IV.—*The Bromine Compounds of Phenanthrene.* *Part I.*

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WHEN it is considered that phenanthrene is one of the principal aromatic hydrocarbons derived from coal-tar, it seems strange that up to now almost the only commercial use to which it has been put is the production of lamp black, by its destruction. Several of the alkaloids, notably morphine, *apomorphine*, and thebaine, have the phenanthrene molecule as the chief basis of their structure, and the hydrocarbon should also be a fruitful source of colouring matters. One of the chief reasons why its value has not been more appreciated is undoubtedly the very meagre knowledge which we have of its more common compounds. Its halogen derivatives offer a promising field for inquiry.

The number of possible isomeric bromophenanthrenes is large, although few have been already described, and still fewer thoroughly investigated.

Of the five possible monobromo-derivatives, only 9-bromophenanthrene (m. p. 63°) is known (Hayduck, *Annalen*, 1873, **167**, 181). Of the twenty-five possible dibromo-derivatives only six are known, namely, the 2:7 (m. p. 199—200°; Hayduck, *loc. cit.*; Schmidt and Mezger, *Ber.*, 1907, **40**, 4562), the 9:10 (m. p. 181—182°; Hayduck, *loc. cit.*; Schmidt and Ladner, *Ber.*, 1904, **37**, 4404), the 3:9 (m. p. 146°; Zetter, *Ber.*, 1878, **11**, 170; Schmidt and Ladner, *Ber.*, 1904, **37**, 3571; Sandqvist, *Ber.*, 1920, **53**, [B], 168), the 4:9 (or 10) (m. p. 113°, Werner, *Annalen*, 1902, **321**, 331), the 10:(1, 4, 5 or 8) (m. p. 123°, Sandqvist, *Ber.*, 1915, **48**, 1146), and a dibromo-derivative melting at 202° (*Annalen*, 1873, **167**, 182). With the exception of two or three imperfectly described ones, nothing is known of the sixty-one possible tribromo-derivatives. In brominating phenanthrene, the 9:10-positions are those most readily attacked, and this dibromide is very unstable, decomposing at 100° with the evolution of hydrogen bromide and the formation of the 9-bromo-derivative (Hayduck, *loc. cit.*).

In the course of this work a 2(?)*-bromophenanthrene dibromide* (I) was isolated, which decomposed exactly as in the case of Hayduck's dibromide (*loc. cit.*), leaving a 2(?):10*-dibromophenanthrene* (II):

This will probably be found to be a general reaction for compounds of this kind.

The preparation of the 9-bromo-derivative has been improved by Austin (T., 1908, **94**, 1762) by using carbon tetrachloride as a diluting medium. A systematic examination of the reaction in this diluent has been made by the author by using varying amounts of bromine. With two atoms Austin's results were confirmed. Three yielded 28 per cent. of the 9-bromo-derivative and 23 per cent. of 2(?)-bromophenanthrene dibromide, whilst four atoms gave 31 per cent. of the 9-bromo-derivative, together with 30 per cent. of 2(?)-bromophenanthrene dibromide, which decomposed to 23 per cent. of the 2(?):10-dibromo-derivative melting at 162°. The dibromo-derivative having the nearest melting point (158°) to this is that of Zetter (*loc. cit.*), but his is readily soluble in alcohol, and crystallises only in plates, whereas the new one is soluble in alcohol only on boiling, and crystallises most readily in needles, but is dimorphous and can also be obtained in plates.

The proof of the position of the bromine atom in position 10 is shown by the formation of a phenanthrone on oxidation. Normally, phenanthrene, or its compounds having the 9:10-positions unoccupied, yield *o*-quinones, but in this instance only one oxygen atom was found in the oxidised product, indicating that one of these positions was already occupied. The reaction may be represented thus:

The phenanthrone yielded a monoxime, but no dioxime, as would have been the case had the 9:10-positions been occupied by oxygen. Additional evidence was forthcoming on nitration, where exactly analogous conditions hold; a mononitrate, but no dinitrate, was obtained. It may therefore be concluded that position 10 is occupied by one of the bromine atoms.

In an attempt to prove the position of the second bromine atom the evidence was of a negative character. If we consider the positions 1, 2, 3, and 4 which it might occupy, number 3 is excluded, because Sandqvist (*loc. cit.*) describes a dibromophenanthrene melting at 143°, which he demonstrates to be the 10:3(or 6)-derivative. Of the remaining positions, 2 was chosen for attack. 2-Ethoxyphenanthrene was subjected to exactly the same conditions of experiment, in which the dibromo-derivative melting at 162° was formed. The sole product was the 10-bromo-2-ethoxyphenanthrene, so that when position 2 is occupied, the bromine enters the bridge only; from this it might be inferred that the second bromine atom

occupies position 2, but this evidence cannot be taken as conclusive, and the matter is still under investigation.

EXPERIMENTAL.

2(?)-Bromophenanthrene Dibromide (I).

A solution of 32 grams of dry phenanthrene in 50 c.c. of dry carbon tetrachloride was treated with 57.4 grams (4 atoms) of previously dried bromine in 50 c.c. of the same solvent. After forty-eight hours 11 grams of pale yellow crystals had formed, which were found to be 9:10-dibromophenanthrene. The filtrate was evaporated to dryness in a current of dry warm air, no heat being applied, when a yellow, crystalline solid remained. On extraction with three successive portions of cold light petroleum, part dissolved, leaving 10 grams of a pale yellow substance, which crystallised from glacial acetic acid in long, flat, lemon-yellow needles melting and decomposing at 100–102 (Found, Br=57.64. $C_{14}H_9Br_3$ requires Br=57.55 per cent.).

The bromine, evolved as hydrogen bromide, was estimated by heating to 110° and passing the gas into silver nitrate solution (Found, Br=18.79. $C_{14}H_9Br_3$ (less HBr) requires Br=19.10 per cent.).

The compound can be boiled in glacial acetic acid solution without change, but it gradually decomposes into the dibromo-derivative and hydrogen bromide if exposed to a warm atmosphere.

2(?):10-Dibromophenanthrene (II).

After heating 10 grams of the preceding compound at 100° until all hydrogen bromide ceased to be evolved, it yielded 8 grams of a white solid, which crystallised from a concentrated solution in boiling alcohol in long, slender, colourless needles, forming throughout the liquid. On allowing the filtrate to remain, no needles appeared, but very small, colourless plates formed on the sides of the dish. These were again crystallised from a concentrated, boiling, alcoholic solution, when they separated in needles like the first crop. The needles (first crop), on the other hand, separated from a dilute solution in boiling alcohol in plates. The needles melted at 162°, the plates at 161° (Found [needles], C=50.00; H=2.68; Br=47.68; [plates], C=49.83; H=2.43. $C_{14}H_8Br_2$ requires C=50.00; H=2.35; Br=47.61 per cent.).

The plates were found to be triclinic, and the needles rectangular. The substance is therefore dimorphous. When kept for some months the needles gradually break down into plates.

2(?) : 10-Dibromophenanthrene is fairly readily soluble in glacial acetic acid, ether, acetone, chloroform, or benzene, less so in light petroleum or alcohol, and insoluble in water. The solubility of the plates in ether, acetone, or glacial acetic acid is slightly less than that of the needles, whilst the latter dissolve in alcohol rather less readily than the plates; in other solvents their solubilities are alike. Both plates and needles yield the same phenanthrene and the same nitro-compound.

2(?) : 10-Dibromophenanthrene (III).

Two grams of the above dibromo-derivative dissolved in 120 c.c. of glacial acetic acid were oxidised by heating for two hours with an equal weight of chromium trioxide. If the solution becomes cold, yellow crystals appear, but a better yield is obtained by cooling to about 30° and pouring into water. The precipitate (1.9 grams) crystallised from alcohol in slender, lemon-yellow needles melting at 203° (Found, C=47.64; H=2.50. $C_{14}H_8OBr_2$ requires C=47.72; H=2.27 per cent.).

The compound is not so soluble in alcohol, ether, or glacial acetic acid as in most of the other organic solvents. Analyses of the substance prepared from both the plates and needles of the dibromo-derivative gave concordant results. It dissolves in warm concentrated sulphuric acid with a dark, greenish-blue colour, and is reprecipitated on dilution with water.

The *monoxime* is readily formed by boiling for three hours a 1 per cent. alcoholic solution of the substance with two-fifths of its weight of hydroxylamine hydrochloride. After evaporating the alcohol, the residue is boiled for some minutes with water and is then left as a greenish-yellow powder, the yield being quantitative. It crystallises from benzene in bulky, dull yellow, hair-like crystals, which shrink considerably on drying, and melt and decompose at 239° (Found, N=4.05; Br=43.44. $C_{14}H_9ONBr_2$ requires N=3.81; Br=43.59 per cent.).

Although very readily soluble in ether, acetone, or alcohol it is insoluble in cold benzene. It does not form an anhydride when treated with alcoholic potassium hydroxide.

A 1 per cent. solution of 2(?) : 10-dibromophenanthrene in glacial acetic acid is heated to 60--70°, and then cold, fuming nitric acid added until a slight permanent cloudiness remains; the solution is

finally boiled for five minutes, and, on cooling, silky crystals (75 per cent. yield) are deposited, which separate from alcohol in lemon-yellow, feathery needles melting at 188° (Found, $N=3.39$. $C_{14}H_7O_2NBr_2$ requires $N=3.61$ per cent.).

The nitro-compound is very readily soluble in chloroform or benzene, but in acetone or alcohol only on boiling. On further addition of nitric acid or continued boiling of the mixture, no dinitro-derivative was formed, although several attempts were made to obtain this; therefore the bromine atom in position 10 is not readily displaceable by the nitro-group.

A similar type of compound, namely, 9-bromo-10-nitrophenanthrene, has been prepared by Schmidt and Ladner (*loc. cit.*).

The reduction of the nitro-compound was effected by boiling for one hour with tin and hydrochloric acid. The amine was washed with hot water, dissolved in warm alcohol, and the solution filtered. On pouring this into much water, a brown, flocculent precipitate was obtained, which, when dry, was extracted with a little cold chloroform. The pale brown solid (35 per cent. yield) crystallised from dilute alcohol in colourless needles melting at 177° (Found, $N=4.08$. $C_{14}H_9NBr_2$ requires $N=3.98$ per cent.).

The substance is very readily soluble in the usual solvents except light petroleum, ether, or chloroform, although it does not crystallise readily from these. On prolonged exposure to light it gradually turns brown. It dissolves on boiling with dilute sulphuric acid, and, on cooling, flocculent crystals of the hydrogen sulphate appear.

The *acetyl* derivative was prepared by heating the amine with twenty times its weight of acetic anhydride at $130\text{--}140^{\circ}$ for six hours. The cold solution was poured into water, and the resulting white, granular solid, after being washed with dilute sodium hydroxide solution and then with warm water, crystallised from boiling alcohol in colourless, flat, tetragonal plates melting at 202° . The yield was 80 per cent. of the theoretical (Found, $C=48.81$; $H=3.01$. $C_{16}H_{11}ONBr_2$ requires $C=48.85$; $H=2.80$ per cent.). It is very readily soluble in cold chloroform, but dissolves in ether or alcohol only on boiling.

Action of Alcoholic Potassium Hydroxide on 2(?) : 10-Dibromophenanthrene.

When the dibromo-compound (one-fifth of the weight of the potassium hydroxide) is gradually added to 10 per cent. alcoholic

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potassium hydroxide and the solution boiled for four hours, the liquid becomes reddish-purple and deposits a 90 per cent. yield of a blood-red precipitate, which is insoluble in water and all the usual organic solvents, with the exception of carbon disulphide and benzene, in which it is sparingly soluble. It crystallises from the latter in small, brilliant scarlet needles, which do not melt below 350°. Its composition was not indicated by analysis (Found, C=52.27; H=3.03 per cent.).

It leaves no residue on burning, and is not acted on by strong acids or alkalis in the cold, but is decomposed by the former on boiling. It is oxidised by chromium trioxide, yielding a clear, yellow solution, which on neutralisation with sodium hydroxide gives a yellow precipitate. The product is therefore not a quinone, neither is the red substance. This is further shown by the fact that neither gives an oxime. The scarlet substance contains bromine. 9-Bromophenanthrene does not yield a red compound.

A Dibromo-hydrocarbon, C₁₇H₁₆Br₂.

The three portions of light petroleum extract from the bromination of phenanthrene (p. 57) were united and evaporated to dryness, leaving a pale brown oil, which solidified after twenty-four hours and crystallised from alcohol in pale yellow needles melting at 216° (Found, C=53.64; H=4.04. C₁₇H₁₆Br₂ requires C=53.68; H=4.21 per cent.).

The compound contains bromine, and is evidently a dibromo-derivative of a hydrocarbon, occurring as an impurity in the phenanthrene.

2-Ethoxyphenanthrene (T., 1906, **89**, 1527) was brominated under exactly the same conditions as when 2(?):10-dibromophenanthrene was formed. The product, when heated at 100°, evolved hydrogen bromide and left a yellowish-white mass, which crystallised from glacial acetic acid in small, colourless leaflets (81 per cent. yield), melting at 148—149° (Found, C=63.87; H=4.72; Br=26.34. C₁₆H₁₃OBr requires C=63.78; H=4.32; Br=26.57 per cent.). It is very readily soluble in the usual solvents except methyl alcohol and glacial acetic acid.

Since bromine attacks the 9 and 10 positions most readily, it is reasonable to suppose that these have been entered, and the fact that hydrogen bromide is evolved on heating the crude product

would substantiate this view, a 9:10-dibromide being first formed and decomposing into the above substance and hydrogen bromide, just as in the case of Hayduck's dibromide (*loc. cit.*). Further evidence is afforded by the fact that 9:10-dinitro-2-ethoxyphenanthrene is not attacked by bromine under the same experimental conditions.

The *dinitro*-compound was prepared by treating a 3 per cent. glacial acetic acid solution of the ether with fuming nitric acid until a permanent cloudiness appeared, and then adding a slight excess, boiling for fifteen minutes, and allowing to remain for twenty-four hours. On pouring into water the dinitro-compound was precipitated, and was dried at 105°. After extracting with a little cold benzene, the residue crystallised from the same boiling solvent in pale yellow, shining, rhombic prisms melting at 247° (Found, N=9.66. $\text{C}_{16}\text{H}_2\text{O}_5\text{N}_2$ requires N=9.46 per cent.).

It is readily soluble in chloroform, but not in carbon tetrachloride. It burns very easily with a small flash, leaving no residue.

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