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It has been shown by mass spectrometric analysis that 3-azidoindazole, the product of the reaction between 3-diazoindazole and azide ion, was formed through acyclic pentazene (IV and V) and cyclic pentazole (VIII and IX) intermediates in the ratio 2:1.

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Sir:

Heterocyclic diazo compounds are important synthons for the synthesis of heterocyclic systems (1) and valuable intermediates in aza-transfer reactions in which 1,3-disubstituted triazenes and 1,4-disubstituted tetrazenes are formed (2,3,4).

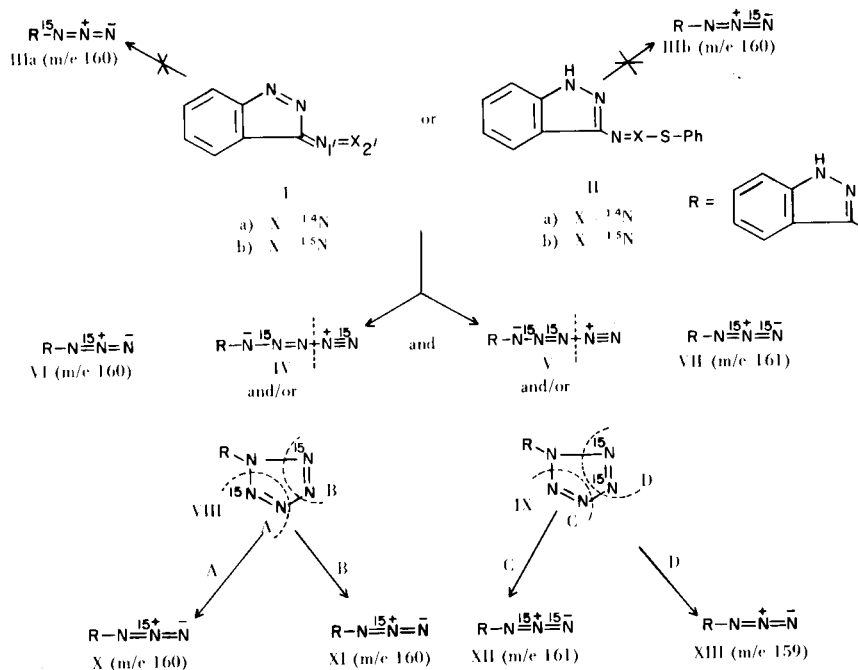
Recently, it has been found that 3-diazoindazole could be converted with hydroxylamine into 3-azidoindazole (2), which exists in the 1-NH form, as has been demonstrated by the observation of $^{11}\text{H}^{-1}\text{H}$ and $^{13}\text{C}^{-1}\text{H}$ coupling (5). Photochemical decomposition of differently ^{15}N -labelled 3-azidoindazoles revealed that nitrogen was eliminated without prior scrambling (2).

In this communication we report, as a continuation of our interest in aza-transfer reactions, the preparation and the mechanism of formation of 3-azidoindazole from 3-diazoindazole or 3-indazolyldiazo phenyl sulphide and potassium azide. It seemed worthwhile to study this reaction for several reasons. Although the reaction between aromatic diazonium salts and hydrazoic acid was first observed by Noeltling and Michel (6) and comprehensive ^{15}N labelling experiments have been carried out by Clusius (7,8), Ugi and Huisgen (9,10) and others (11), no example concerning the mechanism of formation is known in the field

of heterocyclic diazo compounds. The second reason was that $\text{C}_3\text{-N}_1$ bond in 3-diazoindazole was cleaved very easily and indazole was formed as a by-product in all reactions in which 3-diazoindazole was one of the reactants (2,3). This is due to the fact that this bond has a dipolar character with a negative charge on C_3 , as shown recently by X-ray analysis (12).

A solution of 3-diazoindazole (13) or 3-indazolyldiazo phenyl sulphide (2) (20 mg.) in ethanol (2 ml.) was treated with potassium azide (20 mg.) dissolved in a minimum amount of water. After standing for 5 minutes at room temperature the solvent was evaporated *in vacuo* and the residue extracted with chloroform (3 x 5 ml.), the chloroform evaporated *in vacuo* and the residue sublimed (70° , 1 mm Hg) in order to separate 3-azidoindazole from indazole and diphenyl disulphide, m.p. 95° , yield 45-50%. The isolated compound was identical in all respects with 3-azidoindazole prepared previously (2). Similarly, the experiments with ^{15}N labelled compounds were carried out.

3-Azidoindazole could be formed by direct nucleophilic displacement of the diazo group or the diazo sulphide group by the azide ion or by addition of the azide ion to the diazo group or the diazo sulphide group resulting in the forma-



tion of an acyclic pentazene and/or a cyclic pentazole intermediates from which elimination of a molecule of nitrogen took place (Scheme I). The easiest way to differentiate among these three possible mechanisms is ^{15}N labelling techniques including mass spectrometric analysis of the isotope distribution.

By treatment of either unlabelled 3-diazoindazole (Ia) or unlabelled 3-indazolyldiazo phenyl sulphide (IIa) with potassium azide, 95% enriched with ^{15}N on one nitrogen atom, a mixture of unlabelled (m/e 159) and mono-labelled (m/e 160) 3-azidoindazole in a ratio of 1:1 was formed. On this basis the direct nucleophilic displacement of the diazo group or the diazo sulphide group by an azide ion, in which the formation of mono-labelled IIIa (m/e 160) and mono-labelled IIIb (m/e 160) should be expected, was excluded. Therefore, 3-azidoindazole must be formed by addition of the azide ion to the diazo group or the diazo sulphide group followed by elimination of a molecule of nitrogen either *via* pentazene (IV and V) or pentazole (VIII and IX) intermediates. In order to distinguish between these two reaction pathways, mono-labelled 3-diazo($2\text{-}^{15}\text{N}$)indazole (Ib) (2) or 3-indazolyldiazo($2\text{-}^{15}\text{N}$) phenyl sulphide (IIb) (14) were treated with potassium azide, 95% enriched with ^{15}N on one nitrogen atom. If the reaction should proceed only through pentazole intermediates IV and V followed by elimination of a molecule of nitrogen then the mono-labelled azido compound VI (m/e 160) and the bi-labelled azide VII (m/e 161) should be produced in a 1:1 molar ratio. On the other hand, if the azido compound should be formed only through cyclic intermediates VIII and IX, then reaction pathways A and B should produce mono-labelled azides X (m/e 160) and XI (m/e 160), while reaction pathways C and D should produce bi-labelled azide XII (m/e 161) and unlabelled azide XIII (m/e 159) in the ratio m/e 159:160:161 = 1:2:1.

The mass spectrometric analysis of the reaction mixture gave the ratio m/e 159:160:161 = 5:20:16, from which one can calculate and conclude that 3-azidoindazole was formed from 3-diazoindazole (I) or 3-indazolyldiazo phenyl sulphide (II) and potassium azide through acyclic pentazene (IV and V), and cyclic pentazole (VIII and IX) intermediates in the ratio 2:1, according to the Scheme I.

REFERENCES AND NOTES

- (1) For reviews see:
 - (a) J. M. Tedder, *Adv. Heterocyclic Chem.*, **8**, 1 (1967); (b) R. N. Butler, *Chem. Revs.*, **75**, 241 (1975); (c) M. Tišler and B. Stanovnik, *Heterocycles*, **4**, 1115 (1976).
 - (2) M. Kočevar, D. Kolman, H. Kranjc, S. Polanc, B. Porovne, B. Stanovnik, and M. Tišler, *Tetrahedron*, **32**, 725 (1976).
 - (3) B. Stanovnik, M. Tišler, S. Polanc, V. Kovačič-Bratina, and B. Špicer-Smolnikar, *Tetrahedron Letters*, 3193 (1976).
 - (4) L. Dežman, D. Janežič, M. Kokalj, E. Kozak, J. Prime, B. Stanovnik, M. Tišler, and O. Zaplotnik-Naglič, *Tetrahedron*, **33**, 2851 (1977).
 - (5) A. Fruchier, E. Alcalde, and J. Elguero, *Org. Magn. Reson.*, **9** 235 (1977).
 - (6) E. Noelting and O. Michel, *Ber.*, **26**, 86 (1893).
 - (7) K. Clusius and H. Hurzeler, *Helv. Chim. Acta*, **37**, 798 (1954).
 - (8) K. Clusius and M. Vecchi, *ibid.*, **39**, 1469 (1956).
 - (9) R. Huisgen and I. Ugi, *Angew. Chem.*, **68**, 705 (1956).
 - (10) R. Huisgen and I. Ugi, *Chem. Ber.*, **90**, 2914 (1957).
 - (11) For a review see: M. E. C. Biffin, J. Miller, and D. B. Paul, "Introduction of the Azido Group" in "The Chemistry of the Azido Group", S. Patai, Ed., Interscience Publishers, London, New York, 1971, p. 57.
 - (12) I. Leban, B. Stanovnik, and M. Tišler, *Acta Cryst.*, **B**, in press.
 - (13) E. Bamberger, *Ber.*, **32**, 1773 (1899).
 - (14) Prepared from 3-diazo($2\text{-}^{15}\text{N}$)indazole (2) according to the procedure described for the preparation of unlabelled 3-indazolyldiazo phenyl sulphide (2).