

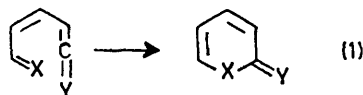
Synthesis of 2*H*-1,3-Oxazin-2-ones

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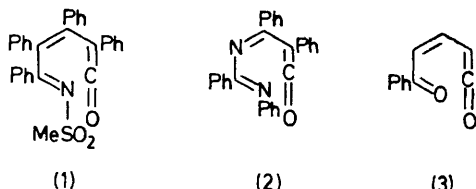
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Summary Thermolysis of the azides of *t*-maleamic acids gave the first derivatives of 2*H*-1,3-oxazin-2-one, 6-morpholine-5-phenyl- and 6-diethylamino-4,5-di-phenyl 1,3-oxazin-2-ones.

A GENERAL method for the formation of six-membered heterocyclic compounds is the electrocyclic ring-closure of 1,3,5-hexatrienes in which one or more carbon atoms are replaced by hetero-atoms. When the open-chain system contains a non-carbon atom at one end and cumulated double bonds at the other, the cyclic valence tautomer is

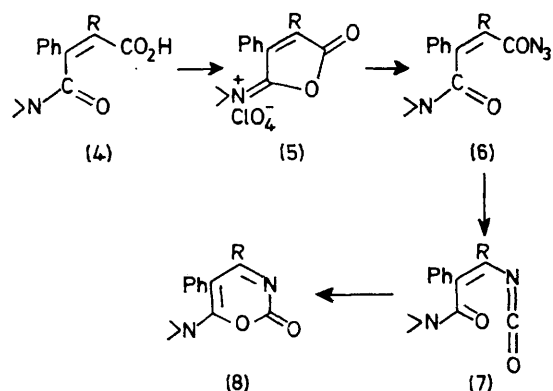


fully conjugated [equation (1)]. Recent examples illustrating this principle include the cyclisation of the ketens (1)—(3) to the corresponding pyridone,¹ pyrimidone,² and



2-pyrone,³ respectively. In each case the keten was an intermediate in a complex reaction sequence and was not directly observed.

We have found that β -carbamoylvinyl isocyanates (7) undergo a reaction of the type discussed to yield the derivatives (8) of 2*H*-1,3-oxazin-2-one, a new heterocyclic system.



a; R = H, >N = morpholino
b; R = Ph, >N = Et₂N

Treatment of (5a), obtained⁴ from the maleamic acid (4a),[†] with sodium azide gave the azide (6a), which under-

[†] Satisfactory analytical and spectral data were obtained for all new compounds; acyl azides were characterised by i.r. and n.m.r. spectra. As a representative of the oxazinones, (8a) showed a parent ion at *m/e* 258, had λ_{\max} 340 (ϵ 17,544) and 250 (14,964) nm; and in the n.m.r. spectrum showed resonances at δ 7.78 (s, 1H, 4-H), 7.2—7.65 (m, 5H, Ph), and 3.72 (s, 8H, morpholine ring).

went a Curtius rearrangement in boiling toluene. The resulting isocyanate (**7a**) cyclised spontaneously to the oxazinone (**8a**) (83%), m.p. 156.5 °C and ν_{CO} 1760 cm^{-1} . A similar sequence, starting with (**4b**), led to the analogue (**8b**) (68%), m.p. 128 °C and ν_{CO} 1742 cm^{-1} . When the reaction (**6a**) \rightarrow (**8a**) was monitored by i.r. spectroscopy it was observed that, as the azide band at 2140 cm^{-1} decayed, it was replaced by a transient isocyanate absorption at 2258 cm^{-1} and, at the same time, the oxazinone carbonyl band appeared; the process was completed in *ca.* 7 min.

Analogous results were obtained for the conversion, (**6b**) \rightarrow (**8b**), which occurred in 20 min.

1,3-Oxazin-2-ones, like other aza-analogues of 2-pyrone, such as the 6*H*-1,3-oxazin-6-ones,⁵ and 2*H*-1,3,5-oxadiazin-2-ones,⁶ are of interest as potential precursors of azetes⁷ and diazetes.

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¹ R. A. Abramovitch and G. N. Knaus, *J.C.S. Chem. Comm.*, 1974, 238.

² T. L. Gilchrist, C. J. Harris, and C. W. Rees, *J.C.S. Chem. Comm.*, 1974, 487.

³ R. Breslow, M. Oda, and J. Pecoraro, *Tetrahedron Letters*, 1972, 4415.

⁴ G. V. Boyd, *Chem. Comm.*, 1969, 1147.

⁵ For the preparation of the parent compound and leading references to 1,*n*-oxazin-6-ones, see A. Krantz and B. Hoppe, *J. Amer. Chem. Soc.*, 1975, **97**, 6590.

⁶ I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc. (C)*, 1971, 1870; R. Gompper and F. Towae, *Synthesis*, 1975, 522.

⁷ G. Maier, *Angew. Chem. Internat. Edn.*, 1974, **13**, 425.