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(22) Samples of 2,4-dichloro-1-nitrobenzene and 1,4-dichloro-2-nitrobenzene were not resolved on several gas chromatographic (GC) columns, and they had a GC retention time identical with that of the unidentified component in the chlorination product mixture.
(23) The reactions are photoinitiated; GC analysis of solutions of chlorine and **1** or **7** in CCl_4 kept in the dark at room temperature for 121 h showed no evidence of reaction products.
(24) *p*-Bromochlorobenzene was reported to undergo free-radical chlorodebromination 91% as rapidly as did bromobenzene, and *p*-bromonitrobenzene was reported not to react under the same conditions.[7c]
(25) GC analyses of product mixtures from **7** excluded the presence of 1,2-dichloro-4-nitrobenzene, 2,4-dichloro-1-nitrobenzene, and 1,4-dichloro-2-nitrobenzene, compounds which would have indicated chloro or nitro migration in ipso intermediates.
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Acid-Catalyzed Dimerization of 10-Methyleneanthrone. Synthesis of Spiro-Substituted Benz[*de*]anthracenes

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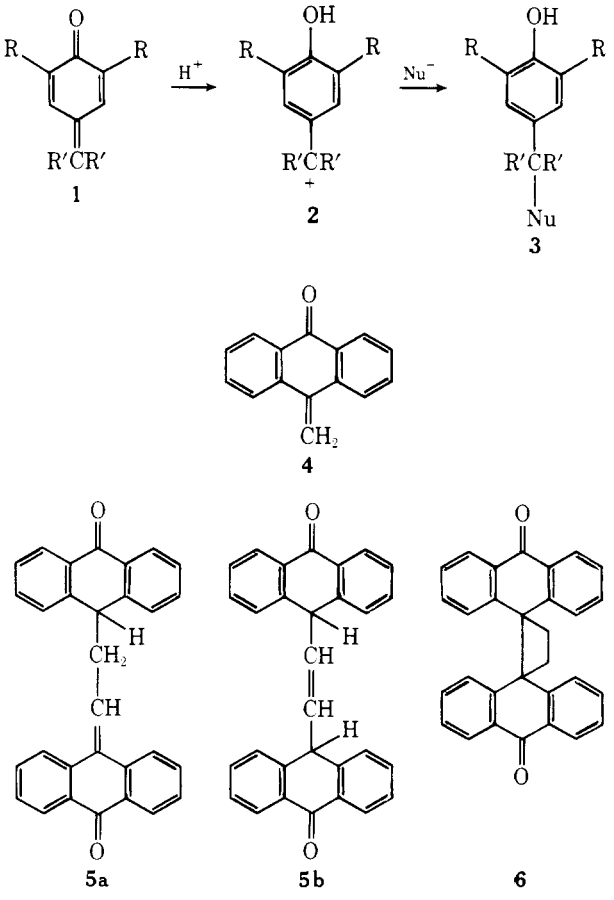
The acid-catalyzed dimerization of 10-methyleneanthrone is found to give 7′-hydroxy-1′,2′-dihydrospiro[anthracene-9(10H),3′-[3*H*]benz[de]anthracen]-10-one (**9a**), which in solution is in equilibrium with its keto tautomer **9b.** Previously proposed structures of the methyleneanthrone dimer are thus being corrected.

p-Quinone methides **1,** in general, are prone to undergo acid-catalyzed reactions with nucleophiles (Nu) to give 1,6-addition products **3** via intermediate hydroxybenzyl cations **2.**[1–3] By contrast, treatment of 10-methyleneanthrone (**4**) with acids at elevated temperature was reported to give a dimer believed to have structure **5a** or **5b.**[4] According to a very recent reinvestigation, this dimer is suggested to have the spiro-substituted cyclobutane structure **6.**[5] However, no evidence whatsoever in support of this structure has been presented.

We had reasons to doubt the correctness of the dianthronylethylene structure **5b** when we recently succeeded in synthesizing the tautomer **7** and found it to be easily dehydrogenated by molecular oxygen to give dianthronylideneethane (**8**) rather than tautomerizing to **5b.**[6]

Repeating the acid-catalyzed reaction of 10-methyleneanthrone according to the literature[4] did afford, though rather sluggishly, the reported dimeric product; however, its 270-MHz NMR spectrum turned out to be incompatible with any of the previously proposed three structures. Therefore, we have reinvestigated the acid-catalyzed reaction of 10-methyleneanthrone and found that the dimerization proceeds smoothly at room temperature in chloroform in the presence of trifluoroacetic acid or boron trifluoride etherate. In the present paper we describe the structure of the 10-methyleneanthrone dimer prepared by this method and its utilization in the preparation of spiro-substituted benz[*de*]anthracenes.



Results and Discussion

10-Methyleneanthrone dimerizes upon treatment with trifluoroacetic acid or boron trifluoride etherate in chloroform solution under nitrogen to give, in about 80% yield, the spiroanthronyl-substituted dihydrobenzanthracene **9a,** which, in solution, is in equilibrium with its keto tautomer **9b.** In the crystalline state, the 10-methyleneanthrone dimer predominantly exists in the keto form, as we conclude from the absence of a hydroxyl absorption in its IR spectrum.

It is essential to carry out the dimerization of 10-methyleneanthrone in an inert atmosphere. In the presence of oxy-

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Table I. Absorption Maxima (nm) of R-Substituted Spiro[Anthronylbenzanthracenes] 13 (X = C=O) in Cyclohexane Solution[a]

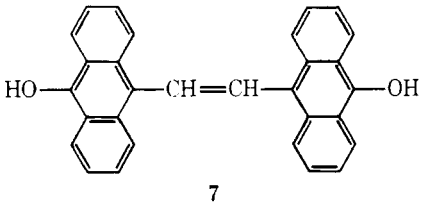
R = H	R = $OCOCF_3$	R = $OCOCH_3$	R = CH_3	R = OCH_3	R = $OSiMe_3$
396 (11.5)	402 (10.9)	404 (11.4)	407 (12.7)	410 (11.1)	422 (8.1)
375 (12.0)	381 (11.7)	382 (11.9)	385 (12.7)	388 (11.8)	398 (9.2)
356 (7.2)	361 (7.1)	362 (6.9)	365 (7.2)	368 (7.1)	376 (7.1)
339 (3.4)	343 (3.3)	345 (3.1)	347 (3.2)	350 (3.4)	359 (3.8)
324 (1.5)	328 (1.6)	329 (1.3)	332 (1.4)	334 (1.5)	340 (1.6)
303 (6.2)	301 (4.3)	303 (5.4)	304 (6.2)	304 (6.0)	305 (5.9)
290 (7.0)	289 (7.3)	290 (6.5)	291 (7.5)	291 (7.3)	292 (7.4)
262 (154)	263 (154)	264 (143)	266 (145)	266 (143)	268 (123)

[a] Molar extinction coefficients ($\epsilon \times 10^{-3}$) are given in parentheses. The two maxima around 300 nm are due to the π–π^* transition of the anthrone chromophore.

Table II. 270-MHz ^{1}H NMR Data (ppm) of Dihydrobenz[*de*]anthracenes 9a [a] and 13a–h [b]

	9a	13a	13b	13c	13d	13e	13f	13g	13h
R	OH	$OCOCH_3$	OCH_3	$OCOCF_3$	$OSiMe_3$	CH_3	CH_3	H	H
X	C=O	C=O	C=O	C=O	C=O	C=O	$C=CH_2$	C=O	CH_2
R[d]		2.67	4.24		0.42	3.23	3.21		
X							5.93		4.38, 4.22[e]
$H_{AA'}$	3.43	3.47	3.50	3.57	3.47	3.59	3.56	3.55	3.39[f]
$H_{BB'}$	2.28	2.34	2.38	2.41	2.37	2.40	2.39	2.40	2.31[f]

[a] In pyridine-d_5. [b] In deuteriochloroform. [c] The chemical shift of the aromatic protons is between 6.70 and 8.50 ppm. [d] Position of hydroxyl proton is not discernible because of peak broadness. [e] Pair of doublets, J_{AB} = 20 Hz. [f] In all cases, the $H_AH_{A'}$–$H_BH_{B'}$ system of the flexible ethano bridge gives rise to two triplets, J_{AB} = 6 Hz.



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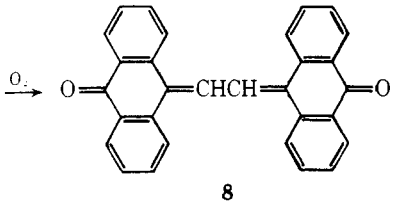
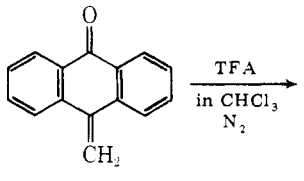
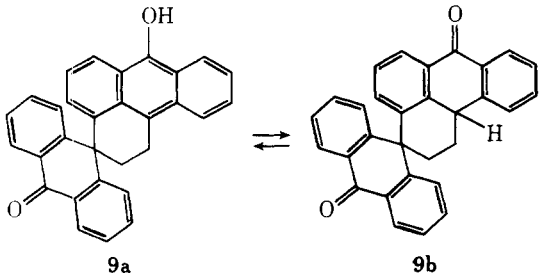


8

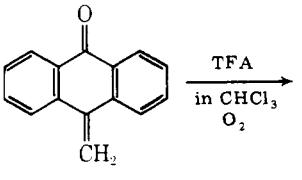
gen, the reaction smoothly leads to the dehydrogenated prodcut **10a**, which, in pyridine solution, tautomerizes to the hydroxy-substituted benzanthracene **10b** (vide infra).

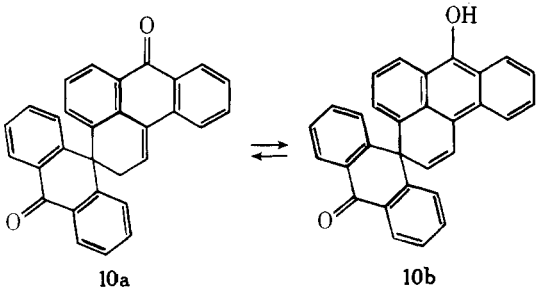
The structural assignment of **9** rests on the following NMR spectroscopic evidence and chemical reactions. The 270-MHz ^{1}H NMR spectrum of **9** in deuterated pyridine shows for the





9a **9b**





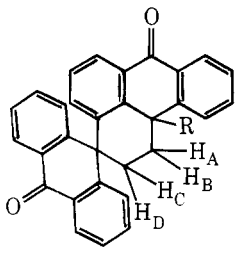
10a **10b**

four nonaromatic hydrogens two triplets (cf. Table II), which we assign to the flexible ethano bridge in the enol structure **9a**. By contrast, the 270-MHz ^{1}H NMR spectrum of **9** in deuteriochloroform is that of the keto tautomer **9b** as we conclude from the appearance of a doublet of doublets (J_{HH_A} = 13 Hz, J_{HH_B} = 4 Hz) centered at 4.30 ppm and attributable to the tertiary hydrogen in **9b**, while the four nonequivalent protons of the now rigid ethano bridge give rise to two sets of multiplets at around 2.30 and 2.75 ppm, respectively (cf. Table III).

As is typical[6,7] of 9-hydroxy-10-alkylanthracenes, **9** in solution is readily autoxidized to give the hydroperoxy compound **11**, which upon treatment with trifluoroacetic acid gives the dehydro compound **10**. We presume, therefore, that the hydroperoxide **11** is an intermediate in the formation of **10** by acid-catalyzed dimerization of 10-methyleneanthrone in the presence of oxygen. Sodium iodide reduces the hydroperoxide **11** to the hydroxy compound **12**. The 270-MHz ^{1}H NMR spectra of **11** and **12**, summarized in Table III, are in support of the assigned structures.

In accordance with the keto–enol equilibrium of the 10-

Table III. 270-MHz ^{1}H NMR Data [ppm, J (Hz)] of 9b,[a] 11,[b] and 12[c]



9b, R = H
11, R = OOH
12, R = OH

	9b	11	12
R	4.30 (dd)	*c*	*c*
H_A		3.25 (dt)	3.50 (td)
H_B		1.97 (dt)	2.04 (dt)
H_C	m at 2.64 and 2.18, resp.	3.17 (td)	2.97 (dt)
H_D		2.60 (td)	2.55 (td)
J_{RA}	13		
J_{RB}	4		
J_{AB}		14	14
J_{AC}		3	3
J_{AD}		14	14
J_{BC}		3	3
J_{BD}		3	2
J_{CD}		14	14

[a] In deuteriochloroform. [b] In pyridine-d_5. [c] Position of hydroxyl proton is not descernible because of peak broadness. The chemical shift of the aromatic protons is between 6.70 and 8.50 ppm.

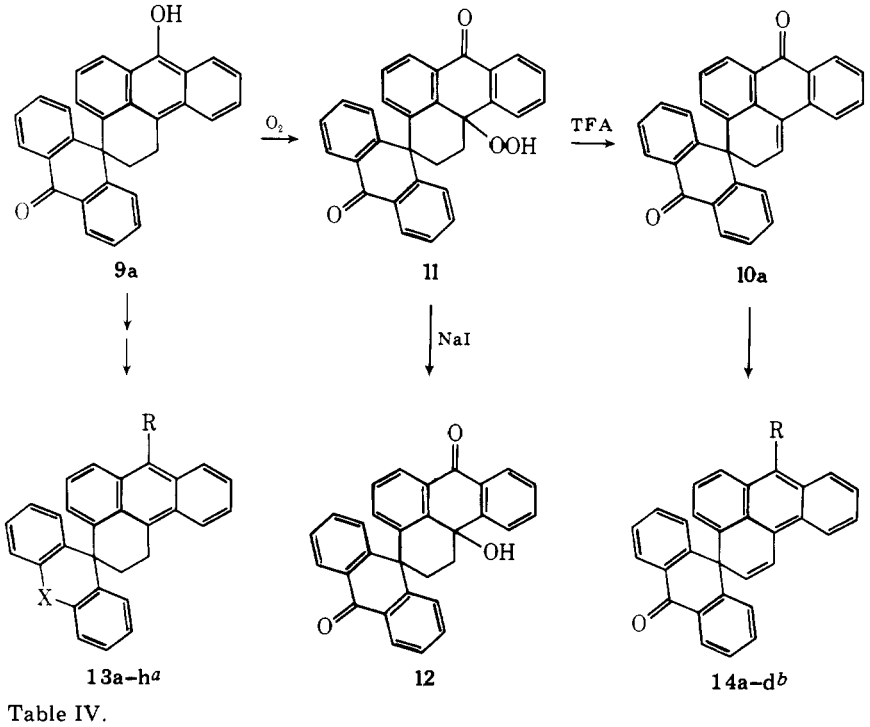
methyleneanthrone dimer **9**, dihydrobenzanthracene derivatives **13a–h** (see Table II) are easily obtained in high yields by more or less conventional procedures. Substitution of the hydroxy group in **9a** by hydrogen to **13g** was accomplished by a sequence of reactions involving reduction of **9** with sodium borohydride, acid-catalyzed elimination of water, and oxidation with potassium permanganate. Reduction of **9** with a large excess of sodium borohydride afforded the parent hydrocarbon **13h** (R = H, X = CH_2). Replacement of the hydroxy group in **9a** by methyl to give **13e** was achieved by reaction of **9** with methyllithium, followed by elimination of water to give **13f** (R = CH_3, X = C=CH_2) and oxidative cleavage of the exocyclic double bond with potassium permanganate.

In the UV spectra of spiro[anthronylbenzanthracenes] **13** (X = C=O), the bathochromic shift of the characteristic anthracene absorption induced by the substituents R was found in the order $OSiMe_3 > OCH_3 > CH_3 > OCOCH_3 > OCOCF_3 > H$ (see Table I). We conclude from these data that the resonance effect of the trimethylsiloxy group exceeds that of the methoxy group.

The NMR spectra of dihydrobenzanthracenes **13a–h** are summarized in Table II. Because of the conformational flexibility of the hydroaromatic ring in compounds **13**, the anthracene moiety represents a plane of symmetry for the spiro substituent whose two aromatic rings, consequently, are geometrically equivalent. Thus, the two protons of the methylidine group in **13f** give rise to a singlet. By contrast, the protons of the diaryl-substituted methylene group in **13h** are geometrically nonequivalent and appear as a pair of doublets.

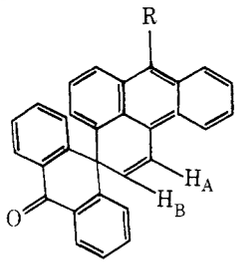
The 270-MHz ^{1}H NMR spectrum in deuteriochloroform of the dehydro compound **10a** obtained by acid-catalyzed dimerization of 10-methyleneanthrone in the presence of oxygen exhibits a doublet (J = 5 Hz) at 3.35 ppm and a triplet (J = 5 Hz) at 7.14 ppm which we attribute to the methylene group and the olefinic hydrogen, respectively. As mentioned above, **10a** tautomerizes in pyridine to give the new hydroxy-substituted benzanthracene **10b**, as we deduce from its NMR spectrum and those of its stable derivatives **14a–c** and that of **14d** (see Table IV), which we prepared from **10** or **13** by conventional methods (see Experimental Section).

The generic relationship between dihydrobenzanthracenes **13** and benzanthracenes **14** was furthermore proven by dehydrogenating **13b** and **13g** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to give benzanthracenes **14b** and **14d**, respectively. Attempts to dehydrogenate 10-methyleneanthrone dimer **9** with DDQ resulted, unexpectedly, in the smooth oxidative dimerization of the primary dehydro-



[a] See Table II. [b] See Table IV.

Table IV. 270-MHz ^{1}H NMR Data [ppm, J (Hz)] of Benz[*de*]anthracenes 10b [a] and 14a-d [b]

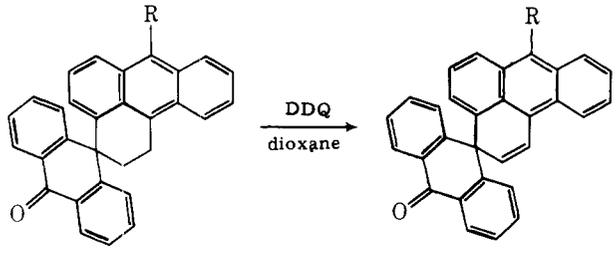


10b, R = OH
14a, R = OAc
14b, R = OCH_3
14c, R = $OSi(CH_3)_3$
14d, R = H

	10b	14a	14b	14c	14d
R	c	4.17	2.65	0.35	
H_A	7.80	7.78	7.81	7.70	7.79
H_B	6.05	6.08	6.12	6.00	6.12
J_{AB}	10	10	10	10	10

[a] In pyridine-d_5. [b] In deuteriochloroform. [c] Position of hydroxyl proton is not discernible because of peak broadness. The chemical shift of the aromatic protons is between 6.40 and 8.60 ppm.

genation product **10** to give a heretofore unknown 10-methyleneanthrone tetramer **15.**



13b, R = OCH_3
g, R = H

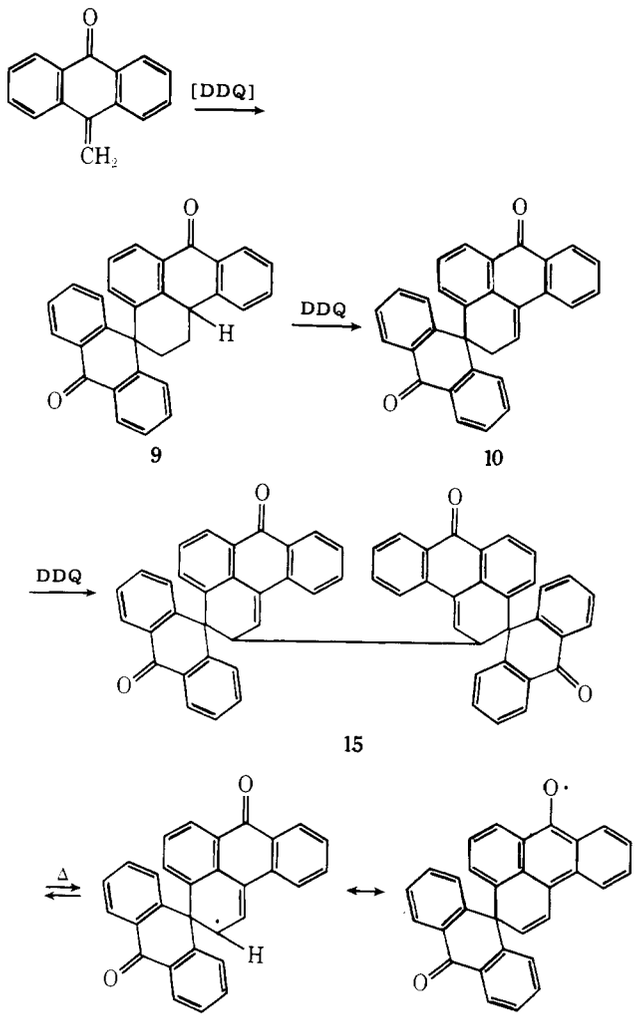
14b, R = OCH_3
d, R = H

Since DDQ not only is an electron acceptor[8] but may act as a Lewis acid as well,[9] tetramer **15** is most conveniently prepared in 80% yield by reaction of 10-methyleneanthrone with 0.75 molar equiv of DDQ.

The structure of **15** is supported by analytical and spectroscopic data. In its 270-MHz ^{1}H NMR spectrum in deuteriochloroform, the four nonaromatic protons are pairwise equivalent, thus giving rise to a pair of doublets (J = 2.7 Hz) at 3.67 and 5.72 ppm, respectively. By off-resonance technique, the corresponding carbon atoms in the ^{13}C NMR spectrum were found at 48.6 and 122.7 ppm, respectively.

Upon warming, solutions of **15** in xylene turn yellow, and the color is discharged upon cooling. Most likely, the coloration is due to reversible homolytic cleavage of the central single bond in **15,** as is supported by the concomitant appearance of an ESR signal. In agreement with this interpretation, treatment of **15** with sodium iodide in warm acetic acid results in the liberation of 1 molar equiv of iodine and smoothly regenerates dimer **10.**

As for the acid-catalyzed formation of the 10-methyleneanthrone dimer **9,** we presume that a mechanism is operative in which the catalyst reacts with 10-methyleneanthrone to form a cationic intermediate **16,** which in turn attacks 10-methyleneanthrone electrophilically as outlined in Scheme I. The reported formation of **13b** by reaction of 10-methyleneanthrone with methyl iodide[10] conceivably can be rationalized by this mechanism as well. Thus, at least in principle, the dimerization of 10-methyleneanthrone resembles that of the acid-catalyzed dimerization of 1,1-diphenylethylene[11] or isopropylidenecyclohexadienones.[12]



The luminescence properties of the benzanthracenes described in this paper are being discussed elsewhere in an appropriate photophysical context.[13]

Experimental Section

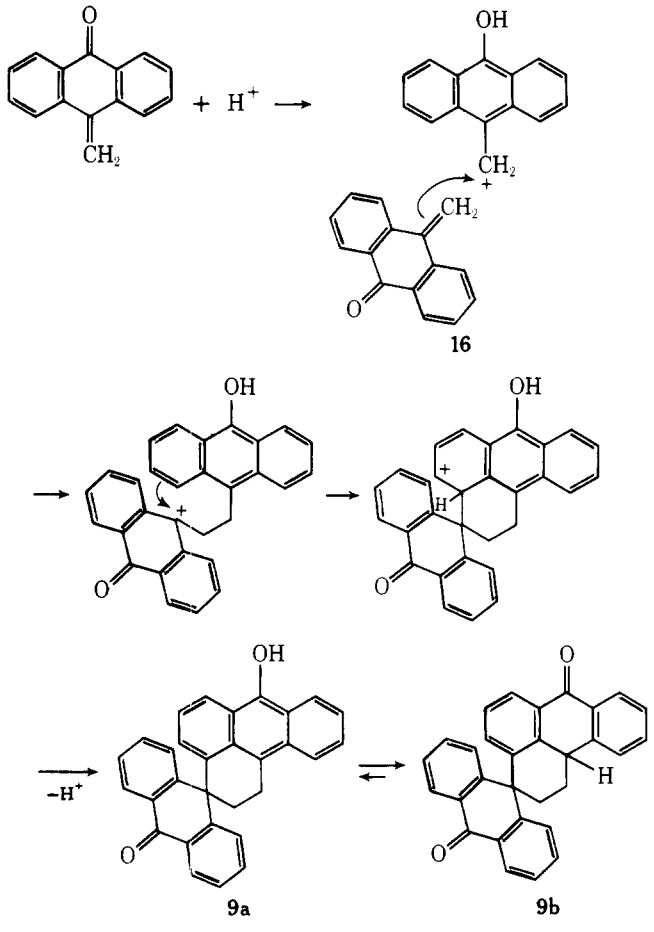
Melting points are determined on a hot-stage microscope and are uncorrected. Analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark. Infrared spectra, in KBr pellets, were recorded on a Beckman IR 9 instrument. NMR spectra were recorded on a Bruker 270 spectrometer. The solvent is indicated for each case. Chemical shifts are given in parts per million downfield from Me_4Si. Mass spectra were obtained on an AEI MS 902 spectrometer.

10-Methyleneanthrone was prepared according to the literature[10] and recrystallized from methylene chloride by precipitation with ethanol.

Acid-Catalyzed Dimerization of 10-Methyleneanthrone under Nitrogen (9). Trifluoroacetic acid or boron trifluoride etherate (5 mL) was added to a solution of 10-methyleneanthrone (4.12 g, 20 mmol) in chloroform (35 mL) under nitrogen blanketing. After 1 h, ethanol (120 mL) was added while nitrogen was passed into the reaction mixture to give a pale yellow crystalline precipitate. Recrystallization under nitrogen from chloroform by precipitating with ethanol gave 3.2 g (77%) of pale yellow crystals: mp 235 °C; IR 1660 cm^{-1} (CO); MS m/e 410 ($M^+ - 2$). Anal. Calcd for $C_{30}H_{20}O_2$ (412.49): C, 87.35; H, 4.89. Found: C, 86.87; H, 4.94.

(a) Acid-Catalyzed Dimerization of 10-Methyleneanthrone in the Presence of Oxygen (10). Oxygen was introduced for 1.5 h into a solution of 10-methyleneanthrone (6.18 g, 30 mmol) in chloroform (50 mL) and trifluoroacetic acid or boron trifluoride etherate

Scheme I



(5 mL). Addition of methanol afforded a yellow crystalline precipitate which was recrystallized from chloroform by addition of methanol: yield 5.1 g (83%); mp 275–278 °C; IR 1660 cm^{-1} (CO); MS *m/e* 410 (M^+). Anal. Calcd for $C_{30}H_{18}O_2$ (410.47): C, 87.78; H, 4.42. Found: C, 87.51; H, 4.35.

(b) From Hydroperoxide 11. Trifluoroacetic acid (10 drops) was added to a suspension of **11** (100 mg, 0.225 mmol) in chloroform (5 mL). As the acid was added, **11** dissolved and the solution became red colored. The solvent was partially evaporated under vacuum, and a yellow crystalline precipitate was obtained upon addition of ethanol: yield 70 mg (76%); mp 274–277 °C.

Synthesis of Hydroperoxide 11 from Dimer 9. A stream of oxygen was introduced for 12 h into a solution of **9** (1.65 g, 4 mmol) in methylene chloride (100 mL) and pyridine (5 mL). Vacuum evaporation of solvents gave a solid residue which was triturated with boiling methylene chloride containing a few drops of acetic acid: yield 1.4 g (79%) of colorless crystals; mp 217–218 °C; IR 3290 (OH), 1665 (CO) cm^{-1}; MS *m/e* 444 (M^+). Anal. Calcd for $C_{30}H_{20}O_4$ (444.49): C, 81.06; H, 4.53. Found: C, 81.01; H, 4.65.

Reduction of Hydroperoxide 11 with Sodium Iodide to Give 12. A stirred suspension of **11** (444 mg, 1 mmol) and sodium iodide (5 g) in acetic acid (50 mL) was refluxed under nitrogen for 1 h, and the liberated iodine (1 mmol) was reduced with 0.1 M aqueous sodium thiosulfate. Recrystallization of the pale yellow crystalline precipitate from boiling nitromethane gave 350 mg (82%) of colorless crystals: mp 260–262 °C; IR 3420 (OH), 1660 (CO) cm^{-1}; MS *m/e* 428 (M^+). Anal. Calcd for $C_{30}H_{20}O_3$ (428.49): C, 84.09; H, 4.70. Found: C, 83.87; H, 4.71.

7′-Acetoxy-1′,2′-dihydrospiro[anthracene-9(10*H*),3′-[3*H*]-benz[*de*]anthracen]-10-one (13a). A suspension of **9** (1.03 g, 2.5 mmol) in acetic anhydride (15 mL) and pyridine (10 drops) under nitrogen was kept at reflux temperature for 2 h to give a yellow solution from which a yellow crystalline product precipitated upon cooling to room temperature. Excess acetic anhydride was decomposed with ethanol (40 mL), and the crystalline product was recrystallized from a chloroform–ethanol mixture: yield 965 mg (85%) of greenish-yellow crystals; mp 272–273 °C; IR 1760 (OAc), 1660 (CO) cm^{-1}; MS *m/e* 454 (M^+). Anal. Calcd for $C_{32}H_{22}O_3$ (454.53): C, 84.56; H, 4.88. Found: C, 84.28; H, 4.87.

7′-Methoxy-1′,2′-dihydrospiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracen]-10-one (13b). Methyl iodide (12 g) was added dropwise under nitrogen to a suspension of **9** (412 mg, 1 mmol) in refluxing methanol (25 mL) containing sodium methoxide (250 mg). After 1 h at reflux temperature, the solvent was partially evaporated from the yellow solution to give a yellow crystalline precipitate which was recrystallized from a methylene chloride–methanol mixture: yield 395 mg (93%) of green-yellow fluorescent plates; mp 226 °C, undepressed upon admixture of an authentic[10] sample prepared from 10-methyleneanthrone and methyl iodide.

7′-(Trifluoroacetoxy)-1′,2′-dihydrospiro[anthracene-9(10-*H*),3′-[3*H*]benz[*de*]anthracen]-10-one (13c). Trifluoroacetic anhydride (5 mL) was added to a warm solution of **9** (1.5 g, 3.65 mmol) in pyridine (10 mL), and the reaction mixture was refluxed under nitrogen for 1 h. Addition of ethanol (50 mL) to the solution after cooling to room temperature gave a crystalline precipitate which was dried for 1 h at 80 °C (10^{-2} torr): yield 1 g (54%) of pale green crystals; mp 238–41 °C; IR 1800 ($COCF_3$), 1660 (CO) cm^{-1}. Anal. Calcd for $C_{32}H_{19}O_3F_3$ (508.50): C, 75.59; H, 3.77. Found: C, 75.79; H, 3.86.

7′-(Trimethylsiloxy)-1′,2′-dihydrospiro[anthracene-9(10-*H*),3′-[3*H*]benz[*de*]anthracen]-10-one (13d). Bis(trimethylsilyl)acetamide (BSA) (1 mL) was added to a suspension of **9** (412 mg, 1 mmol) in dioxane (4 mL) and pyridine (2 mL) under nitrogen. The reaction mixture was refluxed for 1 h to give a yellow solution from which solvents and excess BSA and (trimethylsilyl)acetamide were removed by vacuum distillation and sublimation, respectively. The residue was recrystallized from methylene chloride by addition of ethanol: yield 400 mg (83%) of yellow crystals; mp 179–181 °C; IR 1660 cm^{-1} (CO); MS *m/e* 484 (M^+). Anal. Calcd for $C_{33}H_{28}O_2Si$ (484.67): C, 81.78; H, 5.82. Found: C, 81.72; H, 5.54.

7′-Methyl-1′,2′-dihydrospiro[anthracene-9(10*H*),3′-[3*H*]-benz[*de*]anthracen]-10-one (13e). The oxidation of crude **13f** (1.95 g) in methylene chloride (100 mL) was carried out by adding the solution to potassium permanganate (6 g) in boiling acetone (600 mL) and refluxing the reaction mixture for 2 h. Workup as described for **13g**, followed by column chromatography on silica gel using methylene chloride as eluent gave 1.6 g (82%) of bright green-yellow crystals (after recrystallization from boiling ethyl acetate): mp 290–292 °C; IR 1660 cm^{-1} (CO). Anal. Calcd for $C_{31}H_{22}O$ (410.52): C, 90.70; H, 5.40. Found: C, 90.88; H, 5.53.

7′-Methyl-1′,2′-dihydrospiro[10-methyleneanthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracene] (13f). A methyllithium solution (12 mL, 2 M in ether) was added under nitrogen to a solution of **9** (2.06 g, 5 mmol) in benzene (175 mL). The reaction mixture was refluxed for 1 h and then cooled to room temperature and acidified with trifluoroacetic acid (10 mL). The solid residue obtained after vacuum evaporation of solvents was treated with a water (50 mL) and methylene chloride (50 mL) mixture, and the organic layer was washed with sodium bicarbonate and dried. Partial evaporation of solvents followed by addition of ethanol gave 1.9 g of yellow crystals which were purified by column chromatography on silica gel using methylene chloride as eluent. Recrystallization from boiling ethyl acetate gave bright greenish-yellow crystals, mp 255–258 °C. Anal. Calcd for $C_{32}H_{24}$ (408.54): C, 94.08; H, 5.92. Found: C, 93.35; H, 6.01.

1′,2′-Dihydrospiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracen]-10-one (13g). Sodium borohydride (2 g) was added to a solution of **9** (2.06 g, 5 mmol) in dioxane (100 mL) and methanol (25 mL) under nitrogen. The reaction mixture was refluxed for 15 min, and the residue obtained on vacuum evaporation of solvents was then treated for 15 min with a refluxing mixture of water (25 mL), dioxane (25 mL), and concentrated hydrochloric acid (10 mL). Vacuum evaporation solvents gave a solid residue which was treated with a water (50 mL) and methylene chloride (50 mL) mixture. The organic layer was washed with aqueous sodium bicarbonate and dried over magnesium sulfate. The dried solution was then added to a boiling solution of potassium permanganate (3 g) in acetone (500 mL). The reaction mixture was refluxed for 20 min and then filtered through Celite. The residue obtained after evaporation of solvents from the filtrate was purified by column chromatography on silica gel using methylene chloride as eluent. In order to obtain emission spectroscopically pure material, it is essential to keep the crude product adsorbed on the head of the column for about 16 h before elution: yield 950 mg (48%) of bright light green crystals (from methylene chloride by addition of methanol); mp 213–214 °C; IR 1660 cm^{-1} (CO). Anal. Calcd for $C_{30}H_{20}O$ (396.49): C, 90.88; H, 5.08. Found: C, 90.84; H, 5.12.

1′,2′-Dihydrospiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracene] (13h). Sodium borohydride (20 g) was added to a solution of **9** (2.06 g, 5 mmol) in dioxane (100 mL) and methanol (50 mL) under nitrogen. After the reaction mixture was refluxed for 4 h, vacuum

evaporation of solvents gave a solid residue which was treated with dioxane (25 mL) and concentrated hydrochloric acid (75 mL). The suspension was briefly refluxed (10 min) and then triturated with benzene (500 mL). The organic layer was decanted, washed with sodium bicarbonate, and dried over magnesium sulfate. Vacuum evaporation of the dark colored solution gave a residue which was purified by column chromatography on silica gel, using methylene chloride as eluent. Subsequent recrystallization from boiling ethyl acetate gave pale green needle-shaped crystals: yield 1.0 g (52%); mp 254–256 °C. Anal. Calcd for $C_{30}H_{22}$ (382.51): C, 94.20; H, 5.80. Found: C, 93.84; H, 5.68.

7′-Acetoxyspiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracen]-10-one (14a). The acetylation of **10** (410 mg, 1 mmol) with acetic anhydride in the presence of pyridine was carried out in the same fashion as described for **13a:** yield 400 mg (88%) of yellow crystals; mp 333–336 °C; IR 1765 (OAc), 1660 (CO) cm^{-1}; UV (in cyclohexane) λ ($\epsilon \times 10^{-3}$) 267 (106.2), 370 (3.5), 392 (8.0), 416 (15.5), 442 (17.0) nm; MS *m/e* 452 (M^+). Anal. Calcd for $C_{32}H_{20}O_3$ (452.51): C, 84.94; H, 4.45. Found: C, 84.75; H, 4.56.

7′-Methoxyspiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracen]-10-one (14b). (a) By Methylation of 10. The reaction of **10** (410 mg, 1 mmol) with methyl iodide (20 g) in boiling methanol (25 mL) in the presence of sodium methoxide (250 mg) was performed in the same fashion as described for **13b:** yield 380 mg (90%) of yellow crystals; mp 322 °C; IR 1660 cm^{-1} (CO); UV (in cyclohexane) λ ($\epsilon \times 10^{-3}$) 268 (110), 375 (3.8), 397 (7.8), 420 (13.7), 448 (14.2) nm; MS *m/e* 424 (M^+). Anal. Calcd for $C_{31}H_{20}O_2$ (424.50): C, 87.71; H, 4.75. Found: C, 87.35; H, 4.87.

(b) By Dehydrogenation of 13b with DDQ. A solution of **13b** (426 mg, 1 mmol) and DDQ (227 mg, 1 mmol) in dioxane (30 mL) was refluxed for 2.5 h. Precipitated $DDQH_2$ was removed by filtration of the reaction mixture at room temperature. The solid residue obtained after vacuum evaporation of solvent from the filtrate was recrystallized from methylene chloride by addition of methanol: yield 385 mg (91%); mp 322 °C.

7′-(Trimethylsiloxy)spiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracen]-10-one (14c). The reaction of **10** (300 mg, 0.73 mmol) with BSA (1 mL) in dioxane (10 mL) was performed in the same fashion as described for the preparation of **13c** to give 320 mg (91%) of yellow crystals: mp 242–245 °C; IR 1660 cm^{-1} (CO); UV (in cyclohexane) λ ($\epsilon \times 10^{-3}$) 271 (108), 370 (3.0), 388 (5.3), 410 (7.6), 432 (11.9), 458 (10.5) nm; MS *m/e* 482 (M^+). Anal. Calcd for $C_{33}H_{26}O_2Si$ (482.66): C, 82.12; H, 5.43. Found: C, 81.82; H, 5.37.

Spiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracen]-10-one (14d). The dehydrogenation of **13g** (792 mg, 2 mmol) with DDQ (454 mg, 2 mmol) in dioxane (20 mL) was carried out in the same fashion as described for **13b:** yield 475 mg (60%) of yellow crystals; mp 333–336 °C (from methylene chloride–ethanol); IR 1660 cm^{-1} (CO). Anal. Calcd for $C_{30}H_{18}O$ (394.47): C, 91.35; H, 4.60. Found: C, 91.03; H, 4.42.

Synthesis of Tetramer 15. (a) From 10-Methyleneanthrone. A suspension of 10-methyleneanthrone (2.06 g, 10 mmol) and DDQ (1.71 g, 7.5 mmol) in dioxane (50 mL) under nitrogen was refluxed for 1 h. Precipitated $DDQH_2$ was removed by filtration. Vacuum evaporation of solvent from the filtrate gave a solid residue which was triturated with ethanol to give a colorless crystalline residue. It was recrystallized from methylene chloride by precipitation with ethanol: yield 1.65 g (80%); mp 269–273 °C (green melt); IR 1660 cm^{-1} (CO); MS *m/e* 410 (base peak). Anal. Calcd for $C_{60}H_{34}O_4$ (818.92): C, 88.00; H, 4.18. Found: C, 87.51; H, 4.35.

(b) From 9. The oxidative dimerization of **9** (412 mg, 1 mmol) with DDQ (341 mg, 1.5 mmol) in dioxane (20 mL) was carried out in the same fashion as described under method a, yield 330 mg (80%).

(c) From 10. The oxidation of **10** (410 mg, 1 mmol) with DDQ (114 mg, 0.5 mmol) in dioxane (20 mL), carried out in the fashion as described under method a, afforded 300 mg (73%) of tetramer **15.**

Reductive Cleavage of Tetramer 15 with Sodium Iodide. A suspension of **15** (818 mg, 1 mmol) and sodium iodide (5 g) in acetic acid (50 mL) was refluxed under nitrogen for 1 h. Reduction of liberated iodine by addition of aqueous 0.1 M sodium thiosulfate (20 mL, corrected) gave a yellow crystalline precipitate which was recrystallized from chloroform by precipitation with ethanol: yield 760 mg (93%) of **10a;** mp 269–275 °C.

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Registry No.—**9a,** 69469-53-0; **9b,** 65252-94-0; **10a,** 65252-95-1; **10b,** 69469-59-6; **11,** 65252-96-2; **12,** 65252-97-3; **13a,** 65252-92-8; **13b,** 24215-76-7; **13c,** 69469-54-1; **13d,** 69469-55-2; **13e,** 69469-56-3; **13f,** 69469-57-4; **13g,** 65882-10-2; **13h,** 69469-58-5; **14a,** 65252-98-4; **14b,** 65253-00-1; **14c,** 69469-60-9; **14d,** 69469-61-0; **15,** 69469-62-1; 10-methyleneanthrone, 4159-04-0.

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