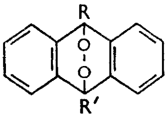
844. *The Thermal Decomposition of some* meso-*Substituted Anthracene Photo-oxides.*

By P. F. Southern and William A. Waters.

The thermal decompositions of the photo-oxides of 9,10-dimethylanthracene, and 9,10-diphenyl-, 9-phenyl-10-methyl-, and 9-hydroxymethyl-10-methyl-anthracene have been studied for solutions in hydrocarbon solvents and in the presence of various phenols and benzoic acid. The natures of the products indicate that a homolysis of the O–O bonds of the peroxides can occur. This is supported by demonstration that certain of the photo-oxides can initiate vinyl polymerisation.

Coal tar very slowly absorbs oxygen and its properties as a binder in road surfaces thereby deteriorate.[1] This oxidation is accelerated by light and it has been suggested that it then involves photo-oxides of anthracenoid hydrocarbons which might conceivably disrupt to give free oxy-radicals, RO•, capable of initiating the autoxidation of other components of coal tar. Already the reactions of oxy-radicals with representative phenols [2] and hydrocarbons [3] have indicated courses of homolytic oxidation, addition, and substitution that would give a rational interpretation of the complex oxidative polymerisation that slowly occurs in coal tar. It has therefore been desirable to examine the thermal decomposition of the photo-oxides of some anthracenoid hydrocarbons and search for evidence of the transient formation of reactive RO• radicals.



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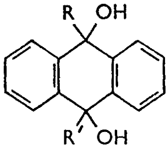

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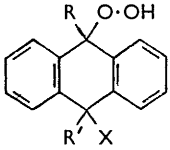

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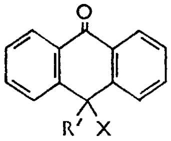

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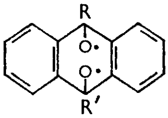

(V)

Though the conditions of formation, the structures, and the relative stabilities of the photo-oxides of many polycyclic aromatic compounds have been studied,[4] little attention has been paid to their chemical reactions or to their thermal decomposition products. Reduction with either Raney nickel [5] or lithium aluminium hydride [6] converts the photo-oxides (I) into *cis*-9,10-dihydroanthracene-9,10-diols (II); dilute mineral acids, water, and hydrogen peroxide can effect heterolysis of a C–O bond, yielding hydroperoxides (III) which decompose rapidly to substituted anthrones (IV).[7]

Photo-oxides can be prepared most easily from *meso*-substituted anthracenes, and these photo-oxides usually liberate a considerable proportion, but rarely the whole, of their oxygen when heated, regenerating the parent anthracene.[4] Homolysis of the peroxide (I) to the radical (V) is unlikely to be efficient on account of the proximity of the unpaired electrons in the diradical (V),[8] but Breitenbach and Kastell [9] have found that anthracene photo-oxide can catalyse the polymerisation of styrene. They estimate the activation

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[1] " The Durability of Road Tar," D.S.I.R. Road Research Technical Paper No. 31, H.M.S.O., 1954; " The Reaction of Oxygen with Tar Oils," D.S.I.R. Road Research Technical Paper No. 16, H.M.S.O., 1949, 1048, **226**, 929.

[2] Moore and Waters, *J.*, 1952, 2432; 1954, 243; Hey and Waters, *J.*, 1955, 2753; Cosgrove and Waters, *J.*, 1951, 388, 1726.

[3] Beckwith and Waters, *J.*, 1957, 1001; 1956, 1108; Beckwith, Norman, and Waters, *J.*, 1958, 171.

[4] Badger, " The Structures and Reactions of the Aromatic Compounds," Chapter 9, Cambridge Univ. Press, 1954.

[5] Dufraisse and Houpillard, *Compt. rend.*, 1937, **205**, 740.

[6] Mustafa, *J.*, 1952, 2435.

[7] Dufraisse and Gerard, *Bull. Soc. chim. France*, 1937, **4**, 2052; Pinazzi, *Compt. rend.*, 1947, **225** 1012; 1948, **226**, 929.

[8] Walling, " Free Radicals in Solution," J. Wiley and Sons, New York, 1957, pp. 182, 474.

[9] Breitenbach and Kastell, *Monatsh.*, 1954, **85**, 676.

energy of the homolysis as 29·8 kcal. mole^{-1}, which is apposite for the fission of an O–O bond (*i.e.*, I $\longrightarrow$ V).

For our studies we selected the photo-oxides of 9-methyl-10-phenylanthracene (I; R = Me, R′ = Ph) which liberates 20% of its oxygen when heated,[10] and of 9,10-dimethylanthracene (I; R = R′ = Me) which does not liberate any oxygen on slow heating.[11] A few tests were conducted with the photo-oxides of 9,10-diphenylanthracene (I; R = R′ = Ph) and of 9-hydroxymethyl-10-methylanthracene (I; R = CH_2·OH, R′ = Me).

The methylphenyl- and the dimethyl-anthracene were prepared by Huang-Minlon reduction of the corresponding 9-formylanthracenes,[12] but for the dimethyl compound a more direct method involving dehydrogenation of 9,10-dihydro-9,10-dimethylanthracene [13] by sulphur proved quicker. By shaking together in ether, anthracene, sodium slices, and glass chips, and treating the resulting purple adduct with methyl iodide, Badger, Goulden, and Warren [13] obtained the *cis*-dihydrodimethylanthracene, m. p. 101—102°. However, we have found that addition of a suspension of anthracene in tetrahydrofuran to one of sodium in liquid ammonia leads to the *trans*-isomer, m. p. 130°. The conflicts with the statement by Badger, Jones, and Pearce [14] that sodium always effects *cis*-addition to anthracenes.

The photo-oxides were prepared in glass flasks in presence of sunlight or under irradiation from a Hanovia mercury-vapour lamp filtered through a sheet of soft glass. Over-irradiation and also photo-oxidation in quartz vessels led to much decomposition of the photo-oxides to anthraquinone.

TABLE 1. *Yields* (%) *of decomposition products of* 9-*methyl*-10-*phenylanthracene photo-oxide* (*reaction time,* 2·5 *hr. in all cases*).

Reactant, solvent	Hydrocarbon	(VI; R, R′ = Me, Ph)	Anthraquinone	(XI)	(II; R = Me, R′ = Ph)	(IV; R′ = Ph, X = OH)
Ethylbenzene	35	25	15	0	0	0
Cumene	40	23	15	0	0	0
Cumene	42	21	—	—	—	—
Toluene (in air)	27	23	41	—	—	—
Phenol (5 g.) in PhCl	21	2·5	0	8	13	0
p-Cresol (5 g.) in PhCl (i)	6	0	7	7	—	—
,, ,, (ii)	4	0·5	—	5	5	0
2,6-Xylenol (2 g.) in PhCl	27	15	—	—	—	—
2,6-Xylenol (5 g.) in PhCl	19	6	12	0	25	0
2,6-Dimethoxyphenol (2 g.) in PhCl	24	10	1	0	21	0
α-Naphthol (2 g.) in PhCl	5	0	0	0	36	0
BzOH (2 g.) in PhCl	45	16	12	0	0	20
,, (2 g.)	—	—	15	0	0	21

TABLE 2. *Yields* (%) *of decomposition products of* 9,10-*dimethylanthracene photo-oxide.*

Reactant	Photo-oxide	(VI; R = R′ = Me)	Anthraquinone	(II; R = R′ = Me)	9-CH_2·OH deriv.	(IV; R′ = Me, X = OH)
Chlorobenzene (2 hr.) ...	60	—	—	2	0	0
Chlorobenzene (12 hr.) ...	0	7	2	0	14	0
2,6-Dimethoxy-phenol (2 g.) in PhCl (2·5 hr.) ...	52	0	—	15	0	0
α-Naphthol (2 g.) in PhCl (2 hr.)	0	0	0·5	0	10	5

At 90°, the photo-oxides of the methylphenyl, dimethyl, and hydroxymethyl compound gave indications of initiating polymerisation of styrene under nitrogen. Similar, but less decisive, results were obtained with methyl methacrylate. In contrast, the decomposition

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[10] Willemart, *Bull. Soc. chim. France*, 1937, **4**, 1447.

[11] Willemart, *Compt. rend.*, 1937, **205**, 866.

[12] Buu-Hoï and Hoán, *J. Org. Chem.*, 1951, **16**, 874.

[13] Badger, Goulden, and Warren, *J.*, 1941, 18.

[14] Badger, Jones, and Pearce, *J.*, 1950, 1700.

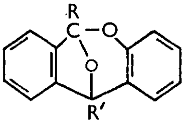
of the photo-oxide of diphenylanthracene to the hydrocarbon and oxygen inhibited polymerisation of both styrene and methyl methacrylate. Though many alkyloxy-radicals dehydrogenate alkylbenzenes, giving dibenzyl derivatives,[3,15] the photo-oxide of methylphenylanthracene under nitrogen had no action on toluene or ethylbenzene. Cumene yielded about 2% of dicumyl, based on the photo-oxide used, but most of this may have been formed by the direct action of the small amount of molecular oxygen liberated by the photo-oxide.

Definite evidence of the homolytic formation of the radical (V) from the peroxide (I) can be adduced from our studies of the thermal decompositions of the photo-oxides. These have been carried out (*a*) by heating the photo-oxides in inert solvents such as ethylbenzene and chlorobenzene and (*b*) in similar solutions containing phenols which might be expected to react with RO$\cdot$ radicals. The products of these reactions have been separated chromatographically and identified as far as possible, both by spectrographic methods and by synthesis.

Tables 1 and 2 summarise the results of this investigation: the following points merit attention.

(i) In inert solvents under nitrogen thermal decomposition of the methylphenyl and the dimethyl photo-oxides yields significant amounts of chemically stable isomers which are of type (VI). In the presence of phenols these yields are reduced.

(ii) Reduction of the methylphenyl photo-oxide could not be detected in the absence of phenols, but was evident in their presence. We suggest that this indicates dehydrogenation of the phenols by radicals (V) though we have failed to isolate the expected oxidation products [2] of the phenols themselves. In the presence of phenols the yield of compound (VI) decreases more rapidly than that of the parent anthracene, as would be expected if the radicals (V) are then hydrogenated to a diol (II) instead of isomerising. For the methylphenyl compound there is evidence of further reduction to the mono-alcohol (XI).



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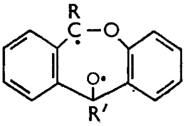

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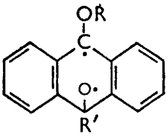

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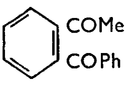

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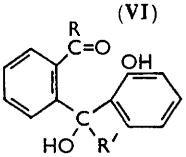

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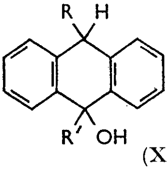

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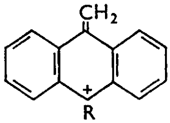

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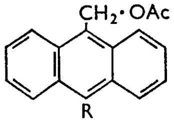

(XIII)

The corresponding reactions of the dimethyl photo-oxide are similar but not so decisive, and a rearrangement product (the hydroxymethyl derivative) from the diol (II; $R = R' = Me$) was also formed. No diol was obtained on decomposition of the diphenyl photo-oxide in the presence of α-naphthol; This was expected, for this oxide, when heated, loses its oxygen completely in molecular form.[16]

(iii) The distinctive action of the phenols is not that of an acid, for the decomposition of the methylphenyl photo-oxide in the presence of benzoic acid gives 20% of a different product, 10-hydroxy-10-phenylanthrone (IV; $R' = Ph$, $X = OH$), which was identified by an authentic synthesis. Evidently this had been produced by the known heterolysis (I) $\longrightarrow$ (III).[7] Decomposition of the dimethyl photo-oxide in the presence of α-naphthol may, to a slight extent, take this route, for a little of the anthronol (IV; $R' = Me$, $X = OH$) was isolated.

The two compounds (VI) which have been isolated from the transannular peroxides

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[15] Gray and Williams, *Chem. Soc. Special Publ.* No. 9, 1958, p. 105; *Chem. Rev.*, 1959, **59**, 239.

[16] Dufraisse and Le Bras, *Bull. Soc. chim. France*, 1937, **4**, 349.

(I; R = R′ = Me; and R = Me, R′ = Ph) are intramolecular rearrangement products of diradicals (V). The methyl phenyl photo-oxide is structurally similar to triphenylmethyl peroxide, with which homolytic decomposition at the weak O–O bond is followed by the rearrangement of an aryl group and eventual formation of a pinacol ether:[17]

$$\mathrm{Ph_3C{-}O{-}O{-}CPh_2} \rightleftharpoons \mathrm{2Ph_3C{-}O\cdot} \longrightarrow \mathrm{2Ph_2\dot{C}{-}OPh} \longrightarrow \mathrm{(Ph_2\overset{|}{C}{-}OPh)_2}$$

Consequently rearrangement of a radical (V) to the isomeric radical (VII) is a likely consequence and the latter could easily afford the ketal (VI). At first, we thought that the radical isomerisation (V) ⟶ (VIII) (cf. rubrene iso-oxide[18]) might have occurred with the methylphenyl photo-oxide, but our product is consistent with a structure of type (VI). Its ultraviolet spectrum shows only a benzene chromophore; its infrared spectrum is that of a ketal [strong absorption at 1258 (aryl ether), 1106 and 116 cm.$^{-1}$ (alkyl ether)] and contains no bonds due to ethylenic linkages. Oxidation with chromic acid in acetic acid to 2-acetylbenzophenone (IX) excluded the rubrene iso-oxide type of structure; and hydrolysis with sulphuric acid in acetic acid gave a phenolic ketone such as (X). The corresponding dioxide from the dimethyl photo-oxide did not contain a methoxy-group and had strong absorption maxima at 1265 and 1090 cm.$^{-1}$, consistently with structure (VI; R = R′ = Me).

The alcohols formed from the methylphenyl photo-oxide in the presence of phenols have been identified by synthesis. The *cis*-diol (II; R = Me, R′ = Ph) was prepared (*a*) by oxidation of 9-methyl-10-phenylanthracene with acidified permanganate[19] and (*b*) from the photo-oxide in 80% yield by hydrogenation in the presence of Raney nickel.[20] Prolonged hydrogenation gave a 65% yield of a monoalcohol (XI), identical with a product isolated on reaction of the photo-oxide with the phenols (see Table 1). The same compound was also obtained from the photo-oxide on prolonged reaction with lithium aluminium hydride in boiling tetrahydrofuran (a similar reduction has been described by Cook and Martin[21]). An isomer (XI; R = Me, R′ = Ph) has been described by Willemart,[10] but on account of possible stereoisomerism this is not conclusive evidence that our product is the structural isomer.

Treatment of the diol (II; R = Me, R′ = Ph) with cold acetyl chloride, or hot acetic acid, yielded 9-acetoxymethyl-10-phenylanthracene (XIII; R = Ph) which was also prepared from 9-formyl-10-phenylanthracene. Evidently dehydration of the diol to the ion (XII; R = Ph), followed by an anionotropic rearrangement,[22] had occurred. Both the alcohols (XI) and (II; R = Me, R′ = Ph) gave coloured carbonium salts on dissolution in concentrated sulphuric acid. Our monoalcohol (XI; R,R′ = Me, Ph) was not dehydrated to 9-methyl-10-phenylanthracene in hot chlorobenzene but was, in part, oxidised to a new diol, probably *trans*-9,10-dihydro-9,10-dihydroxy-9-methyl-10-phenylanthracene.

From the thermal decomposition of the dimethyl photo-oxide in chlorobenzene a little of the diol (II; R = R′ = Me) was obtained and, after prolonged reaction, an appreciable amount of its anionotropic rearrangement product, 9-hydroxymethyl-10-methylanthracene (cf. XIII). This was synthesised by reduction of 9-formyl-10-methylanthracene. The formation of these products, together with some anthraquinone, indicates that this photo-oxide can undergo intermolecular oxidation and reduction.

9-Hydroxymethyl-10-methylanthracene itself easily forms a photo-oxide (I; R = $CH_2{\cdot}OH$, R′ = Me), whose thermal decomposition gave formaldehyde (70%) and 10-hydroxy-10-methylanthrone (IV; R′ = Me, X = OH) (identified by synthesis) together with anthraquinone. Homolysis of the type $\mathrm{R{-}\underset{|}{\overset{|}{C}}{-}O\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{\underset{|}{\overset{|}{C}}{=}O}$ is a well-known route

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[17] Kharasch, Poshkus, Fono, and Nudenberg, *J. Org. Chem.*, 1951, **16**, 1458.

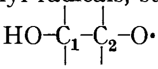
[18] Badger, Pearce, Rodda, and Walker, *J.*, 1954, 3151.

[19] Cf. Enderlin, *Compt. rend.*, 1936, **202**, 1188.

[20] Cf. ref. 5.

[21] Cook and Martin, *J.*, 1940, 1125.

[22] Badger and Pearce, *J.*, 1950, 2314.

for decomposition of alkyloxy-radicals;[15] and 1-hydroxyalkyl radicals, such as $HO{\cdot}CH_2{\cdot}$, are easily oxidised.[23] In fact the easy C–C bond fission of  $HO-C_1-C_2-O\cdot$ (C_2, tertiary) is that of a glycol.[24]

The sequence of reactions, 9,10-dimethylanthracene ⟶ (I; R = R′ = Me) ⟶ (II; R = R′ = Me) ⟶ 9-hydroxymethyl-10-methylanthracene ⟶ (I; R = $CH_2{\cdot}OH$, R′ = Me) ⟶ (IV; R′ = Me, X = OH), explains the removal of *meso*-alkyl substituents from anthracenoid hydrocarbons by mere exposure to air and sunlight. It may perhaps be significant in connection with carcinogenesis.

EXPERIMENTAL

Materials.—9-*Methyl*-10-*phenylanthracene*. The following procedure for the large-scale preparation of this hydrocarbon from 9-formyl-10-phenylanthracene is superior to that of Buu-Hoï and Hoán,[12] followed by Norman and Waters,[25] in which low yields result owing to the separation of as much as 60% of an insoluble azine. 9-Formyl-10-phenylanthracene (65 g.) and 100% hydrazine hydrate (65 ml.) were refluxed in ethanol (700 ml.) until all solid had dissolved (1 hr.). The alcohol was evaporated, potassium hydroxide (45 g.) and ethylene glycol (340 ml.) were added, and the mixture was distilled until the temperature of the residue reached 210°. This was then refluxed for 4 hr. and finally poured into water. 9-Methyl-10-phenylanthracene (60 g., 96%), purified chromatographically in the absence of light, had m. p. 112°.

9,10-*Dimethylanthracene*.—(*a*) Prepared from 9-formyl-10-methylanthracene by a similar procedure,[12] in 70% yield, it had m. p. 180—181°. (*b*) To sodium (10 g.) in liquid ammonia (250 ml.) a slurry of anthracene (20 g.) in dry tetrahydrofuran (100 ml.) was added with stirring. After 20 min. methyl iodide (31 ml.) was slowly added, together with enough liquid ammonia to replenish losses. A day later the material remaining at room temperature was acidified, extracted with benzene, and purified by chromatography in light petroleum. The crude *trans*-9,10-dihydro-9,10-dimethylanthracene (10·7 g.) had m. p. 109—110°, raised to 130—131°[14] by repeated crystallisation from alcohol. Dehydrogenation[13] of this with sulphur at 230° gave 60% of 9,10-dimethylanthracene, m. p. as above.

9-*Hydroxymethyl*-10-*methylanthracene*.—A slurry of 9-formyl-10-methylanthracene[12] (m. p. 167°; 31 g.) in ether (250 ml.) was slowly added to a stirred suspension of lithium aluminium hydride (4 g.) in ether (250 ml.), and the mixture was refluxed for 1 hr. After treatment with ethyl acetate, water and chlorobenzene (500 ml.) were added, the ether was removed, and the product (20 g.) which crystallised from the hot filtered chlorobenzene solution was obtained as pale yellow needles, m. p. 222·5—223° (Found: C, 86·3; H, 6·4. Calc. for $C_{16}H_{14}O$: C, 86·4; H, 6·4%). The m. p. for this substance has been given as 229° by Tardieu,[26] though its first preparation was by Guyot and Staehling[27] who gave m. p. 223°. Its infrared spectrum had peaks at 3350 and 1060 cm.$^{-1}$ ($CH_2{\cdot}OH$) and 760, 750, and 689 cm.$^{-1}$ (Ph and *o*-C_6H_4).

Preparation of the Photo-oxides.—(*a*) The hydrocarbon (10 g.) under methanol (500 g.) was put in sunlight in a glass vessel open to the air but protected from rain. As oxidation proceeded, the yellow hydrocarbon dissolved and white photo-oxide was deposited. This took up to 3 days in summer and 3 weeks in winter; yields of 70—80% were obtained. (*b*) In a slowly rotating vessel similar to that described by Bowen and Tanner[28] the hydrocarbon (2 g.) in purified carbon disulphide (300 ml.) was irradiated under oxygen with a 500 w ultraviolet lamp through a glass sheet that acted as a heat trap. The oxygen was replenished after 2 hr. Lack of fluorescence, in benzene, of evaporated test portions indicated completion of the photo-oxidation. All the photo-oxides were purified by chromatography through alumina in the dark. Unchanged hydrocarbons were eluted with light petroleum–benzene (4 : 1), and the photo-oxides of 9-methyl-10-phenyl- [m. p. 180° (decomp.)], dimethyl- [m. p. 200—205° (decomp.)], and diphenyl-anthracene with light petroleum–benzene (1 : 1). The *photo-oxide* of 9-hydroxymethyl-10-methylanthracene, which was eluted with chloroform, had m. p. 185°

[23] Merz and Waters, *J.*, 1949, S15; Mackinson and Waters, *J.*, 1953, 323.

[24] Drummond and Waters, *J.*, 1953, 3119; Littler and Waters, *J.*, 1960, 2767.

[25] Norman and Waters, *J.*, 1958, 167.

[26] Tardieu, *Compt. rend.*, 1959, **248**, 2885.

[27] Guyot and Staehling, *Bull. Soc. chim. France*, 1905, **33**, 1144.

[28] Bowen and Tanner, *Trans. Faraday Soc.*, 1954, **51**, 475.

(decomp.) (Found: C, 75·2; H, 5·9. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·6%), $\nu_{max.}$ 3300 and 1080 ($CH_2\cdot OH$), 770, 764, and 695 cm.$^{-1}$ (Ph and o-C_6H_4), 831w cm.$^{-1}$ (also found for the methylphenyl photo-oxide; ?O–O [29]).

It was essential to store the photo-oxides in the dark.

Polymerisation Tests.—These were carried out for 10 min. at 90° in Thunberg tubes filled with nitrogen. 10 Mg. samples of the oxides in 0·5 ml. of the monomers were examined by direct comparison with tubes containing monomers only. Styrene, purified by washing with alkali, drying (Na_2SO_4), and double fractionation at 40°/10 mm. under nitrogen from a little picric acid, gave cloudy solutions when the samples that had been heated with the methylphenyl, dimethyl, and hydroxymethyl photo-oxides were diluted with light petroleum (10 ml.; b. p. 40—60°). The control solution gave a very faint cloudiness and that which had contained the diphenyl photo-oxide remained clear and fluoresced. Polymerisation of methyl methacrylate (b. p. 98—98·5°) by the decomposition of the methylphenyl photo-oxide was established by the precipitation of gummy polymer on addition of ethanol (10 ml.); again the diphenyl photo-oxide gave a clear, fluorescent solution.

Decomposition of the Photo-oxides.—The experiments listed in the Tables were carried out by refluxing, under nitrogen, 1 g. samples of the photo-oxides in 100 ml. of the liquid stated. When phenols or benzoic acid had been added the cooled chlorobenzene solutions were extracted with aqueous sodium hydroxide before evaporation under nitrogen. The residues, in benzene, were chromatographed through alumina (100 g.; grade H), with benzene and then chloroform for elution. The early benzene fractions were chromatographed on fresh alumina. Bicumyl and anthracene hydrocarbons then separated in light petroleum, the isomerised dioxides (VI) in benzene–light petroleum (9 : 1), and anthraquinone in pure benzene. The alcohols (II), (IV), and (XI) were eluted only with chloroform or benzene–chloroform. The alcohols were contaminated with large quantities of red oil, especially from mixtures that had contained phenols, but it was not possible to establish the formation of the expected diphenoquinones. Alkali-treatment of the mixture from α-naphthol and the dimethyl photo-oxide precipitated a deep purple solid (0·75 g.), soluble in chloroform, but this could not be crystallised.

The hydroxymethyl photo-oxide (0·50 g.) in refluxing chlorobenzene (80 ml.) was decomposed in a stream of nitrogen and the issuing gas was passed through two successive aqueous solutions of dimedone. In the first of these solutions the formaldehyde condensation product (0·105 g., 43%), m. p. and mixed m. p. 188—189°, was precipitated, whilst in the preceding condenser tube some paraformaldehyde (15 mg., 27%) was deposited (also identified as dimedone derivative). From the chlorobenzene solution were isolated 35% of anthraquinone and 21·5% of 10-hydroxy-10-methylanthrone (IV; R′ = Me, X = OH).

Products. The *dioxide* (VI; R, R′ = Me, Ph), obtained from the methylphenyl photo-oxide, had m. p. 122—123° (from ethanol) (Found: C, 83·5; H, 5·4%; *M*, 246. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·4%; *M*, 300), $\lambda_{max.}$ 2585, 2650, and 2715 Å (ε 492, 710, and 863), $\nu_{max.}$ 1285 (OAr), 1116 and 1106 (OAlk), 752, 747, and 696 cm.$^{-1}$ (o-C_6H_4 and Ph) (no distinctive absorption in the 4000—3100, 1750—1610, 920—880, and 840—820 wave bands). Oxidation of this product (0·1 g.) for 2 hr. at 100° with chromium trioxide (0·5 g.) in acetic acid (10 ml.) gave *o*-acetylbenzophenone (0·02 g.), m. p. 100° (Koelsch and Johnson [30] give 99°) (Found: C, 80·4; H, 5·3. Calc. for $C_{15}H_{12}O_2$: C, 80·4; H, 5·4%), identified by its double C=O absorption at 1660 and 1680 cm.$^{-1}$ and its aromatic absorption at 776, 767, and 710 cm.$^{-1}$. Its disemicarbazone, m. p. 216—217° (decomp.), gave the blue colour in hot acetic acid described by Koelsch and Johnson.

Hydrolysis of this oxide (VI; R, R′ = Me, Ph) (0·1 g.) for 3 hr. with boiling acetic (10 ml.) and 25% aqueous sulphuric acid (4 ml.) gave phenolic material, insoluble in sodium carbonate, that gave a green colour with aqueous ferric chloride. Its infrared spectrum had peaks at 3100—3000, 1700, 1590, 1275, 1260, 754, and 698 cm.$^{-1}$. Compound (VI; R, R′ = Me, Ph) was stable at 200° and resisted reduction with zinc dust in hot acetic acid, hydrogenation in ethanol at room temperature and pressure over Raney nickel, and attack by phenylmagnesium bromide (cf. rubrene [18]).

The isomeric dioxide (VI; R = R′ = Me) from the dimethyl photo-oxide, *i.e.*, 2,5-*benzoylene-2,5-dihydro-2,5-dimethylbenzo*[c]*furan* had m. p. 182° (from ethanol) (Found: C, 80·3; H, 6·0; OMe, nil. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%). Its infrared spectrum had no hydroxyl

[29] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 120.
[30] Koelsch and Johnson, *J. Amer. Chem. Soc.*, 1943, **65**, 572.

or carbonyl peaks but showed strong absorption at 1265 (OAr), 1090 (OAlk) and 761 cm.$^{-1}$ (o-C_6H_4).

cis-*9,10-Dihydro-9,10-dihydroxy-9-methyl-10-phenylanthracene,* when separated after decompositions of the methylphenyl photo-oxide in the presence of phenols, had m. p. 216—217° (from benzene) (Found: C, 83·0; H, 6·1. $C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%). Material made by oxidising the anthracene with acid 0·12% permanganate solution [19] or by hydrogenating the photo-oxide in ethanol at atmospheric pressure over Raney nickel [20] had the same m. p. and unchanged mixed m. p. Its infrared spectrum had peaks at 3350 and 1140 cm.$^{-1}$ (tertiary OH), 762, 736, and 698 cm.$^{-1}$ (Ph and o-C_6H_4), and $\lambda_{max.}$ 2605 Å (ε 702), $\lambda_{min.}$ 2450 (ε 405). The diol dissolved in concentrated sulphuric acid to a dark green solution and in acetic–sulphuric acid mixtures to a bright yellow solution. When treated with acetyl chloride (1 ml.) the diol (0·25 g.) dissolved, with evolution of heat, giving a yellow solution from which *9-acetoxymethyl-10-phenylanthracene* (0·18 g.) was rapidly precipitated; this had m. p. 228—229° and formed yellow needles from acetic acid (Found: C, 84·1; H, 5·7. $C_{23}H_{18}O_2$ requires C, 84·6; H, 5·6%). It had $\nu_{max.}$ 1725 and 1235 cm.$^{-1}$ (AcO), and 770, 757, and 700 cm.$^{-1}$ (Ph and o-C_6H_4), and $\lambda_{max.}$ 3395, 3560, 3745, 3955, and 2620 Å (ε 3400, 7400, 11,800, 11,000, and 120,000), typical of the anthracene ring system. The same product was obtained by refluxing the diol for 20 hr. with acetic acid. Treatment, in ether, with lithium aluminium hydride, followed by decomposition with water, gave *9-hydroxymethyl-10-phenylanthracene,* m. p. 166—167° (from benzene–light petroleum), identical with material obtained by reducing 9-formyl-10-phenylanthracene with lithium aluminium hydride in ether (Found: C, 88·7; H, 6·0. $C_{21}H_{16}O$ requires C, 88·7; H, 5·7%). Its infrared spectrum had peaks at 3350 cm.$^{-1}$ (OH), and 763, 750, and 703 cm.$^{-1}$ (Ph and o-C_6H_4). Acetylation of the synthetic material gave the acetate described above.

*9,10-Dihydro-*meso*-hydroxy-9-methyl-10-phenylanthracene* (as XI), isolated after decomposition of the methylphenyl photo-oxide in the presence of certain phenols (Table 1), had m. p. 205° (decomp.) (from benzene) (Found: C, 88·3; H, 6·0. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%). Specimens made by reduction of this photo-oxide with (*a*) Raney nickel and hydrogen in ethanol (60% yield) and (*b*) lithium aluminium hydride in tetrahydrofuran (33% yield after 19 hr.) had identical m. p.s, unchanged mixed m. p., and the same infrared spectra [peaks at 3500 (OH), 1150 (tertiary OH), 758, 748, and 702 cm.$^{-1}$ (Ph and o-C_6H_4)]. In both concentrated sulphuric acid and acetic–sulphuric acid it gave colour reactions similar to those of the diol (II; R = Me, R′ = Ph). After refluxing for 3 hr. in chlorobenzene, the alcohol (XI) gave a compound, thought to be trans-*9,10-dihydro-9,10-dihydroxy-9-methyl-10-phenylanthracene,* which crystallised from cyclohexane in forms of m. p. 186—187° and 218—220° (Found, for sample of higher m. p.: C, 83·5; H, 6·1. $C_{21}H_{18}O_2$ requires C, 83·4; H, 6·0%). It had $\nu_{max.}$ 3570 (OH), 770, and 700 cm.$^{-1}$ (Ph) and $\lambda_{max.}$ 2540, $\lambda_{min.}$ 2470 Å ($\varepsilon_{max.}/\varepsilon_{min.}$ 1·06).

cis-9,10-Dihydro-9,10-dihydroxy-9,10-dimethylanthracene, obtained on decomposition of the dimethyl photo-oxide in the presence of phenols, had m. p. 180—181° (cf. Guyot and Staehling [27]), unchanged on admixture with material prepared by hydrogenation of this photo-oxide in ethanol over Raney nickel. This substance (0·03 g.), after refluxing for 4 hr. in chlorobenzene (25 ml.), gave 9-hydroxymethyl-10-methylanthracene.

Decomposition of the dimethyl photo-oxide in chlorobenzene in the presence of α-naphthol gave, besides the above compound, about 5% of *10-hydroxy-10 methylanthrone* (IV; R′ = Me, X = OH), m. p. 152—153° (from cyclohexane) (Found: C, 80·1; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·4; H, 5·4%), $\nu_{max.}$ 3350 and 1180 (tertiary OH), 1640 (Ar_2CO), and 768 cm.$^{-1}$ (o-C_6H_4). The same product (no mixed m. p. depression) was obtained in 2% yield by oxidising 9-methylanthracene (2 g.) for 10 min. with potassium dichromate (2 g.) in boiling acetic acid (25 ml.), and purifying the sticky product chromatographically. Its phenyl analogue [31] (IV; R′ = Ph, X = OH), m. p. 215° (Found: C, 83·5; H, 4·6. Calc. for $C_{20}H_{14}O_2$: C, 83·9; H, 4·9%), was obtained in 70% yield from 9-phenylanthracene by a similar procedure; [31] it gave a purple colour with cold concentrated sulphuric acid.

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[31] Baeyer and Schillinger, *Annalen*, 1880, **202**, 58.