1-Azabicyclo[3,2,0]hept-3-ene-2,7-diones. A New Heterocyclic System

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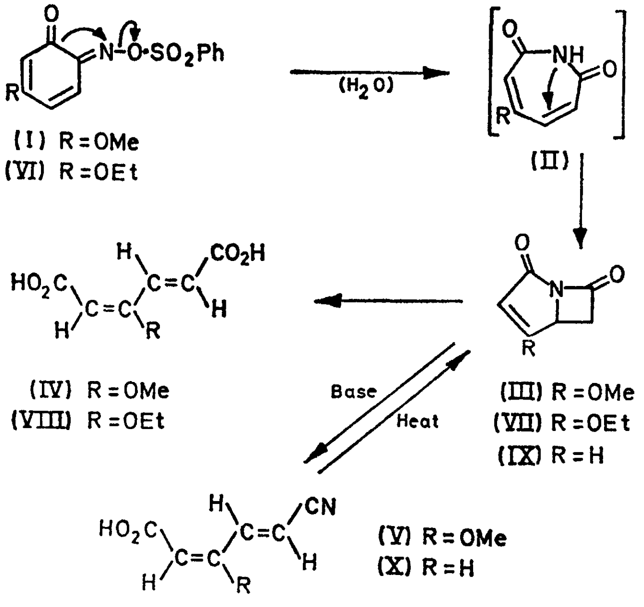
Summary 4-Methoxy-1-azabicyclo[3,2,0]hept-3-ene-2,7-dione (III) has been prepared both by a Beckmann rearrangement of 4-methoxy-*o*-benzoquinone 1-(*O*-phenylsulphonyl)oxime (I) followed by ring contraction and by cyclization of 5-cyano-3-methoxypenta-*cis*-2,*trans*-4-dienoic acid (V).

THE oxime ether (I),[1] m.p. 100—101°, on being heated at 60—70° in aqueous pyridine, gave colourless crystals (40%) of a compound, m.p. 128·5—129·5°, whose structure was established as 4-methoxy-1-azabicyclo[3,2,0]hept-3-ene-2,7-dione (III), a methoxy-derivative of a new class of heterocyclic system (IX). This structure is supported by the following spectral properties: M^+, 153, λ_{max} (EtOH) 219 and 278 nm (log ϵ 4·18 and 1·28, respectively), ν_{max} (KBr) 1615 (C=C) and 1780 and 1760 cm^{-1} (CO stretching vibrations of β- and γ-lactams,[2] respectively), the n.m.r. spectrum (in pyridine) shows signals at δ 5·32 (1H, s, CH=C), 3·68 (3H, s, OMe), 3·00 and 3·22 (1H each, J 17 Hz, CH_2), and this latter signal further coupled to a methine proton at 5·12 p.p.m. (1H, t, J 4·8 Hz), this coupling being confirmed by irradiation at the methine proton frequency. A possible pathway for the formation of (III) is as shown.



The structure of this ring system is further supported by ring opening experiments. The compound (III) was unaffected by heating under reflux with ethanolic HCl, but boiling with NaOH in aqueous ethanol gave a dicarboxylic acid (85%), $C_7H_8O_5$, m.p. 197·5—198·5°. This acid must be (IV), since it gave adipic acid on hydrogenation with platinum oxide in methanol, with concomitant hydrogenolysis of the methoxy-group. Also, the n.m.r. spectrum $[(CD_3)_2SO]$ shows a pair of doublets at δ 6·38 and 8·36 p.p.m. (J_{trans} 16 Hz) which correspond to *trans*-vinylene protons. The corresponding ethoxy-derivatives (VII), m.p. 39—40°, and (VIII), m.p. 165—168°, were prepared in a similar way from (VI), m.p. 89° (decomp.).

Treatment of (III) with sodium methoxide in boiling anhydrous methanol for 7 h afforded a cyanocarboxylic acid (53%) [$C_7H_7NO_3$, m.p. 148—151° (decomp.), ν_{max} (KBr) 2225 cm^{-1} (C≡N)], which was converted into the dicarboxylic acid (IV) (65%) on alkaline hydrolysis in aqueous ethanol. The n.m.r. spectrum $[(CD_3)_2SO]$ of the cyanocarboxylic acid exhibits signals due to vinylene protons at δ 6·15 and 8·10 p.p.m. (J_{trans} 16 Hz), which are shifted to higher field than the corresponding peaks of the dicarboxylic acid (IV). Evidently this shift is caused by structural change in the substituent attached to the vinylene group;[3] therefore the cyanocarboxylic acid is the 3-methoxy-acid (V) rather than the 4-methoxy-isomer. Similarly, treatment of (III) with sodium hydride in boiling 1,2-dimethoxyethane or with sodium borohydride in ethanol at room temperature gave the same acid (V) (53 and 81%, respectively), but no reduction products. Evidently, the ring opening begins with proton abstraction from C-6 by a methoxide or hydride ion, probably with synchronous scission of the C–5–N bond, formation of a double bond between C-5 and C-6, and migration of oxygen which may be envisaged as occurring from C-7 to C-2 with simultaneous breaking of the C–N bond to form a carboxylate and a nitrile group.

Heating the cyanocarboxylic acid (V) at 168° for 30 min resulted in the reformation of the heterocycle (III) in 58% yield. This finding enabled us to prepare the parent compound, 1-azabicyclo[3,2,0]hept-3-ene-2,7-dione (IX), as a colourless oil (32%) by pyrolysis of the corresponding acid[4] (X) at 160° for 20 min. Its n.m.r. spectrum ($CDCl_3$) is in accord with the structure: δ 6·30 and 7·58 (each 1H, dd, J_{cis} 6 and $J_{vinylene}$ 2 Hz), 2·90 and 3·04 p.p.m. (2H, J_{gem} 17 Hz, both resonances further split by interaction with the methine proton, J 6 Hz), and a methine proton signal comprising nine peaks centred at δ 5·30 p.p.m. ($J_{methylene}$ 6 and $J_{vinylene}$ 2 Hz). Although acid (X) contains a double bond in the *trans*-configuration, it seems possible that a muconimide structure (II) is an intermediate in this transformation in keeping with the mechanism proposed for the formation of (III) from (I); in fact it is known that *o*-cyanobenzoic acid, on being heated, gives phthalimide.[5]

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