Nitrile Imide–Imidoylnitrene–Carbodi-imide Rearrangement

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Summary Gas-phase generation of benzonitrile *N*-methylimide (**3**) leads to rearrangement to 1-methylene-2-benzylidenehydrazine (**5**) and methylphenylcarbodi-imide (**9**); the latter is also obtained in 85% yield by flash vacuum pyrolysis of 1-methyl-5-phenyltetrazole.

THE thermolysis of 2,5-diaryltetrazoles in the gas-phase or in inert solvents gives nitrile imides which, in the absence of trapping agents, undergo intramolecular cyclisation with the formation of indazoles.[1] The ground states of the nitrile imides can be formulated as resonance hybrids of dipolar and carbenic forms[2] (**1**).

$$R^1\text{–}C{\equiv}\overset{+}{N}\text{–}\overset{-}{N}\text{–}R^2 \longleftrightarrow R^1\text{–}\overset{-}{C}{=}\overset{+}{N}{=}N\text{–}R^2 \longleftrightarrow R^1\text{–}\overset{\bullet\bullet}{C}\text{–}N{=}N\text{–}R^2$$

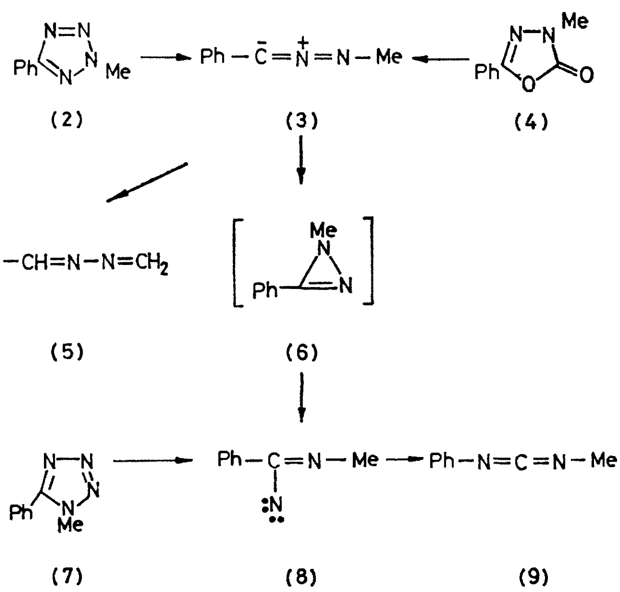
(1a) **(1b)** **(1c)**

We now report two new reactions of nitrile imides which occur when the intramolecular cyclisation is inhibited (R^2 = alkyl), namely, a 1,4-hydrogen shift to give an azine (**5**), and a rearrangement to a carbodi-imide (**9**).

Flash vacuum pyrolysis of 2-methyl-5-phenyltetrazole (**2**) at 550 °C (10^{-4} Torr) gave the azine (**5**) (10%), methylphenylcarbodi-imide (**9**) (*ca.* 1%), styrene (9%), benzonitrile (44%), and a gaseous product which was shown by i.r. spectroscopy to be a mixture of HCN and NH_3 (*ca.* 70:30). The yield of (**9**) increased with temperature, 8% being formed at 960 °C. In contrast, (**5**) was not detectable above 800 °C.

A series of pyrolyses of an authentic sample of the azine (**5**) established that this product decomposes at 550 °C to benzonitrile, styrene, the 70:30 mixture of HCN and NH_3, as well as other, unidentified products also formed in the pyrolyses of (**2**). (The products were analysed by g.l.c.–mass spectrometry and i.r. spectroscopy.)

The same products as above were also obtained, together with CO_2, by similar pyrolyses of 3-methyl-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one (**4**) at 700—960 °C. The carbodi-imide (**9**) was isolated in 85% yield by pyrolysis of 1-methyl-5-phenyltetrazole (**7**) at 600 °C (10^{-4} Torr). Compound (**9**) is extremely unstable,[3] polymerising even at −20 °C. It cannot be distilled, but can be gas chromatographed at 65 °C on a SE 30 column [i.r. (film) 3010m, 2920m, 2120vs, 1585s, 1490s, 1398s, 1150s, 885s, 745s, and 680s cm^{-1}; ^1H-n.m.r. δ ($CDCl_3$) 3·15 (s, 3H), 7·7—7·0 (m, 5H); mass spectrum, *m/e* 132 (100%), 131 (32), 104 (34), and 77 (34)]. The instability of (**9**) indicates that the actual yields of this compound in the pyrolyses of (**2**) and (**4**) could have been somewhat higher than the 8—9% isolated.



Evidence for the thermal formation of the nitrile imide (**3**) from the tetrazole (**2**) in the condensed phase has been reported by Huisgen, *et al.*[4] The Wolff-type rearrangement of imidoylnitrenes to carbodi-imides is well known.[5] The above results indicate that the azine (**5**) and the carbodi-imide (**9**) are the only primary rearrangement products of the nitrile imide (**3**). A 1,4-hydrogen shift analogous to the reaction (**3**) → (**5**) is also known in nitrile ylides.[6] The isolation of (**9**) from (**2**) and (**4**) is the first evidence for a nitrile imide–imidoylnitrene rearrangement (**3**) → (**6**) → (**8**). This reaction is isoelectronic with the well known nitrile oxide–isocyanate rearrangement.[7] If the nitrile imide is regarded as a carbene (**1c**), this rearrangement is also analogous to the rearrangement of oxocarbenes to oxirens and ketens.[7] *Ab initio* calculations[8] indicate that the antiaromatic 1*H*-diazirine [unsubstituted (**6**)] is *ca.* 14 kcal mol^{-1} less stable than nitrile imide (HCNNH), whereas carbodi-imide (HNCNH) lies *ca.* 50 kcal mol^{-1} below HCNNH.

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