Flash-vacuum Pyrolysis of 1,3-Oxazin-2- and -6-ones

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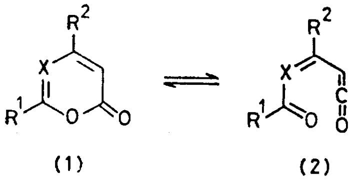
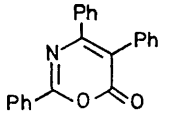
Summary On flash-vacuum pyrolysis, the oxazinone (**3**) is fragmented to diphenylacetylene, benzonitrile, and carbon dioxide; the oxazinones (**4**) and (**6**), on the other hand, undergo ring-opening to the isocyanates (**5**) and (**7**), respectively, which cyclise at room temperature.

An obvious extrapolation of the successful generation of cyclobutadiene by photolysis of α-pyrone[1] would be the formation of azetes (azacyclobutadienes) from 1,*n*-oxazin-2- or -6-ones. Photolysis of 1,3-oxazin-6-ones (**1b**) has been reported[2] to give either electrocyclic ring-opening (**1b** $\rightleftharpoons$ **2b**) or photo-fragmentation to acetylenes and nitriles, probably through a transient azete.

Flash-vacuum pyrolysis (f.v.p.) of 1,3-oxazin-6-ones also leads to fragmentation. Thus triphenyloxazinone (**3**) on sublimation through a hot tube at 750 °C and 10^{-2} Torr, followed by condensation of the pyrolysate at −78 °C, gave diphenylacetylene and benzonitrile. The pyrolysate contained several other minor products but pentaphenylpyridine, the diazabenzenes, and hexaphenyldiazacyclo-octatetraene, products expected from triphenylazete by addition to diphenylacetylene, benzonitrile, or by dimerisation, respectively, were not detected. Spectral examination of the pyrolysate gave no evidence for electrocyclic ring-opening of the type (**1b** ⇌ **2b**).



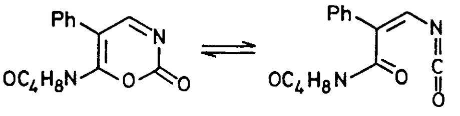
(1) (2)



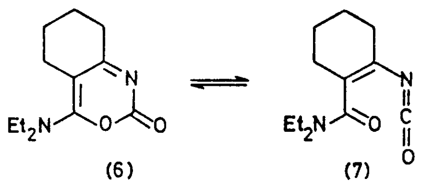
(3)

a: X = CH
b: X = N
c: X = CH,
R^1 = pyrrolidino,
R^2 = Ph

The recently available 6-amino-substituted 1,3-oxazin-2-ones[3] are attractive potential precursors to azetes, which are stabilised by the electron-releasing amino group. However, 6-morpholino-5-phenyl-2*H*-1,3-oxazin-2-one (**4**) was recovered unchanged from photolysis and, in contrast to the oxazin-6-one, pyrolysis led to electrocyclic ring-opening rather than fragmentation. Thus flash-vacuum pyrolysis at 650 °C and 0·007 Torr gave a pyrolysate whose i.r. and ^1H n.m.r. spectra† showed that it was a 1 : 1 mixture of unchanged oxazinone (ν_{CO} 1740 cm^{-1}) and the isocyanate (**5**) (ν_{NCO} 2270 cm^{-1}). The ^1H n.m.r. spectrum ($CDCl_3$) of this mixture was unchanged below −5 °C but over 15 h at 35 °C it gradually reverted to that of the pure oxazinone. The tetrahydrobenzoxazinone (**6**), m.p. 42 °C, ν_{CO} 1750 cm^{-1}, which was prepared[3] from 3,4,5,6-tetrahydrophthalic anhydride, behaved similarly on flash-vacuum pyrolysis, yielding substantial amounts of the valence tautomer (**7**) (ν_{NCO} 2265 cm^{-1}), which was stable at 0 °C but reverted completely to the tetrahydrobenzoxazinone during 12 h at room temperature.



(4) (5)



(6) (7)

Both photochemical [4,5] and thermal (f.v.p)[6] conversions of α-pyrones into vinylketens (**1a** ⇌ **2a**) are known. However, thermal ring-closure of the vinylketens is so rapid as to preclude their direct observation[5,6] and, for example, we found no evidence (i.r. or attempted trapping with methanol or dimethylamine) for the keten (**2c**) from pyrolysis of the pyrrolidinopyrone (**1c**).‡ Thus the 1,3-oxazin-2-ones (**4**) and (**6**) provide the first examples of this type of system where thermal ring-opening leads to a directly observable valence tautomer. The results also illustrate the use of flash-vacuum pyrolysis to produce mixtures of equilibrating isomers which are enriched in the less stable form.[7]

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† Compound (**4**) showed δ ($CDCl_3$) 7·78 (s, CH), 7·65—7·2 (m, Ph), and 3·74 (br s, morpholino), the isocyanate (**5**) 7·23 (br s, Ph), 6·46 (s, CH), and 3·9—3·3 (m, morpholino).

‡ Compound (**1c**), yellow prisms, m.p. 165 °C, ν_{CO} 1720 cm^{-1}, was prepared from β-phenylglutaconic anhydride by successive treatment with pyrrolidine, acetic anhydride–perchloric acid, and triethylamine.

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