

However, three of the four coupling constants differ substantially from those reported previously.<sup>2</sup> Uv had  $\lambda$  258  $m\mu$  shoulder, 265.5 ( $\epsilon$  1026), 272.5 (1036).

**cis-9,10-Diisopropyl-9,10-DHA.**—To 9-isopropyl-9,10-DHA (1.25 g, 5.6 mmol) in dry THF (50 ml) at  $-60^\circ$  was added *n*-butyllithium (6.0 mmol). The reaction mixture was stirred at  $0^\circ$  for 1 hr and the reaction was terminated by the rapid addition of excess isopropyl iodide. After separation of salts with water and removal of ether solvents, an nmr spectrum indicated the presence of 12.5% *cis*- and 87.5% *trans*-9,10-diisopropyl-9,10-DHA by integration of the benzylic hydrogen doublets at  $\delta$  3.78 ( $J = 5.0$  Hz for the *trans* isomer) and 3.27 ( $J = 9.5$  Hz for the *cis* compound). See earlier literature.<sup>3</sup>

After chromatography over dry basic alumina (hexane), 0.85 g of *trans*-9,10-diisopropyl-9,10-DHA (57%), mp  $73-74^\circ$ , was obtained after recrystallization from ethanol (lit.<sup>3</sup> mp  $76-77^\circ$ ); uv 257  $m\mu$  (shoulder), 265 ( $\epsilon$  647), 272 (588).

In later fractions the *cis* isomer appeared predominantly as an oil which crystallized upon trituration with ethanol to yield 60 mg of *cis*-9,10-diisopropyl-9,10-DHA (4%, mp  $99.5-105^\circ$ ), lit.<sup>3</sup> mp  $109-110^\circ$ ; uv  $\lambda$  258  $m\mu$  ( $\epsilon$  822), 265 (1084), 272 (1221).

**Methylithium Addition to Anthracene.**—Anthracene (0.5 g, 2.8 mmol) in 50 ml of THF was mixed with excess methylithium (14 mmol) in ether. After refluxing for 4 hr, excess isopropyl iodide was added quickly. After 1 hr stirring, salts were separated with water and gas chromatography showed the presence of five components. The ratio of *cis*- and *trans*-9-isopropyl-10-methyl-9,10-DHA was  $40:60 \pm 1$  as determined by vpc. Unchanged anthracene was recovered.

**trans-9-Ethyl-10-methyl-9,10-DHA.**<sup>15</sup>—Lithium (0.15 g)—am-

(15) We thank Mr. Isaac Angres (NSF undergraduate participant) for running this experiment.

monia (300 ml) reduction of 9-ethyl-10-methylantracene (2 g) in THF (120 ml) for 3.5 hr was followed by addition of ethanol (10 ml) and H<sub>2</sub>O (10 ml). Solvents were evaporated and the oil obtained from ether-water treatment was recrystallized from absolute ethanol to give 1.3 g of white needles (65%), mp  $33-34^\circ$ .

*Anal.* Calcd for C<sub>17</sub>H<sub>18</sub>: C, 91.84; H, 8.16. Found: C, 91.73; H, 8.25; C, 91.75; H, 8.38.

Uv had  $\lambda$  212.2  $m\mu$  ( $\epsilon$  19,480), 264.5 (1140), 271.8 (1067); nmr  $\delta$  0.887 (t, 3, CH<sub>3</sub>CH<sub>2</sub>-,  $J = 7.0$  Hz), 1.71 (d, 3, CH<sub>3</sub>C<sub>10</sub>H,  $J = 6.7$  Hz), 3.80 (t, 1, C<sub>9</sub>HCH<sub>2</sub>-,  $J = 7.5$  Hz), 3.99 (q, 1, C<sub>10</sub>HCH<sub>3</sub>,  $J = 6.7$  Hz), 7.22 (m, 8, aromatic).

These chemical shifts and coupling constants do not agree well with those published previously.<sup>5</sup> This sample was purified by recrystallization before nmr spectroscopy and spectra were obtained on an HA-100 instrument better suited for careful determination of coupling constants. There is no doubt, however, of the identity of this material with that described previously.<sup>5</sup>

**Registry No.**—*cis*-2, 21438-93-7; *trans*-2, 33608-27-4; 9-isopropyl-9,10-dihydroanthracene, 17573-50-1; *trans*-9,10-diisopropyl-9,10-dihydroanthracene, 25340-82-3; *cis*-9,10-diisopropyl-9,10-dihydroanthracene, 24316-21-0; *trans*-9-ethyl-10-methyl-9,10-dihydroanthracene, 23660-35-7.

**Acknowledgment.**—This investigation was supported in part by Undergraduate Science Education Program Grants GY-5723 and GY-7540, National Science Foundation.

## The Synthesis of 9,10-Cyclobutenophenanthrene from 9,10-Dimethylene-9,10-dihydrophenanthrene

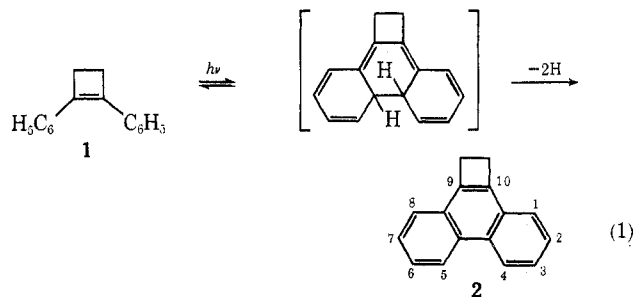
JOHN P. ANHALT,\* EARL W. FRIEND, JR., AND EMIL H. WHITE<sup>1</sup>

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

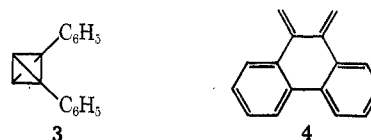
Received May 18, 1971

9,10-Dimethylene-9,10-dihydrophenanthrene (4) has been prepared from trimethyl(10-methyl-9-phenanthryl-methyl)ammonium chloride (6) and characterized by its physical data and the formation of an adduct with maleic anhydride. Irradiation of compound 4 yielded 9,10-cyclobutenophenanthrene (2), the proof of structure of which is discussed.

Our interest in 9,10-cyclobutenophenanthrene (2) was first aroused during a study of the photochemistry of 1,2-diphenylcyclobutene (1), in which it is a possible product (eq 1).<sup>2</sup> We were stimulated to the synthesis



of 2 by the subsequent report by Masamune and Kato of diphenyltetrahydrene (3).<sup>3</sup> This report drew our attention because of our interest in 3 and because the physical properties attributed to 3 by Masamune and Kato appeared to match better the predicted proper-



ties of 2.<sup>4</sup> We wish now to report the full synthesis and characterization of 2.

During the progress of this synthesis, we were able to demonstrate the intermediacy of 9,10-dimethylene-9,10-dihydrophenanthrene (4). Previously, this compound had been reported as a reactive intermediate and its presence was inferred only by trapping with various dienophiles.<sup>5</sup> The instability of 4 with respect to dimerization and polymerization prevented our complete characterization of it; however, we were able to obtain its ultraviolet spectrum in dilute solution. The direct observation of 4 in the ultraviolet is to our knowledge the first such observation of an *o*-quinodi-

(1) Author to whom inquiries should be addressed.

(2) E. H. White and J. P. Anhalt, *Tetrahedron Lett.*, 3927 (1965).

(3) (a) S. Masamune and M. Kato, *J. Amer. Chem. Soc.*, **87**, 4190 (1965);

(b) S. Masamune and M. Kato, *ibid.*, **88**, 610 (1966).

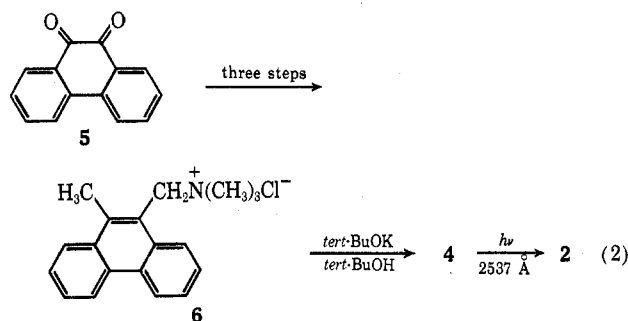
(4) E. H. White, G. E. Maier, R. Graeve, U. Zirngibl, and E. W. Friend, *ibid.*, **88**, 611 (1966).

(5) (a) I. T. Millar and K. V. Wilson, *J. Chem. Soc.*, 2121 (1964); (b) J. K. Stille and R. T. Foster, *J. Org. Chem.*, **28**, 2708 (1963); (c) P. D. Gardner and H. S. Sarrafzadeh R., *J. Amer. Chem. Soc.*, **82**, 4287 (1960).

methane not substituted in the terminal methylene positions.<sup>6</sup>

**9,10-Cyclobutenophenanthrene (2).**—The synthesis of **2** was achieved in five steps starting with the readily available 9,10-phenanthroquinone (**5**). The conversion of **5** to trimethyl(10-methyl-9-phenanthrylmethyl)-ammonium chloride (**6**) was effected by known procedures.<sup>5</sup> This intermediate was purified as the monohydrate.

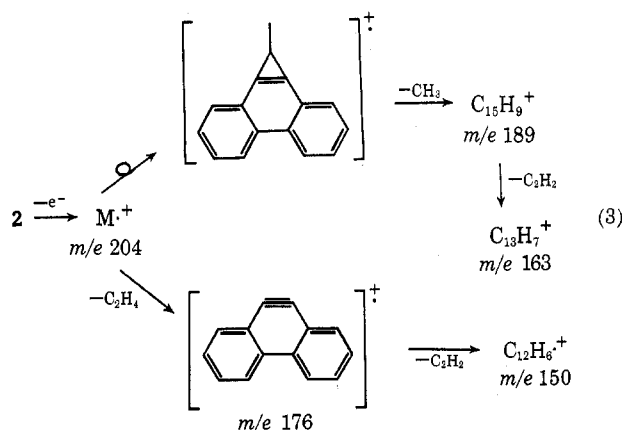
The conversion of the monohydrate of **6** to cyclobutenophenanthrene (**2**) was straightforward (eq 2).



It was found that best yields are obtained when dry *tert*-butyl alcohol is used, and when both steps in the reaction are carefully monitored (see Experimental Section). Early irradiation of **6** before elimination is completed appeared to give more complicated reaction mixtures. In addition, compound **2** is photodecomposed by prolonged irradiation.

The physical data found for the product are completely consistent with the assigned structure of **2**. In particular (see Experimental Section for other data) the ultraviolet spectrum of **2** [ $\lambda_{\text{max}}^{\text{hexane}} 255 \text{ m}\mu$  ( $\log \epsilon 4.83$ )] is very similar to that of 9,10-dimethylphenanthrene and clearly indicates a phenanthrene chromophore.<sup>4</sup>

The mass spectrum of **2** shows apparent successive losses of 15, 13, 13, and 13 mass units. The pattern of fragmentation may be explained by two parallel processes (eq 3).



The nmr spectrum is consistent in detail with structure **2**. The methylenic protons of **2** at  $\delta$  3.35 are shifted 0.70 ppm downfield from the methyl protons of 9,10-dimethylphenanthrene; this shift is consistent with the presence of a fused cyclobutane ring (Table I).

(6) G. Quinkert, M. Finke, J. Palmowski, and W-W Wiersdorff, *Mol. Photochem.*, **1**, 433 (1969), and G. Quinkert, *Photochem. Photobiol.*, **7**, 783 (1968), have observed diphenyl- and tetraphenyl-*o*-xylylene at low temperature.

TABLE I

POSITION OF BENZYLIC PROTONS AS A FUNCTION OF RING SIZE IN BENZOCYCLOALKENES

	Benzylic protons, $\delta$
<i>o</i> -Xylene <sup>a</sup>	2.23
Tetralin <sup>a</sup>	2.76
Indan <sup>a</sup>	2.91
Benzocyclobutene <sup>b,c</sup>	3.14
9,10-Dimethylphenanthrene <sup>c</sup>	2.65
Cyclobutenophenanthrene <sup>c</sup>	3.35

<sup>a</sup> N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalogue," Vol. II, Varian Associates, Palo Alto, Calif., 1963. In chloroform-*d*<sub>1</sub>. <sup>b</sup> G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1964). <sup>c</sup> In carbon tetrachloride.

Furthermore, the increased downfield shifts of the 1,8 protons in 9,10-substituted phenanthrenes<sup>7a</sup> (van der Waals deshielding)<sup>7b</sup> are not observed in **2** (Table II), a

TABLE II

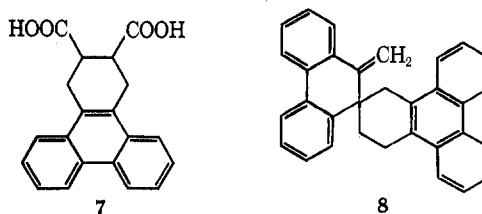
POSITION OF RING PROTONS AS A FUNCTION OF SUBSTITUTION IN PHENANTHRENES<sup>a</sup>

	Ring protons, $\delta^b$		
	2,3,6,7	1,8	4,5
Phenanthrene	7.51	7.74	8.56
9,10-Dideuterio-2,7-dimethylphenanthrene <sup>c</sup>	7.3	7.6	8.4
9,10-Cyclobutenophenanthrene ( <b>2</b> )	7.45	7.65	8.60
9,10-Dimethylphenanthrene	7.47	7.98	8.57
9-Methoxymethyl-10-methylphenanthrene	7.61	8.15	8.67

<sup>a</sup> Spectra, except where noted, were obtained in carbon tetrachloride using a Varian Associates HA-100 spectrometer. <sup>b</sup> Centers of multiplets in most cases. Positional assignments are made in accord with assignments given in ref 7 for phenanthrenes. <sup>c</sup> L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4085 (1964); no conditions given.

result, presumably, of the smaller size of the cyclobutane ring relative to two methyls.

**9,10-Dimethylene-9,10-dihydrophenanthrene (4).**—The intermediacy of quinodimethane **4** in the synthesis of compound **2** (eq 2) was demonstrated by trapping it with maleic anhydride (in experiments without irradiation). The nearly quantitative yield of 1,2,3,4-tetrahydro-2,3-triphenylene-*cis*-dicarboxylic acid (**7**)<sup>6b</sup> isolated after hydrolysis indicates that almost complete conversion of **6** to **4** had occurred (Table III). The small amount of dimer **8**<sup>6c</sup> found may have formed after addition of maleic anhydride. The formation of **8**



was not evident in ultraviolet spectra of reaction mixtures immediately after being quenched with acetic acid; however, it is not certain that such a small quantity would be detected. When the addition of maleic anhydride to **4** was delayed, dimerization of the

(7) (a) P. M. Bavin, K. D. Bartle, and J. A. S. Smith, *Tetrahedron*, **21**, 1087 (1965); (b) N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 183.

TABLE III  
PRODUCT YIELDS FOR THE REACTION OF 9,10-DIMETHYLENE-9,10-DIHYDROPHENANTHRENE (4) WITH MALEIC ANHYDRIDE

Aliquot	Time of addn of maleic anhydride, hr <sup>a</sup>	Yields					
		Compd 7			Compd 8		
		mg	mmol	% <sup>b</sup>	mg	mmol	% <sup>b</sup>
A <sub>1</sub>	0.1	29.0	0.091	91.0	0.7	0.0017	3.4
A <sub>2</sub>	0.1	29.0	0.093	93.0	0.5	0.0012	2.4
B	8.0	12.3	0.038	38.0	10.3	0.025	50.0
C	103.0	2.8	0.0087	8.7	17.1	0.042	84.0

<sup>a</sup> After ultraviolet spectra indicated complete conversion to 4. <sup>b</sup> Based on 0.100 mmol of 6.

TABLE IV  
ULTRAVIOLET SPECTRA OF MODEL 2,3-DIPHENYL-1,3-DIENES

	$\lambda_{\max}$ , m $\mu$ (log $\epsilon$ )
9,10-Dimethylene-9,10-dihydrophenanthrene (4)	216 sh (4.56), 244 (4.42), 260 sh (4.25), 300 (3.79) <sup>a</sup>
2,3-Diphenylbutadiene <sup>c</sup>	243 (4.26), 280 sh (3.22), 287 sh (2.70) <sup>b</sup>
2,3-Diphenyl-1,3-cyclooctadiene <sup>c</sup>	247 (4.41), 295 sh (3.00) <sup>b</sup>

<sup>a</sup> In *tert*-butyl alcohol. <sup>b</sup> In cyclohexane. <sup>c</sup> A. C. Cope and D. S. Smith, *J. Amer. Chem. Soc.*, **74**, 5136 (1952).

unstable 4 did occur to yield compound 8. The yields of 7 and 8 as a function of time (Table III) indicate that quinodimethane 4 has a half-life of about 8 hr at room temperature at a concentration of  $10^{-3}$  M in *tert*-butyl alcohol.

Comparison of the ultraviolet spectrum of the quinodimethane with model systems (Table IV) indicates that the spectrum is consistent with structure 4. Since the quinodimethane 4 could not be isolated, concentration of solutions of 4 leading to dimer 8 and polymer, the  $\epsilon$  values we report are approximate and are calculated by assuming the concentration of 4 to be the same as the initial concentration of 6. This assumption is justified since high yields (93%) of the maleic anhydride adduct 7 were obtained (Table III). Furthermore, the ultraviolet spectra of solutions of 4 briefly irradiated with a 4-W germicidal lamp were interpretable as the sum of just the two components 2 and 4 (see Experimental Section). Since the reactant 6 and known products 2 and 8 have greater extinction coefficients at the position of maxima for 4, the presence of small amounts of these compounds would lead to an increase in the calculated  $\epsilon$  values for 4. The absence of these compounds in the reaction mixture after apparent complete conversion of 6 to 4 is evident from the constant  $\epsilon$  values obtained for 4 over a range in concentrations from  $2.0 \times 10^{-5}$  to  $5.3 \times 10^{-4}$  M.

Each of the model compounds in Table IV shows some evidence of long wavelength absorption between 280 and 300 m $\mu$ . The presence of a well-defined maximum at 300 m $\mu$  in 4 may be the expression of a relatively rigid structure compared to the model compounds.

### Experimental Section

Melting points, except where noted, were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by either Mr. Joseph Walters in this department or Galbraith Laboratories, Inc., Knoxville, Tenn.

Infrared spectra were determined on Perkin-Elmer Model 337 or 521 infrared spectrometers and were calibrated against known absorption bands of polystyrene. Ultraviolet spectra were determined on a Cary Model 14 spectrometer. Proton magnetic resonance spectra (nmr) were determined on Varian Associates A-60 or HA-100 spectrometers using tetramethylsilane as an internal standard for nonaqueous solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for aqueous solutions.

Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6 mass spectrometer.

Thin layer chromatography (tlc) was performed on Eastman chromatogram sheets containing a fluorescent indicator. Visualization was with 2537-Å light.

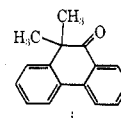
**9-Chloromethyl-10-methylphenanthrene.**—9-Chloromethyl-10-methylphenanthrene was prepared by a modification of the method of Millar and Wilson.<sup>5a</sup> To a suspension of 9,10-dimethyl-9,10-dihydroxy-9,10-dihydrophenanthrene<sup>8</sup> (10.58 g, 44.0 mmol) in ether (60 ml), thionyl chloride (12.7 ml, 21.0 g, 0.18 mol) was added with stirring. The reaction mixture was protected from atmospheric moisture with a drying tube. After stirring for 1.5 hr the mixture was heated to reflux for 5.5 hr at which time the reaction mixture became homogeneous. Reflux was allowed to continue for 2 hr, after which time the ether was allowed to distill off until stirring became impossible and hydrogen chloride evolution commenced. The mixture was then placed under aspirator vacuum and heated on a steam bath until hydrogen chloride evolution ceased (1 hr). Ethyl acetate (100 ml) was added and the mixture was heated to reflux overnight. The nearly homogeneous hot solution was filtered and allowed to cool to give 4.25 g of 9-chloromethyl-10-methylphenanthrene (17.7 mmol, 40%): mp 152.5–154° (lit.<sup>5c</sup> 155–156°); ir (KBr) 1254, 780, 760, and 720  $\text{cm}^{-1}$ . The ethyl acetate mother liquor was evaporated to dryness on a rotary evaporator and the residue was dissolved in hot benzene. Addition of an equal volume of isooctane gave nicely shaped, slightly colored crystals of 9-chloromethyl-10-methylphenanthrene (1.40 g, 5.8 mmol, 13%), mp 146–148.5°. Tlc of each batch on silica gel (benzene–hexane, 1:2) gave a single spot of  $R_f$  0.48.

The benzene–isooctane mother liquor on evaporation gave a crystalline mass (4.52 g) which on tlc on silica gel (benzene–hexane, 1:2) gave two spots of  $R_f$  0.27 and 0.48. This material was chromatographed on silica gel (100 g) using a benzene–hexane mixture (1:2) as eluent. The fractions containing the slow-moving material were evaporated to crystalline solids and combined. Recrystallization from hexane gave 2.45 g (10.6 mmol, 24%) of 10,10-dimethyl-9(10*H*)-phenanthrene (i), mp 72.0–73.5° (lit.<sup>9</sup> 75°).<sup>10</sup> The infrared spectrum (KBr) was identical with that reported in the literature for i<sup>12</sup> with prominent bands at

(8) 9,10-Dimethyl-9,10-dihydroxy-9,10-dihydrophenanthrene was prepared by the addition of 9,10-phenanthraquinone to a solution of methylmagnesium iodide in ether according to the method of Gardner and Sarrafzadeh.<sup>5c</sup> The product after recrystallization from benzene melted at 162.5–163.8° (lit.<sup>5c</sup> 163–164°).

(9) T. Zincke and W. Tropp, *Justus Liebigs Ann. Chem.*, **362**, 242 (1908).

(10) The production of i had not previously been reported in the synthesis of 9-chloromethyl-10-methylphenanthrene by this method.<sup>11</sup> The occurrence here may have been due to the somewhat more vigorous conditions employed.



(11) S. Hauptmann, *Chem. Ber.*, **93**, 2604 (1960).

(12) A. Schönberg and G. Schütz, *ibid.*, **95**, 2386 (1962).

1675, 982, 783, 756, and 732  $\text{cm}^{-1}$ ; uv (hexane) 238  $\text{m}\mu$  ( $\log \epsilon$  4.39), 248 (4.33), 267 (3.99), 276 (4.05), 292 sh (3.74), and 320 (3.50); nmr ( $\text{CCl}_4$ )  $\delta$  7.92 (m, 3.2 H), 7.38 (m, 5.2 H), and 1.50 (s, 6.0 H). The fraction containing the faster moving material gave a crystalline solid after evaporation. Tlc on silica gel (benzene-hexane, 1:2) of this material was identical with that of 9-chloromethyl-10-methylphenanthrene.

**Trimethyl(10-methyl-9-phenanthrylmethyl)ammonium Chloride Monohydrate (6).**—The procedure of Millar and Wilson<sup>5a</sup> for the synthesis of trimethyl(10-methyl-9-phenanthrylmethyl)ammonium chloride (6) was followed. Complications attend the synthesis, and thus our procedure is described in detail. Trimethylamine generated by stirring the corresponding hydrochloride (9.6 g, 0.10 mol) with barium oxide (26 g, 0.27 mol) was bubbled into a stirred suspension of 9-chloromethyl-10-methylphenanthrene (3.000 g, 12.45 mmol) in a mixture of chloroform (210 ml) and absolute methanol (70 ml). After stirring for 1.5 hr at room temperature, the reaction mixture was heated to reflux for 1.0 hr at which time the solution was homogeneous. The reaction mixture was allowed to cool with stirring for an additional 3 hr. Tlc on silica gel (benzene-hexane, 1:2) showed the presence of considerable starting material. Additional trimethylamine generated by adding dropwise a solution of the hydrochloride (14.4 g, 0.150 mol) in water (50 ml) to a huge excess of sodium hydroxide (200 g) was bubbled through the reaction mixture for 1.0 hr at room temperature. Tlc under the same conditions no longer showed starting material; however, a new spot at  $R_f$  0.18 was present in addition to the expected spot at the origin corresponding to the title quaternary chloride. The reaction mixture was then heated to reflux for 2.0 hr, after which time the tlc was unchanged. The solvents were removed from the reaction mixture on a rotary evaporator and the resulting solid was placed under high vacuum overnight. The solid was then dissolved in absolute ethanol and the solution was filtered. Addition of ether to the filtrate gave 1.958 g of material which gave only a very faint spot of  $R_f$  0.20 in addition to the spot at the origin. The nmr ( $\text{CDCl}_3$ ) of this material showed a doublet at  $\delta$  2.93 ( $J = 5$  Hz) attributable to trimethylamine hydrochloride.<sup>13</sup> The only other peaks in the spectrum were attributable to the quaternary chloride 6 at  $\delta$  8.72 (m, 3.0 H), 8.17 (m, 1.2 H), 7.70 (m, 3.7 H), 5.82 [broad doublet (unresolved AB quartet), 1.7 H,  $\text{CH}_2$ ], 3.50 (s, 9.0 H), and 3.02 (s, 3.6 H). Integration of this spectrum indicated 9.0% (31 mol %) of trimethylamine hydrochloride was present. When the spectrum was taken using deuterium oxide as solvent the doublet attributed to trimethylamine hydrochloride coalesced to a singlet at  $\delta$  3.17,<sup>14</sup> which also indicated the presence of about 9% of trimethylamine hydrochloride. The presence of trimethylamine hydrochloride was further confirmed by weak infrared bands (Nujol) at 2515, 2470, and 987  $\text{cm}^{-1}$ . The quaternary chloride 6 readily formed a chloroform insoluble hydrate. The impure quaternary chloride 6 was crystallized twice from water to give 1.103 g (3.47 mmol, 28%) of analytically pure trimethyl(10-methyl-9-phenanthrylmethyl)ammonium chloride monohydrate (6): uv max (*tert*-butyl alcohol) 224  $\text{m}\mu$  ( $\log \epsilon$  3.38), 250 (4.63), 257 (4.69), 272 sh (4.11), 278 sh (3.99), 292 (3.96), 303 (3.93), 334 (2.53), 340 sh (2.26), and 350 (2.26); ir (Nujol) 3430, 3350, 875, and 760  $\text{cm}^{-1}$ ; nmr ( $\text{D}_2\text{O}$ )  $\delta$  8.21 (m, 2.0 H), 7.91 (m, 1.9 H), 7.68 (m, 3.8 H), 4.82 [broad doublet (unresolved AB quartet), 1.7 H], 2.98 (s, 8.9 H), and 2.52 (s, 3.1 H).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{22}\text{NCl}\cdot\text{H}_2\text{O}$ : C, 71.80; H, 7.61; N, 4.41. Found: C, 71.81; H, 7.36; N, 4.22.

The mother liquor from the initial precipitation of the quaternary ammonium chloride with ether was evaporated to a crystalline solid (1.638 g) which gave a principal spot on tlc on silica gel (benzene-hexane, 1:2) of  $R_f$  0.20. This material was dissolved in carbon tetrachloride (10 ml) and filtered. The clear solution was then evaporated to give a crystalline solid which was recrystallized from ethanol to give 0.598 g (2.54 mmol, 20%) of 9-methoxymethyl-10-methylphenanthrene: mp 108.7–111.0° (lit.<sup>5c</sup> 113–114°); ir (KBr) 1099, 953, 755, and 720  $\text{cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ )  $\delta$  8.67 (m, 2.2 H), 8.15 (m, 2.2 H), 7.61 (m, 4.0 H), 4.96 (s, 2.0 H), 3.48 (s, 2.8 H), and 2.76 (s, 3.0 H).

**9,10-Dimethylene-9,10-dihydrophenanthrene (4).**—A freshly

(13) A nearly saturated solution of trimethylamine hydrochloride in  $\text{CDCl}_3$  gave a singlet at  $\delta$  2.95; however, a dilute solution gave a doublet at  $\delta$  2.88 ( $J = 5$  Hz).

(14) The nmr ( $\text{D}_2\text{O}$ ) of trimethylamine hydrochloride gave a singlet at  $\delta$  2.91. Addition of trimethyl(10-methyl-9-phenanthrylmethyl)ammonium chloride (<50 mol %) shifted this peak to  $\delta$  3.07.

prepared solution of potassium *tert*-butoxide (0.10 ml of 0.37 *M*, 37  $\mu\text{mol}$ ) was added to 5 ml of a  $5.25 \times 10^{-4}$  *M* solution of 6 (2.63  $\mu\text{mol}$ ) in *tert*-butyl alcohol. The solution was mixed well and then placed in an ultraviolet cell of 0.5-mm path length. The disappearance of the fine structure and maxima characteristic of 6 and the appearance of maxima at 244 and 300  $\text{m}\mu$  (characteristic of 4) were observed. After 21 min there was no longer any evidence of 6, and the maxima at 244 and 300  $\text{m}\mu$  showed no further decrease in intensity (the decrease results from the low extinction of 4 relative to 6 in this region). After an additional 8 min the spectrum was unchanged. The ultraviolet spectrum of this solution showed max ( $\log \epsilon$ ) 216 sh (4.56), 244 (4.42), 260 sh (4.25), and 300  $\text{m}\mu$  (3.79).

A portion of this reaction solution was diluted with *tert*-butyl alcohol to  $3.17 \times 10^{-5}$  *M* and placed in a 1-cm path length cell. After irradiation for 2 min with a 4-W germicidal lamp, the ultraviolet spectrum showed maxima at positions identical with 9,10-cyclobutenophenanthrene (2). The intensities corresponded to a mixture comprised of 56% 2 ( $1.76 \times 10^{-5}$  *M*) and 44% 4 ( $1.41 \times 10^{-5}$  *M*). Further irradiation caused a net decrease in the concentration of 2.

**Adduct of 9,10-Dimethylene-9,10-dihydrophenanthrene with Maleic Anhydride.**—Trimethyl(10-methyl-9-phenanthrylmethyl)ammonium chloride monohydrate (159 mg, 0.500 mmol) was dissolved in *tert*-butyl alcohol (500 ml, Baker Analyzed) and protected from atmospheric moisture by a drying tube. A freshly prepared solution of potassium *tert*-butoxide (27 ml of 0.34 *M*, 7.5 mmol) was then injected. After stirring for 2 min, a sample was withdrawn and placed in an ultraviolet cell of 0.5-mm path length. The reaction was followed in the ultraviolet until no further decrease in the maximum at 244  $\text{m}\mu$  was observed. This occurred 14 min after addition of the potassium *tert*-butoxide. Glacial acetic acid (0.50 ml, 817 mmol) was then added to give approximately a pH of 7.0. The reaction was allowed to stir an additional 4 min, after which time four 100-ml aliquots were withdrawn. After the addition of potassium *tert*-butoxide (20 min), maleic anhydride (1.1 g, 11 mmol) was added to each of two of the aliquots ( $A_1$  and  $A_2$ ). Upon addition of the maleic anhydride, a cloudy precipitate formed and the solution turned pink. After 8 hr at room temperature, the same amount of maleic anhydride was again added to  $A_1$  and  $A_2$  (to ensure complete reaction) as well as to a third aliquot (B). After an additional 8 hr,  $A_1$  and  $A_2$  were worked up as described below and additional maleic anhydride was added to B. This aliquot was worked up after an additional 8 hr. The fourth aliquot (C) was treated exactly the same as the first three with addition of maleic anhydride commencing 103 hr after maleic anhydride was added to  $A_1$  and  $A_2$ .

After the addition of maleic anhydride (16 hr), each aliquot was concentrated on a rotary evaporator until only a few milliliters of *tert*-butyl alcohol remained. A solution of potassium hydroxide (5 g) in water (100 ml) was then added and the mixture was heated to 80–90° for 2.5 hr. Upon cooling, the mixture was vacuum filtered through Whatman No. 50 filter paper and the precipitate was washed well with water and dried *in vacuo*. The clear filtrate was then acidified with 1 *N* hydrochloric acid. The precipitate was collected by vacuum filtration through a medium grade sintered glass filter and washed well with water followed by drying *in vacuo*. The base-insoluble precipitates each melted at 234–237° dec (Kofler). The literature values for 2-methylene-3,4,5,6-dibenzo-3',4'-(9,10-phenanthro)spirobicyclohexane (8) are 228.5–229° and 252–253° depending on the solvent for crystallization.<sup>15</sup> The infrared (KBr and  $\text{CS}_2$ ), ultraviolet (ethanol), and nmr ( $\text{CDCl}_3$ ) spectra of the combined base-insoluble product were identical with those of 8 prepared by the method of Stille and Foster.<sup>16</sup> The tlc on silica gel (benzene-hexane, 1:2) showed a large spot at  $R_f$  0.38 identical with 8 and barely perceptible spots at  $R_f$  0.19 and at the origin. A portion of this product after recrystallization from ethanol gave an ir (KBr) identical with the spectrum of the crude product and melted at 245–247° dec. A second portion recrystallized from cyclohexane melted at 229–231° dec. The ir (KBr) of this sample showed a strong band at 913  $\text{cm}^{-1}$  characteristic of the lower melting form of 8.<sup>5b</sup> Tlc on

(15) The lower melting form was obtained by crystallization from cyclohexane by Stille and Foster.<sup>5b</sup> The higher melting form was obtained by crystallization from ethanol.<sup>5b,c</sup>

(16) Gardner and Sarrafzadeh<sup>5c</sup> report uv max (EtOH) 245  $\text{m}\mu$  ( $\log \epsilon$  4.44), 256 (4.46), and 272 (4.44) for 8. In our hands, compound 8 prepared by the method of Stille and Foster<sup>5b</sup> gave uv max (EtOH) 215  $\text{m}\mu$  ( $\log \epsilon$  4.72), 225 (4.71), 247 (4.81), 256 (4.81), 268 (4.46), 272 (4.45), 278 (4.39), 287 (4.32), 300 (4.19), 336 (2.83), 342 (2.63), and 351 (2.85).

silica gel (benzene-hexane, 1:2) of both forms and **8** prepared by the method of Stille and Foster<sup>5b</sup> gave a single spot of  $R_f$  0.43.

The acid-precipitated material sublimed readily upon melting. Material from the first two aliquots melted at 280–290° dec (Kofler). Due to the small amount of sample, only the melting point of the sublimate could be determined for the second two aliquots. In each case, the sublimed material melted at 305–308°. The values reported for 1,2,3,4-tetrahydro-2,3-triphenylene-*cis*-dicarboxylic acid (**7**) are 279–282° dec (sublimate, 308–313°).<sup>5b</sup> Recrystallization from an ethyl acetate-ethanol mixture (1:1) gave crystals which melted at 282–284° dec: ir (KBr) 1690  $\text{cm}^{-1}$  [lit.<sup>5b</sup> (Nujol mull) 1698  $\text{cm}^{-1}$  (C=O str)]; uv max (EtOH) 349  $\text{m}\mu$  (log  $\epsilon$  2.90), 333 (2.76), 298 (4.05), 286 (4.03), 278 (4.15), 272 (4.19), 255 (4.79, lit.<sup>5b</sup> 4.78), 247 (4.70), 224 (4.37), and 215 (4.47). A small sample of this material was sublimed in an 8-mm glass tube sealed at 20 mm and heated to 275–300° to give very nice needles. The ir (KBr) was identical with that of Stille's 1,2,3,4-tetrahydro-2,3-triphenylene-*cis*-dicarboxylic anhydride.<sup>17</sup> The yields of **7** and **8** for each aliquot are summarized in Table III.

**9,10-Cyclobutenophenanthrene (2).**—Trimethyl(10-methyl-9-phenanthrylmethyl)ammonium chloride monohydrate (239 mg, 0.75 mmol) and *tert*-butyl alcohol (Baker Analyzed, 1.0 l.) were placed in a 1.0-l. quartz round-bottom flask with a single 24–40  $\frac{1}{8}$  joint. To the other member of this joint was attached a coarse porosity gas dispersion tube and a section of 8-mm-o.d. glass tubing. The 8-mm tubing was closed with a rubber septum through which a long stainless steel needle was inserted. This needle normally functioned to allow the nitrogen being bubbled through the reaction solution to escape; however, the tip could be inserted below the surface of the liquid for the withdrawing of aliquots. The flask also contained a magnetic stir bar.

The solution of **6** was then flushed for 8 hr with nitrogen (Aircro Prepurified) dried by passage through a glass coil immersed in a Dry Ice-ethanol bath. During this period, a solution of potassium *tert*-butoxide in *tert*-butyl alcohol was prepared under argon and diluted with *tert*-butyl alcohol to 0.76 *N* as determined by titration with hydrochloric acid. The clear, colorless solution of potassium *tert*-butoxide (14.0 ml, 10.6 mmol) was injected below the surface of the nitrogen flushed solution of quaternary chloride over a 5-min period. An aliquot was withdrawn and placed in an ultraviolet cell of 0.5-mm path length. The formation of 9,10-dimethylene-9,10-dihydrophenanthrene (**4**) in this aliquot was monitored in the ultraviolet until no further change (decrease) in the maximum at 244  $\text{m}\mu$  was observed (20 min). Irradiation was begun using a Rayonet photochemical reactor<sup>18</sup> equipped with 2537- $\text{\AA}$  lamps. The photolysis was followed in the ultraviolet by periodically withdrawing aliquots. The concentration of cyclobutenophenanthrene appeared to reach a maximum after 25 min of irradiation; irradiation was stopped after a total of 30 min. Glacial acetic acid (1.0 ml, 17.4 mmol) was added to the cloudy reaction mixture to give a neutral solution. The *tert*-butyl alcohol was then removed on a rotary evaporator at 40–50° to give a white solid which was dried at  $5 \times 10^{-3}$  Torr overnight. This solid was stirred with a mixture of hexane (100 ml) and water (100 ml). The mixture was then filtered to give an amorphous solid (67.0 mg) which did not melt below 290°; however, it appeared to decompose slowly above 200°. This material did not contain any cyclobutenophenanthrene by tlc on silica gel (benzene-hexane, 1:2).

The hexane solution on tlc on silica gel (benzene-hexane, 1:2) gave a major spot at  $R_f$  0.58 corresponding to cyclobutenophenanthrene. A minor spot at the origin as well as extremely light spots at  $R_f$  0.47 and 0.27 were present. Evaporation of the hexane solution gave a semicrystalline mass. Attempted recrystallization of this material from ethanol-water mixtures kept under nitrogen gave solid products which on tlc showed that decomposition had occurred. From the tlc of the combined solids, cyclobutenophenanthrene was now estimated to constitute only one-half of the total. The combined solids were chromatographed on 12 g of silica gel using cyclohexane as eluent. The fractions were collected under argon and yielded 23 mg (0.113 mmol, 15%) of cyclobutenophenanthrene, mp (Kofler) 135–137°

(17) We wish to thank Professor Stille for a generous sample of this material.

(18) The Southern New England Ultraviolet Co., Middletown, Conn.

(lit.<sup>4</sup> 130–131°). Recrystallization from hexane gave an analytical sample: mp 135.5–136° (Kofler); ir (KBr) 2955, 1204, 948, 942, 744, and 721  $\text{cm}^{-1}$ ; uv max<sup>19</sup> (EtOH) 220  $\text{m}\mu$  (log  $\epsilon$  4.33), 247 (4.70), 255 (4.80), 270 (4.23), 279 (4.06), 289 (4.01), 301 (4.14), 324 (2.83), 339 (3.10), and 357 (3.23); uv max (*n*-hexane) 220  $\text{m}\mu$  (log  $\epsilon$  4.37), 247 (4.73), 255 (4.83), 270 (4.27), 278 (4.10), 288 (4.04), 301 (4.20), 324 (2.70), 332 (2.67), 339 (3.06), 343 (2.75), 348 (2.74), 352 (2.73), and 357 (3.34); fluorescence max<sup>20</sup> (diethyl ether, 340- $\text{m}\mu$  excitation) 362  $\text{m}\mu$  (rel intensity 1.29), 382 (1.55), and 398 sh (1.00); nmr ( $\text{CCl}_4$ )  $\delta$  8.60 (m, 2.1 H), 7.65 (m, 2.0 H), 7.45 (m, 4.0 H), and 3.35 (s, 4.0 H); mass spectrum (70 eV) *m/e* (rel intensity) 204 (100), 203 (67), 202 (48), 201 (12), 200 (11), 189 (7.5), 176 (6.0), 163 (2.6), 150 (3.5), 102 (6.7), 101.5 (6.2), 101 (25), 100.5 (4.6), 100 (8.4), 89 (7.4), 88 (9.3), and 76 (5.7).

*Anal.* Calcd for  $\text{C}_{16}\text{H}_{12}$ : C, 94.08; H, 5.92; mol wt, 204. Found: C, 94.03; H, 5.94; mol wt, 215 (Mechrolab osmometer in chloroform); 204 (mass spectrum).

**Unsuccessful Approach to the Synthesis of 9,10-Cyclobutenophenanthrene (2).**—Trimethyl(10-methyl-9-phenanthrylmethyl)ammonium chloride monohydrate (108 mg, 0.34 mmol) dissolved in ethanol (10 ml) was converted to trimethyl(10-methyl-9-phenanthrylmethyl)ammonium hydroxide by passage through a column of Amberlite IRA-400 (OH) resin according to the method of Millar and Wilson.<sup>5a</sup> The solution was diluted to 225 ml with additional ethanol and then placed in a cylindrical quartz vessel (5  $\times$  18 cm). The solution was stirred and flushed with nitrogen (Aircro Prepurified) for 30 min. So far, the procedure was performed in a refrigerated room at 5°. Tlc on silica gel (benzene-hexane, 1:2) showed a single spot at the origin. The reaction solution was then irradiated with stirring in a Rayonet photochemical reactor<sup>18</sup> at 2537  $\text{\AA}$  at 35°. The reaction was followed by tlc on silica gel (benzene-hexane, 1:2). Irradiation was stopped after 30 min. Tlc showed the absence of starting material. Spots were present at  $R_f$  0.048, 0.25, 0.41, and 0.56. The spot at  $R_f$  0.56 corresponded in position to both 9,10-dimethylphenanthrene and 9,10-cyclobutenophenanthrene. The reaction solution contained a fine precipitate and gave a strong odor of trimethylamine. The precipitate (27 mg) was separated by filtration. The solution was evaporated to dryness at 25° on a rotary evaporator. This residue was chromatographed on a preparative tlc plate (20  $\times$  20 cm) prepared with 30 g of alumina using a benzene-hexane (1:2) mixture for development. During this chromatography, the products were protected from oxygen by an argon atmosphere. Five bands of material were evident; however, only the two apparently major bands were extracted and the material was identified. One band ( $R_f$  0.51–0.67) gave 7.0 mg (0.034 mmol, 10%) of dimethylphenanthrene, mp (Kofler) 138.5–141° (lit.<sup>10</sup> 139°). The ir [(KBr) 1602, 1580, 1435, and 749  $\text{cm}^{-1}$ ], uv ( $\text{Et}_2\text{O}$ ), and mass spectrum [(70 eV) *m/e* (rel intensity) 206 (100) and 191 (97)] were identical with those of authentic 9,10-dimethylphenanthrene. The second band ( $R_f$  0.23–0.32) gave 2.0 mg (8  $\mu\text{mol}$ , 2.4%) of 9-ethoxymethyl-10-methylphenanthrene: mp (Kofler) 96.0–97.2° (lit.<sup>5c</sup> 91–92°); uv max (EtOH) 224  $\text{m}\mu$  (log  $\epsilon$  4.25), 248 (4.56), 255 (4.63), 272 (4.04), 278 (3.94), 287 (3.83), 299 (3.83), 333, and 350; ir (KBr) 1120, 1097, 1010, and 755  $\text{cm}^{-1}$ ; nmr ( $\text{CCl}_4$ )  $\delta$  8.59 (m, 2.1 H), 8.09 (m, 2.1 H), 7.50 (m, 3.8 H), 4.94 (s, 1.9 H), 3.57 (q, 2.1 H,  $J = 7$  Hz), 2.74 (s, 3.0 H), and 1.19 (t, 3.4, H,  $J = 7$  Hz); mass spectrum (70 eV) *m/e* (rel intensity) 250 (0.76), 206 (14), 204 (13), 191 (15), and 44 (100).

**Registry No.**—**2**, 33482-75-6; **4**, 33537-23-4; **6**, 33482-76-7; **7**, 33495-80-6; **8**, 33482-77-8; 9-methoxymethyl-10-methylphenanthrene, 33482-78-9; 9-ethoxymethyl-10-methylphenanthrene, 33482-79-0.

**Acknowledgment.**—Financial support by the Petroleum Research Fund of the American Chemical Society (PRF 328-A1) is gratefully acknowledged.

(19) The low-intensity absorptions (log  $\epsilon$  less than 2.80) between 320 and 360  $\text{m}\mu$  are not reported for the ethanol spectrum because of the low solubility of cyclobutenophenanthrene (**2**) in this solvent.

(20) Fluorescence spectrum and molecular weight (osmometer) as reported by E. W. Friend, Dissertation, The Johns Hopkins University, 1967.