

Substituted Anthracene Derivatives. Part VII. An Examination of Some Naphthacene endoOxide Derivatives.*

By G. M. BADGER, R. S. PEARCE, H. J. RODDA, and I. S. WALKER.

[Reprint Order No. 5212.]

Several compounds with postulated structures (*e.g.*, IV, V, VI) involving transannular mono-oxide bridges have been examined.

Bergmann's compound (supposedly VI) has been identified as *o*-dibenzoylbenzene.

It has been confirmed that the original rubrene skeleton (I) is retained in rubrene mono-oxide (IV) and that the three oxides of rubrene have similar absorption spectra. On the other hand, the original rubrene skeleton is not present in rubrene *isooxide*, for it is reduced by iron and acetic acid to the phenoxytriphenylnaphthacene (XIV). Other degradations of rubrene *isooxide* have also been investigated and the structure (X) is now proposed for this substance. Tetra-*p*-tolyl-naphthacene *isooxide* ("tetramethylrubrene *isooxide*") has been synthesised and reduced with magnesium and methylmagnesium iodide to 5 : 6 : 11-tri-*p*-tolyl-naphthacene and *p*-cresol.

THE bright red hydrocarbon rubrene (5 : 6 : 11 : 12-tetraphenylnaphthacene) (I; Ar = Ph) forms three oxides. When irradiated in the presence of molecular oxygen, it forms a photo-oxide having a transannular peroxide structure (II; Ar = Ph) (Dufraisse, *Bull. Soc. chim.*,

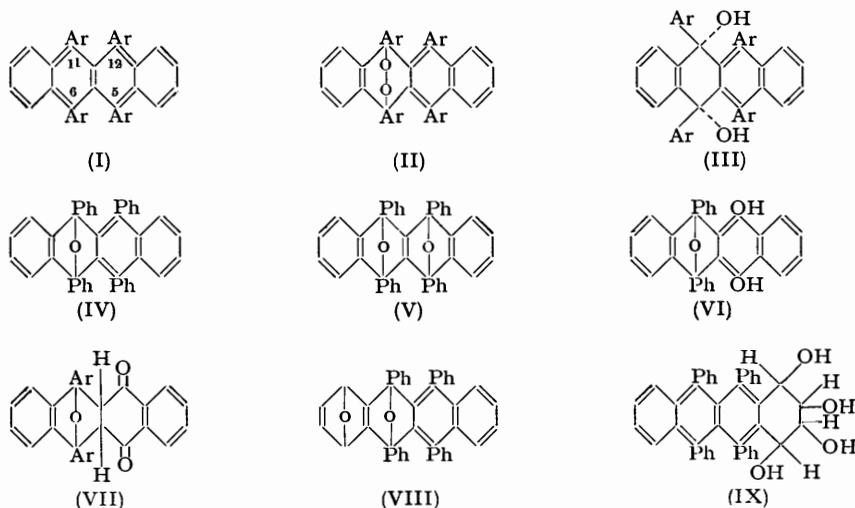
* Part VI, *J.*, 1952, 1175.

1939, 6, 422). This structure seems to be established, more especially by the observation that the photo-oxide is reduced, on catalytic hydrogenation, to the *cis*-diol (III; Ar = Ph) (Dufraisse and Houpillart, *Compt. rend.*, 1937, 205, 740). When rubrene is oxidised with dilute nitric acid or with certain other oxidising agents, however, a mono-oxide is formed (Moureu, Dufraisse, and Enderlin, *ibid.*, 1929, 188, 1528), which is also obtained by reduction of the photo-oxide with zinc and acetic acid (Dufraisse and Enderlin, *Bull. Soc. chim.*, 1932, 51, 132) and by thermal dehydration of the *cis*-diol (III; Ar = Ph) (Enderlin, *Ann. Chim.*, 1938, 10, 5). The endocyclic mono-oxide structure (IV) has been proposed for this substance (Enderlin, *loc. cit.*; *Compt. rend.*, 1936, 202, 669). Similar mono-oxides have been obtained from rubrene derivatives (Enderlin, *loc. cit.*), but it is noteworthy that no such oxide of 9 : 10-diphenylanthracene could be obtained by direct oxidation, by partial reduction of the photo-oxide, or by thermal dehydration of the 9 : 10-diol (Dufraisse and Le Bras, *Bull. Soc. chim.*, 1937, 4, 349, 1037).

The *isooxide* of rubrene is obtained by isomerisation of the photo-oxide with magnesium iodide (Dufraisse and Badoche, *Compt. rend.*, 1930, 191, 104). The structure (V) was proposed for this (Enderlin, *loc. cit.*, 1938; *Compt. rend.*, 1936, 203, 192) and received some support from the facts that such isomerisations are known only in the *meso*-tetra-aryl-naphthacene series, and that 9 : 10-diphenylanthracene photo-oxide does not isomerise (Dufraisse and Le Bras, *Bull. Soc. chim.*, 1937, 4, 349).

It has already been pointed out (Badger and Pearce, *J.*, 1950, 2311) that although transannular dioxides (such as II) are little strained (see also Dufraisse, *loc. cit.*, 1939), a mono-oxide bridge as in (IV or V) involves considerable distortion of the normal valency angles for oxygen and carbon and of the normal oxygen-carbon bond length. For this reason, it was thought desirable to re-investigate the oxides of rubrene and its derivatives. As part of the same investigation, the supposed transannular mono-oxide (VI) obtained by Bergmann (*J.*, 1938, 1147) has also been re-examined.

Bergmann obtained the Diels-Alder adduct (VII; Ar = Ph) from 1 : 4-naphthaquinone and 1 : 3-diphenylisobenzofuran, and treated this with hydrobromic acid in acetic acid. Part of the material was dehydrated to the known 6 : 11-diphenylanthracene-5 : 12-quinone (XIII); but a colourless compound was also obtained. From the analytical figures, and by analogy with some work of Diels, Alder, and Stein (*Ber.*, 1929, 62, 2337),



Bergmann concluded that some of the adduct had enolised, and he therefore assigned the structure (VI) to his product. It has now been found, however, that the colourless substance obtained in this way is far too stable to have the structure indicated, and it has been identified as *o*-dibenzoylbenzene. The Diels-Alder reaction is, of course, reversible, and

the *o*-dibenzoylbenzene is probably formed by aerial oxidation of the diphenylisobenzofuran which is obtained by partial dissociation of the adduct into its components.

However, the (other) three rubrene oxides are undoubtedly derivatives of naphthacene, and their properties are known in some detail (Dufraisse, *loc. cit.*, 1939; Enderlin, *loc. cit.*, 1938).

For example, rubrene mono-oxide is reduced to rubrene by iron and acetic acid (Moureu *et al.*, and Dufraisse and Enderlin, *loc. cit.*) and by methylmagnesium iodide and excess of magnesium (present work). Moreover, it showed no hydroxyl absorption in the infra-red. The structure (IV) therefore seems to be established in spite of the steric distortion.

Enderlin's structure (V) for the *isooxide* can be quickly dismissed, for the absorption spectrum of the *isooxide* is almost identical with that of rubrene mono-oxide and of rubrene photo-oxide (Fig. 1), indicating that the three compounds have the same chromophore. While this work was in progress, the same conclusion was reached by Gillet (*Compt. rend.*, 1949, 229, 936; *Bull. Soc. chim.*, 1950, 17, 1141), who also pointed out that all three spectra resemble that of 1 : 4-diphenylnaphthalene. Gillet concluded that this conjugated system must be present in all three rubrene oxides : he proposed structure (VIII) for the *isooxide*. This also seems to be erroneous : it includes an unhindered ethylenic double bond and would therefore be expected to show the usual double-bond reactivity, but in fact, rubrene *isooxide* does not react with osmium tetroxide under the usual conditions. Rubrene mono-oxide and photo-oxide are also unreactive towards osmium tetroxide, but rubrene itself behaves as an ordinary reactive aromatic hydrocarbon (such as anthracene; see Cook and Schoental, *Nature*, 1948, 161, 237). Osmium tetroxide added to the 1 : 2- and 3 : 4-bonds, for 1 : 2 : 3 : 4-tetrahydro-1 : 2 : 3 : 4-tetrahydroxyrubrene (IX) was isolated after hydrolysis of the complex. The structure of this tetrol is confirmed by its absorption spectrum, which is of the general "anthracene" type.

When the *isooxide* is treated with a large excess of magnesium and methylmagnesium iodide, 5 : 6 : 11-triphenylnaphthacene (XI) and phenol are obtained in almost quantitative yield (Dufraisse and Badoche, *Compt. rend.*, 1931, 193, 242; Badoche, *Bull. Soc. chim.*, 1936, 3, 2040). This suggests that the two oxygen atoms are not bound in the same way. This reaction has been confirmed, and the structure of the triphenylnaphthacene (XI) established unequivocally by synthesis. For this purpose diphenylnaphthacenequinone (XIII) was reduced to the diphenylbenzanthrone (XII), which by treatment with phenylmagnesium bromide and subsequent dehydration gave 5 : 6 : 11-triphenylnaphthacene (XI).

To be able to perform this degradation on the *isooxide* of a rubrene derivative having substituents in the four phenyl rings, the synthesis of 5 : 6 : 11 : 12-tetra-*p*-tolyl naphthacene (I; Ar = *p*-tolyl) was undertaken. 1 : 4-Naphthaquinone and 1 : 3-di-*p*-tolylisobenzofuran, gave the adduct (VII; Ar = *p*-tolyl), which was then dehydrated with ice-cold sulphuric acid to 6 : 11-di-*p*-tolyl naphthacene-5 : 12-quinone (cf. Bergmann, *loc. cit.*; Dufraisse and Compagnon, *Compt. rend.*, 1938, 207, 585). This with *p*-tolyl-lithium gave the *cis*-diol (III; Ar = *p*-tolyl), which was reduced with iron and acetic acid to the desired "tetramethylrubrene" (I; Ar = *p*-tolyl) (cf. Allen and Gilman, *J. Amer. Chem. Soc.*, 1936, 58, 937; Dufraisse and Velluz, *Compt. rend.*, 1935, 201, 1394; *Bull. Soc. chim.*, 1936, 3, 1905). It is of interest that an attempt to dehydrate the *cis*-diol by heat in *vacuo* resulted only in isomerisation, the *trans*-diol being obtained. The new derivative has a visible absorption spectrum almost identical with that of rubrene (cf. Badger and Pearce, *Spectrochim. Acta*, 1951, 4, 280) except that the intense band in the ultra-violet is at a longer wavelength. The photo-oxide (II; Ar = *p*-tolyl) was obtained in the usual way, and on isomerisation with magnesium iodide gave the *isooxide*, the absorption spectrum of which was almost identical with that of rubrene *isooxide* (cf. Fig. 1).

When tetra-*p*-tolyl naphthacene *isooxide* was reduced with excess of magnesium and methylmagnesium iodide, 5 : 6 : 11-tri-*p*-tolyl naphthacene was obtained, together with *p*-cresol. This isolation of the *p*- rather than of *m*-cresol excludes the possibility that the *isooxides* contain an oxygen bridge between the 11 (or 12)-position and a position in a phenyl group which is *meta* to the methyl substituent. The absorption spectrum of the tri-*p*-tolyl naphthacene was similar to that of triphenylnaphthacene (see Table; cf. Badoche, *loc. cit.*).

A hydroperoxide structure for the *isooxides* would account for the observed results in this reaction ; but rubrene *isooxide* shows none of the reactions of a hydroperoxide. It is stable to heat, contains no active hydrogen, and has no hydroxyl absorption in the infra-red.

The reducing action of magnesium and methylmagnesium iodide is identical with that of the Gomberg-Bachmann reagent ($\text{Mg} + \text{MgI}_2$), for dissociation occurs according to the equations, $2\text{MeMgI} + \text{Mg} \rightleftharpoons \text{Me}_2\text{Mg} + \text{MgI}_2 + \text{Mg} \rightleftharpoons \text{Me}_2\text{Mg} + 2\text{MgI}$ (Allen and Bell, *J. Amer. Chem. Soc.*, 1940, **62**, 2408; Kharasch and Weinhouse, *J. Org. Chem.*, 1936, **1**, 209; Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 236, 2548; 1928, **50**, 2762). It is very unlikely that this reagent could bring about the fission of a carbon-carbon bond. The reduction of the *isooxides* to triarylnaphthacene and a phenol therefore seems to indicate that the *isooxide* contains a phenoxy-group, and this has been confirmed by the finding that cold concentrated sulphuric acid, or fusion with potassium hydroxide converts rubrene *isooxide* into phenol and the triphenylbenzanthrone (XVII). The structure of this product

FIG. 1. Absorption spectra of rubrene mono-oxide (—), *isooxide* (.....), and photo-oxide (-----), in ethanol.

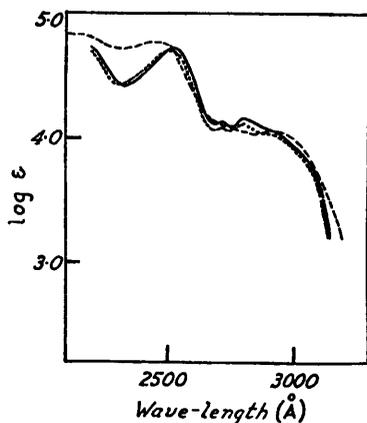
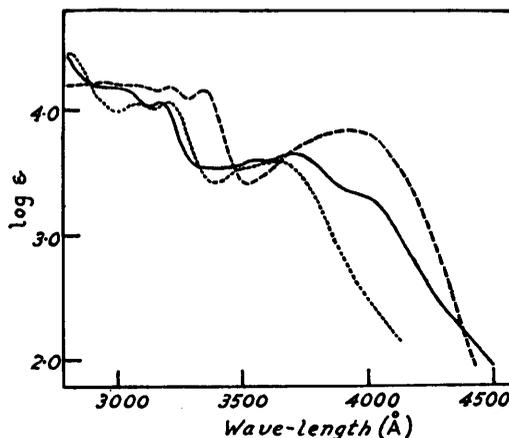


FIG. 2. Absorption spectra of (—) diphenylbenzanthrone (XII), (-----) triphenylbenzanthrone (XVII), and (.....) hydroxytriphenylbenzanthrone (XV), in benzene.



is supported by its absorption spectrum (Fig. 2), which is very similar to that of the diphenylbenzanthrone (XII).

Reduction of rubrene *isooxide* with iron and acetic acid gave a compound which had the same appearance and m. p. as rubrene and gave no m. p. depression when mixed with it (cf. Enderlin, *loc. cit.*, 1938; Dufraisse and Badoche, *loc. cit.*, 1930). However, its empirical formula was $\text{C}_{42}\text{H}_{28}\text{O}$. Its absorption spectrum (see Table) was almost identical

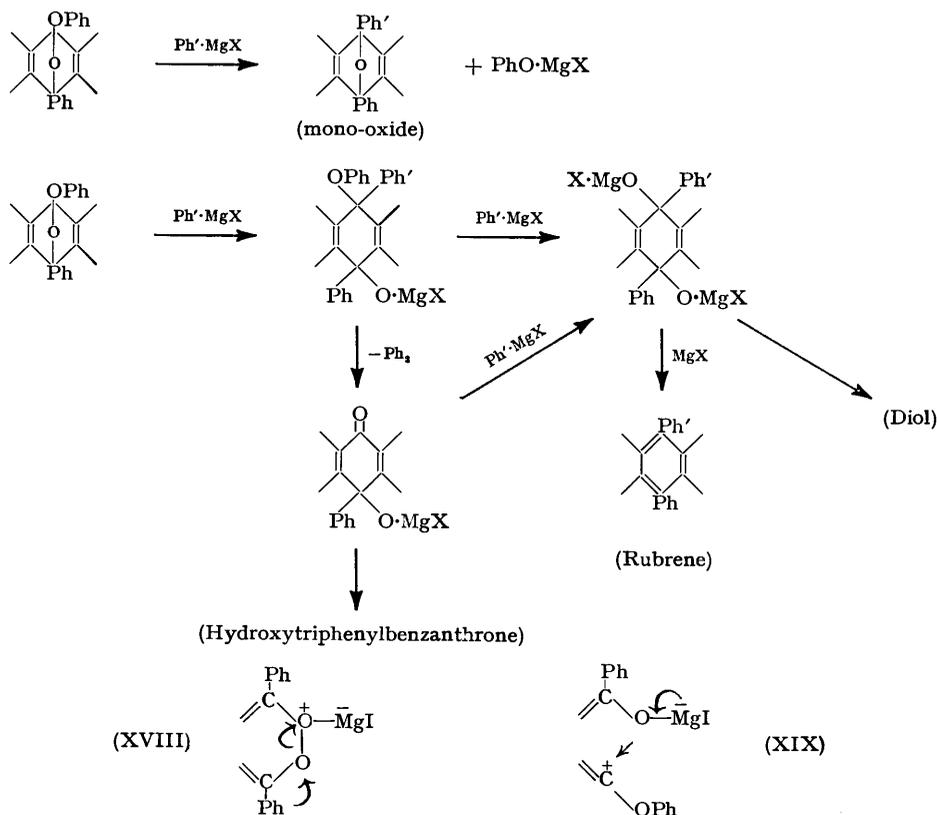
Absorption maxima (Å) and intensities (log ε) (in parentheses) of naphthacene derivatives in benzene.

	Band : *	A	C	D	E
Rubrene		3030 (5.07)	4650 (3.79)	4950 (4.07)	5300 (4.08)
5 : 6 : 11 : 12-Tetra- <i>p</i> -tolyl-naphthacene		3040 (5.12)	4640 (3.79)	4940 (4.07)	5300 (4.11)
5 : 6 : 11-Triphenyl-naphthacene (XI)		2950 (5.02)	4450 (3.64)	4730 (3.93)	5050 (4.06)
5 : 6 : 11-Tri- <i>p</i> -tolyl-naphthacene		2960 (5.06)	4450 (3.75)	4730 (4.05)	5060 (4.10)
5-Phenoxy-6 : 11 : 12-triphenyl-naphthacene (XIV) ...		2990 (5.04)	4600 (3.77)	4900 (4.05)	5250 (4.08)

* The nomenclature is that used by Badger and Pearce (*Spectrochim. Acta*, 1951, **4**, 280).

with that of rubrene, except that the absorption bands were shifted about 50 Å to shorter wave-lengths. It showed no hydroxyl absorption in the infra-red. It must therefore be 5-phenoxy-6 : 11 : 12-triphenyl-naphthacene (XIV). On oxidation with hot dilute nitric acid, or with cold dilute permanganate, it gave the hydroxytriphenylbenzanthrone

positive charge so that cyclisation occurs (see XIX) to give the isooxide (X) with liberation of the magnesium, and re-formation of the magnesium iodide.



EXPERIMENTAL

Bergmann's Compound.—The Diels–Alder adduct was obtained from 1 : 3-diphenylisobenzofuran and 1 : 4-naphthaquinone, and after treatment with acetic and hydrobromic acid at 37° for 2 days, two products were isolated as described by Bergmann (*loc. cit.*). One was identified as the known yellow diphenylnaphthacenequinone in agreement with Bergmann, and the second was obtained in colourless needles, m. p. 149—150° (Bergmann gives m. p. 150°).

The colourless product dissolved in cold concentrated sulphuric giving a red colour, and was recovered unchanged on dilution with water. It was recovered unchanged after attempted oxidation with chromic acid in glacial acetic acid. On refluxing with zinc and acetic acid, the solution became yellow and exhibited an intense bluish-green fluorescence identical with that given by 1 : 3-diphenylisobenzofuran. The mixed m. p. with *o*-dibenzoylbenzene showed no depression, and the substance was further characterised by the formation of 1 : 4-diphenylphthalazine, m. p. and mixed m. p. 192°, from hydrazine hydrate in boiling alcohol. Bergmann's analytical figures agree with those for *o*-dibenzoylbenzene (Found : C, 83.9; H, 4.9. Calc. for C₂₀H₂₄O₂ : C, 83.9; H, 4.9%).

Reduction of Rubrene Mono-oxide with Magnesium and Methylmagnesium Iodide.—Rubrene mono-oxide (500 mg.) was shaken for 8 days with the Grignard reagent, prepared from magnesium (4 g.), methyl iodide (8 g.) and ether (50 c.c.). The resulting dark solution was poured on cracked ice, and the mixture steam-distilled. The distillate contained no phenol. The red residue was extracted from the aqueous suspension with benzene, and after drying and evaporation to small volume this deposited red crystals of rubrene, identified by m. p. and absorption spectrum.

*Addition of 1 : 3-Di-*p*-tolylisobenzofuran to 1 : 4-Naphthaquinone.*—An intimate mixture of

1 : 3-di-*p*-tolylisobenzofuran (23.6 g.; Guyot and Vallette, *Ann. Chim.*, 1911, **23**, 363) and 1 : 4-naphthaquinone (12.5 g.) was moistened with chloroform. The mixture immediately became black, but after a few minutes white. A little ether was then added. After 1 hr. the solid was collected and recrystallised from ethyl acetate. The adduct (30 g., 86%) formed colourless flat rectangular crystals, m. p. 163° (Found : C, 84.4; H, 5.3. $C_{32}H_{24}O_3$ requires C, 84.2; H, 5.3%).

6 : 11-Di-*p*-tolyl-naphthacene-5 : 12-quinone.—The adduct (27 g.) was dissolved in concentrated sulphuric acid (150 c.c.) at -10° , and set aside for 1 hr. The solution was then poured on cracked ice, and the excess of acid neutralised with aqueous alkali; this also flocculated the quinone. After recrystallisation from ethyl acetate, 6 : 11-di-*p*-tolyl-naphthacene-5 : 12-quinone (15 g., 58%) formed lemon-yellow needles, m. p. 288° (Found : C, 87.3; H, 4.9. $C_{32}H_{22}O_2$ requires C, 87.6; H, 5.1%).

cis-5 : 12-Dihydro-5 : 12-dihydroxy-5 : 6 : 11 : 12-tetra-*p*-tolyl-naphthacene.—A solution of *p*-tolyl-lithium, prepared from *p*-bromotoluene (61 g.), lithium (6 g.) and ether (1 l.) and filtered under nitrogen pressure, was refluxed, the returning liquid dropping on to 6 : 11-di-*p*-tolyl-naphthacene-5 : 12-quinone (13 g.) in a Soxhlet thimble (cf. Bachmann and Chemerda, *J. Org. Chem.*, 1939, **4**, 583). After 9½ hr., all the quinone had dissolved. Heating was continued for a further 2½ hr., and the mixture then poured on 1½ kg. of cracked ice. The ether layer was separated, filtered, dried, and evaporated to small volume, whereupon the crystalline diol separated. After recrystallisation from benzene, it formed colourless prisms (15.5 g., 84%), m. p. indefinite, depending on the rate of heating (Found : C, 89.1; H, 6.3. $C_{46}H_{38}O_2$ requires C, 88.7; H, 6.15%). This diol was not reduced when shaken for 8 days with excess of magnesium and ethereal methylmagnesium iodide.

6 : 11-Di-*p*-tolyl-5 : 6-11 : 12-ditolyl-naphthacene.—In one attempt to prepare the above diol, the crude product was steam-distilled and then added to hot *n*-propanol. Dehydration took place, and the colourless, sparingly soluble 6 : 11-di-*p*-tolyl-5 : 6-11 : 12-ditolyl-naphthacene was formed, having m. p. 402° (from xylene) (Found : C, 94.1; H, 5.8. $C_{46}H_{34}$ requires C, 94.2; H, 5.8%), giving a very intense violet fluorescence in solution. Dehydration of rubrenediol gives a similar hydrocarbon (see, e.g., Dufraisse and Velluz, *Bull. Soc. chim.*, 1936, **3**, 1905).

trans-5 : 12-Dihydro-5 : 12-dihydroxy-5 : 6 : 11 : 12-tetra-*p*-tolyl-naphthacene (?).—In an attempt to prepare the mono-oxide, the *cis*-diol (500 mg.) was heated *in vacuo* at 260° for 30 min. After cooling, the pink brittle solid was recrystallised from benzene and the product, which seems to be the *trans*-diol, was obtained as colourless needles, m. p. 305° (Found : C, 88.9; H, 6.3%). It gave an intense colour with concentrated sulphuric acid.

5 : 6 : 11 : 12-Tetra-*p*-tolyl-naphthacene.—A finely powdered intimate mixture of the *cis*-diol (5 g.) and iron powder (40 g.) was refluxed for 1 hr. in purified glacial acetic acid (500 c.c.), then poured into cold water (5 l.) and set aside for 3 hr. The solid was collected, dried, and extracted with benzene in a Soxhlet apparatus, in a dark room. The benzene solution was evaporated to small volume and the hydrocarbon obtained in 83% yield. After recrystallisation from benzene, 5 : 6 : 11 : 12-tetra-*p*-tolyl-naphthacene formed short red prisms, m. p. 325° (Found : C, 93.7; H, 6.2. $C_{46}H_{36}$ requires C, 93.8; H, 6.2%). Solutions of this hydrocarbon were very rapidly photo-oxidised on exposure to light and air, and the solid itself was slowly photo-oxidised on exposure in thin layers to the ordinary light of the laboratory. In the latter respect it differs from rubrene.

5 : 6 : 11 : 12-Tetra-*p*-tolyl-naphthacene 6 : 11-Photo-oxide.—A stream of oxygen was passed into a solution of tetra-*p*-tolyl-naphthacene (1 g.) in benzene (1 l.) in direct sunlight. After a few minutes the solution became colourless, and was then evaporated to small volume. After recrystallisation from ether, the photo-oxide formed colourless prisms, m. p. 223° after preliminary reddening [Found : C, 87.35; H, 6.2. $C_{46}H_{36}O_2$, $\frac{1}{2}C_{46}H_{10}O$ requires C, 87.6; H, 6.3%). Rubrene photo-oxide also crystallises with $\frac{1}{2}$ molecule of ether (Moureu, Dufraisse, and Gerard, *Compt. rend.*, 1928, **186**, 1027).

5 : 6 : 11 : 12-Tetra-*p*-tolyl-naphthacene isoOxide.—A solution of magnesium iodide was prepared by allowing iodine (3 g.) and excess of magnesium turnings to react in anhydrous ether (200 c.c.). The clear solution was cooled in an ice-bath and then added to an ice-cold solution of the photo-oxide (2 g.) in anhydrous benzene (150 c.c.). The mixture was kept in an ice-bath for 5 min., and then poured on cracked ice, and the organic layer was separated, washed with sodium thiosulphate solution, dried, and evaporated. Recrystallisation from ether gave 5 : 6 : 11 : 12-tetra-*p*-tolyl-naphthacene isooxide as colourless hexagonal plates, m. p. 198° (Found : C, 89.0; H, 5.8%. $C_{46}H_{36}O_2$ requires C, 89.0; H, 5.85%).

5 : 6 : 11-Tri-*p*-tolyl-naphthacene.—The above isooxide (0.5 g.) was shaken with a Grignard solution prepared from methyl iodide (10 g.), magnesium turnings (4 g.) and anhydrous ether

(100 c.c.) for 8 days. The whole was then poured on cracked ice and steam-distilled, and the ether layer of the distillate separated and combined with a second ethereal extract of the aqueous distillate. The combined extracts were evaporated, and the residue was heated with aqueous sodium hydroxide (0.4 c.c.; 33%) and aqueous chloroacetic acid (0.24 c.c.; 50%) for 1 hr. on a water-bath. After cooling, it was diluted slightly and acidified to pH 5 with hydrochloric acid. The liberated acid was taken up in ether (10 c.c.), extracted with aqueous sodium carbonate, and reprecipitated with hydrochloric acid. Recrystallisation from water gave colourless needles, m. p. 138° alone or mixed with an authentic specimen (m. p. 138°) of *p*-tolylxyacetic acid. The material which was not volatile in steam was extracted with benzene, the resulting solution being orange-red with an intense green fluorescence. After evaporation, the product was collected and recrystallised from benzene-light petroleum. The 5 : 6 : 11-*tri-p*-tolyl-naphthacene was formed as orange-red prisms, m. p. 244° (Found : C, 93.8; H, 6.4. C₃₅H₃₀ requires C, 93.9; H, 6.1%).

Rubrene isoOxide.—*Test for ethylenic double bond*. Pyridine (3 drops) and a benzene solution of osmium tetroxide (0.4 c.c.; 10%) were added to a solution of rubrene *isooxide* (15 mg.) in benzene (0.5 c.c.). No change of colour was apparent after 3 days. Tetramethylrubrene *isooxide* likewise showed no colour change, although ethylenic substances (*e.g.*, stilbene) reacted immediately with the formation of a brown colour or precipitate. Rubrene mono-oxide and rubrene photo-oxide also gave no colour change.

Oxidation of Rubrene with Osmium Tetroxide.—A suspension of rubrene (1.5 g.) in benzene (40 c.c.) and pyridine (0.5 c.c.) was treated with osmium tetroxide (1 g.) in benzene (10 c.c.). The colour darkened and the yellow fluorescence diminished immediately. After 3 days the mixture was diluted with light petroleum, and the brown solid collected, dissolved in methylene chloride (200 c.c.), and shaken with 1% aqueous potassium hydroxide (200 c.c.) containing mannitol (20 g.). After 3 hr., the organic layer, which was light yellow, was separated and evaporated. Recrystallisation from benzene gave the 1 : 2 : 3 : 4-*tetrahydro*-1 : 2 : 3 : 4-*tetrahydroxy*-5 : 6 : 11 : 12-*tetraphenyl*naphthacene (1.0 g.) as very small yellow prisms, m. p. 250° with decomposition (Found : C, 83.5; H, 5.7. C₄₂H₃₂O₄ requires C, 84.0; H, 5.4%).

1 : 4-*Diphenyl*-2 : 3-*benzanthrone* (XII).—A suspension of finely divided 6 : 11-diphenyl-naphthacene-5 : 12-quinone (XIII; Dufraisse and Compagnon, *Compt. rend.*, 1938, **207**, 585) in glacial acetic acid (150 c.c.) was boiled with granulated tin (9 g.). The quinone gradually dissolved to a red solution, which faded to brown when the reduction was complete (10—15 hr.). The hot solution was filtered and concentrated to half its volume, and concentrated hydrochloric acid (10 c.c.) was added, whereupon the crude product crystallised. After purification by chromatography on alumina from benzene solution, and recrystallisation from 1 : 1 benzene-light petroleum (b. p. 90—120°) 1 : 4-*diphenyl*-2 : 3-*benzanthrone* (XII) (2.75 g.) was obtained as yellow prisms, m. p. ca. 260° depending on the rate of heating (Found : C, 90.8; H, 5.1. C₃₀H₂₀O requires C, 90.8; H, 5.1%).

5 : 6 : 11-*Triphenyl*naphthacene. —A 0.4M-solution of phenylmagnesium iodide in ether (13 c.c.) and anhydrous benzene (60 c.c.) was boiled under reflux, 1 : 4-diphenyl-2 : 3-*benzanthrone* (1.0 g.) being suspended in a Soxhlet thimble under the condenser. After 24 hr. the red solution was poured on cracked ice and concentrated hydrochloric acid (20 c.c.). The organic layer was shaken for a few minutes with concentrated hydrochloric acid (4 × 25 c.c.), washed with distilled water, dried (Na₂SO₄), and evaporated to small volume. The resulting semi-solid mass was purified by chromatography on alumina, from benzene solution. Elution of the orange band, followed by evaporation and recrystallisation from benzene, gave 5 : 6 : 11-triphenyl-naphthacene (0.35 g., 30%) as orange crystals, m. p. 175° unchanged after recrystallisation from benzene. The m. p. was not depressed by admixture with a specimen prepared from rubrene *isooxide* by reduction with magnesium and methylmagnesium iodide according to Badoche (*loc. cit.*; see also Dufraisse and Badoche, *loc. cit.*, 1931). The specimen obtained by this method also had m. p. 175° unchanged by recrystallisation from benzene (*lit.*, m. p. 177—178°).

5-*Phenoxy*-6 : 11 : 12-*triphenyl*naphthacene. —An intimate mixture of rubrene *isooxide* (1.0 g.) and iron powder (10 g.) was refluxed with glacial acetic acid (150 c.c.) for 15 min., then poured into distilled water (750 c.c.). The solid was collected, washed until acid-free, air-dried, and extracted with benzene (Soxhlet) in the dark. After chromatography on alumina, the solution was concentrated, and the product collected and recrystallised from benzene-hexane. 5-*Phenoxy*-6 : 11 : 12-*triphenyl*naphthacene (0.3 g.) was obtained as short red laths, m. p. 325° (Found : C, 91.9; H, 5.2; O, 2.6. C₄₂H₂₈O requires C, 91.9; H, 5.2; O, 2.9%). Unchanged *isooxide* (0.4—0.5 g.) was also obtained from the chromatogram.

The m. p. of the phenoxytriphenyl-naphthacene was not depressed on admixture with rubrene,

m. p. 325°. It was rapidly photo-oxidised but a homogeneous product could not be isolated. It was recovered unchanged after being shaken for 2 weeks in the dark with magnesium and methylmagnesium iodide.

1 : 4 : 10-Triphenyl-2 : 3-benzanthrone (XVII).—(a) Rubrene isooxide (1.0 g.) was dissolved in concentrated sulphuric acid (15 c.c.) at -10° , and set aside for 1 hr. The solution was poured on cracked ice, and the precipitated solid filtered off and washed until acid-free. The filtrate and washings were treated with bromine water, and the resulting 2 : 4 : 6-tribromophenol was collected (0.44 g., 75%) and identified by comparison with an authentic specimen. The initially precipitated solid was chromatographed on alumina. A small colourless band having a blue-violet fluorescence preceded the main yellow band. Elution of the former gave a few mg. of a pale yellow hydrocarbon, m. p. $>400^{\circ}$ (Found : C, 94.6; H, 5.6%). The absorption spectrum in chloroform had a maximum at 3180 Å (log ϵ 4.5). Elution of the main yellow band and recrystallisation from benzene–light petroleum gave 1 : 4 : 10-triphenyl-2 : 3-benzanthrone (XVII) as yellow prisms, m. p. 244° (0.59 g.) (Found : C, 91.9; H, 5.3. $C_{36}H_{24}O$ requires C, 91.5; H, 5.1%).

(b) Rubrene isooxide (40 mg.) was added slowly, with stirring, to just-molten potassium hydroxide (1.2 g.), in a nickel crucible. After cooling, the mixture was treated with water, and the solid collected and recrystallised from acetic acid. The triphenylbenzanthrone was obtained as yellow prisms, m. p. and mixed m. p. 244° (17 mg., 50%).

10-Hydroxy-1 : 4 : 10-triphenyl-2 : 3-benzanthrone (XV).—(a) A suspension of 6 : 11-diphenyl-naphthacene-5 : 12-quinone (1.0 g.) in anhydrous benzene (60 c.c.) and 0.25M-phenylmagnesium bromide in ether (9.8 c.c.) was refluxed for 24 hr., then poured on ice and sulphuric acid. Further benzene was added to keep the solid in solution. The organic layer was dried (Na_2SO_4) and then chromatographed on alumina, benzene being used for development. A broad bright yellow band, which was eluted first, contained unchanged quinone. A second, pale yellow band, was held firmly on the upper half of the column. This was cut out and extracted with chloroform (Soxhlet). After evaporation to small volume and addition of a little hexane, the product separated. Recrystallisation from dry ether gave 10-hydroxy-1 : 4 : 10-triphenyl-2 : 3-benzanthrone (XV) as pale yellow needles (0.3 g., 25%), m. p. 281–284° (decomp.) (Found : C, 88.8; H, 5.1; O, 6.6. $C_{36}H_{24}O_2$ requires C, 88.5; H, 4.9; O, 6.6%).

(b) A solution of 5-phenoxy-6 : 11 : 12-triphenyl-naphthacene (0.5 g.) in boiling benzene (30 c.c.) was treated with nitric acid (15% ; 0.25 c.c.) during 30 min., by which time the colour and fluorescence had disappeared. The benzene solution was washed, dried, and evaporated. After recrystallisation from dry ether the hydroxytriphenylbenzanthrone was obtained as pale yellow needles, m. p. and mixed m. p. 282–283° (decomp.).

(c) A mechanically shaken solution of 5-phenoxy-6 : 11 : 12-triphenyl-naphthacene (0.1 g.) in benzene (30 c.c.) was treated with cold 1% potassium permanganate (to which sulphuric acid, 0.5 c.c./l., had been added) a few c.c. at a time. The addition was stopped when the benzene layer had been decolorised. Sodium hydrogen sulphite solution was added to dissolve the manganese dioxide, and the benzene solution was then washed with water and dried (Na_2SO_4). After concentration and recrystallisation from ether, hydroxytriphenylbenzanthrone (80 mg., 90%) identical with that prepared as above was obtained.

Specimens made by all methods gave a characteristic grass-green colour with concentrated sulphuric acid in the cold. On heating, the colour changed to a reddish-brown. This type of colour reaction is given by many *meso*-hydroxyanthrones.

Action of Filtered Phenylmagnesium Bromide on Rubrene isoOxide.—(a) A solution of rubrene isooxide (1 g.) in anhydrous benzene (30 c.c.) was added to filtered Grignard reagent prepared from bromobenzene (6.0 g.), magnesium turnings (0.9 g.) and ether (25 c.c.). The mixture was refluxed for 65 hr., the ether being allowed to escape in the first hour, and then poured on ice and sulphuric acid. The hydrolysate was steam-distilled, and the residue heated at 160–180°/0.01 mm. to remove diphenyl by sublimation. After further purification by chromatography and recrystallisation from ether–light petroleum, the product was obtained as red crystals (0.3 g.), m. p. 316° unchanged by further recrystallisation. It was identified as rubrene by analysis (Found : C, 94.3; H, 5.8. Calc. for $C_{42}H_{28}$: C, 94.7; H, 5.3%) and by its absorption spectrum. The m. p. was not depressed on admixture with rubrene.

In the purification of this product by chromatography, the fraction eluted from the column immediately after the red band yielded rubrene photo-oxide (90 mg.), identified by direct comparison with an authentic specimen. This product was evidently formed by photo-oxidation of the rubrene during the working up. Further elution of the column gave gums.

(b) A filtered ethereal solution of phenylmagnesium bromide (14 c.c. ; 0.25M) was added to

rubrene isooxide (1 g.) in benzene (30 c.c.), and the mixture refluxed for 24 hr., the ether being allowed to escape. After hydrolysis and steam-distillation as above, the product was chromatographed on alumina from benzene. Elution of the first band, followed by recrystallisation of the product from ethyl acetate, gave rubrene mono-oxide (0.18 g.), m. p. and mixed m. p. 320°. A little unchanged isooxide was also isolated, but no other homogeneous material.

(c) A similar experiment was conducted but with 10.5 c.c. of the 0.25M-Grignard solution. Elution of the lowest band on the column gave no homogeneous material. A second yellow band was held firmly, and this was cut out and extracted with ether. Evaporation and recrystallisation of the product from ether gave 10-hydroxy-1 : 4 : 10-triphenyl-2 : 3-benzanthrone (78 mg.), m. p. and mixed m. p. 280° (decomp.), giving the characteristic colour reactions (see above).

trans-6 : 11-Dihydro-6 : 11-dihydroxy-5 : 6 : 11 : 12-tetraphenylnaphthacene (XVI).—Ethereal phenylmagnesium iodide (10 c.c.; 0.4M) and anhydrous benzene (60 c.c.) were boiled under reflux, hydroxytriphenylbenzanthrone (XV) (1.0 g.) being suspended in a Soxhlet thimble under the condenser. After 24 hr. the mixture was poured on ice and sulphuric acid, and the organic layer worked up in the usual way. Recrystallisation from ethyl acetate gave the colourless *trans*-diol (XVI), m. p. 251°, not depressed on admixture with a specimen prepared according to Dufraisse and Compagnon (*Compt. rend.*, 1938, **207**, 585; see also Allen and Bell, *J. Amer. Chem. Soc.*, 1940, **62**, 2408).

We thank Dr. A. R. H. Cole for the infra-red spectra. Analyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA.

[Received, March 17th, 1954.]
