207. *Polycyclic Aromatic Hydrocarbons. Part XXIV.*

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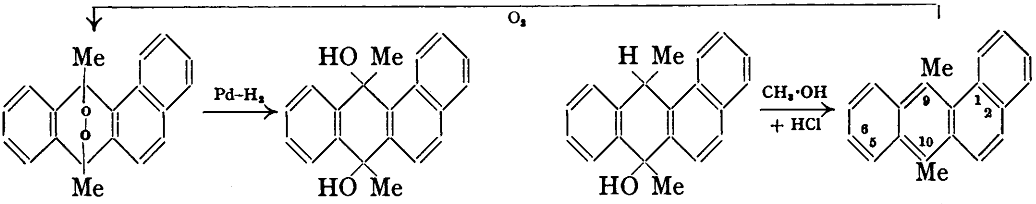
Homologues of 1 : 2-benzanthracene with substituents at position 9 or 10 (or both) give photo-oxides when oxygen is passed through their dilute solutions in carbon disulphide, exposed to light. This behaviour appears unrelated to the carcinogenic activity of the hydrocarbons. The *photo-oxide* of 9 : 10-dimethyl-1 : 2-benzanthracene is shown to have structure (I).

The rubrenes, well known for their ability to combine with oxygen in the presence of sunlight to give oxides which liberate their oxygen when heated, are all derived from 2 : 3-benzanthracene, and it is now recognised that the capacity to form photo-oxides is widespread among anthracene derivatives but is not shown by other groups of polycyclic aromatic compounds (for review with bibliography, see Dufraisse, *Bull. Soc. chim.*, 1939, **6**, 422). The experiments now recorded, of which a preliminary account has been published (Cook, Martin, and Roe, *Nature*, 1939, **143**, 1020), were undertaken in order to determine whether the formation of photo-oxides of the type studied by Dufraisse and his collaborators is involved in the cellular changes which occur in the tissues under the influence of the carcinogenic hydrocarbons of the 1 : 2-benzanthracene group. This appears not to be the case, for tumours did not result from injection into mice of suspensions in sesame oil of the pure photo-oxide of the highly carcinogenic 9 : 10-dimethyl-1 : 2-benzanthracene (IV), and it has not been possible to isolate photo-oxides from 1 : 2 : 5 : 6-dibenzanthracene or 3 : 4-benzpyrene.

The photo-oxide of anthracene was obtained by Dufraisse and Gérard (*Bull. Soc. chim.*, 1937, **4**, 2052) by irradiation of a solution of the hydrocarbon with a carbon arc, but for the most part sunlight has been used hitherto as the source of light. We have found that an ordinary gas-filled lamp furnishes a convenient source for the facile photo-oxidation of 9 : 10-dimethyl-1 : 2-benzanthracene and its derivatives. In the case of 1 : 2-benzanthracene there were indications of the formation of a photo-oxide, but this could not be isolated on account of its high solubility and contamination with amorphous by-products. Benzanthracene derivatives with only one *meso*-substituent (9-methyl, 10-methyl, and 10-*iso*propyl derivatives) also gave photo-oxides, although less readily than the 9 : 10-disubstituted compounds. A photo-oxide could not be obtained from 1 : 2-dimethylchrysene, a carcinogenic hydrocarbon not related to 1 : 2-benzanthracene (Hewett, this vol., p. 293). Since this work was completed, Velluz (*Bull. Soc. chim.*, 1939, **6**, 1541) has described the photo-oxides of 9 : 10-diphenyl-1 : 2-benzanthracene and 9 : 10-diphenyl-1′ : 2′ : 3′ : 4′-tetrahydro-1 : 2-benzanthracene, and Allsopp (*Nature*, 1940, **145**, 303) has reported experiments on the photo-oxidation of 3 : 4-benzpyrene, under somewhat different conditions, to labile water-soluble products.

The photo-oxides of the anthracene hydrocarbons are undoubtedly peroxides involving both *meso*-carbons atoms. 9 : 10-*Dimethyl*-1 : 2-*benzanthracene photo-oxide* (I) gave by catalytic hydrogenation the same 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (II) which Bachmann and Bradbury (*J. Org. Chem.*, 1937, 2, 175) obtained from 1 : 2-benzanthraquinone and methylmagnesium iodide. In another hydrogenation



(I.) (II.) (III.) (IV.)

experiment carried out under the same conditions the product was a well-defined crystalline compound (probably III), which was quantitatively converted into 9 : 10-dimethyl-1 : 2-benzanthracene (IV) by treatment in warm methyl-alcoholic solution with a trace of hydrochloric acid. We attribute the different results of these two experiments to the influence, in the second case, of hydrogen chloride formed by hydrogenation of chloroform of crystallisation which was present in the sample used in this, but not the earlier experiment.

The relative stability of the photo-oxides is noteworthy. 5 : 6 : 9 : 10-*Tetramethyl*-1 : 2-*benzanthracene photo-oxide* was recovered unchanged after its solution in 8% alcoholic potash had been boiled for two hours.

EXPERIMENTAL.

The irradiation experiments were carried out by passing a slow stream of oxygen through a solution of the hydrocarbon (0·2 g.) in carbon disulphide (400 c.c.) exposed to the light of a 200-watt gas-filled lamp. The solution was contained in a 600 c.c. beaker surrounded by a larger glass vessel through which cold water was continuously circulated. The lamp was placed in position below this outer vessel and the whole apparatus was enclosed in a white enamelled iron pan which ensured good reflection. In some of the earlier experiments a little eosin was added as a sensitiser, and in such an experiment 1 : 2-benzanthracene on one occasion gave a small quantity of a colourless crystalline product, m. p. about 110°. In general, however, the use of eosin presented very little advantage and was discontinued.

The irradiation with passage of oxygen was carried out until a sample of solution gave on evaporation a residue which did not show a fluorescence when examined by the ultra-violet light of a screened mercury-vapour lamp. The time required (2½—4½ hours) varied with the compound. With 1 : 2 : 5 : 6-dibenzanthracene, only unchanged hydrocarbon was isolated after 24 hours' exposure in presence of eosin.

After oxidation the carbon disulphide was evaporated in the dark at 20—25° under reduced pressure, the receiver being cooled in ice and salt. Purification of the residual photo-oxide was effected by dissolving it in carbon disulphide at 25° and allowing the solution to crystallise in the refrigerator. Except in the case of the photo-oxide of 10-*iso*propyl-1 : 2-benzanthracene, which formed small colourless prisms, all the photo-oxides crystallised in colourless silky needles. Melting points were determined by immersing the capillary tube containing the substance in a bath previously heated to about 10° below the m. p. and then heating the bath slowly. In this way reproducible values were obtained. The following table gives the m. p.'s and analytical figures for the compounds prepared :

		Found.		Calc.		
Photo-oxide of	M. p.	C, %.	H, %.	Formula.	C, %.	H, %.
9-Methyl-1 : 2-benzanthracene	122—123°	83·3	4·7	$C_{19}H_{14}O_2$	83·2	5·1
10-Methyl-1 : 2-benzanthracene	129—130	83·5	5·3	$C_{19}H_{14}O_2$	83·2	5·1
10-*iso*Propyl-1 : 2-benzanthracene	166—167	82·8	5·9	$C_{21}H_{18}O_2$	83·4	6·0
9 : 10-Dimethyl-1 : 2-benzanthracene *	193—194	83·1	5·6	$C_{20}H_{16}O_2$	83·3	5·6
5 : 9 : 10-Trimethyl-1 : 2-benzanthracene	212—213	83·2	6·0	$C_{21}H_{18}O_2$	83·4	6·0
6 : 9 : 10-Trimethyl-1 : 2-benzanthracene	205—206	83·4	6·1	$C_{21}H_{18}O_2$	83·4	6·0
5 : 6 : 9 : 10-Tetramethyl-1 : 2-benzanthracene	228—229	83·3	6·3	$C_{22}H_{20}O_2$	83·5	6·4
9 : 10-Dimethyl-1 : 2 : 5 : 6-dibenzanthracene	222—223	85·0	5·5	$C_{24}H_{18}O_2$	85·2	5·4

* The photo-oxide of 9 : 10-dimethyl-1 : 2-benzanthracene crystallised from chloroform in long colourless needles, m. p. 188—189°, which contained a molecule of chloroform of crystallisation (Found : C, 62·5; H, 4·2. $C_{20}H_{16}O_2$,$CHCl_3$ requires C, 61·8; H, 4·2%).

Catalytic Hydrogenation of 9 : 10-*Dimethyl*-1 : 2-*benzanthracene Photo-oxide.*—(a) A solution of the photo-oxide (0·4 g.) in pure acetone (50 c.c.) was shaken in the dark for 20 hours with hydrogen and palladium-black. The product, after crystallisation from benzene, had m. p. 183—184°, not depressed by admixture with authentic 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthracene (Bachmann and Bradbury, *loc. cit.*). Identification was completed by conversion with methyl-alcoholic hydrochloric acid into the dimethyl ether of this diol, described by Bachmann and Chemerda (*J. Amer. Chem. Soc.*, 1938, **60**, 1023).

(b) Hydrogenation carried out for 24 hours as described under (a) gave a product, m. p. 185°, which depressed the m. p. of the original photo-oxide and also that of the diol of Bachmann and Bradbury. Addition of a few drops of methyl-alcoholic hydrochloric acid to a warm methyl-alcoholic solution of this product (III or an isomeride) gave pure 9 : 10-dimethyl-1 : 2-benzanthracene (Bachmann and Chemerda, *loc. cit.*).

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