[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

THE STRUCTURE OF THE SO-CALLED "6-PHENYL-1,4-DIHYDRO-*as*-TRIAZINE"

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Biquard's report (1) of the formation of 6-phenyl-1,4-dihydro-*as*-triazine (I) in 60% yield by the action of either the ethyl or the methyl Grignard reagent on acetophenone semicarbazone at 80° is of interest because of the apparently unique nature of both the synthesis and the product. This appears to be the only preparation of the dihydro-*as*-triazine ring which is not fused with another ring, and one of the few syntheses of the unfused *as*-triazine ring.

The evidence for the reported structure consisted of a carbon-hydrogen-nitrogen analysis and the preparation and analyses of a chloroplatinate and of the mono- and di-acetyl derivatives. Unfortunately, the possibility of an isomeric structure was not seriously considered; however, it would seem likely that ring-closure by an aldol-type condensation might produce the isomeric 3(5)-amino-5(3)-phenylpyrazole (II). This aminopyrazole (II) has been described twice previously, having been prepared in two other ways (2, 3), but the literature disagrees as to its melting point and the melting point of derivatives.

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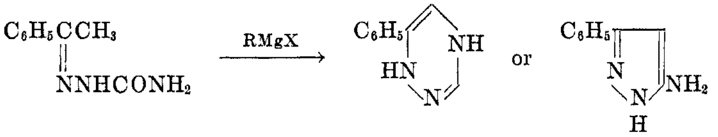

I II

The Biquard synthesis was repeated, although in much lower yield than previously reported in spite of improvements in the isolation procedure. The product was compared with authentic II prepared by condensation of hydrazine with β-imino-β-phenylpropionitrile. The identical melting points, mixture melting points and infrared spectra of these two products, together with similar melting point data on their picrates and diacetyl derivatives and the identical infrared spectra of the diacetyl compounds, demonstrate clearly that the correct structure for the Biquard product is II.

EXPERIMENTAL

The Biquard condensation was carried essentially as described previously (1). The time of reflux (not stated by Biquard) was one hour after addition of the acetophenone semicarbazone, and six hours after the ether had been replaced by benzene. The isolation was modified by extracting the dried magnesium salts, which were precipitated by the ammonium chloride hydrolysis, with boiling ethyl acetate. Addition of petroleum ether (b.p. 90–100°) to these extracts precipitated the crude product, which was recrystallized from hot water; white plates, m.p. 125–126°. From 80 g. of acetophenone semicarbazone, 5 g. (10%) of the purified condensation product was obtained.

Authentic 3(5)-amino-5(3)-phenylpyrazole. To a solution of 8.5 g. (0.05 mole) of β-imino-β-phenylpropionitrile in 100 ml. of 95% alcohol, 7.5 g. (0.15 mole) of 85% hydrazine hydrate was added. After six hours of refluxing, the solvent was removed by vacuum-distillation. The residue solidified on standing a few hours and was crystallized alternately from ethyl acetate-petroleum ether (b.p. 90–100°) and hot water, to give 5 g. (62%) of white plates, m.p. 125–126°. The m.p. was not affected by mixing with the Biquard product, and both gave the same infrared spectrum in a Nujol mull with principal bands at 3.37, 6.27, 6.50, 9.18, 9.35, 10.12, 10.88, and 13.1 μ.

Derivatives. The picrates were prepared in the usual manner from each preparation. The m.p. of each and the mixture m.p. was 202–203°. The diacetyl derivatives were prepared by heating the free bases 15 minutes with a ten-fold amount of acetic anhydride. The derivative crystallized out on cooling and was recrystallized from alcohol, m.p. 156–157° (from each base and mixture). The infrared spectra (Nujol mull) of the two diacetyl derivatives were identical and showed principal bands at 3.27, 5.74, 5.99, 6.60, 7.97, 8.70, 9.74, 10.75, 12.02, 12.60 and 12.92 μ.

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SUMMARY

The reaction of acetophenone semicarbazone with Grignard reagents under "forcing" conditions has been shown to give 3(5)-amino-5(3)-phenylpyrazole, rather than 6-phenyl-1,4-dihydro-*as*-triazine, as previously reported.

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