Furazan *N*-Oxides: a Convenient Source of both Nitrile Oxides and Isocyanates

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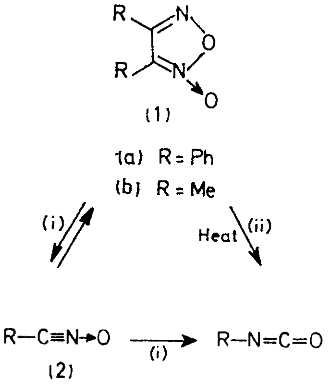
Summary Thermolysis of furazan *N*-oxides results in ring cleavage to nitrile oxides which may be trapped in good yield as 1,3-dipolar cycloadducts; in the absence of dipolarophiles the intermediate nitrile oxides rearrange to isocyanates.

Furazan *N*-oxides (furoxans) (**1**) have long been regarded[1a] as the stable products resulting from the dimerisation of nitrile oxides (**2**) but until recently little attention had been paid to their thermal decomposition, despite early reports[2] suggesting that phenyl isocyanate† had been formed during an attempted distillation of (**1a**).

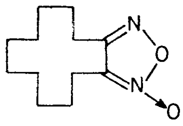
The hypothesis [2a,3] that the formation of the isocyanate involves dissociation of the furoxan to nitrile oxide fragments, followed by the well established [1b] rearrangement of nitrile oxides to isocyanates [*i.e.*, route (i) rather than (ii) in the Scheme], has found support with the observations[4,5] that strained furoxans and furoxans with bulky substituents decompose at moderate temperatures with formation of nitrile oxides which may be trapped as cycloadducts in the presence of a dipolarophile.



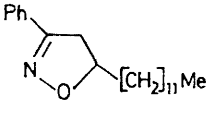
Scheme

We report that thermolytic ring opening of (**1a**), (**1b**), and (**3**), which does not depend upon special structural features such as bulky substituents or high ring strain, but takes place under more forcing conditions, may be utilised for the generation *in situ* of both nitrile oxides and isocyanates.

When (**1a**) and (**1b**) were heated under reflux in dodecan-1-ol (257 °C) phenyl and methyl isocyanate, respectively, were trapped as their carbamates in yields of 81 and 20% respectively. Phenyl isocyanate was also isolated directly (42%) by distillation from (**1a**) at atmospheric pressure. At > 200 °C the rearrangement of the intermediate nitrile oxide is expected to be rapid;[1b] however, when (**1a**) was heated for 2 h at 245 °C in tetradec-1-ene, and then cooled, the isoxazoline cycloadduct (**4**) of the alkene with benzonitrile oxide was isolated in 82% yield, showing that the 1,3-cycloaddition is faster than the isomerisation of nitrile oxide to isocyanate.

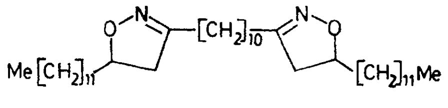


(3)

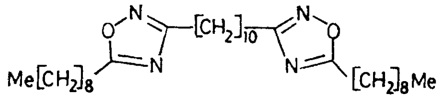


(4)

Whereas disubstituted furoxans (**1**) produce monofunctional nitrile oxides and isocyanates, bicyclic analogues such as (**3**), which are conveniently prepared from the appropriate cycloalkene by the neglected method of Klamann,[6] should give rise to a series of bis-nitrile oxides and di-isocyanates which are not readily obtainable by other routes. In accord with this expectation, thermolysis of (**3**) in tetradec-1-ene and decanonitrile (b.p. 244 °C) afforded the cycloadducts (**5**) (65%) and (**6**) (51%) derived from (**7**), while in decan-1-ol at 228 °C (**8**), formed from (**9**), was isolated (70%). Thermolysis of (**3**) in hexadecane leads directly to (**9**) (67%).



(5)



(6)

$O \leftarrow N{\equiv}C{-}[CH_2]_{10}{-}C{\equiv}N \rightarrow O$

(7)

$Me[CH_2]_9OCONH{-}[CH_2]_{10}NHCO_2{-}[CH_2]_9Me$

(8)

$O{=}C{=}N{-}[CH_2]_{10}N{=}C{=}O$

(9)

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† The phenyl cyanate described in ref. 2a has since been assumed to be phenyl isocyanate.[3]

These results taken with those previously reported[4,5] suggest the ring opening of furoxans is a general reaction with a threshold temperature that is critically dependent on substituent, and furthermore that bicyclic furoxans may find use both as thermally triggerable sources of bis-nitrile oxides suitable for applications such a the formation of polymer cross-links of high thermal stability,[7] and as intermediates in a phosgene-free route to di-isocyanates from commercially available cycloalkenes.[8]

(*Received, 2nd February* 1976; *Com.* 107.)

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[1] (a) C. Grundmann and P. Grünanger, 'The Nitrile Oxides,' Springer-Verlag, West Berlin and Heidelberg, 1971, pp. 75—81, and references therein; (b) *ibid.*, pp. 62—67.

[2] (a) S. Gabriel and M. Koppe, *Ber.*, 1886, **19**, 1145; (b) K. Auwers and V. Meyer, *ibid.*, 1889, **22**, 705.

[3] J. H. Boyer in 'Heterocyclic Compounds,' Vol. 7, ed. R. C. Elderfield, Wiley, New York and London, 1961, Ch. 6, p. 498.

[4] J. Ackrell, M. Altaf-ur-Rahman, A. J. Boulton, and R. C. Brown, *J.C.S. Perkin I*, 1972, 1587.

[5] A. Dondoni, G. Barbaro, A. Battaglia, and P. Giorgianni, *J. Org. Chem.*, 1972, **37**, 3196.

[6] D. Klamann, W. Koser, P. Weyerstahl, and M. Fligge, *Chem. Ber.*, 1965, **98**, 1831.

[7] West German Patent, 2,336,403 (*Chem. Abs.*, 1974, **81**, P49257a).

[8] West German Patent, 2,422,764 (*Chem. Abs.*, 1975, **82**, P141047a).