10b** could also be prepared in ca. 90% yields by the reaction of **2** with diethyl sulfate or dimethyl sulfate in hot ethanolic potassium hydroxide. The structures of these compounds were confirmed by direct comparisons with the authentic samples prepared independently.[2c,3b]

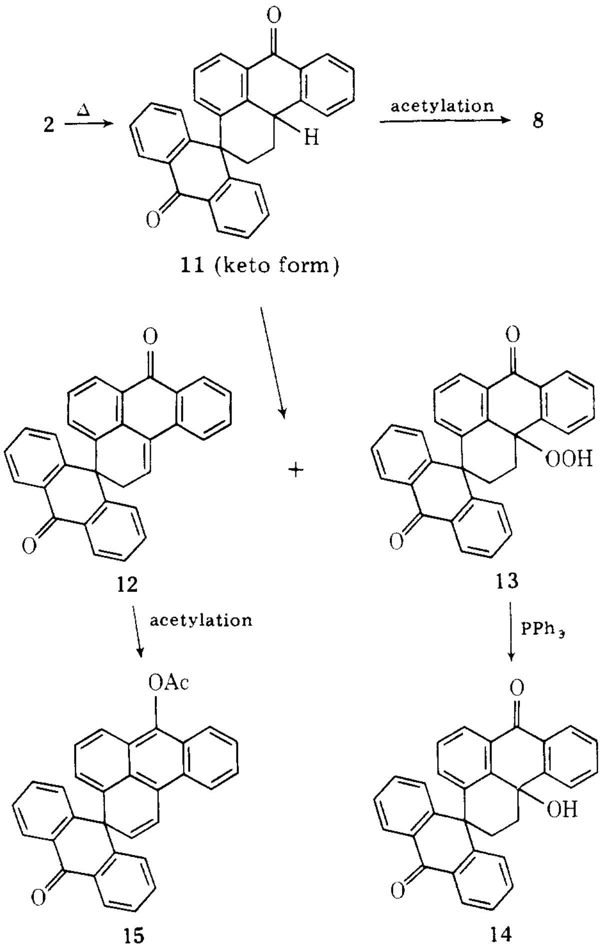


Spiroanthrone **2** readily rearranged in refluxing solvents with ring expansion followed by autoxidation or dehydrogenation to benzanthrone derivatives. Under the atmosphere, the thermal reaction of **2** in benzene led to 1,2,3,11b-tetrahydrobenz[*de*]anthrone-3-spiro-10′-anthrone (**11**), 2,3-dihydrobenz[*de*]anthrone-3-spiro-10′-anthrone (**12**, 15%), and 1,2,3,11b-tetrahydro-11b-hydroperoxybenz[*de*]anthrone-3-spiro-10′-anthrone (**13**). The thermal reaction of **2** using other organic solvents also gave similar results. In this reaction, the formation of hydroperoxide was suggested by a positive peroxide test, the presence of a strong parent peak for **13** at *m/e* 444 in the mass spectrogram, and its infrared absorption for hydroxy group at 3350 cm^{-1}. The structure of **13** was confirmed by the fact that it formed 1,2,3,11b-tetrahydro-11b-hydroxybenz[*de*]anthrone-3-spiro-10′-anthrone (**14**) on reduction with triphenylphosphine. The formation of **11** was suggested by the fact that the acetylated product of the thermal reaction mixture contained **8**. Under the atmosphere spiroanthrone **11** could not be isolated due to its extreme reactivity, and attempts to isolate it led to **12** and/or **13**. The thermal reaction of **2** in solvents under a nitrogen atmosphere mainly yielded **11**. In this case, the analysis of the acetylated products of the reaction sample in benzene by NMR showed that these contained **8** and **15**. Quantitative calculations based on the NMR spectrum showed that the composition of the acetylated products was **8** (95%) and **15**

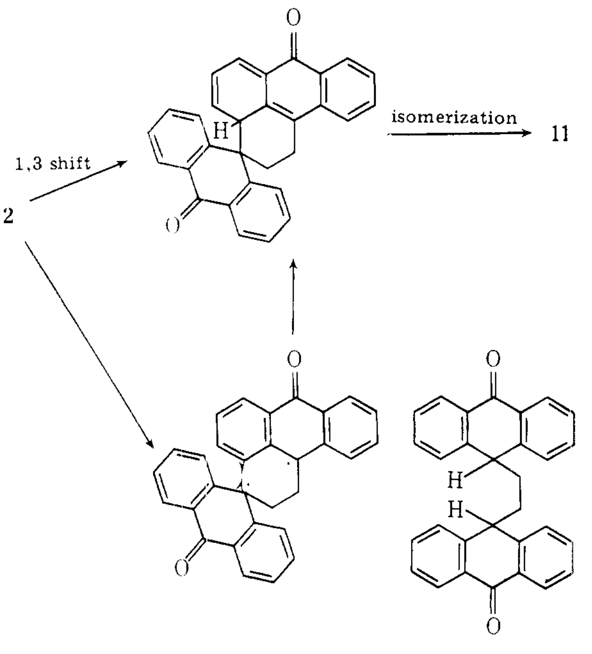
Table I. Reaction of 10-Methyleneanthrone with Acid Catalysts[a]

Catalyst (mmol)[b]	Solvent (mL)[c]	Yield, %[d]
HCl (20)	CH_3OH (500)	82
HCl (20)	C_2H_5OH (500)	65
HCl (20)	n-C_3H_7OH (200)	52
HCl (20)	n-C_4H_9OH (50)	97
HCl (20)	CH_3COOH (150)	41
H_2SO_4 (20)	CH_3OH (500)	74
$AlCl_3$ (15)	CH_3OH (500)	82
$FeCl_3$ (60)	CH_3OH (500)	76
$BF_3 \cdot O(C_2H_5)_2$ (15)	C_6H_6 (100)	54
p-$CH_3C_6H_4SO_3H$ (20)	CH_3OH (500)	51
$H_6P_4O_{13}$ (20)	CH_3OH (500)	50

[a] Reaction of 1 (10.3 g, 50 mmol) was carried out at the temperature of the refluxing solvent. [b] The minimum amount of acid catalysts required to react. [c] The minimum volume of solvents required to dissolve 1. [d] Isolated yields of pure dimeric product; not corrected for the recovered starting material and by-products.



Scheme I



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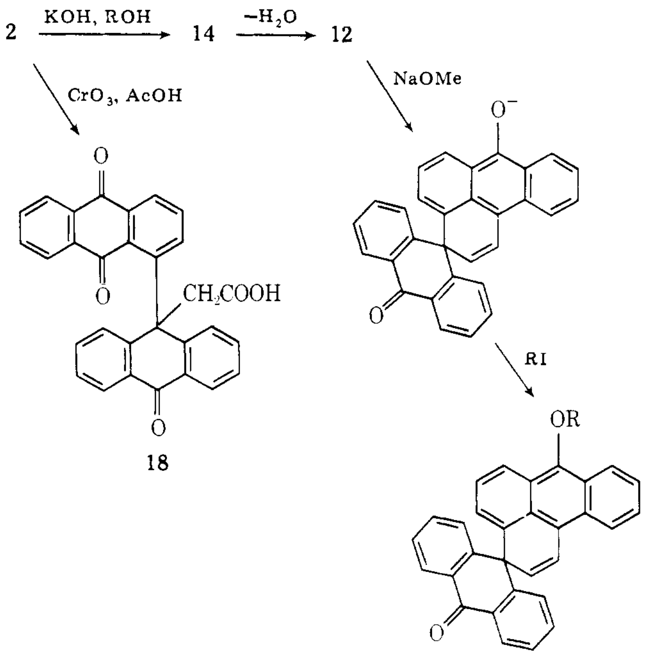

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17a, R = Et
b, R = Me

(5%). The bulk thermal reaction of **2** at its melting point gave **12** (68%).

Two pathways (the biradical and 1,3-sigmatropic pathways) for the rearrangement of **2** are conceivable. If the biradical pathway is operative, **2** would be expected to give 1,2-dianthronylethane (**16**)[5] from the reaction of biradical which abstracts a proton from solvent. However, **16** was not detected in any of the thermal reaction products from **2** even in solvents, such as alcohols, diphenylmethane, or decalin. The presence of the biradical was not confirmed by the ESR measurements of the thermal reactions of **2**. For this rearrangement the sigmatropic pathway rather than the biradical one in Scheme I is seemingly demanded by these facts. However, it does not seem likely that the rearrangement proceeds by the sigmatropic pathway, since thermal 1,3-antarafacial shift with retention is rendered inaccessible by the steric situation at the migrating center. It is probable that the intramolecular cyclization is favorable over the intermolecular reaction, so that **16** is not produced, and also that the cyclization proceeds too fast to detect the ESR signal of the biradical. Therefore, it seems likely that the rearrangement proceeds by the biradical pathway, being followed by isomerization. Analogous reactions have been reported in conversion of vinylcycloalkanes to cycloalkenes[6] and of dibenz[2,4]spirenes to pentalene derivatives.[7]

The reaction of **2** with potassium hydroxide in methanol gave **14** (44%), which was dehydrated to **12** (93%) by refluxing in acetic acid. Although the mechanism of this reaction has not been established, spiroanthrone **14** appears to be obtained by oxidation of **11** which is produced as an intermediate in the rearrangement of **2**. Spiroanthrones **12** and **14** were acetylated in acetic anhydride, yielding acetylated product **15** (67–69%). Alkylation of **12** by the way described for **2** gave 7-ethoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**17a**) and 7-methoxy compound (**17b**). Acetylation and alkylation of **12** involve enolization by a transfer of hydrogen from C-2.[8] Oxidation of **2** by chromium trioxide in acetic acid gave **18** as the main product (47%) along with a small quantity (<2%) of anthraquinone. Under the same conditions, oxidation of **8**, **10**, and **12** gave similar results. The oxidation product **18** reacted with alcohols in the presence of a small amount of hydrogen chloride to yield esters (**19**).

It now appears that 10-methyleneanthrone (**1**) is dimerized by acid catalyst to give spiroanthrone **2** which rearranges readily into the benzanthrone derivatives. It seems reasonable that the reactivity in the rearrangement of **2** depends primarily on strains in the cyclobutane ring. In this case it is almost certain that steric repulsion by the large anthronyl groups may increase these strains. Similar rearrangement of various 2′,2′-disubstituted spirocyclopropaneanthrones will be described in subsequent publications.

Experimental Section

Melting points were determined with a Meihoh thermoanalyzer MP-2. Elemental analyses were performed on a Coleman Model 33 carbon hydrogen analyzer. Infrared, 60-MHz NMR, and mass spectra were obtained with JASCO Model IRA-1, JEOL JNM-3H-60, and JEOL JMS-01SG-2, respectively. The NMR measurements were made at ambient temperature on dilute solutions containing Me_4Si as internal standard. The column chromatography was carried out on silica gel M and the TLC used on 0.25 mm thick silica gel G layers. Substances were visualized on these plates either by exposure to iodine vapor or by spraying an alkaline sodium dithionite solution.

Materials. The chemicals used were either highly purified articles of commerce or materials prepared by standard literature, as indicated below. Purities were verified by spectral measurements, TLC, VPC analyses, and the determination of appropriate physical constants.

Reaction of 10-Methyleneanthrone (1) with Acid Catalysts. Fine powder of **1**[3b] was completely dissolved in solvent with stirring and refluxing. Acid catalyst was then introduced dropwise into the mixture during 5 min, while stirring and refluxing were continued. Almost immediately the color of the mixture changed to light brown and the product precipitated slowly. After an additional 20 min of stirring and heating, the hot mixture was filtered, and the recovered solid was washed several times with methanol; the product was pure anthrone-10-spiro-1′-cyclobutane-2′-spiro-10″-anthrone (**2**) as light yellow microcrystals: mp 248–250 °C (lit.[1] 254 °C); IR (KBr) 1670 cm^{-1} (ArCOAr C=O), no OH; mass spectrum (75 eV) *m/e* 412 (M^+), 410, 394, 383, 326, 206, 193, and 178. Anal. Calcd for $C_{30}H_{20}O_2$: C, 87.36; H, 4.89. Found: C, 87.40; H, 4.96. The results are summarized in Table I.

Acetylation of 2. A solution of concentrated sulfuric acid (1 mL) in acetic anhydride (5 mL) was added to a suspension of **2** (5.16 g, 12.5 mmol) in acetic anhydride (200 mL). The mixture was stirred and heated under reflux for 1 h. The color of the mixture gradually changed from yellow to greenish yellow. The hot mixture was filtered, and water (500 mL) was added. The mixture was shaken until acetic anhydride was completely hydrolyzed. The yellow solid was collected by filtration and washed with water; the solid then weighed 5.07 g and melted at 273–275 °C. Two recrystallizations of the product from acetic acid gave 3.64 g (64%) of 7-acetoxy-1,2-dihydro-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**8**) as microcrystals: mp 283 °C; IR (KBr) 1754 (ester C═O), 1665 cm^{-1} (ArCOAr C═O); NMR ($CDCl_3$) δ 2.35 (t, 2, J = 6.2 Hz, CH_2CH_2Ar), 2.67 (s, 3, CH_3), 3.48 (t, 2, J = 6.2 Hz, CH_2Ar), and 6.5–8.5 (m, 15, aromatic **H**); mass spectrum (75 eV) *m/e* 454 (M^+), 412, 383, and 193. Anal. Calcd for $C_{32}H_{22}O_3$: C, 84.56; H, 4.88. Found: C, 84.58; H, 4.94.

Reduction of 8. A solution of **8** (4.54 g, 10.0 mmol) in acetic acid (150 mL) was stirred and heated under reflux with zinc powder (20 g) for 15 h. The color of the mixture gradually changed to yellow with a blue fluorescence. The hot mixture was filtered, and water (500 mL) was added to the filtrate. The light yellow solid was recovered by filtration and washed with water; the solid then weighed 4.50 g. The product was purified by column chromatography using benzene as developer. Evaporation of appropriate fractions yielded 2.55 g (58%) of 7-acetoxy-1,2-dihydro-3*H*-benz[*de*]anthracene-3-spiro-10′-(9′,-10′-dihydroanthracene) (**9**) as light yellow microcrystals (single spot on TLC): mp 258–259 °C; IR (KBr) 1760 cm^{-1} (ester C═O); NMR ($CDCl_3$) δ 2.28 (t, 2, J = 6.2 Hz, CH_2CH_2Ar), 2.67 (s, 3, CH_3), 3.36 (t, 2, J = 6.2 Hz, CH_2Ar), 4.25 (center of AB quartet, 2, J = 21.0 Hz, $\delta_A - \delta_B$ = 13.5 Hz, 9′-**H**), and 6.7–8.3 (m, 15, aromatic **H**); mass spectrum (75 eV) *m/e* 440 (M^+), 398, 319, 289, and 207. Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49. Found: C, 87.40, H, 5.39.

Reaction of 2 with Alkyl Iodides and Sodium Methoxide in Methanol. Sodium methoxide (1.60 g, 29.6 mmol) was added with stirring to a gently refluxing mixture of **2** (2.00 g, 4,85 mmol) in methanol (100 mL). Ethyl iodide (58.5 g, 0.375 mol) was then introduced dropwise into the dark red-brown mixture during 20 min while stirring and heating were continued. After an additional 35 min of heating, the mixture (now a pale yellow solution) was concentrated at the boiling point until precipitation occurred, cooled to room temperature, and filtered. The recovered solid was washed with several small portions of cold methanol; the solid then weighed 1.08 g. The product was purified by the column chromatography using benzene as developer. A recrystallization of the appropriate fraction from methanol–benzene gave 0.96 g (45%) of pure 1,2-dihydro-7-ethoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**10a**) as bright yellow microcrystals, mp 238–239 °C (lit.[2c,3a] mp 236–237.5 °C), which were shown to be identical with an authentic sample of **10a** by NMR and IR spectral comparisons and mixture melting point test.

Similar reaction of **2** with methyl iodide gave 1,2-dihydro-7-methoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**10b**, 42%) as bright yellow microcrystals, mp 240 °C (lit.[2c,3a] mp 237–239 °C), which were shown to be identical with an authentic sample of **10b**.

Reaction of 2 with Dialkyl Sulfates. A solution of potassium hydroxide (0.56 g, 10 mmol) in absolute ethanol (10 mL) was added to 2.06 g (5.00 mmol) of **2** dispersed in absolute ethanol (50 mL) and the mixture was heated to 50 °C during 2 min with stirring. Diethyl sulfate (2 mL) was added, and stirring was continued at 50 °C until the color of the mixture changed to pale yellow (5–10 min required). Increments of potassium hydroxide and diethyl sulfate were added alternately in a similar manner until a solution of base (5.6 g, 0.10 mol) in absolute ethanol (100 mL) and 20 mL (23 g, 0.10 mol) of the sulfate had been introduced. After cooling to room temperature, the mixture was filtered, and the recovered solid (largely inorganic) was washed several times with fresh portions of ethanol. The filtrate and washing were combined, concentrated by distillation, and diluted with water until the boiling solution exhibited a slight turbidity. Cooling yielded a precipitate, which was collected in the usual way. This product weighed 2.06 g and melted at 234–235 °C. The product was recrystallized from methanol–benzene to give 1.09 g (86%) of pure **10a**. Analogous reaction of **2** with dimethyl sulfate gave **10b** (93%).

Thermal Reaction of 2. A. In Solvents. A suspension of **2** (2.06 g, 5.00 mmol) in dry benzene (300 mL) was heated under reflux for 5 h. The color of the mixture gradually changed from initial light yellow to colorless at the end. TLC (benzene) of the initial mixture showed a major spot having R_f 0.30 corresponding to **2** and two minor spots having R_f 0.35 and 0.12 corresponding to 2,3-dihydrobenz[*de*]anthrone-3-spiro-10′-anthrone (**12**) and hydroperoxide (**13**), respectively. At the end of the reaction TLC showed a minor spot having R_f 0.30 and two major spots having R_f 0.35 and 0.12. The final mixture contained a white solid, which was recovered by filtration and washed several times with fresh benzene. This solid (fraction A) weighed 1.06 g and gave a positive test for peroxide(s) with potassium iodide in acetic acid. Evaporation of the combined filtrate and washings yielded 0.34 g of pale yellow powder (fraction B). Two recrystallizations of fraction B from benzene gave 0.30 g (15%) of pure **12** as light yellow microcrystals: mp 298–300 °C; IR (KBr) 1665 cm^{-1} (ArCOAr C═O); NMR ($CDCl_3$) δ 3.66 (d, 2, CH_2Ar), and 6.9–8.6 (m, 16, aromatic **H** and CH═Ar); mass spectrum (75 eV) *m/e* 410 (M^+), 382, 354, 326, and 324. Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42. Found: C, 87.50; H, 4.60.

Fraction A was slightly soluble in usual organic solvents, and the TLC (benzene) showed a spot having R_f 0.12. The mass and infrared spectra of fraction A indicated a strong parent peak for hydroperoxide (**13**) at *m/e* 444 and absorption for hydroxy group at 3350 cm^{-1}, respectively. Attempts to isolate **13** from fraction A were unsuccessful. A suspension of fraction A (0.44 g) in benzene (50 mL) was stirred and heated under reflux with triphenylphosphine (0.325 g, 1.2 mmol) for 3 h. The mixture was concentrated at the boiling point until precipitation occurred, cooled to room temperature, and filtered. The solid was recrystallized from chlorobenzene to yield 0.21 g of 1,2,3,11b-tetrahydro-11b-hydroxybenz[*de*]anthrone-3-spiro-10′-anthrone (**14**) as colorless microcrystals: mp 299–300 °C; IR (KBr) 3390 (OH), 1663 cm^{-1} (ArCOAr C═O); mass spectrum (75 eV) *m/e* 428 (M^+), 410, 400, 383, and 193. Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.09; H, 4.70. Found C, 84.10; H, 4.80.

A solution of fraction A (0.5 g) in benzene (300 mL) was heated for 5 h. TLC (benzene) of a portion from the reaction mixture showed two spots having R_f 0.35 and 0.12 corresponding to **12** and **13**, respectively. Fraction A was acetylated with acetic anhydride in the manner described for **2**. Analysis of the acetylated products by NMR showed that it contained **8** and 7-acetoxy-3*H*-benz[*de*]anthracene-3-spiro-10-anthrone (**15**). These identifications were confirmed by NMR peak enhancements resulting from addition of the pure substance. Quantitative calculations based on the NMR spectrum showed that the composition of the acetylated products was **8** (29%) and **15** (71%). Acetylation of fraction A indicated that its fraction contained 1,2,3,11b-tetrahydrobenz[*de*]anthrone-3-spiro-10′-anthrone (**11**). The thermal reaction of **2** using toluene, chlorobenzene, carbon tetrachloride, alcohols, chloroform, diphenylmethane, decalin, acetic acid, and dimethyl sulfoxide as solvent gave similar results.

When a suspension of **2** in benzene under a nitrogen atmosphere was refluxed for 10 h, TLC (benzene) of the final mixture showed a minor spot having R_f 0.35 and a major spot having R_f 0.12 corresponding to **12** and **11**, respectively. The composition of the acetylated products of the final mixture was estimated by NMR as **8** (95%) and **15** (5%).

A mixture of **2** (1.03 g, 2.50 mmol) and dimethyl sulfoxide (50 mL) was degassed with nitrogen and allowed to stand at 100 °C for 1 h under a nitrogen atmosphere. After cooling to room temperature, water (300 mL) was added. The yellow solid (**11**) was then collected by filtration and washed with water. Crude **11** weighed 1.01 g (98%) and TLC (benzene) of **11** showed a spot having R_f 0.12. Owing to its instability it was examined without further treatment: mp 180–185 °C dec; IR (KBr) 1662 cm^{-1} (ArCOAr C═O); NMR (DMSO-d_6) δ 2.05–2.50 (m, 2, CH_2CH_2Ar), 3.20–3.65 (m, 2, CH_2Ar), 3.38–3.65 (m, 1, 11b-**H**), and 6.8–8.9 (m, 15, aromatic **H**); mass spectrum (75 eV) *m/e* 412 (M^+), 410, 394, 393, 383, 326, 276, 206, 193, and 178. Anal. Calcd for $C_{30}H_{20}O_2$: C, 87.36; H, 4.89. Found: C, 87.34; H, 4.96.

B. Bulk Thermal Reaction. Spiroanthrone **2** (2.06 g, 5.00 mmol) was heated without solvent at its melting point for 10 min. The product was purified by column chromatography using chloroform as developer. Evaporation of appropriate fractions yielded 1.39 g (68%) of pure **12**. The presence of the biradical was not confirmed by the ESR measurements (JEOL JES-ME spectrometer) of the thermal reaction sample.

Reaction of 2 with Alcoholic Potassium Hydroxide. A solution of **2** (4.12 g, 10.0 mmol) in methanol (50 mL) containing potassium hydroxide (28 g) was heated with stirring for 24 h under reflux. After cooling to room temperature, water (300 mL) was added. The solid was recovered by filtration and washed well with water; the solid then weighed 4.02 g. Two recrystallizations of the product from chlorobenzene gave 1.09 g (44%) of **14**.

A solution of **14** (1.07 g, 2.50 mmol) in acetic acid (50 mL) was refluxed with stirring for 5 h. The volume of the mixture was reduced to 10 mL by distillation. After cooling, the mixture was filtered, and the collected solid was washed with water; the solid then weighed 1.01 g. The product was recrystallized from chloroform to yield 0.95 g (93%) of pure **12**. On the dehydration of **14**, chloroform and sulfuric acid served as a substitute for acetic acid.

Acetylation of 12 and 14. The procedure employed was similar to that for acetylation of **2**. Spiroanthrone **12** (4.10 g, 10.0 mmol) was acetylated in acetic anhydride (100 mL) in the presence of sulfuric acid (1 mL). Two recrystallizations of the product from acetic acid gave 3.10 g (67%) of pure 7-acetoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**15**) as yellow microcrystals: mp 307–309 °C; IR (KBr) 1754 (ester C═O), 1665 cm^{-1} (ArCOAr C═O); NMR ($CDCl_3$), δ 2.62 (s, 3, CH_3), 6.15 (d, 1, J = 10 Hz, CH═CHAr), 7.82 (d, 1, J = 10 Hz, CHAr), and 7.8–8.5 (m, 15, aromatic **H**); mass spectrum (75 eV) *m/e* 452 (M^+), 410, 381, 363, and 350. Anal. Calcd for $C_{32}H_{20}O_3$: C, 84.94; H, 4.45. Found: C, 84.94; H, 4.30.

The acetylated product **15** was also obtained analogously from **14** in a 69% yield.

Alkylation of 12 with Alkyl Iodide and Sodium Methoxide in Methanol. The procedure employed for alkylation was similar to that of **10a.** 7-Ethoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**17a**) was obtained as yellow microcrystals in a 35% yield: mp 300–301 °C; IR (KBr) 1672 cm^{-1} (ArCOAr C=O); NMR ($CDCl_3$) δ 1.65 (t, 3, J = 7.5 Hz, CH_3), 4.30 (q, 2, J = 7.5 Hz, CH_2), 6.08 (d, 1, J = 10 Hz, CH=CHAr), 7.80 (d, 1, J = 10 Hz, CHAr), and 6.7–8.2 (m, 15, aromatic **H**); mass spectrum (76 eV) *m/e* 438 (M^+), 410, 409, 350, 276, and 274. Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.65; H, 5.06. Found: C, 87.44; H, 5.00.

Methylation of **12** gave 7-methoxy-3*H*-benz[*de*]anthracene-3-spiro-10′-anthrone (**17b,** 30%) as yellow microcrystals: mp 305 °C; IR (KBr) 1670 cm^{-1} (ArCOAr C=O); NMR ($CDCl_3$) δ 4.18 (s, 3, CH_3), 6.10 (d, 1, J = 10 Hz, CH=CHAr), 7.82 (d, 1, J = 10 Hz, CHAr), and 6.7–8.2 (m, 15, aromatic **H**); mass spectrum (75 eV) *m/e* 424 (M^+) and 409. Anal. Calcd for $C_{31}H_{20}O_2$: C, 87.71; H, 4.75. Found: C, 87.54; H, 4.87.

Oxidation of 2 with Chromium Trioxide. A solution of chromium trioxide (10.0 g, 0.100 mol) in water (30 mL) was added to 4.12 g (10.0 mmol) of **2** suspended in 160 mL of acetic acid, and the resulting dark red-brown mixture was stirred and heated under reflux for 2 h. The hot mixture was filtered, the filtrate was diluted with water (1.5 L), and the solid that separated was recovered by filtration. The solid then weighed 2.51 g and melted at 290–294 °C. Two recrystallizations of the product from acetic acid gave 2.14 g (46.7%) of 10-(1-anthraquinonyl)-10-carboxymethylanthrone (**18**) as yellow microcrystals: mp 295–296 °C; IR (KBr) 1760 (acid C=O), 1668, 1640 cm^{-1} (ArCOAr and quinone C=O, respectively); NMR (DMSO-d_6) δ 3.50 (s, 2, CH_2), and 6.8–8.8 (m, 16, aromatic **H,** COOH); mass spectrum (75 eV) *m/e* 458 (M^+), 399, 313, and 206. Anal. Calcd for $C_{30}H_{18}O_5$: C, 78.59; H, 3.96. Found: C, 78.38 H, 3.99.

The oxidation product **18** was obtained in ca. 45–50% yields on similar oxidations of **8, 10, 11,** and **12,** respectively.

Esterification of 18. Methyl Ester (19a). A solution of 1.00 g (2.18 mmol) of **18** in methanol (60 mL) containing 5 g of hydrogen chloride was refluxed for 2 h; removal of excess reagents in vacuo and a recrystallization of the product from methanol gave 0.78 g (76%) of the methyl ester of **18** as yellow microcrystals: mp 251 °C; IR (KBr) 1745 (ester C=O), 1680, 1675, 1660 cm^{-1} (ArCOAr and quinone C=O); NMR ($CDCl_3$) δ 3.17 (s, 3, CH_3), 3.35 (s, 2, CH_2), and 6.6–8.7 (m, 15, aromatic **H**); mass spectrum (75 eV) *m/e* 472 (M^+), 399, 313, and 256. Anal. Calcd for $C_{31}H_{20}O_5$: C, 78.80; H, 4.27. Found: C, 78.87; H, 4.47.

Ethyl Ester (19b). The oxidation product **18** was esterified with ethanol in the manner described above for methyl ester. A recrystallization of the product from ethanol gave the ethyl ester of **18** as yellow microcrystals in a 80% yield: mp 253 °C; IR (KBr) 1740 (ester C=O), 1674, 1658 cm^{-1} (ArCOAr and quinone C=O, respectively); NMR ($CDCl_3$) δ 0.81 (t, 3, J = 7.5 Hz, CH_3), 3.36 (s, 2, CH_2), 3.63 (q, 2, J = 7.5 Hz, CH_2CH_3), and 6.7–8.8 (m, 15, aromatic **H**); mass spectrum (75 eV) *m/e* 486 (M^+), 399, 312, and 279. Anal. Calcd for $C_{32}H_{22}O_5$: C, 79.00; H, 4.56. Found: C. 78.90; H, 4.6.

Registry No.—**1,** 4159-04-0; **2,** 65252-91-7; **8,** 65252-92-8; **9,** 65252-93-9; **10a,** 24165-82-0; **10b,** 24215-76-7; **11,** 65252-94-0; **12,** 65252-95-1; **13,** 65252-96-2; **14,** 65252-97-3; **15,** 65252-98-4; **16,** 58382-11-9; **17a,** 65252-99-5; **17b,** 65253-00-1; **18,** 65253-01-2; **19a,** 65253-02-3; **19b,** 65253-03-4; ethyl iodide, 75-03-6; methyl iodide, 74-88-4; diethyl sulfate, 64-67-5; dimethyl sulfate, 77-78-1; 1,2-bis(9-acetoxy-10-anthryl)ethane, 58382-04-0.

References and Notes

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(5) (a) In ref 3d, it was reported that reductive dimerization of **1** by ketyl radicals gave **16.** (b) The compound **16** was prepared independently in a 96% yield by the hydrolysis of 1,2-bis(9-acetoxy-10-anthryl)ethane formed on reductive acetylation of **1** with zinc and acetic anhydride: mp 232 °C (lit.[3d] 245 °C); IR (KBr) 1665 cm^{-1} (ArCOAr C=O); NMR ($CDCl_3$) δ 1.48 (t, 4, CH_2), 4.10 (m, 2, 10-, and 10-**H**), and 7.0–8.3 ppm (m, 16, aromatic **H**); mass spectrum 414 (M^+).

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Octopus Molecules in the Cyclotriveratrylene Series

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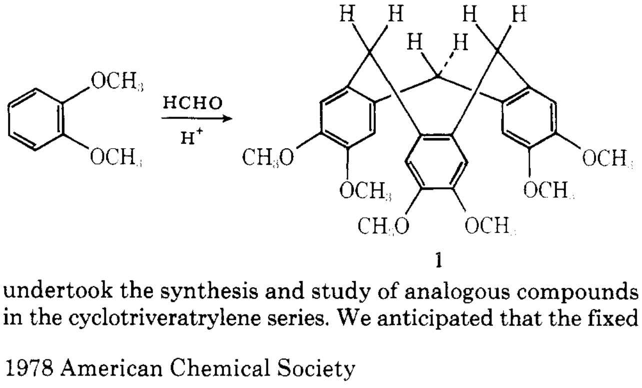
Received October 3, 1977

Cyclotriveratrylene (**1**) was converted into a series of oligo(ethylene glycol) ether derivatives (**3a–f**). These many-armed polyethers (octopus molecules) are capable of adopting cavity-containing conformations and possess complexing properties typical of crown ethers. Analogous derivatives of macrocycle **9** do not show crown ether behavior; this is attributed to their lack of conformational rigidity. The length of polyether arms is of less importance than the stereochemistry and conformational rigidity of the framework to which they are attached.

The condensation product of veratrole and formaldehyde, originally described by Robinson[1] and formulated as a dimer, has been shown by Lindsey[2] and by Erdtman and co-workers[3] to possess the conformationally stable[4,5] cyclotriveratrylene structure **1**. Despite the novel crown structure and known clathrate-forming ability of **1**,[6] relatively little chemistry in the series has been reported.[7-9]



1

Recently, Vögtle and Weber[10] demonstrated that acyclic, many-armed polyether benzene derivatives of the structural type **2** (octopus molecules) act as complex-forming ligands capable of solubilizing alkali-earth salts in aprotic organic solvents. Since such behavior is of considerable utility,[11] we undertook the synthesis and study of analogous compounds in the cyclotriveratrylene series. We anticipated that the fixed