Tetrahedron Letters Vol. 21, pp 559 - 560 0040-4039/80/0201-0559$02.00/0
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NEW PERSPECTIVES IN THE CHEMISTRY OF 1-AZIDOHYDRAZONES

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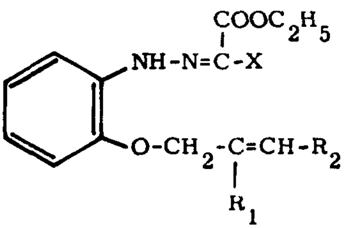
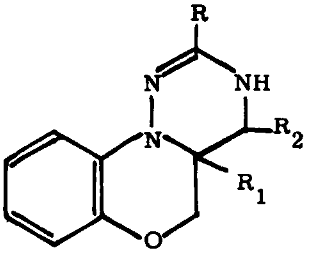
Summary. Thermal decomposition of 1-azidohydrazones [I] results in tricyclic products [III], probably arising from nitrene intermediates through an intramolecular cycloaddition to the ethylenic bond.

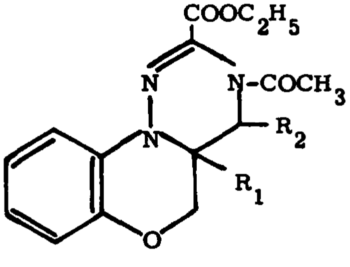
Despite 1-azidohydrazones may be seen as potential intermediates in heterocyclic syntheses, little attention has been hitherto devoted to them.(1, 2) The present preliminary report deals with an unprecedented reaction pattern we have evidenced on investigating the thermal behaviour of the functionalised 1-azidohydrazones [Ia-c]. These substrates were accessible by reacting the corresponding 1-chlorohydrazones [IIa-c] with sodium azide (2 mol.eq.) in benzene - water system (0.1 mol.eq. of hexadecyltributylphosphonium bromide, 5-8 hours at 40°, 55-65% yield).(3)



[I] : X = N_3
[II]: X = Cl



[III]: R = $COOC_2H_5$
[IV]: R = H

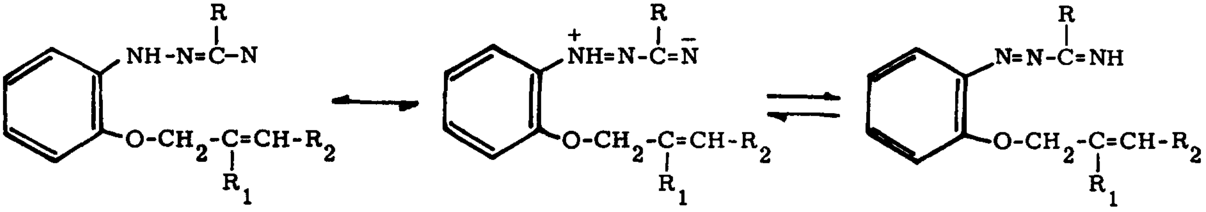


[V]

a: $R_1 = R_2 = H$; b: $R_1 = CH_3$, $R_2 = H$; c: $R_1 = H$, $R_2 = C_6H_5$

The azidohydrazones [Ia-c] underwent in boiling benzene (0.2 *M* concentration, 2-3 hours) a rather clean reaction providing 3, 4, 4a, 5-tetrahydro-[1, 2, 4]triazino[6, 1-*c*][1, 4]benzoxazines [IIIa-c] in 63, 69, and 79% yield respectively. Hydrolysis of these products by ethanolic sodium hydroxide led to unstable carboxylic acids, which were readily decarboxylated to give the corresponding 2-unsubstituted compounds [IVa-c]. On the other hand, the treatment of [IIIa, b] with boiling acetic anhydride resulted in the *N*-acetylderivatives [Va, b]; such a reaction did not occur in the case of [IIc], reasonably because of steric hindrance by the bulky R_2 substituent.

All formulae [III], [IV], and [V] are consistent with elemental analyses, molecular weights measured by mass spectrometry, and IR and NMR data.(4) In addition, they were proved to be correct on submitting one compound of the series ([IVa]) to the X-ray diffraction study.(5)



[VI] [VII]

The formation of [III] from [I] can be interpreted as involving the preliminary loss of nitrogen to originate the unusual nitrene species [VI], which then reacts intramolecularly (as such or in the tautomeric form [VII]) according to a 1, 4-cycloaddition on the neighbouring ethylenic bond. Of course, the actual mechanism of the latter reaction cannot be stated at thepresent, both concerted and stepwise pathways being conceivable a priori.(6)

Further work is in progress with the aim of providing more intramolecular as well as intermolecular examples of this novel pattern of behaviour.

References and Notes

(1) S. Patai (Ed.), "The Chemistry of the Azido Group", Interscience, London, 1971, p. 90, 93, and 517.

(2) A.F. Hegarty, M.P. Cashman, and F.L. Scott, J.C.S. Perkin II, 44 (1972).

(3) Compounds [Ia-c] gave proper IR and NMR spectra; however, samples of analytical purity could not be obtained because of their thermal instability.

(4) Analytical and spectral data of [III], [IV], and [V] will be reported in a future paper. Melting points are: [IIIa], 100°; [IIIb], 151°; [IIc], 216°; [IVa], 152°; [IVb], 138°; [IVc], 155°; [Va], 141°; [Vb], 129°.

(5) T. Pilati (C.N.R., Centro per lo studio delle relazioni tra struttura e reattivita' chimica, Milano), personal communication.

(6) A somewhat similar case of 1, 4-cycloaddition leading to the 1, 2, 4-triazine ring has been recently reported: in fact, 3-diazopyrazoles react with electron-rich olefins to afford pyrazolo[5, 1-c][1, 2, 4]triazines.(7, 8)

(7) W.L. Magee and H. Shechter, J.Am.Chem.Soc., **99**, 633 (1977).

(8) H. Dürr and H. Schmitz, Chem.Ber., **111**, 2258 (1978).

(Received in UK 6 December 1979)