

**397. Phenanthrene Chemistry. Part III.\* 9,10-Phenanthraquinodimethane and 9,10-Anthraquinodimethane.**

By IAN T. MILLAR and K. V. WILSON.

Some reactions of 9,10-disubstituted phenanthrenes and anthracenes, which appear to proceed through the reactive intermediates named in the title, have been studied.

The dehydration of appropriate tertiary diols in boiling diethyl phthalate affords a useful route to some polycyclic quinodimethanes.

QUINODIMETHANES have been postulated or demonstrated as reactive intermediates in a number of reactions.<sup>1-4</sup>

By the thermal decomposition of trimethyl-10-methyl-9-phenanthrylmethylammonium hydroxide (V; X = OH), Gardner and Sarrafzadeh<sup>5</sup> obtained a polymer, and a compound which they formulated as a spirocyclic hydrocarbon. They deduced that the latter resulted from the dimerization of initially-formed 9,10-phenanthraquinodimethane (9,10-dihydro-9,10-dimethylenephenanthrene) (III). We have re-examined the preparation and thermal decomposition of the quaternary hydroxide (V; X = OH), and have been able to improve yields and to confirm and extend earlier results. Other routes to the quinodimethane have been studied, and new evidence is presented in favour of the view that it is formed in these reactions as a short-lived reactive intermediate, under normal conditions.

We found that the quaternary hydroxide (V; X = OH) is conveniently prepared by the route shown in overall yield of 40% from phenanthraquinone, compared with 16% in the earlier work.<sup>5</sup> Much of this improvement is due to the use of 9-chloromethyl-10-methylphenanthrene (IV), rather than the corresponding bromo-compound. The chloro-compound (IV) was prepared in good yield by chloromethylation of 9-methylphenanthrene.

It is possible that the quinodimethane is an intermediate in the reaction of the diol (I) with thionyl chloride to give the chloromethyl compound (IV), as shown; thus, the

\* Part II, Ali, Carey, Cohen, Jones, Millar, and Wilson, *J.*, 1964, 387.

<sup>1</sup> Mann and Stewart, *J.*, 1954, 2826.

<sup>2</sup> Errede and Landrum, *J. Amer. Chem. Soc.*, 1957, **79**, 4952.

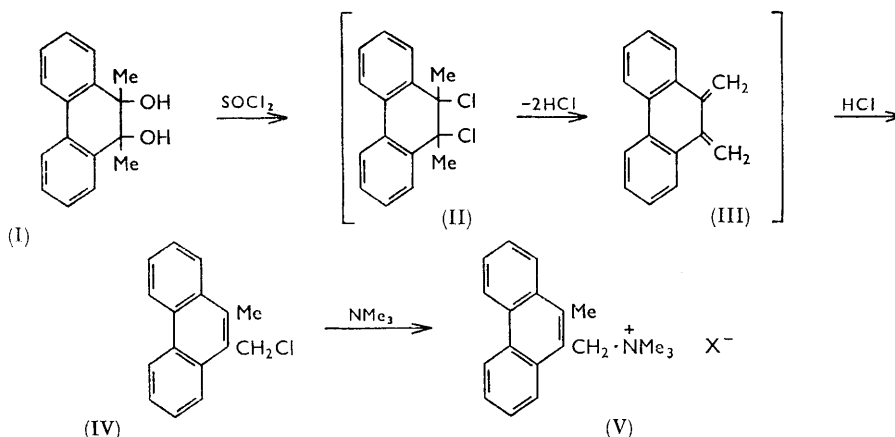
<sup>3</sup> Errede and Szwarc, *Quart. Rev.*, 1958, **12**, 301.

<sup>4</sup> Tedder, *Ann. Reports*, 1961, **58**, 225.

<sup>5</sup> Gardner and Sarrafzadeh, *J. Amer. Chem. Soc.*, 1960, **82**, 4287.

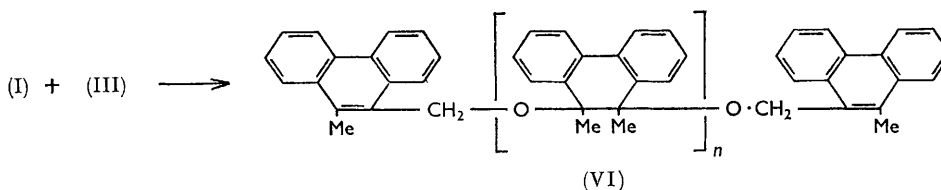
isolation of "a dichloro-compound" from the reaction mixture has been reported,<sup>5</sup> and we found that the quinodimethane (III) reacts readily with hydrogen chloride to give the chloromethyl compound (IV), as described below.\*

The quaternary hydroxide (V; X = OH) is unstable at or above room temperature. We have examined its decomposition when an ethanolic solution was dropped into a



"flash distillation" apparatus at temperatures of 100 and 210°, under reduced pressure. The major product was non-volatile, and consisted of a mixture of polymeric material and the spirocyclic dimer of 9,10-phenanthraquinodimethane. Some of the product of thermal decomposition was volatile, and co-distilled with ethanol, to be trapped at  $-78^\circ$ . This distillate apparently contained the monomeric quinodimethane (III), since with hydrogen chloride at  $-78^\circ$  it gave 9-chloromethyl-10-methylphenanthrene. This result implies that 9,10-phenanthraquinodimethane is as stable as *o*-benzoquinodimethane, as expected. Attempts to detect the monomer by decomposing the quaternary hydroxide (V; X = OH) in a vapour-phase chromatography apparatus failed, although *p*-benzoquinodimethane ("p-xylylene") is relatively stable in the gas phase.<sup>6</sup>

The observation<sup>7</sup> that alumina catalyses elimination of acetic acid from some alkyl and aryl acetates under mild conditions suggested another possible route to the quinodimethane (III) from the diol (I). However, our attempts to prepare the diacetate of the diol (I), by use of acetic anhydride and sulphuric acid, gave only polymeric material and a product which was possibly the diether (VI;  $n = 1$ ), arising by condensation of the diol with the quinodimethane formed by dehydration of the diol.



This result finds analogy in the observation<sup>8</sup> that thermal decomposition of trimethyl-4-methylbenzylammonium hydroxide gives some di-(4-methylbenzyl) ether, which could

\* Added in proof: The reaction of *cis*- and *trans*-1,2-dimethylacenaphthene-1,2-diol with thionyl chloride at  $50^\circ$  to give 2-chloromethyl-1-methylacenaphthylene (Hauptmann and Franke, *J. prakt. Chem.*, 1963, **19**, 180) may follow a similar course, *via* acenaphthene-1,2-quinodimethane (Campbell and Gow, *J.*, 1959, 1955).

<sup>6</sup> Szwarc, *Discuss. Faraday Soc.*, 1947, **2**, 46.

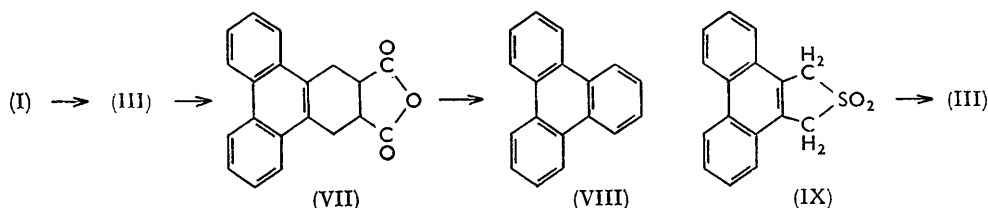
<sup>7</sup> Taylor, *Chem. and Ind.*, 1962, **88**, 1684.

<sup>8</sup> Errede, *J. Amer. Chem. Soc.*, 1961, **83**, 949; Cram and Knox, *ibid.*, p. 2204.

arise by condensation of *p*-benzoquinodimethane with 4-methylbenzyl alcohol, the expected primary products.

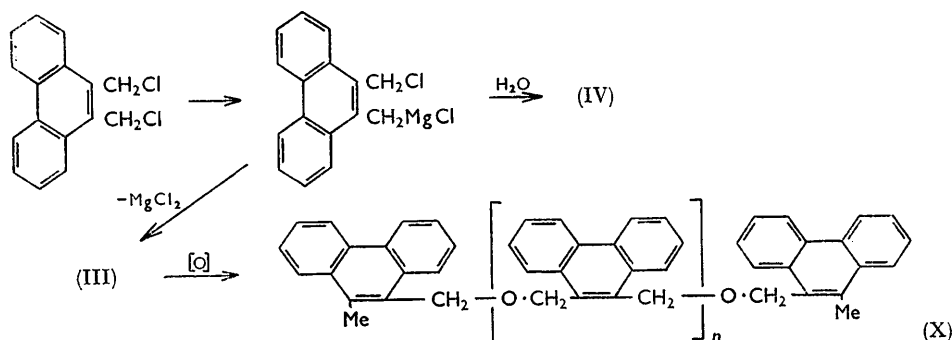
The product from the attempted diacetylation of the diol (I) may also have contained a polymeric ether (as VI;  $n > 1$ ).

We found, however, that the direct dehydration of the diol (I) in boiling diethyl phthalate gave the quinodimethane (III), as we reported previously,<sup>9</sup> since in the presence of maleic anhydride, Diels–Alder addition occurred to give the adduct (VII), whose structure was confirmed by aromatization and decarboxylation to triphenylene (VIII). In the absence of maleic anhydride, the product of dehydration was polymeric.



We have also obtained the adduct (VII) by thermally decomposing the sulphone (IX) in diethyl phthalate in the presence of maleic anhydride. The thermal decomposition of the appropriate cyclic sulphone has been used in syntheses of cyclobuta[*a*]- and cyclobuta[*b*]-naphthalene, reactions in which 1,2- and 2,3-naphthaquinodimethane, respectively, have been shown to be intermediates.<sup>10</sup> The sulphone (IX) was prepared by reaction of 9,10-bisbromomethylphenanthrene with sodium sulphide, and oxidation of the resulting sulphide with peracetic acid.

Mann and Stewart<sup>1</sup> studied the reaction of “*o*-xylylene” dichloride with magnesium, and obtained a product which was probably a polymer of *p*-benzoquinodimethane. We found that 9,10-bisbromomethylphenanthrene with magnesium in diethyl ether or tetrahydrofuran gave an oxygen-containing polymer and an ether, probably (X;  $n = 2$ ) or the related cyclic oligomer  $[-O\cdot CH_2\cdot(C_{14}H_{10})\cdot CH_2-]_n$ . Also isolated from this reaction, which consumed one molar equivalent of metal, was 9-chloromethyl-10-methylphenanthrene. These products presumably arise by the reactions shown.

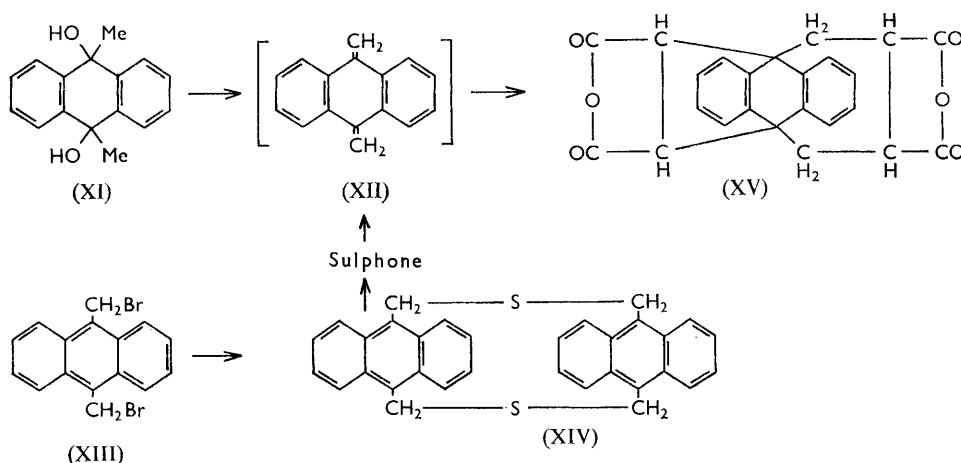


We have also applied the dehydration to *cis*-9,10-dihydro-9,10-dimethylantracene-9,10-diol (XI), a vinylogue of a vicinal diol. The primary product in this case is apparently 9,10-anthraquinodimethane (9,10-dihydro-9,10-dimethyleneanthracene) (XII) since, in the presence of maleic anhydride, the isolated product was an adduct (presumably XV) whose composition corresponded to two maleic anhydride residues per anthracene nucleus. In the absence of maleic anhydride, polymer resulted. A similar or identical adduct was

<sup>9</sup> Millar and Wilson, *Proc. Chem. Soc.*, 1963, 217.

<sup>10</sup> Cava and Shirley, *J. Amer. Chem. Soc.*, 1960, **82**, 654; Cava, Shirley, and Erickson, *J. Org. Chem.*, 1962, **27**, 755.

obtained by Golden<sup>11</sup> by heating tetrabenz-[2,2]-paracyclophane [bi(anthracene-9,10-dimethylene)] with maleic anhydride in benzene. We found that the adduct was also formed when the paracyclophane was heated with maleic anhydride at 350° in boiling diethyl phthalate, a temperature much above that at which polymerization of the paracyclophane occurs.<sup>11</sup> These observations suggest that the adduct is formed through the



9,10-anthraquinodimethane only in reactions at high temperature, and that its formation in benzene solution does not involve this intermediate.

It is of interest that Tardieu<sup>12</sup> failed to obtain 9,10-anthraquinodimethane by the dehydration of 9,10-dihydro-9,10-bishydroxymethylanthracene, although he obtained evidence that the quinodimethane is formed by the action of strong base on the dimethane-sulphonate of the *cis*- or *trans*-diol.

9,10-Bisbromomethylanthracene (XIII) gave, with dry ethanolic sodium sulphide, a 36% yield of an organic sulphide. El-Hewehi and Runge<sup>13</sup> obtained an apparently identical product in 5% yield from 9,10-bischloromethylanthracene and potassium trithiocarbonate, but formulates it as 9,10-(methanothiomethano)anthracene. The latter structure appears most unlikely stereochemically, and determination of molecular weight shows that our sulphide is bi(anthracene-9,10-dimethylene) disulphide (XIV). In both these reactions the major product is a compound,  $C_{32}H_{24}S_3$ , considered by El-Hewehi and Runge<sup>13</sup> to be a cyclic sulphide, as (XIV) but having a disulphide group in place of one sulphur atom.

Oxidation of the sulphide (XIV) to the corresponding sulphone and thermal decomposition of the latter in boiling diethyl phthalate containing maleic anhydride, gave an adduct identical with that described above, indicating that this thermal decomposition also yields 9,10-anthraquinodimethane (XII).

## EXPERIMENTAL

Compounds are colourless unless otherwise described. Melting points were determined on a Kofler hot-stage apparatus, and ultraviolet and infrared spectra on a Unicam S.P. 700 and a Perkin-Elmer Infracord spectrophotometer, respectively.

9-Chloromethyl-10-methylphenanthrene (IV).—(a) 9,10-Dihydro-9,10-dimethylphenanthrene-9,10-diol<sup>5</sup> (29 g.), suspended in dry ether (175 ml.), and thionyl chloride (55 g.) were stirred at

<sup>11</sup> Golden, *J.*, 1961, 3741.

<sup>12</sup> Tardieu, *Compt. rend.*, 1959, **248**, 2885.

<sup>13</sup> El-Hewehi and Runge, *J. prakt. Chem.*, 1959, **9**, 33.

30° for 10 hr. The ether was removed under reduced pressure on a steam-bath until vigorous evolution of hydrogen chloride commenced; heating was continued for  $\frac{1}{2}$  hr., or until the gas evolution ceased. The residue was boiled with ethyl acetate (220 ml.) and charcoal, filtered, and the filtrate evaporated, to give a residue which was crystallized from ethyl acetate–light petroleum (b. p. 60–80°) or from benzene–light petroleum (20 g., 70%), m. p. 154·5–155·5° (lit.,<sup>5</sup> 155–156°).

(b) 9-Methylphenanthrene (19·2 g.) was added to a mixture of acetic acid (75 ml.), hydrochloric acid (*d* 1·18; 40 ml.), phosphoric acid (*d* 1·7; 8 ml.), and paraformaldehyde (5·5 g.), which had previously been stirred at 60° while hydrogen chloride was passed through for 3 hr., and cooled to 20°. The complete mixture was heated to 60° during 3 hr., to 70° in the ensuing 4 hr., and finally on a steam-bath for 2 hr. The cooled mixture was extracted with chloroform and the extracts were washed with aqueous sodium hydrogen carbonate and with water, dried, and evaporated; the product (15 g., 63%) crystallized from benzene–light petroleum (b. p. 40–60°), m. p. 155·5°.

*Trimethyl-10-methyl-9-phenanthrylmethylammonium Hydroxide* (V; X = OH).—Dry trimethylamine was passed into a solution of 9-chloromethyl-10-methylphenanthrene (2 g.) in chloroform (50 ml.) and methanol (150 ml.). After boiling for 1 hr. under reflux, the solvents were removed and the residue was dissolved in the minimum of absolute ethanol. Dilution with ether precipitated the very hygroscopic chloride (V; X = Cl). A sample in ethanol with aqueous sodium picrate gave the corresponding *picrate*, yellow crystals, m. p. 222–224° (decomp.) (Found: C, 59·9; H, 4·9; N, 11·1.  $C_{25}H_{25}N_4O_7 \cdot \frac{1}{2}H_2O$  requires C, 59·9; H, 5·2; N, 11·15%). Another sample of the chloride (0·5 g.) passed in ethanol solution through a column (25 × 1·5 cm.) of Amberlite IRA-400 (Br<sup>−</sup>) resin, gave a quantitative yield of the bromide (V; X = Br), m. p. 222–224° (from ethanol) (lit.,<sup>5</sup> 223–225°).

The chloride (1 g.) in ethanol (60 ml.) was passed through a column (40 × 2 cm.) of Amberlite IRA-400 resin previously washed with aqueous potassium hydroxide and with ethanol. The eluate was evaporated below room temperature in a rotary evaporator, yielding long needles of the hydroxide.

*Thermal Decomposition of the Hydroxide* (V; X = OH).—(a) The hydroxide, on warming to room temperature, decomposed with liberation of trimethylamine; the addition of a little water then precipitated amorphous polymer and crystals of the spiro-dimer, m. p. 249–250° (lit.,<sup>5</sup> 252–253°), identified from its infrared and ultraviolet spectra.

(b) A 1% solution of the hydroxide in ethanol was dropped into a “hot” flask at 100°, at such a rate that the flask was dry between the addition of drops. The pressure in the apparatus was held at *ca.* 25 mm. of nitrogen; it was connected to a trap at −78°, in which ethanol and decomposition products collected. This condensate, mixed with a cooled solution of hydrogen chloride in ether, gave, after evaporation, 9-chloromethyl-10-methylphenanthrene identified by m. p., mixed m. p., and ultraviolet spectrum. The bulk of the reaction product remained in the “hot” flask, and consisted of a mixture of the spiro-dimer (extractable by acetone) and polymer. The *polymer* could be partly purified by dissolution in benzene and precipitation with ethanol, but it then retained benzene tenaciously [Found: C, 93·05; H, 6·4.  $(C_{16}H_{12})_n$  requires C, 94·05; H, 5·9%]. It was a plastic solid, not melting below 350°.

In experiments in which the “hot” flask was kept at temperatures up to 210°, similar results were obtained.

*Attempted Acetylation of 9,10-Dihydro-9,10-dimethylphenanthrene-9,10-diol*.—The diol (I) (1 g.), in acetic anhydride (10 ml.) and sulphuric acid (0·4 ml.), was shaken at room temperature for 12 hr. The precipitated product (0·6 g.) was collected, washed with water, and dried. Extraction with benzene left a residue (0·15 g.), insoluble in common organic solvents and apparently polymeric (m. p. >350°) (Found: C, 90·75; H, 5·7%). The extract was chromatographed on alumina in benzene, giving crystals of the *diether* (VI; *n* = 1), m. p. 284–286° (from benzene) [Found: C, 89·9; H, 6·3%; *M* (Rast), 600.  $C_{48}H_{40}O_2$  requires C, 89·3; H, 6·2%; *M*, 648]. The infrared spectra of both compounds were simple and identical; both showed absorption characteristic of four adjacent aromatic CH groups. The ultraviolet spectra in dioxan were almost identical, and showed the typical form of the phenanthrene chromophore. In an experiment in which perchloric acid was used in place of sulphuric acid, similar results were obtained but yields of both compounds were much lower.

*Dehydration of the Diol* (I).—A solution of the diol (0·7 g.) and maleic anhydride (0·4 g.) in diethyl phthalate (1·5 ml.) was boiled gently for 5 min., cooled, and triturated with ether

to precipitate 1,2,3,4-tetrahydrotriphenylene-2,3-dicarboxylic anhydride (VII) (0.25 g.).\* Recrystallization from benzene and sublimation at  $165\text{--}170^\circ/6 \times 10^{-4}$  mm. gave needles, m. p.  $301\text{--}302^\circ$  (Found: C, 77.75; H, 4.25.  $\text{C}_{20}\text{H}_{12}\text{O}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  requires C, 77.6; H, 4.25%). The yield was not significantly increased by the addition of alumina; dehydration in the absence of maleic anhydride gave polymeric phenanthraquinodimethane, identified from its infrared spectrum. Dehydration did not occur when the diol was boiled in glacial acetic acid for 15 min.

The anhydride (0.042 g.) and 10% palladium-carbon (0.1 g.) were mixed and covered with more palladium-carbon. The mixture was heated slowly to  $360^\circ$  in a nitrogen atmosphere and maintained at  $360^\circ$  for 30 min. The cooled residue was ground with soda-lime (0.1 g.) and covered with more soda-lime (0.1 g.). The mixture was heated slowly to  $360^\circ$  under nitrogen, this temperature being maintained for 45 min. The residue was extracted with hot benzene (25 ml.) and the benzene evaporated, leaving a trace of triphenylene (VIII), m. p.  $193\text{--}197^\circ$ , identified from its ultraviolet spectrum.

**1,3-Dihydrophenanthro[9,10-c]thiophen** (as IX).—To a solution of 9,10-bisbromomethylphenanthrene <sup>14</sup> (4 g.) in dioxan (100 ml.) was added a solution of sodium sulphide (excess), prepared by half-saturating at  $0^\circ$  with hydrogen sulphide a solution prepared by dissolving sodium (2 g.) in absolute ethanol (80 ml.). The complete mixture was boiled under reflux for 15 hr., diluted with water (20 ml.), chilled in ice, and the solid filtered off, washed with water, and dried (2.3 g.). This product was pure enough for conversion into the sulphone. A sample twice recrystallized from acetone gave the pale yellow compound, m. p.  $202\text{--}205^\circ$  (Found: C, 77.7; H, 5.6.  $\text{C}_{18}\text{H}_{12}\text{S} \cdot \frac{1}{2}\text{H}_2\text{O}$  requires C, 78.2; H, 5.4%).

**1,3-Dihydrophenanthro[9,10-c]thiophen 1,1-Dioxide** (IX).—A cooled mixture of freshly prepared peracetic acid (40%; 25 ml.) and acetic acid (20 ml.) was added to a stirred suspension of the above thiophen (2.3 g.) in acetic acid (20 ml.) at  $15\text{--}20^\circ$ . The mixture was stirred at this temperature for 12 hr., diluted with water (20 ml.), and kept at  $0^\circ$  for 2 days before the crude crystalline compound (2.05 g., 79%) was filtered off, m. p.  $258\text{--}260^\circ$  (decomp.). It was insoluble in common organic solvents and decomposed in high-boiling solvents (Found: C, 70.9; H, 4.7; S, 12.4.  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{S}$  requires C, 71.6; H, 4.5; S, 12.0%)  $\nu_{\text{max}}$ . 1300 (S=O symmetric stretching), 1110 (S=O asymmetric stretching), and 751 and 791  $\text{cm}^{-1}$  (four adjacent aromatic CH).

**Thermal Decomposition of the Dioxide** (IX).—The dioxide (0.2 g.) was boiled in diethyl phthalate (1 ml.) until evolution of sulphur dioxide ceased ( $1\frac{1}{2}$  hr.). The cooled mixture was mixed with ether and the solid collected, washed with ether, and dried (0.1 g.), m. p.  $>350^\circ$ , identified as 9,10-phenanthraquinodimethane polymer from its infrared spectrum.

A mixture of the dioxide (1 g.) and maleic anhydride (0.55 g., 1.5 moles) in diethyl phthalate (3.2 ml.) was boiled for  $1\frac{1}{2}$  hr., during which time it became homogeneous. The cooled mixture was mixed with ether, to precipitate 1,2,3,4-tetrahydrotriphenylene-2,3-dicarboxylic anhydride (0.7 g., 65%), m. p.  $301\text{--}302^\circ$  (after sublimation at  $165\text{--}170^\circ/6 \times 10^{-4}$  mm.), identical with a sample obtained from the diol (I) as described above.

**Reaction of 9,10-Bischloromethylphenanthrene with Magnesium**.—The dichloride <sup>14</sup> (1 g.) in benzene (60 ml.), and ether or tetrahydrofuran (60 ml.), was added to magnesium (0.18 g., 2 equiv.) and ether (5 ml.) under nitrogen. The mixture was boiled and stirred under reflux for 7 hr., reaction being initiated by addition of a little iodine or methyl iodide. The ether was removed, benzene (300 ml.) added to dissolve solids, and the solution decanted from the excess of magnesium (0.087 g., 1 equiv.). The solution was concentrated, ether (300 ml.) added, and the resulting precipitate collected (0.48 g.), washed with hot water and with methanol, dissolved in benzene, filtered, and reprecipitated by addition of methanol. Hot acetone then extracted a trace of 9-chloromethyl-10-methylphenanthrene, identified from its ultraviolet spectrum; the residue, insoluble in acetone, was dissolved in benzene and reprecipitated by methanol; the resulting ether (X;  $n = 2$ ) had m. p.  $>350^\circ$  (Found: C, 88.7; H, 5.85.  $\text{C}_{64}\text{H}_{50}\text{O}_3$  requires C, 88.65; H, 5.8%).

**9,10-Dimethylantracene**.—9,10-Bischloromethylantracene <sup>15</sup> (22 g.) in purified tetrahydrofuran (350 ml.) was stirred and boiled under reflux under nitrogen with lithium

\* Added in proof: In a recent paper by Stille and Foster (*J. Org. Chem.*, 1963, **28**, 2708) this and some other compounds now reported are described.

<sup>14</sup> Hauptmann, *Chem. Ber.*, 1960, **93**, 2604.

<sup>15</sup> Moshchinskaya and Ogii, *Chem. Abs.*, 1962, **57**, 7189.

aluminium hydride (7 g.) for 24 hr. The mixture was hydrolysed by the addition of aqueous ethyl acetate, and the solid filtered off and extracted with benzene. The combined organic extracts were evaporated; the resulting crude solid (13.4 g., 82%) had m. p. 180—182°. Recrystallisation from ethanol gave the pale yellow compound, m. p. 181° (lit.,<sup>16</sup> 180—181°).

9,10-Dimethylphenanthrene was prepared similarly.

9,10-Bisbromomethylanthracene (XIII).—This was prepared as described by Golden,<sup>11</sup> or by adding bromine (16 g.) in carbon tetrachloride (75 ml.) to 9,10-dimethylanthracene (10 g.) in carbon tetrachloride (500 ml.) containing benzoyl peroxide (250 mg.). The mixture was boiled under reflux and illuminated by a 500w tungsten lamp for 9 hr., with further addition of the peroxide (250 mg.), cooled in ice, and the solid filtered off (15 g., 85%), yellow crystals, m. p. >340° (from chloroform) (lit.,<sup>11</sup> >300°), infrared spectrum identical with that of a sample prepared by Golden's method.<sup>11</sup>

Bi(anthracene-9,10-dimethylene) Disulphide (XIV).—A solution of sodium sulphide, prepared by half-saturating a solution from sodium (5 g.) in ethanol (200 ml.) with hydrogen sulphide at 0°, was added to 9,10-bisbromomethylanthracene (10 g.) in dioxan (500 ml.), and the mixture boiled and stirred under reflux for 17 hr., diluted with water (200 ml.), and cooled. The solid was collected and washed with hot water, and the residue of sulphides extracted (Soxhlet) with tetrahydrofuran (200 ml.). The extract was evaporated to 50 ml. and ethanol added to precipitate the sulphide (XIV) (2.5 g., 36%), m. p. 255—260°. Percolation of a solution in methylene chloride through neutral alumina, and evaporation, gave the pale yellow compound, m. p. 272—274° (decomp.) (lit.,<sup>13</sup> 266°) [Found: C, 81.25; H, 5.15%; *M* (Rast), 500. Calc. for C<sub>32</sub>H<sub>24</sub>S<sub>2</sub>: C, 81.3; H, 5.1%; *M*, 470]. The residue insoluble in tetrahydrofuran (4.5 g.) was recrystallized from ethanolic dimethylformamide, to give the trisulphide, m. p. 220—222° (lit.,<sup>13</sup> 222°).

Bi(anthracene-9,10-dimethylene) Disulphone (as XIV).—A suspension of the sulphide (2.0 g.), in acetic acid (60 ml.) and peracetic acid (40%; 20 ml.), was stirred at 15—20° for 48 hr. Dilution with water (25 ml.) and cooling deposited the corresponding *sulphone* (1.7 g., 76%), pale yellow needles, m. p. >300°. The infrared spectrum was in accord with the assigned structure. No suitable solvent for recrystallization was found (Found: S, 11.7. C<sub>32</sub>H<sub>24</sub>O<sub>4</sub>S<sub>3</sub> requires S, 12.0%).

Thermal Decomposition of the Sulphone.—The sulphone (0.9 g.) with maleic anhydride (0.5 g.) was boiled in diethyl phthalate (2.5 ml.) for 15 min.; the mixture was cooled, mixed with ether, and the solid collected (0.7 g., 70%), m. p. >350°, infrared spectrum identical with that of a specimen of the adduct formed from tetrabenzo-[2,2]-paracyclophane and maleic anhydride, prepared by Golden's method.<sup>11</sup> This adduct was also formed if the paracyclophane (1 g.) and maleic anhydride (0.75 g.) were boiled in diethyl phthalate (3 ml.) for 10 min. (yield, 1.15 g.).

Dehydration of *cis*-9,10-Dihydro-9,10-dimethylanthracene-9,10-diol (XI).—(a) The diol<sup>17</sup> (1 g.) was boiled under reflux in benzene (7 ml.) for 10 min. The crystalline residue was washed with ether, leaving a trace of an amorphous solid, m. p. >350°, having an infrared spectrum identical with that of polymeric 9,10-anthraquinodimethane prepared by heating tetrabenzo-[2,2]-paracyclophane as described by Golden.<sup>11</sup>

(b) The diol (1 g.) and maleic anhydride (0.5 g.), in diethyl phthalate (2.5 ml.), were boiled for 10 min., cooled, and ether added, to give the adduct (0.75 g.) having an infrared spectrum identical with that of a sample prepared as described above.

We are indebted to Unilever Ltd. for a Research Studentship (to K. V. W.), and to Dr. F. G. Mann, F.R.S., for helpful discussions.

DEPARTMENT OF CHEMISTRY,  
THE UNIVERSITY, KEELE, STAFFORDSHIRE.

[Received, September 10th, 1963.]

<sup>16</sup> Gibson and Johnson, *J.*, 1931, 753.

<sup>17</sup> Beckett and Lingard, *J.*, 1961, 588.