CCXXII.—*Bromination of Acyl Derivatives of Phenylhydrazine. Preparation of 2 : 4-Dibromophenylhydrazine.*

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BROMINATION, even with excess of the halogen, of the acetyl and benzoyl derivatives of phenylhydrazine in cold chloroform or carbon tetrachloride does not produce diazonium salts (compare Michaelis, *Ber.*, 1893, **26**, 2190; Vaubel, *J. pr. Chem.*, 1894, **49**, 540; 1897, **55**, 220). The formation of diazonium salt in Michaelis's experiment appears to have been due to the action of the bromine on phenylhydrazine formed from its acetyl derivative by hydrolysis by the hydrochloric acid used as solvent.

In our experiments, no evidence was obtained of the existence of *N*-bromo-compounds, proved by Chattaway (J., 1908, **93**, 852) to be formed in the bromination of phenylhydrazine.

The experiments were carried out at —5° to —10°. After the initial experiments chloroform was used as solvent, since the acyl derivatives are more soluble in it than in carbon tetrachloride. The brominated phenylhydrazines produced were identified by conversion into the bromophenylhydrazones of benzophenone or benzaldehyde. Tests for diazonium compounds were carried out with an alkaline solution of β-naphthol.

Acetylphenylhydrazine. (1) Bromine (1 mol.) was added gradually to the solution, which became red and turbid. *Acetyl-*p-*bromophenylhydrazine hydrobromide* slowly separated as a white, crystalline solid, m. p. 132° (decomp.) (Found: total Br, 51·5; HBr, by titration with baryta, 26·4. $C_8H_9ON_2Br,HBr$ requires total Br, 51·6; HBr, 26·1%). The compound dissolved immediately in alcohol and from the solution acetyl-*p*-bromophenylhydrazine, m. p. 164°, was soon deposited (Found: Br, 34·7. Calc., Br, 34·9%).

(2) A solution of 12 g. (1 mol.) of acetylphenylhydrazine in 400 c.c. of chloroform was cooled to 0°, slowly treated with 8·2 c.c. (2 mols.) of bromine, and kept for 12 hours at the ordinary temperature, when the heavy, red oil that had separated solidified (from more dilute solutions it separated in crystals). The crystalline mass, which was washed with chloroform, was *acetyl-2 : 4-dibromophenylhydrazine hydrobromide*, m. p. 146° (decomp.); it decomposed in the air, giving off hydrogen bromide (Found: total Br, 61·85; HBr, 20·9. $C_8H_8ON_2Br_2,HBr$ requires total Br, 61·7; HBr, 20·8%). The compound was dissolved in cold alcohol and water added to the solution, when acetyl-2 : 4-dibromophenylhydrazine, m. p. 146°, was formed in theoretical yield (24—25 g.) (Found: Br, 51·7. Calc., Br, 51·9%). The hydrochloride of the hydrazine was easily obtained by warming the acetyl derivative with concentrated hydrochloric acid.

Benzoylphenylhydrazine. The solution turned red and turbid when the bromine (2 mols.) was added and after a short time white needles of 2 : 4-dibromophenylhydrazine hydrobromide separated (Found: Br, 68·9. Calc., Br, 69·2%).

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