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Rearrangement of *N*-Nitro-1,2,4-triazoles into 3-Nitro-1,2,4-triazoles

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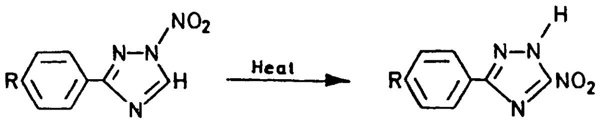
Summary Syntheses of the *N*-nitro-1,2,4-triazoles (**1**) and (**2**) and their thermal isomerization into the 3-nitro-derivatives (**3**) and (**4**) is described; this thermal rearrangement of *N*-nitro-azoles to their corresponding *C*-nitro-compounds is suggested to be an example of a [1,5] sigmatropic shift of the NO_2 group.

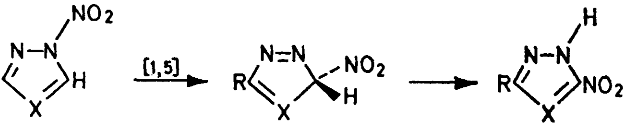
Recently we reported on a novel reaction, the thermal isomerization of *N*-nitro-pyrazoles[1] and *N*-nitro-indazoles[2] into their corresponding 3-nitro-derivatives. We report here the thermal isomerization of the *N*-nitro-1,2,4-triazoles (**1**) and (**2**) into the 3-nitro-compounds (**3**) and (**4**). *N*-Nitration[1,3] of 3-phenyl- and 3-(*p*-nitrophenyl)-1,2,4-triazole[4,5] easily afforded in good yields the triazoles (**1**) and (**2**).† The structures of (**1**) and (**2**) were assigned on the basis of their n.m.r. spectra. Introduction of the NO_2 group in the triazole ring did not alter the chemical shift of the phenyl protons indicating that this group is not located on one of the nitrogen atoms adjacent to the phenyl group.



(1) R = H
(2) R = NO_2
(3) R = H
(4) R = NO_2

When heated at 120° for 8—18 h (temp. raised from 20° to 120° in 2·5 h) either neat or in anisole solution, (**1**) and (**2**) rearranged into the corresponding 3-nitro-compounds (**3**), m.p. 215° (decomp.), and (**4**) m.p. 260°.†

The synthesis of the nitro-compounds described here seems to be the first example of direct nitration of the 1,2,4-triazole ring. In addition, the isomerization provides another example of an apparently characteristic property of *N*-nitro-azoles[1,2] to rearrange thermally into their corresponding *C*-nitro-derivatives. In the case of the *N*-nitro-pyrazoles this isomerization has been found, kinetically as well as chemically, to be a first-order intramolecular rearrangement. Such an intramolecular migration of an NO_2 group from one position to another in the aromatic ring can be visualized as a [1,5] sigmatropic shift followed by tautomerization.‡



X = N; R = Ph or *p*-$NO_2 \cdot C_6H_4$
X = CH; R = H or Me

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† Satisfactory elemental analyses were obtained for all new compounds.

‡ We thank Dr. David Dalrymple (University of Delaware) for his suggestion concerning the mechanism of this isomerization of *N*-nitro-azoles.

So far no sigmatropic shifts of a NO_2 group have been reported in the literature, but there are examples of other groups undergoing sigmatropic shifts in N-heteroaromatic rings,[6,7] the most thoroughly investigated example being the thermal isomerization of 1-substituted pyrroles into the corresponding 2- and 3-substituted pyrroles.[7]

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