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STEREOELECTRONIC CONTROL OF THE RATE OF RING OPENING IN AZIDOFURANS[1]

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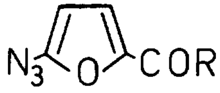
Summary. 5-Azido-2-furyl alkyl ketones are converted into nitrogen and 4,5-dioxo-2-alkenenitriles in a reaction whose facility depends on the nature of the alkyl group.

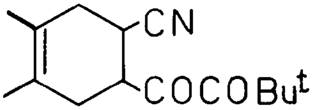
The recent report of thermally induced fragmentation of azidoisoxazoles[2] prompts us to report a facile, but substituent dependent ring-opening reaction in some azidofurans. The azides (1) and (2) were found to decompose quantitatively in deuterochloroform at 20° in first-order processes with half-lives of approximately 11 and 40 h to give the nitriles (3)[3] and (4)[3] respectively. These nitriles gave i.r., ^{13}C and ^{1}H n.m.r., and mass spectral data consistent with the proposed structures, but underwent *(Z)* to *(E)* isomerization and also decomposed on standing. Accordingly they were further characterized. For example (3) gave the stable Diels-Alder adduct (5) with 2,3-dimethyl-1,3-butadiene and the quinoxaline (6) with *o*-phenylenediamine.



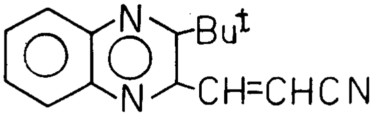
(1) R = Bu^t
(2) R = Pr^i
(7) R = H

NC-CH=CH-COCOR

(3) R = Bu^t
(4) R = Pr^i



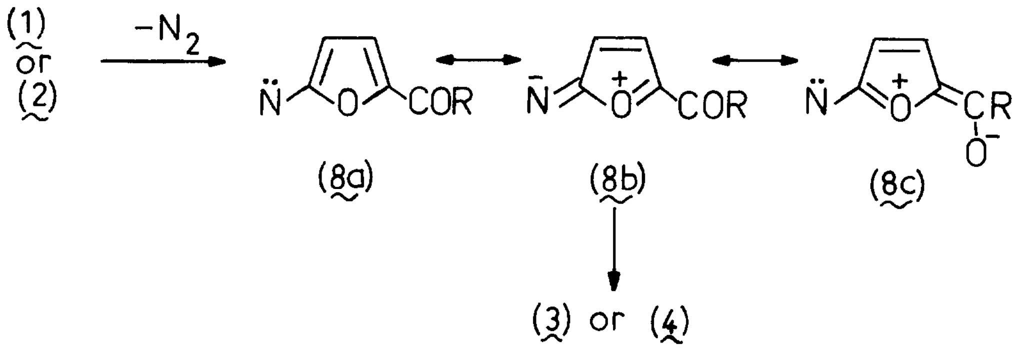
(5)



(6)

The mechanism for the ring-opening reaction is outlined in the Scheme. This system is isoelectronic with diazo(2-furyl)- and diazo(5-isoxazoyl)-methanes which lose nitrogen and undergo ring opening under somewhat more forcing conditions (vacuum pyrolysis) to give acetylenic products.[4]

By way of contrast with the facility with which (1) and (2) undergo the above reaction, the azido aldehyde (7), under the same conditions was found to have a half-life in excess of 900 h.[5] This remarkable difference in stability can be correlated with the degree of planarity of the carbonyl group with the furan ring. It is generally agreed in aromatic and heteroaromatic aldehydes and ketones, that whereas the formyl group is coplanar with the aromatic ring, increasing the bulk of the group attached to the carbonyl group leads to increasing deviation from planarity.[6] When one considers the stability of the intermediate (8) in the Scheme, it is apparent that an in-plane carbonyl group will favour contributions from canonical form (8c) and reduce contributions from (8b).



Scheme

When the carbonyl group is not in-plane, contribution (8b) is significant and the electron deficient nitrogen, as shown in the nitrene contributor (8a), accepts electron density from the furanoid oxygen with resultant stabilization of the intermediate (8) and increase in the rate of reaction.

The decomposition of the azides (1), (2) and (7) thus appears to be a reaction which is stereoelectronically controlled by the bulk of the substituent attached to the carbonyl group.

FOOTNOTES AND REFERENCES

1. This study was supported by a grant from the Australian Research Grants Committee.
2. G. Kumar, K. Rajagopalan, S. Swaminathan and K.K. Balasubramanian, *Tetrahedron Letts.*, 4685 (1979).
3. Mixtures of the (*E*)- and (*Z*)-isomers with the latter predominating (>85%); a similar stereochemical result has been obtained in the isoelectronic azido(2-furyl)methanes.[4]
4. R.V. Hoffman, G. Gorphanides and H. Schechter, *J. Am. Chem. Soc.*, **100**, 7927 (1978); S.-I. Hayashi, M. Nair. D.J. Houser and H. Schechter. *Tetrahedron Letts.*, 2961 (1979).
5. After 7 days 12% of (7) had decomposed to unidentifiable products.
6. A.R. Katritzky, R.F. Pinzelli and R.D. Topsom, *Tetrahedron*, **28**, 3449 (1972); and C.G. Andrieu, P. Metzner, D. Debruyne, D.M. Bertin and H. Lumbroso, *J. Mol. Struct.*, **39**, 263 (1977) and references therein.

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