

282. Carbenic Behaviour of Isocyanamines generated by Flash Pyrolysis of 4-Arylhydrazono-isoxazol-5-ones. Rearrangement to Cyanamides and Indazoles

Preliminary communication

by **Werner Reichen** and **Curt Wentrup**¹⁾

Institut de Chimie Organique de l'Université, CH-1005 Lausanne, Switzerland

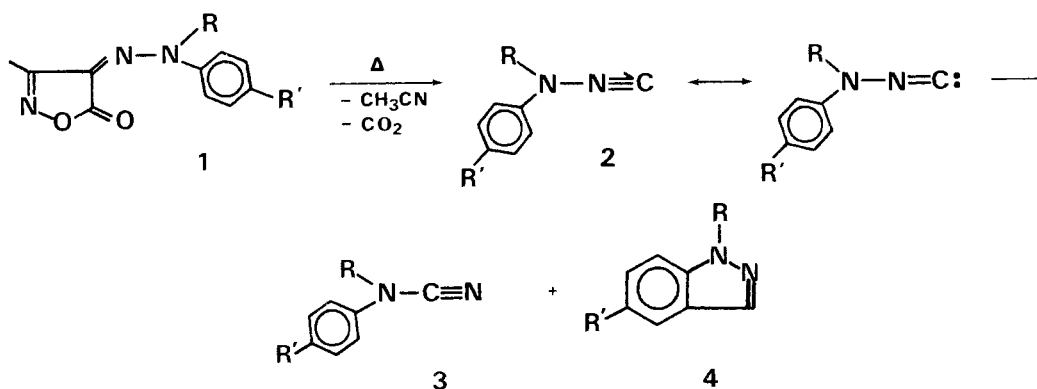
(21. IX. 76)

Summary. Flash pyrolysis of the 4-arylhydrazono-3-methyl-isoxazol-5-one (**1**) yields carbon dioxide, acetonitrile, and isocyanarylamines **2** which under the reaction conditions rearrange to either arylcyanamides **3** or indazoles **4**. It is shown by deuterium labelling that only the isocyanamines not the isomeric nitrile imines are intermediates in the formation of indazoles.

In the accompanying paper we describe a method which offers considerable promise for the production of methylenecarbenes in the gas-phase [1]. We now report (a) an extension of this procedure, allowing the facile generation of highly reactive isocyanamines, and (b) the carbenic behaviour of such compounds.

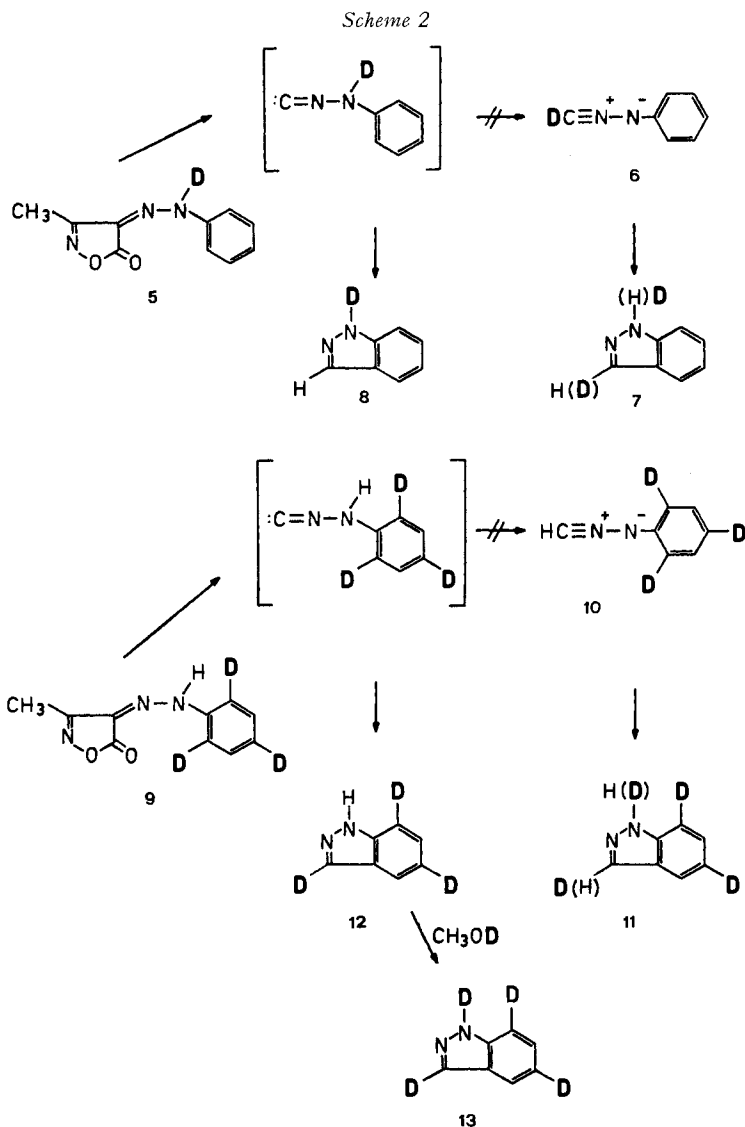
4-Arylhydrazono-3-methyl-isoxazol-5-ones (**1**) are easily obtained from the one-pot reaction between ethyl acetoacetate, hydroxylamine hydrochloride, the appropriate arylamine, and sodium nitrite [2]. Flash pyrolysis of **1a** at temperatures be-

Scheme 1



a	b	1-4	c	d	e
H	CH ₃	R	H	H	H
H	H	R'	COOH	OH	NO ₂

¹⁾ Present address: Fachbereich Chemie der Universität, D-3550 Marburg/Lahn, Lahnberge.

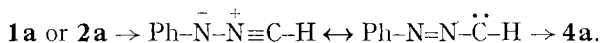


tween 400° and $550^\circ/10^{-3}$ – 10^{-2} Torr²⁾ resulted in a clean fragmentation into acetonitrile and carbon dioxide, identified by IR. spectroscopy of the condensable gas. The less volatile product consisted of phenylcyanamide (3a) and indazole (4a)³⁾. The nature of the products suggests that the key intermediate is isocyanamide 2a. The corresponding indazoles and/or cyanamides were also obtained by pyrolysis of 1b–e (Scheme 1).

²⁾ Two types of apparatus were used; one [3] consisting of a 30×2 cm quartz tube, operating at 10^{-3} Torr; the other a 40×3.5 cm quartz tube at 10^{-2} – 10^{-1} Torr.

³⁾ Identified by IR., NMR., and mass spectrometrical comparison with authentic materials after separation by column chromatography ($\text{SiO}_2/\text{CCl}_4-\text{CHCl}_3$).

Since we have shown previously that thermally generated nitrile imines cyclize quantitatively to indazoles in the gas-phase [4], the question arises whether the isocynoamines **2** or the isomeric nitrile imines are the true intermediates:



The following deuterium labelling experiments demonstrate unequivocally that only the isocynoamines **2** are the reactive intermediates.

The pyrolysis of compound **5** (obtained by exchange between **1a** and D₂O) at 550°/10⁻² Torr resulted in the exclusive formation of 1-[D]-indazole (**8**) which easily exchanged back to indazole with H₂O (in fact, it did so already partially during isolation). No diminution of the H-C(3) singlet at δ 8.22 ppm in the NMR. spectrum of indazole [5] was observable (absence of **7**) (*Scheme 2*). Similarly, the 2,4,6-trideuterio-phenylhydrazone **9** (obtained from 2,4,6-trideuterioaniline using the standard procedure [2]) yielded only 3,5,7-trideuterioindazole (**12**), and not 1,5,7-trideuterioindazole (**11**) (*Scheme 2*), as shown by NMR. spectroscopy (absence of the H-C(3) singlet at δ 8.22 ppm). Repeated boiling of **12** with methanol caused no change in the NMR. and mass spectra (continued presence of three deuterium atoms). However, treatment with deuteriomethanol resulted in the rapid formation of 1,3,5,7-tetradeuterioindazole (**13**) (*Scheme 2*). From these results it is clear that no isocynoamine/nitrile imine rearrangement takes place. Furthermore, a hydrazone-azo tautomerism in the starting material **1** (**5**, **9**) can be excluded, as can a thermal 1,3-hydrogen shift in indazole itself under the reaction conditions. These hydrogen shifts are, of course, formally forbidden by the *Woodward-Hoffmann* rules of orbital symmetry [6], but could nevertheless not be excluded *a priori*.

In conclusion, we have demonstrated a near-quantitative formation of isocynoamines **2** by flash pyrolysis of the hydrazones **1**. The isocynoamines behave in the same way as methylenecarbenes [1] [7], undergoing an aromatic C-H insertion reaction leading to indazoles **4**, or rearranging to cyanamides **3** by a 1,2-shift.

The financial support of this work by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (Project No. 2.258.074) and this Institute (Prof. H. Dahn) is gratefully acknowledged.

REFERENCES

- [1] C. Wentrup & W. Reichen, *Helv. 59*, 2615 (1976).
- [2] R. Schiff, *Ber. deutsch. chem. Ges.* **28**, 2732 (1895).
- [3] R. Gleiter, W. Rettig & C. Wentrup, *Helv. 57*, 2111 (1974).
- [4] By pyrolysis of 1,3,4-oxadiazolin-5-ones: W. Reichen, *Helv. 59*, 1639 (1976); by pyrolysis of 2,5-diaryltetrazoles: C. Wentrup, unpublished work.
- [5] P. J. Black & M. L. Heffernan, *Austral. J. Chemistry* **16**, 1051 (1963).
- [6] R. B. Woodward & R. Hoffmann, 'The Conservation of Orbital Symmetry', Verlag Chemie, Weinheim/Bergstr. 1970.
- [7] R. F. C. Brown, F. W. Eastwood, K. J. Harrington & G. L. McMullen, *Austral. J. Chemistry* **27**, 2393 (1974).