Acid-catalysed Isomerisation of a Bicyclic Diazetidine to an *N*-Amino-2-pyridone

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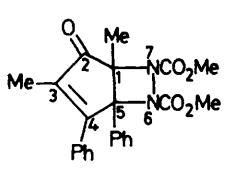
Summary The bicyclic diazetidine ester (**3**) is isomerized by trifluoroacetic acid to the *N*-amino-2-pyridone ester (**4**) which on heating loses methanol to give the bicyclic mesoionic compound (**5**); both reactions are quantitative.

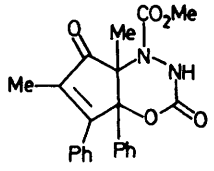
WE have recently shown[1] that trifluoroacetic acid (TFA) causes demethylation and expansion of the diazetidine ring in the bicyclic compound (**1**)[2] to give the 1,3,4-oxadiazin-2-one (**2**). We now report that if the ester group at N-7 in (**1**) is first removed by alkaline hydrolysis the resulting compound (**3**) undergoes a more profound skeletal change with TFA to give an isomeric monocyclic structure identified as the *N*-amino-2-pyridone derivative (**4**).

Treatment of (**1**) with cold 1N methanolic sodium hydroxide for 12 h gave the basic ester (**3**) m.p. 159—160°. The preservation of the diazetidine ring in (**3**) follows from its

conversion back into (**1**) with methyl chloroformate, and from its n.m.r. spectrum which shows a highly shielded methoxy signal at τ 6·8, diagnostic of the ester group on N-6.[2]



(1)



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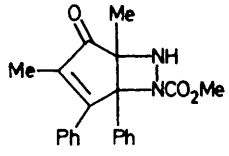

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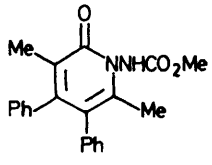

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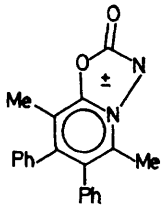
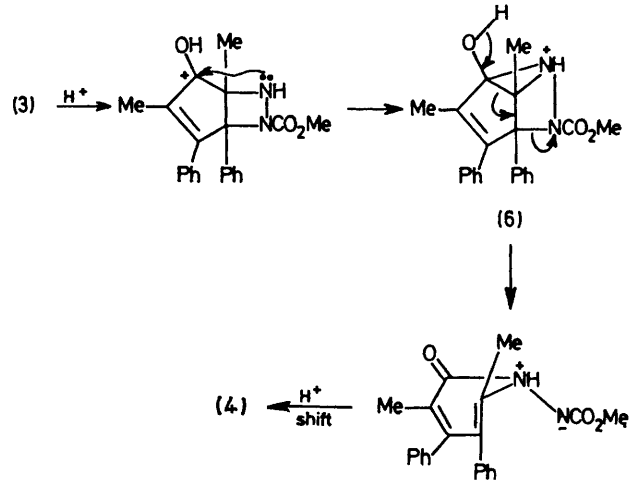


(5)

Addition of (**3**) to TFA at room temperature caused immediate and quantitative isomerisation. The product, m.p. 232—233°, had i.r. bands at 3140, 1756, and 1640 cm^{-1} (Nujol), a very different u.v. absorption (λ_{max} 245, 317 nm) from that of the enone chromophore in (**1**)—(**3**) (λ_{max} *ca.* 284 nm), and an n.m.r. spectrum with vinylic methyl peaks at τ 7·8 and 8·0 and an unshielded methoxy peak at τ 6·1. These data are fully consistent with (**4**) and the structure has been confirmed by *X*-ray analysis.[3]

When (**4**) was maintained above its m.p. methanol was rapidly lost giving an analytically pure NH and OH free compound, m.p. 300—301°, whose phenyl and *C*-methyl absorptions were similar to those of (**4**), but with quite different i.r. (C=O, 1780 cm^{-1}) and u.v. (λ_{max} 278, 305sh nm) spectra. On this evidence and on the basis of its chemical reactions we assign it the mesoionic structure (**5**) the parent ring-unsubstituted analogue of which has been described.[4]



SCHEME

The isomerisation, which in effect transposes the *C*-methyl and the adjacent nitrogen, requires the formal breaking of the 1,2 and 5,6 bonds and the formation of a 2,7 bond. A reasonable mechanism is through the tricyclic aziridinium ion (**6**) (Scheme).

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[1] D. Mackay and C. W. Pilger, *Canad. J. Chem.*, 1974, **52**, 1114.
[2] D. Mackay, C. W. Pilger, and L. L. Wong, *J. Org. Chem.*, 1973, **38**, 2043.
[3] M. Mathew and G. J. Palenik, Centre for Molecular Structure, Department of Chemistry, University of Florida, Gainesville, Florida, unpublished results.
[4] K. Hoegerle, *Helv. Chim. Acta*, 1958, **41**, 548.