1-Azabicyclo[3,2,0]hept-3-ene-2,7-dione. A Correction

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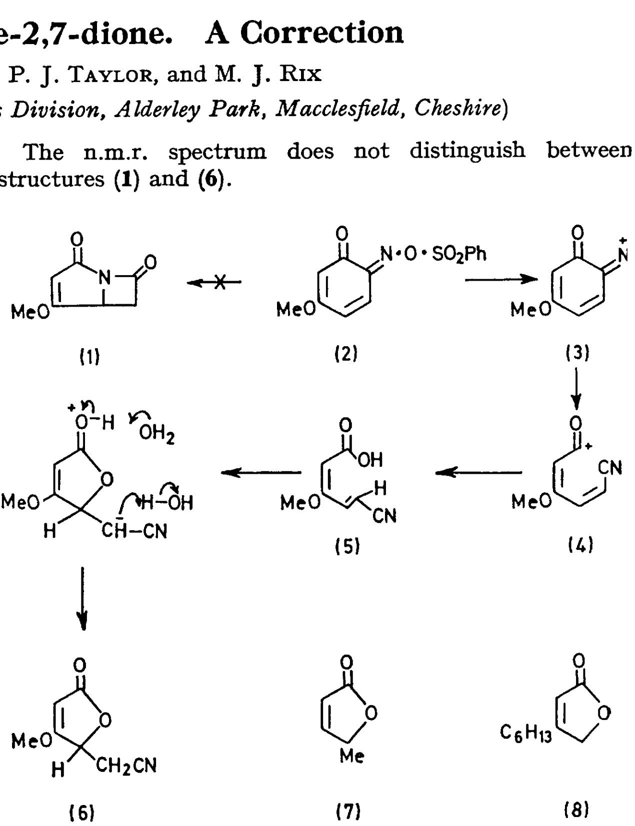
Summary Beckmann rearrangement of 4-methoxy-*o*-benzoquinone *O*-phenylsulphonyloxime (**2**) gives 3-methoxy-4-cyanomethylbut-2-enolide (**6**) and not 1-azabicyclo-[3,2,0]hept-3-ene-2,7-dione (**1**) as reported.

The recently reported synthesis[1] of 4-methoxy-1-azabicyclo[3,2,0]hept-3-ene-2,7-dione (**1**) prompted us to repeat its synthesis as the first step in an examination of the chemistry of this novel ring system which has essentially the same stereochemistry as the penicillin nucleus. Our product is identical in all respects with that of Hatanaka *et al.*,[1] but a closer examination of the physical data leads us to a different conclusion—the Δ^2-butenolide structure (**6**).

The molecular ion of the product is correctly reported as *m/e* 153, but its base peak at *m/e* 113 corresponds to a loss of C_2H_2N, determined by accurate mass measurements. This cannot be accommodated by structure (**1**), but is readily explained by the loss of CH_2CN from structure (**6**). In agreement with this the i.r. spectrum (Nujol) shows a weak nitrile band[2] (not reported by Hatanaka) at 2255 cm^{-1}. The two strong bands at 1782 cm^{-1} and 1758 cm^{-1} which were originally assigned to the CO stretching vibrations of a β- and γ-lactam, are much too close for structure (**1**) where a rough estimate allowing for coupling would place them 50—100 cm^{-1} apart. They in fact result from Fermi resonance which is common in five-membered rings[3] and well-documented in Δ^2-butenolides.[4] 4-Methylbut-2-enolide (**7**) shows bands at 1782 cm^{-1} and 1765 cm^{-1},[4] and 3-hexyl-but-2-enolide (**8**) at 1785 cm^{-1} and 1750 cm^{-1}.[5] A characteristic of this type of absorption is the variation in intensity of the bands with solvent polarity, the upper frequency being stronger in non-polar solvents and the lower stronger in polar solvents.[4]

The present compound shows bands of roughly equal intensity in Nujol, but in dioxan the 1782 cm^{-1} band is much the stronger, while in chloroform its intensity is intermediate between the two. The n.m.r. spectrum does not distinguish between structures (**1**) and (**6**).



Our suggested mechanism involves formation of the nitrenium cation (**3**) by solvolysis of the tosylate (**2**), its fission to the acylium cation (**4**), and the subsequent hydration and cyclisation of this in the manner shown. The acid (**5**) is identical with the hydrolysis product [their formula (V)] of Hatanaka *et al.*;[1] all the reported reactions of (**1**) and its analogues are readily understood in terms of (**6**) and related compounds.

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[1] N. Hatanaka, H. Ohta, O. Simamura, and M. Yoshida, *Chem. Comm.*, **1971**, 1364.

[2] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' 2nd edn., Methuen, London, 1958, p. 266.

[3] L. J. Bellamy, 'Advances in Infrared Group Frequencies', Methuen, London, 1968, p. 127.

[4] R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith, *Canad. J. Chem.*, 1959, **37**, 2007.

[5] G. Eglinton in 'Physical Methods in Organic Chemistry,' ed. J. C. P. Schwarz, Oliver & Boyce, London, 1964, p. 78, 122.