CLXV.—*The Reactivity of* meso-*Substituted Anthracenes. Part I.*

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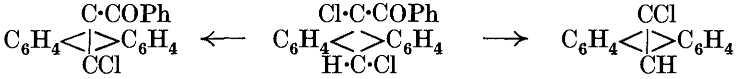
It has already been shown (Barnett, Cook, and Grainger, J., 1922, **121**, 2060; Barnett, Cook, and Matthews, J., 1923, **123**, 1997; Barnett and Cook, J., 1923, **123**, 2631; 1924, **125**, 1084; Barnett, J., 1925, **127**, 2040) that in many cases *meso*-substituents in the anthracene ring system render compounds formed by addition to the " bridge " unstable or incapable of existence. The investigation of 9-benzoylanthracene (anthraphenone) has now shown that the presence of the benzoyl group hinders the formation of additive compounds. Thus with bromine no additive compound could be obtained, the sole product being 10-bromoanthraphenone. With chlorine, a similar result was obtained, although in one instance an additive compound (I) was isolated which, slowly at the ordinary temperature and rapidly on heating, lost both hydrogen chloride and benzoyl chloride and passed into a mixture of 10-chloroanthraphenone (II) and 9-chloroanthracene (III) :



$$\mathrm{C_6H_4}\!<\!\overset{\mathrm{C{\cdot}COPh}}{\underset{\mathrm{CCl}}{|}}\!>\!\mathrm{C_6H_4} \longleftarrow \mathrm{C_6H_4}\!<\!\overset{\mathrm{Cl{\cdot}C{\cdot}COPh}}{\underset{\mathrm{H{\cdot}C{\cdot}Cl}}{\;}}\!>\!\mathrm{C_6H_4} \longrightarrow \mathrm{C_6H_4}\!<\!\overset{\mathrm{CCl}}{\underset{\mathrm{CH}}{|}}\!>\!\mathrm{C_6H_4}$$

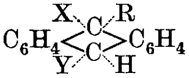
(II.) (I.) (III.)

This behaviour suggests that the additive compound had the *trans*-configuration, but unfortunately all attempts to repeat the preparation failed, the sole product being 10-chloroanthraphenone.

The action of nitric acid on anthraphenone leads to 10-nitroanthraphenone (IV) (compare Lippmann and Keppich, *Ber.*, 1900, **33**, 3086), no additive compound being isolated, but with nitrogen dioxide addition takes place easily and leads to a moderately stable dinitro-compound (V) which readily loses nitrous acid under the influence of cold pyridine and passes into 10-nitroanthraphenone :

$$\begin{array}{c} NO_2\cdot C\cdot COPh \\ C_6H_4<\;>C_6H_4 \\ NO_2\cdot C\cdot H \end{array} \longrightarrow \begin{array}{c} C\cdot COPh \\ C_6H_4<|>C_6H_4 \\ C\cdot NO_2 \end{array}$$

(V.) (IV.)



$$\begin{array}{c} X\diagdown\;\diagup R \\ C \\ C_6H_4<\;>C_6H_4 \\ C \\ Y\diagup\;\diagdown H \end{array}$$

(VI.)

The " negative " or unsaturated benzoyl group thus resembles other negative groups in its ability to render *meso*-additive compounds unstable, and this behaviour is in general harmony with the idea of valency developed by Werner. Thus an unsaturated group at position 9 will appropriate some of the free affinity of that carbon atom ; the carbon atom at 10 will accordingly have relatively more free affinity, encouraging substitution by addition at 10 rather than by addition to the " bridge." In derivatives of 9 : 10-dihydroanthracene (VI) the union of each *meso*-carbon atom with two unsaturated benzene nuclei results in a comparatively small amount of affinity being available for holding the other groups. These groups are thus endowed with considerable free affinity and are consequently very reactive. Thus, direct bromination of dihydroanthracene takes place with great ease, and in anthracene dibromide ($R = H$; $X = Y = Br$) the bromine atoms are very much more reactive than in a simple aliphatic bromo-compound. The tenacity with which X is held should be decreased by increasing the unsaturated nature of R, since unsaturation in R will lead to this group appropriating more affinity and hence leaving less available for holding X. A phenyl group is more unsaturated in nature than a benzoyl group (Werner, *Ber.*, 1906, **39**, 1278), so that phenylanthracene should give less stable additive compounds than benzoylanthracene. This is in accordance with fact, since, as already stated, benzoylanthracene gives an additive compound with nitrogen dioxide, whereas phenylanthracene does not (Barnett, *loc. cit.*). On the basis of the above argument the more saturated benzylanthracene should show greater capacity for undergoing additive reactions and should yield more stable additive compounds. That this is the case will be shown in a future communication.

The nature of the group R is not, of course, the only factor which influences the stability of these additive compounds. The influence of their geometrical configuration has been shown in the case of the two stereoisomeric 1 : 5-dichloro-9 : 10-dihydroanthraquinols (Barnett, Cook, and Matthews, *Rec. trav. chim.*, 1925, **44**, 729) and the ease with which re-establishment of the " bridge " takes place must also be affected by the affinity which the groups at 9 have for the groups at position 10.

The acyl group in the *meso*-ketones of the anthracene series is less firmly held than is usually the case with aromatic ketones. Thus anthraphenone and its chloro- and bromo-derivatives are completely hydrolysed by brief boiling with sulphuric acid in acetic acid (compare Krollpfeiffer, *Ber.*, 1923, **56**, 2360) and anthroylbenzoic acid exhibits similar instability (Heller, *ibid.*, 1921, **54**, 3627). It has already been shown (Barnett, Cook, and Matthews, *loc. cit.*) that the facile hydrolysis of anthranyl ethers is due to primary addition to the " bridge," and the hydrolysis of the ketones may be due to a similar cause, but rigorous proof is lacking. The fact that hydrogen bromide is liberated during the hydrolysis of bromoanthraphenone cannot be cited as an argument, as 9-bromoanthracene behaves in the same way under similar experimental conditions. This view of the mechanism receives support from the observation that 10-nitroanthraphenone, 10-benzoylanthraphenone and 9 : 10-dihydroanthraphenone are not hydrolysed by boiling with sulphuric acid in acetic acid. In the first two cases the attachment of an unsaturated group at position 10 may be regarded as diminishing the free affinity of this carbon atom and thus inhibiting 9 : 10-addition. In the last case addition of this nature is not possible.

Neither anthraphenone nor any of its derivatives shows any signs of visible fluorescence, so that the carbonyl group is presumably a powerful bathoflore.

EXPERIMENTAL.

Anthraphenone.—The condensation of anthracene with benzoyl chloride in presence of aluminium chloride or zinc dust (Perrier, *Ber.*, 1900, **33**, 816; Lippmann and his co-workers, *ibid.*, 1899, **32**, 2249; 1900, **33**, 3086; 1901, **34**, 2766; Krollpfeiffer, *loc. cit.*) is troublesome to carry out and tarry by-products are formed. Benzoic anhydride was therefore substituted for benzoyl chloride (compare Noller and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1889).

To a suspension of finely ground anthracene (90 g.) in carbon disulphide (750 c.c.) was added powdered anhydrous aluminium chloride (150 g.), followed by benzoic anhydride (175 g.*). Reaction took place with liberation of hydrogen chloride and was brought to completion by 4 hours' heating on the water-bath.

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* If only one molecule of benzoic anhydride is employed there is formed the eutectic mixture of anthraphenone and anthracene, m. p. 158°, described by Lippmann and Keppich (*loc. cit.*) and the anthracene cannot be removed by any simple treatment.

The dark aluminium compound was decomposed with water and hydrochloric acid, the carbon disulphide removed by steam distillation, and the benzoic acid extracted from the residue by treatment with sodium hydroxide solution. After drying, the brown reaction product was treated with boiling glacial acetic acid (750 c.c.). The filtered solution, on cooling, deposited crystals which, recrystallised from benzene and then from acetic acid, yielded 85 g. of pure anthraphenone, m. p. 148°. This developed a fugitive, pure blue coloration in sulphuric acid.

The residue insoluble in acetic acid was recrystallised twice from nitrobenzene (yield, 15 g.), then from pyridine and alcohol, and finally from xylene. It formed a cream-coloured, crystalline powder, m. p. 320°, and gave a purplish-red solution in sulphuric acid (Found : C, 87·0 ; H, 4·8 ; *M*, in naphthalene, 401. Calc. for 9 : 10-dibenzoylanthracene : C, 87·0 ; H, 4·7% ; *M*, 386). Lippmann and Fleissner (*Ber.*, 1899, **32**, 2249) obtained this substance as a by-product in the preparation of anthraphenone, but in a later paper (Lippmann and Keppich, *ibid.*, 1900, **33**, 3086) the by-product was described as tribenzoylanthracene. This compound gave anthraquinone on oxidation and this and other properties of the substance indicate that it was really impure dibenzoylanthracene.

9 : 10-Dibenzoylanthracene is obtained in 20% yield when anthraphenone is treated with an excess of benzoic anhydride in presence of anhydrous aluminium chloride. The positions assigned to the benzoyl groups follow from a study of the reduction products (future communication).

10-*Bromoanthraphenone*.—A suspension of anthraphenone (2·5 g.) in carbon disulphide (15 c.c.) was cooled in a freezing mixture, and bromine (0·5 c.c. ; 1 mol.), dissolved in carbon disulphide (5 c.c.), was added slowly. Hydrogen bromide was liberated and since the addition of pyridine yielded only pyridine hydrobromide and no quaternary salt it is unlikely that addition of bromine had occurred. The bromo-derivative was obtained by evaporating the solution and crystallising the residue from acetic acid, benzene, and finally ethyl acetate (Found : Br, 22·0. $C_{21}H_{13}OBr$ requires Br, 22·2%).

10-*Bromoanthraphenone* forms pale yellow nodules, m. p. 175—176°. It gives a deep blue solution in sulphuric acid, the colour being less fugitive than in the case of anthraphenone itself. The same compound is obtained when the bromination is carried out in boiling glacial acetic acid solution. If two molecules of bromine are employed and the boiling is continued for an hour, the bromoanthraphenone is contaminated with 9 : 10-dibromoanthracene, this compound being formed by partial hydrolysis of the bromoanthraphenone and subsequent bromination.

10-*Chloroanthraphenone*.—Anthraphenone (5·6 g.) was added to a solution of chlorine in carbon tetrachloride (20 c.c.; 7·5%, wt.-vol.), the mixture boiled for 15 minutes, cooled, and light petroleum added. The resulting solid crystallised from glacial acetic acid, benzene and finally ethyl acetate in yellow nodules, m. p. 164—165° (Found: Cl, 11·3. $C_{21}H_{13}OCl$ requires Cl, 11·2%).

9 : 10-*Dichloro*-9 : 10-*dihydroanthraphenone*.—A solution of anthraphenone (11·4 g.) in carbon tetrachloride (40 c.c.) was cooled in ice, chlorine in carbon tetrachloride solution (40 c.c.) added, the mixture kept in ice for 2 hours, and light petroleum added. The resulting solid crystallised from warm benzene–light petroleum in colourless needles, m. p. 110—111° (decomp.). After being kept in a vacuum desiccator for 2 days, the substance smelled strongly of benzoyl chloride, so the sample for analysis was recrystallised from benzene and light petroleum and dried in a vacuum desiccator for 3½ hours (Found: Cl, 19·8. $C_{21}H_{14}OCl_2$ requires Cl, 20·1%).

The dichloride (0·5 g.) was suspended in cold pyridine (1 c.c.) and after an hour ether was added and the solid recrystallised from alcohol and ether. It formed colourless needles completely soluble in water, and although analysis showed that the substance was not pure it was evident that both chlorine atoms of the dichloride had suffered displacement by pyridinium groups (Found: Cl, 14·4. $C_{31}H_{24}ON_2Cl_2$ requires Cl, 13·9%).

Thermal Decomposition of Anthraphenone Dichloride.—The dichloride (0·1 g.) was heated to its melting point; hydrogen chloride and benzoyl chloride (identified by its smell) were then liberated. The resulting mixture was fractionally crystallised from alcohol into (*a*) 10-chloroanthraphenone, identified by the method of mixed melting points, and (*b*) slender, yellow needles, m. p. 96—98°, which gave solutions having a strong violet fluorescence. The identification was completed by direct comparison with an authentic sample of 9-chloroanthracene.

10-*Nitroanthraphenone*.—Anthraphenone, suspended in acetic acid, was slowly nitrated by nitric acid (1 mol.; *d* 1·42) in the cold without the production of an additive compound. The reaction was best completed by heating on the water-bath for a few minutes; the nitro-compound was then obtained pure without the elaborate purification recommended by Lippmann and Keppich (*loc. cit.*).

9 : 10-*Dinitro*-9 : 10-*dihydroanthraphenone*.—A stream of nitrogen dioxide (2·6 g.) prepared by heating a mixture of lead nitrate and sand, was led into a solution of anthraphenone (5·6 g.) in chloroform (10 c.c.), cooled in a freezing mixture; after an hour light petroleum was added. The resinous substance that separated became solid when ground under ether. Thrice recrystallised from chloroform

and light petroleum and dried in a vacuum desiccator, it was obtained in colourless needles, m. p. 175° (decomp.) (Found: N, 7·8. $C_{21}H_{14}O_5N_2$ requires N, 7·5%). Suspended over-night in cold pyridine diluted with alcohol, it lost nitrous acid and passed into 10-nitroanthraphenone (identified by the method of mixed melting points).

Fission of Anthraphenone Derivatives.—In order to compare the influence of the substituent in the 10-position the same conditions were employed in all cases. Krollpfeiffer (*loc. cit.*) has shown that if this substituent is hydroxyl, hydrolysis can be effected by boiling with hydrochloric acid in acetic acid, whereas anthraphenone itself is unaffected under these conditions.

10-Chloro-, 10-bromo-, and 10-nitro-anthraphenone were all recovered unchanged after 4 hours' boiling with hydrochloric acid in acetic acid. Chloroanthraphenone was not affected by heating for 5 hours at 170° with acetic acid saturated with hydrogen chloride.

Hydrolysis with sulphuric acid was attempted by boiling the substance (1 g.) with acetic acid (10 c.c.) containing sulphuric acid (1 c.c.) for ½ hour. Krollpfeiffer's observation that anthraphenone is completely decomposed into benzoic acid and anthracene was confirmed. Bromoanthraphenone and chloroanthraphenone gave tarry products (in the former case hydrogen bromide was liberated), whilst 9 : 10-dihydroanthraphenone, 10-nitroanthraphenone and 9 : 10-dibenzoylanthracene were recovered unchanged (in the last case after 3 hours' boiling).

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this investigation, and to Dr. E. de Barry Barnett for gifts of materials.

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[*Received, January 20th*, 1926.]