194. *The Influence of* Bz.-*Substituents upon Some Reactions of the Anthrones. Part I.*

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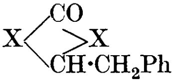
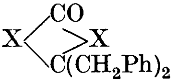
SUBSTITUENTS in the side rings often profoundly affect the course of reactions involving the *meso*-carbon atoms, and, so far as can be judged at present, a methyl group exerts an influence very similar to that of a chlorine atom in the same position. This, however, is not an invariable rule, as is shown by the slight stability of 1 : 4-dimethylanthracene dibromide (Barnett and Low, *Ber.*, 1931, **64**, 49) as compared with the very much greater stability of 1 : 4-dichloroanthracene dibromide (Barnett, Matthews, and Wiltshire, *Rec. trav. chim.*, 1926, **45**, 926). In the case of an anthrone the reactions shown both by the methylene group and by the carbonyl group are affected by *Bz*.-substitution, and as several *Bz*.-dichloro- and *Bz*.-dimethyl-anthrones are now available it is proposed to study this point as systematically as possible.

The condensation of anthrone with benzyl chloride in the presence of caustic potash leads to 10 : 10-dibenzylanthrone (II) (Hallgarten, *Ber.*, 1888, **21**, 2508), and 1-chloroanthrone (Barnett and Cook, J., 1928, 566), 2- and 3-chloroanthrone (Barnett and Goodway, J., 1930, 1348) behave in the same way. On the other hand, 1 : 4-, 1 : 5-, 1 : 8-, and 4 : 5-dichloroanthrone (Barnett and Goodway, Barnett and Cook, *loc. cit.*; Barnett and Wiltshire, *Ber.*, 1929, **62**, 3063) all give the 10-benzylanthrone (I). 2 : 3-Dichloroanthrone is exceptional and gives the benzylanthranyl benzyl ether (III) (Barnett, Goodway, and Savage, *Ber.*, 1931, **64**, 2185). It has now been found that 1 : 3- and 2 : 3-dimethylanthrone both give dibenzyl compounds, and that 1 : 4-dimethylanthrone remains almost unaffected under the same conditions. 2 : 4-Dimethylanthrone, like 4-chloroanthrone (Barnett and Cook, *loc. cit.*), gives only resinous products.


(I.)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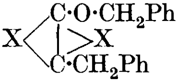
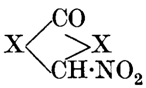
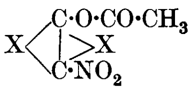

(III.)

10-Nitroanthrone (IV) is readily converted into 10-nitroanthranyl acetate (V) by the action of acetic anhydride in cold pyridine solution (Barnett and Cook, J., 1923, **123**, 2003), and 1-, 2-, and 3-chloroanthrone all behave in the same way, whereas 4-chloro- and 1 : 5- and 1 : 8-dichloroanthrone undergo complete decomposition, and 4 : 5-dichloroanthrone is unaffected (Barnett and Wiltshire, *Ber.*, 1930, **63**, 1690).

(IV.) 

$$X\Big\langle\begin{matrix}CO\\ \\ CH\cdot NO_2\end{matrix}\Big\rangle X$$

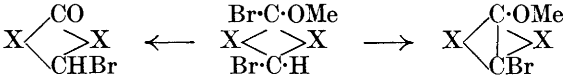
 (V.)

$$X\Big\langle\begin{matrix}C\cdot O\cdot CO\cdot CH_3\\ |\\ C\cdot NO_2\end{matrix}\Big\rangle X$$

The general conclusion drawn from these results was that a chlorine atom in position 4 or 5 prevents the conversion of a 10-nitroanthrone into the nitroanthranyl acetate by the pyridine–acetic anhydride method, and an examination of 1 : 4- and 2 : 3-dichloro-10-nitroanthrone has shown that they conform to this rule, the former undergoing complete decomposition and the latter giving a well-defined acetate.

An examination of the *Bz.*-dimethyl-10-nitroanthrones has indicated that a methyl group at 1 exerts a similar influence to that of a chlorine atom at 4, although the results obtained are less definite than was hoped owing to the unforeseen difficulty in preparing 10-nitro-2 : 4-dimethylanthrone. Of the three isomeric *Bz.*-dimethyl-10-nitroanthrones which have been prepared, only the 2 : 3-dimethyl compound is converted into an acetate, both the 1 : 3- and the 1 : 4-dimethyl isomeride undergoing profound decomposition.

The action of bromine on an anthranyl methyl ether almost certainly consists primarily in addition to the *meso*-positions. The resulting dibromide (VI) is too unstable to isolate and can conceivably undergo decomposition in two ways, *viz.*, by loss of methyl bromide with formation of the bromoanthrone (VII), or by transannular loss of hydrogen bromide with formation of the bromoanthranyl methyl ether (VIII) :

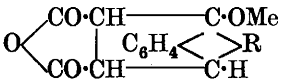


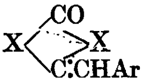
$$X\Big\langle\begin{matrix}CO\\ \\ CHBr\end{matrix}\Big\rangle X \longleftarrow X\Big\langle\begin{matrix}Br\cdot C\cdot OMe\\ \\ Br\cdot C\cdot H\end{matrix}\Big\rangle X \longrightarrow X\Big\langle\begin{matrix}C\cdot OMe\\ |\\ CBr\end{matrix}\Big\rangle X$$

(VII.) (VI.) (VIII.)

Both types of reaction are known, the latter taking place when anthranyl methyl ether is brominated (K. H. Meyer and Schlösser, *Annalen*, 1919, **420**, 129), and the former when 1 : 5-dichloroanthranyl methyl ether is treated in the same way (Barnett, Cook, and Matthews, *Ber.*, 1925, **58**, 976). This is rather surprising in view of the very depressed tendency for 1 : 5-dichloroanthracene dihalides to undergo transannular loss as compared with the corresponding compounds in which the *Bz.*-halogen atoms are absent.

An examination of a series of *Bz.*-chloro- and *Bz.*-methyl-anthranyl methyl ethers has now been carried out, and the rather remarkable fact has emerged that those ethers in which a chlorine atom or a methyl group is in the *peri*-position to the methoxyl group show no visible fluorescence, even when their solutions are examined in the light of the arc lamp. The acetates, however, are all strongly fluorescent and so also are those ethers in which *peri*-substituents are absent. No exceptions to this rule, which is empirical at present and for which no explanation is offered, have been discovered, and all the following ethers have been found to obey it: 1- and 4-chloro-, 1 : 4-, 1 : 5-, 1 : 8-, 4 : 5-, and 2 : 3-dichloro-, 1 : 3-, 1 : 4-, 2 : 3- and 2 : 4-dimethyl-anthranyl methyl ether. All the above were obtained in the pure state with the exceptions of the 1-chloro- and the 1 : 4-dimethyl compound. Both of these refused to crystallise, but the solutions of the crude substances showed no fluorescence and the ethers were brought to analysis in the form of their maleic anhydride additive compounds (IX; R = C_6H_3Cl or $C_6H_2Me_2$):


(IX.)


(X.)

The ethers on bromination fall sharply into two classes, *viz.*, those in which little or no hydrogen bromide is evolved and the bromoanthrone (VII) is formed (1 : 4-, 1 : 5-, and 4 : 5-dichloro- and 1 : 4- and 2 : 4-dimethyl-anthranyl methyl ethers), and those in which there is copious evolution of hydrogen bromide and formation of the bromoanthranyl methyl ether (VIII) (anthranyl methyl ether, 1 : 8- and 2 : 3-dichloro- and 1 : 3- and 2 : 3-dimethyl-anthranyl methyl ethers). A substituent in the *peri*-position to the methoxyl group does not, therefore, affect the reaction, the production of the bromoanthrone depending on the presence of a substituent in the *peri*-position to the *meso*-hydrogen atom. The yields of the products indicate that in each case only one reaction takes place to any appreciable extent.

The production of an alkylideneanthrone (X) by the condensation of an anthrone with an aromatic aldehyde in the presence of piperidine is also a reaction which is easily inhibited by *Bz.*-substituents. Thus anthrone readily gives 10-benzylideneanthrone (Cook, J., 1928, 2160, where references to earlier work will be found), and 1 : 8-dichloroanthrone behaves in the same way, whereas 1 : 5- and 4 : 5-dichloroanthrone fail to react (Barnett, Goodway, and Wiltshire, *Ber.*, 1930, **63**, 1690). It has now been found that 1 : 4-dichloro- and 1 : 4- and 2 : 4-dimethylanthrone all fail to give benzylidene derivatives, whereas benzylidene compounds are readily formed by 1 : 3- and 2 : 3-dimethylanthrone. 2 : 3-Dichloroanthrone also gave a benzylidene derivative, but the reaction was slow and the product contained unchanged anthrone.

EXPERIMENTAL.

1 : 8- *and* 4 : 5-*Dichloroanthrone.*—The reduction of 1 : 8-dichloroanthraquinone to 1 : 8- and 4 : 5-dichloroanthrone by tin and hydro-

chloric and acetic acids was unaffected by the rate of addition of the hydrochloric acid (contrast the reduction of 1-chloroanthraquinone to 4-chloroanthrone: Speitel, Thèses, Strasbourg, 1929; Barnett and Matthews, J., 1923, **123**, 2631). Indeed the reduction was most quickly and conveniently done by boiling 50 g. of 1 : 8-dichloroanthraquinone with 110 g. of crystallised stannous chloride, 125 c.c. of concentrated hydrochloric acid, and 800 c.c. of glacial acetic acid until the colour of the solution became pale (1—2 hours); the isomerides were separated in the way previously described (Barnett, Goodway, and Wiltshire, *Ber.*, 1930, **63**, 472), and 24 g. of pure 4 : 5-dichloroanthrone obtained.

10 : 10-*Dibenzyl*-1 : 3-*dimethylanthrone* (II).—8 G. of 1 : 3-dimethylanthrone and 10 c.c. of benzyl chloride were boiled for 2 hours with a solution of 9 g. of potassium hydroxide in 30 c.c. of water. After being cooled and washed with water, the product was triturated with ether in a freezing mixture, and the resulting solid recrystallised from *cyclo*hexane containing a little benzene. It then formed colourless crystals, m. p. 206° (Found : C, 89·3; H, 6·4. $C_{30}H_{26}O$ requires C, 89·5; H, 6·5%).

10 : 10-*Dibenzyl*-2 : 3-*dimethylanthrone* (II), similarly prepared and purified (it was found advantageous to remove volatile matter with steam before triturating with ether), formed colourless crystals, m. p. 199° (Found : C, 89·5; H, 6·6%).

Nitroanthrones and Nitroanthranyl Acetates (IV and V).—In all cases the anthranyl acetate (0·02 mol.) was suspended in glacial acetic acid (25—50 c.c.) and 2·2 g. of nitric acid (*d* 1·42), diluted with 5 c.c. of glacial acetic acid, were added slowly at the ordinary temperature; the reaction was completed by warming for a few minutes at 50—70°. After cooling, the nitroanthrone was washed with glacial acetic acid and with methyl alcohol and recrystallised from benzene, with or without the addition of *cyclo*hexane or light petroleum according to the solubility of the substance. The nitroanthrones all formed colourless crystals.

Acetylation was effected by adding 3 c.c. of acetic anhydride to a solution or suspension of 3 g. of the nitroanthrone in 10 c.c. of cold pyridine. As soon as the red colour had faded (2—5 minutes) the whole was cooled in a freezing mixture and the crystals were collected and washed with methyl alcohol. It is essential that the preparation be carried out as rapidly as possible. Recrystallisation was effected from benzene or toluene. The acetates formed brilliant yellow crystals.

In the following table the analytical figures refer to nitrogen, the calculated values being given in parentheses. All the compounds decompose at the melting point.

Bz.-Substituents.	Nitroanthrone.	Nitroanthranyl acetate.
1 : 3-Me_2	m. p. 150°; 5·3 (5·2%)	—
1 : 4-Me_2	m. p. 159°; 5·3%	—
2 : 3-Me_2	m. p. 150°; 5·1%	m. p. 242°; 4·6 (4·5%)
1 : 4-Cl_2	m. p. 162°; 4·5 (4·55%)	—
2 : 3-Cl_2	m. p. indefinite; 4·6%	m. p. 225—230°; 4·0 (4·0%)

Anthranyl Methyl Ethers.—These were all prepared by boiling the anthrone (0·03 mol.) with alcohol (50—100 c.c.) under reflux and adding methyl *p*-toluenesulphonate and potassium hydroxide (50% aqueous solution) alternately in very small amounts until there was only a very slight difference in colour of the solution when alkaline and when neutral. It was then made strongly alkaline and boiled for a few minutes to destroy the excess of methyl toluenesulphonate. The less soluble chloro-ethers were isolated by dilution with methyl alcohol and cooling in a freezing mixture, the resulting solid being thoroughly washed with water to remove potassium toluenesulphonate. The more soluble methyl compounds were isolated by dilution with water, followed in the case of 1 : 3-dimethylanthranyl methyl ether by distillation in steam and extraction with ether. Purification was effected by recrystallisation (charcoal) from methyl alcohol (A) or glacial acetic acid (B) and finally from light petroleum (C), *cyclo*hexane (D), or benzene (E). The ethers were, with the exception of the 1-chloro- and the 1 : 4-dimethyl-compound, yellow crystalline solids. They were all obtained in good yield with the exception of the 1 : 3-dimethyl compound. Owing to the production of resinous matter the purification of this was difficult and the yield of the pure product did not exceed 10—15%.

In the following table the analytical figures refer to carbon and hydrogen, the calculated figures being given in parentheses. The figures in the last column indicate the solvents used for purification (see above).

Bz.-Substituents.	M. p. and analysis.		Solvents used.
1 : 3-Me_2	58°.	86·1; 6·8 (86·4; 6·8)	A, C
2 : 3-Me_2	117°.	86·3; 6·8	A, D
2 : 4-Me_2	87°.	86·2; 6·9	A, C
4-Cl	120°.	74·0; 4·6 (74·2; 4·5)	A, D
1 : 4-Cl_2	130°.	65·2; 3·7 (65·0; 3·6)	B, E
1 : 8-Cl_2	173°.	65·0; 3·8	B, E
2 : 3-Cl_2	147°.	64·9; 3·6	B, E
4 : 5-Cl_2	145°.	64·7; 3·7	B, E

1-*Chloro*-9-*methoxy*-9 : 10-*dihydroanthraquinyl*-9 : 10-endo-αβ-*succinic Anhydride* (IX; R = C_6H_3Cl).—1-Chloroanthrone was methylated as described above, and the solution diluted with water and extracted with xylene. To the washed and dried (calcium chloride) xylene solution, maleic anhydride (0·03 mol.) was added, and the whole boiled. Crystals commenced to separate in about 10 minutes, and sufficient xylene was added to maintain a clear solution. After 30 minutes the filtered solution was cooled, and the solid recrystallised twice from xylene and dried at 170°. The resulting colourless crystals melted at 266° (Found : C, 66·8; H, 3·9. $C_{19}H_{13}O_4Cl$ requires C, 66·9; H, 3·8%).

9-*Methoxy*-1 : 4-*dimethyl*-9 : 10 - *dihydroanthraquinyl* - 9 : 10 - endo-αβ-*succinic anhydride* (IX; $R = C_6H_2Me_2$) was prepared from the crude methylation product of 1 : 4-dimethylanthrone in the same way as the compound described above, but the boiling with maleic anhydride in xylene solution was prolonged for 4 hours and, owing to the solubility of the product, it was necessary to isolate it by the addition of light petroleum. After extraction with boiling ether to remove unchanged maleic anhydride the product was recrystallised from toluene and dried at 145°. It then formed colourless crystals, m. p. 259° (Found : C, 75·4; H, 5·5. $C_{21}H_{18}O_4$ requires C, 75·5; H, 5·4%).

Bromination Experiments.—In all cases the ether was dissolved or suspended in carbon disulphide, cooled in a freezing mixture, and bromine (1 mol.), diluted with carbon disulphide, was added slowly. After being kept for 30 minutes at the ordinary temperature, the whole was very gently warmed for 2 or 3 minutes, and the solvent then removed in a vacuum at the ordinary temperature. Bromoanthrones (yield, usually about 90%) were identified, after recrystallisation, by comparison, as such and also as the derived piperidinoanthrones, with authentic samples.

1 : 4-*Dichloro*-10-*bromoanthrone*, not previously obtained in the pure state, was prepared by the bromination of 1 : 4-dichloroanthrone (Barnett, Goodway, and Wiltshire, *Ber.*, 1930, **63**, 1696); it separated from benzene in almost colourless crystals, m. p. 196° (Found : C, 48·9; H, 2·1. $C_{14}H_7OCl_2Br$ requires C, 49·1; H, 2·05%).

The bromoanthranyl methyl ethers were well-crystallised yellow solids with the exception of the 1 : 3-dimethyl compound, which refused to crystallise. There can, however, be no reasonable doubt but that it was produced by the bromination of 1 : 3-dimethylanthranyl methyl ether, since the reaction was accompanied by copious evolution of hydrogen bromide, and no trace of a piperidino-compound could be detected after the product had been treated with piperidine.

10-*Bromo*-2 : 3-*dimethylanthranyl methyl ether* formed yellow crystals, m. p. 151°, from benzene. Its solutions were fluorescent (Found : C, 64·4; H, 4·8. $C_{17}H_{15}OBr$ requires C, 64·7; H, 4·8%).

1 : 8-*Dichloro*-10-*bromoanthranyl methyl ether* formed brilliant greenish-yellow crystals, m. p. 155°, from benzene–light petroleum. Its solutions were not fluorescent (Found : C, 50·4; H, 2·5. $C_{15}H_9OCl_2Br$ requires C, 50·6; H, 2·5%).

2 : 3-*Dichloro*-10-*bromoanthranyl methyl ether* formed silky golden-yellow needles, m. p. 164°, from benzene. Its solutions were fluorescent (Found : C, 50·5; H, 2·7%).

Benzylideneanthrones.—In all cases the anthrone (0·025 mol.) was boiled for 4 hours with pyridine (15 c.c.), benzaldehyde (3 c.c.), and piperidine (6 drops). The solution was then diluted with aqueous methyl alcohol, and the solid obtained on cooling in a freezing mixture was washed with methyl alcohol. In cases in which the solid was the unchanged anthrone this was identified by comparison with an authentic sample, and all such anthrones were subsequently tested for their behaviour towards furfuraldehyde under the conditions given above, but in no case was an alkylideneanthrone obtained. The alkylideneanthrones obtained were recrystallised from *cyclo*hexane and were then pale yellow. They all gave crimson solutions in concentrated sulphuric acid.

10-*Benzylidene*-1 : 3-*dimethylanthrone* melts at 145° (Found : C, 88·9; H, 6·0. $C_{23}H_{18}O$ requires C, 89·0; H, 5·8%) and 10-*benzylidene*-2 : 3-*dimethylanthrone* at 166° (Found : C, 89·0; H, 5·9%).

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