390. *The Reaction of Acetonylacetone with Cyanoacetamide.*

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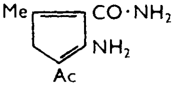
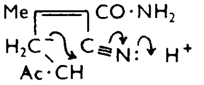
The reaction of acetonylacetone with cyanoacetamide has been claimed[1] to afford an oxepine. A more likely product was thought[2] to be the cyclopentadiene (I), formed from the carbanion (II) by internal attack on the nitrile. The latter structure has now been proved correct and the detailed structures of the salts have since been shown[3] by *X*-ray analysis to be as in (III). The chemical evidence upon which the structure (I) was based is now given.

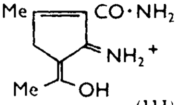
Diazocyclopentadiene[4] is very stable and heterocyclic analogues are known.[5] They are characterised by the presence of the strong diazo-band in the infrared spectrum of the solid. A diagnostic test of the structure (I) was therefore sought by diazotisation, which gave the expected compound (IV).



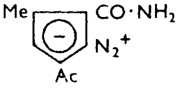
(I)



(II)



(III)



(IV)

In an attempt to demonstrate the presence of the keto-group, the amine (I) was reduced with sodium borohydride. A colourless dihydro-derivative resulted that showed no hydroxyl band in the infrared spectrum and thus contained a reduced ring (though it may have arisen by reduction of the carbonyl group followed by isomerisation). Catalytic hydrogenation gave a different product ($\lambda_{max.}$ 294 mμ) which however is suspected as being a mixture.

Despite the failure of the ketone (I) to give a dinitrophenylhydrazone, there is no reason to suppose that it is enolised and the compound does not give a colour with ferric chloride solution.

Experimental.—The cyclopentadienylamine[1] (I) has $\nu_{max.}$ 5·95 μ (C=O) (shoulder at 6·0 μ) (Found: *C*-Me, 17·7%; *M*, 220. Calc. for $C_9H_{12}N_2O_2$: 2*C*-Me, 16·7%; *M*, 180). The *hydrochloride* had m. p. 242° (Found: C, 50·3; H, 5·9; Cl, 16·4; N, 12·8. $C_9H_{13}ClN_2O_2$ requires C, 49·9; H, 6·0; Cl, 16·4; N, 13·0%).

Diazotisation. The amine (I) (3·6 g.) was diazotised at $<5°$ in complete aqueous solution and, on storage, the solution deposited the *diazo-derivative* (IV) (0·3 g.) which formed yellow needles, m. p. 200° (decomp.), from alcohol (Found: C, 56·3; H, 4·8; N, 22·0; O, 17·1. $C_9H_9N_3O_2$ requires C, 56·5; H, 4·8; N, 22·0; O, 16·7%), $\nu_{max.}$ 4·65 (N_2^+) and 6·0 and 6·05 μ (C=O), $\lambda_{max.}$ 233 and 351 mμ (log ε 4·2 and 4·1, respectively).

Borohydride reduction. The amine (1·0 g.) in 2 : 1 aqueous propanol (30 ml.) was treated with a large excess of sodium borohydride. When the solution began to darken, ammonium sulphate (10 g.) was added and the propanol layer was separated, dried, and evaporated, giving a white *substance*, m. p. 152° (from ethanol) (Found: C, 59·1; H, 7·9; N, 15·0. $C_9H_{14}N_2O_2$ requires C, 59·3; H, 7·7; N, 15·3%), $\nu_{max.}$ 5·95s, 5·9sh μ, $\lambda_{max.}$ 195 and 319 mμ (log ε 3·8 and 4·0, respectively) in neutral or acid solution (in alkali the first band was at 205 mμ).

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[1] Westoo, *Acta Chem. Scand.*, 1959, **13**, 604.

[2] Woodward, Post-doctoral Group Discussion, Harvard, 1959.

[3] Buchanan, Hamilton, Hamor, and Sim, *Acta Chem. Scand.*, 1962, **16**, 776.

[4] Doering and DePuy, *J. Amer. Chem. Soc.*, 1953, **75**, 5955.

[5] Shealy, Struck, Holum, and Montgomery, *J. Org. Chem.*, 1961, **26**, 2396.