X-Ray Structure of 4-Acetyl-5-methyl-2-phenylimidazole formed from 3-Hydroxyiminopentane-2,4-dione and Benzylamine

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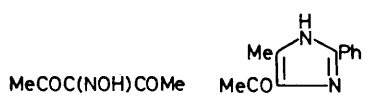
Summary 3-Hydroxyiminopentane-2,4-dione and benzylamine react giving 4-acetyl-5-methyl-2-phenylimidazole, whose *X*-ray structure and conformation are reported.

DURING a current investigation on regiospecific reactions of nucleophiles with 3-hydroxyimino- and 3-acyloxyimino-2,4-diketones, we studied the reaction of 3-hydroxyiminopentane-2,4-dione (**1**) with benzylamine under various conditions. Upon 2 h reflux of equimolecular amounts of the reagents in acetonitrile or ethyl acetate, a product with



(1) (2)

m.p. 200—201 °C was obtained in high yields. Elemental analyses indicated that two water molecules had been eliminated. The product had λ_{max} (MeOH) 287; (N-HCl) 278; (N-NaOH) 320 nm (ϵ 29,600; 31,100; 34,500), pointing to a β-amino-enone derivative; ν_{max} ($CHCl_3$) 3440 (free NH), 3250 (bonded NH), and 1640 (conj. CO); (KBr) 3200 (bonded NH) and 1640 cm^{-1} (conj. CO); δ [$(CD_3)_2SO$] 2·50 and 2·54 (6H, 2 MeC=C), 7·47 (3H, m, Ar), 8·02 (2H, Ar), and 13·0 (NH).

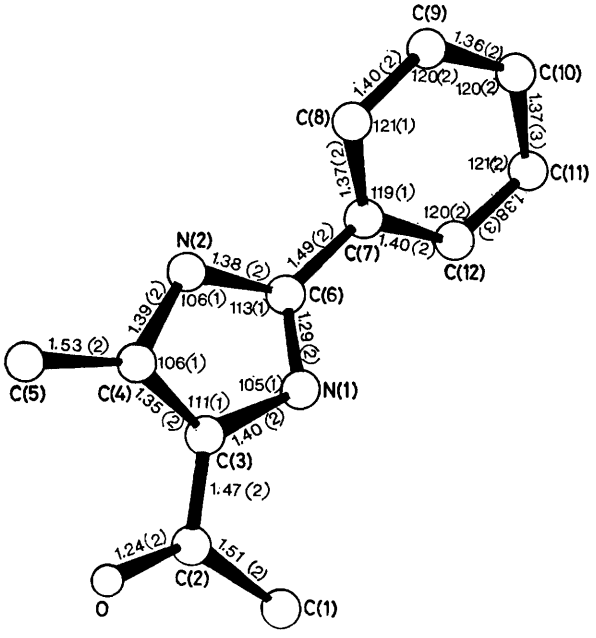


FIGURE. Structure of (2); bond lengths are given in Å and angles in degrees.

An *X*-ray crystal structure analysis demonstrated unequivocally that the product was the acetyl-imidazole (**2**).

Whereas imidazole oxides are formed from (**1**) and analogues with aldehyde–ammonia, aldoximes,[1] or a ketimine,[2] the formation of imidazoles in reactions of the type described here has not been reported.

Crystal data: $C_{12}H_{12}N_2O$, $M = 200{\cdot}24$, $a = 23{\cdot}067(6)$, $b = 13{\cdot}344(4)$, $c = 7{\cdot}088(2)$ Å, $U = 2181{\cdot}73$ Å^3, space group *Pbca*, $Z = 8$, $D_m = D_c = 1{\cdot}22$ g cm^{-3}. Three-dimensional diffraction data were collected on a Philips PW 1100 four-circle diffractometer, using graphite-monochromatized Mo-K_α radiation.

Data collection in the range $0<2\theta\leqslant 30°$ gave 1900 measurements; correction for Lorentz and polarisation effects, and for long-term intensity variation of the radiation yielded 412 unique observed [$I \geqslant 2{\cdot}5\sigma(I)$] reflections. Absorption and extinction corrections were not applied. The structure was solved by the MULTAN direct method and refined by full-matrix least-squares to a final R value of 0·062. All hydrogen atoms were found in the difference Fourier map. The Figure shows a perspective view of the molecule.†

The imidazole ring and the methyl and acetyl groups lie in the same plane, thus indicating some delocalization over this system. However, the considerable shortening of the N(1)–C(6) bond with respect with the other three N–C bonds as well as the length of the C(3)–C(4) bond which is close to that of a double bond, suggest delocalization is limited and is not extended to the phenyl ring, as demonstrated by the value (17·1°) of the dihedral angle between the planes of the phenyl and imidazole rings. An additional feature of this structure is an intermolecular O · · · · H–N hydrogen bond (O · · · · N = 2·9 Å).

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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[2] B. A. J. Clark, T. J. Evans, and R. G. Simmonds, *J.C.S. Perkin I*, 1975, 1803.
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