CXC.—*The Union of Benzoylacetonitrile with Organic Bases in the Presence of Salicylaldehyde. Part I.*

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SALICYLALDEHYDE and benzoylacetonitrile condense together in the presence of a few drops of piperidine to give a poor yield of 3-benzoylcoumarin (Krishnamurti and Dey, *Proc.* 13*th Ind. Sci. Cong.*, 1926); at the same time there is produced a *base*, $C_{14}H_{18}ON_2$. This base is obtained in good yield when piperidine and benzoylacetonitrile react together in molecular proportion in the presence (but not otherwise) of a few drops of salicylaldehyde. It is a mono-acid base which is stable towards mineral acids, with which it forms characteristic, crystalline salts, and towards boiling dilute aqueous alkalis, but is decomposed by alcoholic potash with the liberation of piperidine. It is converted into piperidine and benzoic acid by the action of alkaline permanganate.

No definite acetyl or benzoyl derivative could be prepared, but the base readily yields a *nitroso-hydrochloride* with hydrochloric acid and sodium nitrite, which is decomposed by sodium bicarbonate to give a bright yellow iso*nitroso*-derivative. This compound readily yields diacyl derivatives, and gives benzoic acid on distillation with 70% sulphuric acid. The original base, when heated above its m. p., is decomposed into its constituents.

That it is the *N*-hydrogen atom of piperidine that takes part in the reaction is shown by the fact that the *N*-alkylpiperidines do not give this reaction. The constitution of the base may therefore be represented by (I) $CH_2Bz\cdot C(:NH)\cdot NC_5H_{10}$ or (II) $CH_2Bz\cdot C:NH\cdot NC_5H_{10}$. Formula (II) is more in accordance with the properties of the base, especially its instability towards heat and its stability towards concentrated acids and towards alkalis. The *iso*nitroso-derivative may be represented thus: (III) $OH\cdot N:CBz\cdot C:NH\cdot NC_5H_{10}$.

The action of salicylaldehyde as catalyst may be explained by assuming that it first condenses with benzoylacetonitrile in the presence of piperidine to form the salicylidene derivative; the nitrogen atom of the CN group in this then reacts additively with piperidine by migration of the hydrogen atom of the NH group of the latter; finally, the compound thus produced is hydrolysed, salicylaldehyde being regenerated.

Nitro-, bromo-, and *p*-methoxy-salicylaldehydes—and also β-naphtholaldehyde, but to a lesser extent—similarly act as catalysts, whereas the reaction fails with *o*-methoxybenzaldehyde and *m*- and *p*-hydroxybenzaldehydes, which do not contain the necessary hydroxyl group in the ortho-position to the aldehyde group.

EXPERIMENTAL.

The Base (II).—A mixture of benzoylacetonitrile (1 mol.), piperidine (2 mols.), salicylaldehyde (2—3 drops), and absolute alcohol (50 c.c.) was heated under reflux for about 3 hours. A portion of the alcohol was then distilled off, and the reddish-brown solution was diluted with much water, mixed with concentrated hydrochloric acid (5 c.c.), and, after 12 hours, decanted from the resinous matter and treated with excess of sodium hydroxide. The thick, white precipitate, after being washed, crystallised from alcohol in colourless, rectangular prisms, m. p. 173° (yield, about 80%). The base is insoluble in water, ether, or petroleum, and easily soluble in benzene, alcohol, acetone, chloroform, or dilute acids; from the last it is precipitated unchanged by alkalis (Found: C, 72·85; H, 8·0; N, 12·2. $C_{14}H_{18}ON_2$ requires C, 73·0; H, 7·8; N, 12·2%).

When heated, the base first melted to a clear liquid and then boiled, piperidine being evolved; the residue was charred and insoluble in acids.

A suspension of the base (0·5 g.) in 2% sodium hydroxide solution (50 c.c.) was slowly treated with potassium permanganate (3 g.); subsequent boiling produced a copious evolution of piperidine. The liquid, after being concentrated and acidified, gave a good yield of benzoic acid, m. p. 121°.

The *hydrochloride* slowly crystallised from dilute hydrochloric acid (1 : 1) in broad, glistening plates, m. p. 235—242° (Found: Cl, 13·2. $C_{14}H_{18}ON_2,HCl$ requires Cl, 13·3%). The *chloroplatinate* formed orange crystals (Found: Pt, 22·6. $2C_{14}H_{18}ON_2,H_2PtCl_6$ requires Pt, 22·4%). The *picrate*, obtained as an oil which solidified slowly, crystallised from alcohol in yellow, glistening prisms which lost alcohol of crystallisation at 98° and melted to a clear liquid at 138°.

The iso*Nitroso-derivative* (III).—The sparingly soluble *hydrochloride* was obtained by adding a dilute solution of sodium nitrite to a solution of the base in dilute hydrochloric acid. After recrystallisation from very dilute alcohol it melted at 258° (decomp.) (Found:

N, 14·2. $C_{14}H_{17}O_2N_3,HCl$ requires N, 14·2%). When warmed with a little water and a slight excess of sodium bicarbonate, it gave the iso*nitroso*-compound as a bright yellow solid, which crystallised from alcohol in slender needles, m. p. 183° (decomp.) (Found: C, 65·3; H, 6·4; N, 16·15. $C_{14}H_{17}O_2N_3$ requires C, 65·0; H, 6·6; N, 16·2%).

The *dibenzoyl* derivative of (III) was readily prepared by the Schotten–Baumann method. It crystallised from alcohol in clusters of colourless needles, m. p. 148° (Found: C, 72·1; H, 5·3; N, 9·05. $C_{28}H_{25}O_4N_3$ requires C, 71·95; H, 5·35; N, 9·0%). The *diacetyl* derivative, m. p. 180—181° (decomp.), also was easily obtained by heating the base or its hydrochloride with acetic anhydride for a few minutes (Found: N, 12·4. $C_{18}H_{21}O_4N_3$ requires N, 12·35%).

The reactions of benzoylacetonitrile and of other nitriles of the type $CH_2R{\cdot}CN$ with various reactive bases are under investigation.

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