

## The Condensation of Acetone with Urea: The Formation of a Spirobishexahydropyrimidine

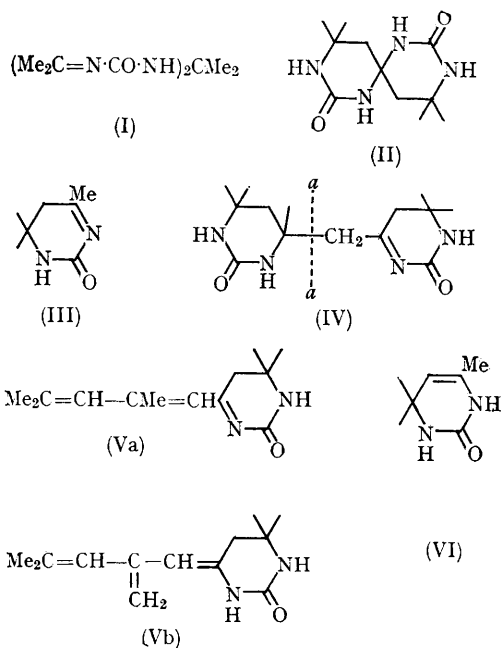
By H. H. HATT and A. C. K. TRIFFETT

(Chemical Research Laboratories, C.S.I.R.O., G.P.O. Box 4331, Melbourne, Australia)

WEINSCHENK<sup>1</sup> obtained a compound  $C_{11}H_{20}N_4O_2 \cdot 3H_2O$  by the condensation of anhydrous acetone and urea in the presence of hydrogen chloride. The structure (I) which he assigned seems to have been generally accepted,<sup>2</sup> apart from Harvey, who in his patents<sup>3</sup> assigned an alternative structure, but without supporting evidence. We have shown its structure to be 4,4,10,10-tetramethyl-2,8-dioxo-1,3,7,9-tetra-azaspirodecane (II). Its solutions show no absorption in the ultraviolet above 210  $m\mu$ . In the infrared region a paraffin mull shows one strong band at  $1660\text{ cm}^{-1}$ , attributable to amide carbonyl. The n.m.r. spectrum in  $D_2O$  at  $80^\circ$  (sodium 3-trimethylsilylpropane-1-sulphonate as internal reference) shows, apart from absorbance due to HDO, two bands: a singlet at 2.08 p.p.m. (4 protons of two methylene groups), and a doublet at 1.30 p.p.m.,  $J$  0.7 c./sec. (12 protons of two geminal dimethyl groups). A molecular weight of 240 was obtained from a mass spectrum.

The structure was confirmed by a synthesis from phorone either by heating with urea alone at  $130^\circ$  or in presence of a crystal of iodine at  $80^\circ$ . The compound owes its ease of isolation from the products of condensation of acetone and urea to the crystallisation from these of the addition compound:  $C_{11}H_{20}N_4O_2 \cdot CO(NH_2)_2 \cdot \frac{1}{2}HCl$ . This gives the trihydrate in water. In hot dilute aqueous acid (II) decomposes rapidly giving, besides the acetone and mesityl oxide Weinschenk noticed, a compound (IV)  $C_{14}H_{24}N_4O_2$ , m.p.  $290-295^\circ$  (dec.) and a compound (V)  $C_{13}H_{20}N_2O$ , m.p.  $200-203^\circ$ . (IV) is readily made, as Harvey<sup>3</sup> showed, by condensing either mesityl oxide or

diacetonealcohol with urea in presence of hydrogen chloride. He wrongly thought the products of the two condensations to differ and reported them as isomers of molecular formula  $C_7H_{12}N_2O$ , to one of which he gave structure (III). We have found the two products are identical, with a molecular weight of 280 obtained from mass spectra. Structure (IV) is assigned on the following evidence. A solution



<sup>1</sup> A. Weinschenk, *Ber.*, 1901, **34**, 2185.

<sup>2</sup> E. H. Rodd, "Chemistry of Carbon Compounds", Elsevier, Amsterdam, 1952, Vol. IB, p. 910.

<sup>3</sup> M. T. Harvey, U.S.P., 2592565 (1952); 2782197-8 (1957).

in methanol absorbs at  $\lambda_{\max}$  242  $m\mu$  ( $\epsilon$ , 3000). In the infrared a paraffin mull gives strong peaks at 1660, 1670, and 1690  $\text{cm}^{-1}$ , attributed to two amide carbonyls and to a conjugated  $\text{C}=\text{N}$ . The base peak of its mass spectrum at  $m/e$  125 is almost equalled in intensity by  $m/e$  141. This is consistent with the expected ease of fission at  $a \cdots a$  in (IV). The related compounds (V) and (VI) both have mass spectra with the ion  $M-15$  as base peak together with an appropriate metastable ion to establish that either a methyl or an imine radical is the first product of breakdown. The peak at  $M-15$  (265) for (IV) is very much weaker, but is the only one of significance between  $M$  280 and  $M/e$  141. Fission at  $a \cdots a$  is therefore the principal first reaction.

Compound (IV) in aqueous acid yields the compound  $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}$  ( $M$ , 220 from mass spectrum) to which either structure (Va) or that of the corresponding enamine, (Vb), is assigned. A solution in methanol absorbs at  $\lambda_{\max}$  280  $m\mu$  ( $\epsilon$ , 10,700). In the infrared a paraffin mull shows peaks

at 1650, 1670, and 1695  $\text{cm}^{-1}$  attributed to amide carbonyl and to conjugated  $\text{C}=\text{N}$ . Features of its n.m.r. in deuteriochloroform are a doublet at 0.95 p.p.m. (cyclic *gem*-dimethyl), a doublet at 1.46 p.p.m. (isopropylidene group) and singlets, 4.85 and 4.72 p.p.m. (olefinic protons). There is evidence that both *cis*- and *trans*-forms of (Va) may be present.

Traube<sup>4</sup> prepared (VI), the isomer of (III), from diacetoneamine oxalate and potassium cyanate. We have confirmed this structure. In methanolic solution, (VI) shows  $\lambda_{\max}$  236  $m\mu$  ( $\epsilon$ , 3200) and in the infrared a paraffin mull gives a strong peak at 1680  $\text{cm}^{-1}$ . The integrated n.m.r. spectrum in deuteriochloroform contained five absorption areas in the ratio 6:3:1:1:1 respectively at 1.23, 1.73 (doublet,  $J$  1.0 c./sec.), 4.30, 5.60, and 7.70 p.p.m. Compound (VI) also gives rise to (IV) and (V) in hot aqueous acid.

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<sup>4</sup> W. Traube, *Ber.*, 1894, 27, 277.