LXVII.—N-*Acylpyrazolones as Acylating Agents.*

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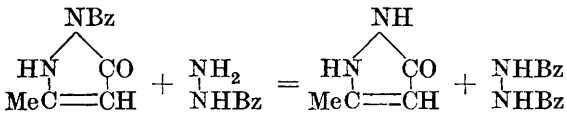
Ethyl acetoacetate reacts with benzoylhydrazine at 100°, *s*-dibenzoylhydrazine and 3-methyl-5-pyrazolone being formed. Their production may be explained by the fact that 1-benzoyl-3-methyl-5-pyrazolone, which can be isolated when the above condensation is carried out at 10—16°, reacts readily with compounds containing an amino-group, 3-methyl-5-pyrazolone and the benzoyl derivative of the amine being formed.



Under the same conditions, benzoylhydrazine does not benzoylate a primary amine.

Similar results are obtained when phenylacetylhydrazine is substituted for benzoylhydrazine in the above reactions.

Bongert (*Compt. rend.*, 1901, **132**, 973) has obtained 3-methyl-5-pyrazolone and butyrylhydrazine by the interaction of methyl β-butyryloxycrotonate and hydrazine.

Experimental.

Interaction of Phenylacetylhydrazine and Ethyl Acetoacetate. Formation of s-*Diphenylacetylhydrazine and* 3-*Methyl-5-pyrazolone.*—Phenylacetylhydrazine (7·5 g.), ethyl acetoacetate (6·5 g.), absolute alcohol (1·3 c.c.), and 3 or 4 drops of piperidine were heated together

on the steam-bath for 3 hours. The solid product was extracted with hot water, and the residue crystallised from absolute alcohol, colourless needles of *s*-diphenylacetylhydrazine (4·0 g.), m. p. 232—233°, being obtained; Pinner and Gobel (*Ber.*, 1897, **30**, 1889) give m. p. 231° (Found : N, 10·65. Calc. for $C_{16}H_{16}O_2N_2$: N, 10·4%). The aqueous extract on concentration gave 3-methyl-5-pyrazolone, m. p. (after recrystallisation) and mixed m. p. with an authentic specimen, 215°.

s-*Dibenzoylhydrazine*.—A mixture of benzoylhydrazine (7 g.), ethyl acetoacetate (6 g.), alcohol (2 c.c.), and piperidine (3 or 4 drops) was heated on the steam-bath as in the preceding case. The product, isolated in a similar way and recrystallised from alcohol, gave colourless plates (3·5 g.), m. p. 235°, of *s*-dibenzoylhydrazine (Struve, *J. pr. Chem.*, 1894, **50**, 299, gives m. p. 233°) (Found : N, 11·8. Calc. for $C_{14}H_{12}O_2N_2$: N, 11·7%).

1-*Phenylacetyl*-3-*methyl*-5-*pyrazolone*.—A mixture of phenylacetylhydrazine (7·5 g.), ethyl acetoacetate (6·5 g.), and piperidine (3 or 4 drops) was kept at the ordinary temperature for 12 hours. The solid product crystallised from hot xylene in pale brownish needles, m. p. 134—136° (Found : N, 13·3. $C_{12}H_{12}O_2N_2$ requires N, 13·0%). A small quantity of a substance, m. p. 228—230°, insoluble in hot xylene was not investigated.

1-*Phenylacetyl*-3-*methyl*-5-*pyrazolone* (0·8 g.) was heated with an equivalent quantity of aniline at 130—140° for an hour or at 100° for 3 hours. Phenylacetanilide, m. p. 116° after recrystallisation, was isolated from the reaction mixture, and 3-methyl-5-pyrazolone from the acid extract (see below).

Phenylacetanilide.—A mixture of phenylacetylhydrazine (5 g.), ethyl acetoacetate (4·3 g.), and a few drops of piperidine was kept over-night, aniline (3 g.) added, and the mixture heated at 130—140° for an hour. The cooled mass was ground with dilute hydrochloric acid, the liquid filtered, and the residue extracted with tepid alcohol. The alcoholic extract on concentration and dilution with water furnished phenylacetanilide (1·9 g.) which, after recrystallisation from hot dilute alcohol, melted, alone or mixed with an authentic specimen, at 116°; a further quantity (0·9 g.) was isolated, by fractional crystallisation, from the residue from the alcohol extraction.

A mixture of phenylacetylhydrazine (3 g.) and aniline (2 g.), heated at 130° for 1 hour, gave no phenylacetanilide.

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