

LVI.—*The Union of Benzoylacetoneitrile with Organic Bases in the Presence of Salicylaldehyde. Part II.*

By PANCHAPAKESA KRISHNAMURTI.

CORRESPONDING to the compound formed when benzoylacetoneitrile reacts with piperidine in the presence of salicylaldehyde as catalyst (J., 1927, 1349), compounds have now been obtained from aniline, *p*-toluidine, and *m*-4-xylydine. In all these cases, the addition of piperidine in small amounts almost doubled the yields, in accordance with the view that the first stage of this type of reaction is the formation of a salicylidene derivative under the influence of this base (Krishnamurti and Dey, *loc. cit.*).

o- and *m*-Toluidines did not react with benzoylacetoneitrile under the conditions mentioned above. A similar behaviour has been noticed in the addition of bases to nitrostyrene (Worrall, *J. Amer. Chem. Soc.*, 1927, 49, 1598): Aniline and *p*-toluidine reacted in the normal way to give the derivatives, whereas *o*- and *m*-toluidines failed to react, and the author came to the conclusion that a substituent in the ortho- and even in the meta-position to the amino-group hinders the mobility of its hydrogen atoms. If this is so, the reactivity of *m*-4-xylydine towards benzoylacetoneitrile can only be explained by assuming that the steric effects of one substituent are modified by the presence of other groups in more favourable positions.

In most respects, the compounds of benzoylacetoneitrile with aniline and with *p*-toluidine were similar to that with piperidine, but they differed from it in that (a) they easily gave dibenzoyl derivatives and (b) the *isonitroso*-compounds did not yield acyl derivatives, benzoylation in the usual way producing the benzoyl derivatives of the primary amines.

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The p-Toluidine Compound.—A solution of benzoylacetoneitrile (1 mol.) and *p*-toluidine (1 mol.) in absolute alcohol containing

salicylaldehyde (2—3 drops) and piperidine (1—2 drops) was heated on the water-bath for 8 hours, alcohol being added from time to time to replace that lost by evaporation. The reddish-brown solution was then diluted with much water and acidified with hydrochloric acid, and after 12 hours the clear solution was decanted and treated with an excess of alkali. The compound thus precipitated crystallised from alcohol in pale yellow, rhombic prisms (yield, about 50%), m. p. 182° (Found: C, 76.3; H, 6.4; N, 11.3. $C_{16}H_{16}ON_2$ requires C, 76.2; H, 6.35; N, 11.1%).

The *hydrochloride* crystallised from hot dilute hydrochloric acid in colourless needles, m. p. 194—195° (Found: Cl, 12.2. $C_{16}H_{16}ON_2 \cdot HCl$ requires Cl, 12.3%). The *dibenzoyl* derivative formed pale yellow, glistening needles, m. p. 166°, from alcohol (Found: C, 78.0; H, 5.1; N, 6.0. $C_{30}H_{24}O_3N_2$ requires C, 78.3; H, 5.2; N, 6.1%).

The *isonitroso-derivative*. A solution of the base in hot dilute hydrochloric acid was cooled rapidly and a dilute solution of the requisite quantity of sodium nitrite was added, followed after a few minutes by an excess of dilute sodium hydroxide solution. After filtration, the light brown solution was acidified with dilute acetic acid; the *isonitroso-derivative* thus precipitated crystallised from alcohol in bright orange plates, m. p. 158°, to a reddish-brown liquid (Found: C, 68.5; H, 5.4; N, 15.1. $C_{16}H_{15}O_2N_3$ requires C, 68.3; H, 5.3; N, 14.95%).

Its *silver* salt was obtained as a light pink, curdy precipitate (Found: Ag, 28.0. $C_{16}H_{14}O_2N_3Ag$ requires Ag, 27.8%).

The *Aniline Compound*.—The conditions of experiment were practically the same as those described for preparing the *p*-toluidine compound. The yield was somewhat lower (about 40%). The substance crystallised from alcohol in light yellow prisms, m. p. 163° (Found: N, 11.7. $C_{15}H_{14}ON_2$ requires N, 11.8%).

The *hydrochloride* crystallised from dilute hydrochloric acid in glistening plates, m. p. 94—96°. The *dibenzoyl* derivative was obtained from alcohol in pale yellow needles, m. p. 168° (Found: N, 6.2. $C_{29}H_{22}O_3N_2$ requires N, 6.3%). The *isonitroso-derivative* crystallised from alcohol in blood-red plates, m. p. 182° (decomp.) (Found: N, 15.75. $C_{15}H_{13}O_2N_3$ requires N, 15.7%).

The *m*-4-*xylidine* compound was obtained under the same conditions as the *p*-toluidine compound, the heating, however, being continued for 16 hours (yield, about 20%). It crystallised from benzene in colourless plates, m. p. 145—146° (Found: N, 10.5. $C_{17}H_{18}ON_2$ requires N, 10.5%). Its *benzoyl* derivative crystallised from alcohol in colourless, shining needles, m. p. 153°, and the *isonitroso-derivative* in yellow plates, m. p. 150—151° to a scarlet liquid.

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INDIAN ASSOCIATION FOR THE CULTIVATION
OF SCIENCE, 210, BOWBAZAR STREET,
CALCUTTA, INDIA.

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