Fragmentation of 3,6-Diphenyl-4,5-dehydropyridazine to Diphenylbutadiyne

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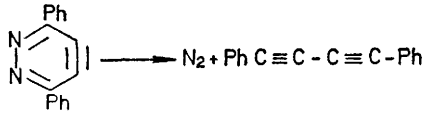
Summary When 3,6-diphenyl-4,5-dehydropyridazine (**1**) is generated in the vapour phase, by pyrolysis of the pyridazotriazine (**2**) or by pyrolysis of its furan adduct (**5**), it reacts by extrusion of nitrogen to give diphenylbutadiyne rather than by dimerisation.

BENZYNE and most other dehydroaromatic intermediates dimerise when they are generated in the vapour phase. 3,4-Dehydropyridine is exceptional in that, although a small amount of dimer is formed, the major reactions involve unimolecular fragmentation of the aromatic

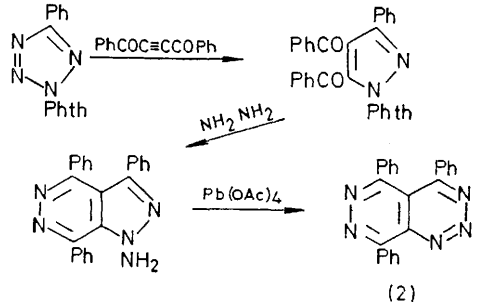


(1)

SCHEME 1

system.[1] The difference has been ascribed to differences in bond energies and resonance energies, totalling about 38 kcal mol^{-1}, which should favour the fragmentation of 3,4-dehydropyridine compared with that of benzyne. On this basis, 4,5-dehydropyridazine derivatives should be particularly prone to fragmentation because of the possibility of extruding molecular nitrogen (Scheme 1).

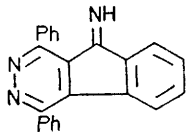
4,5-Dehydropyridazines have not previously been generated. One method of generation of 3,6-diphenyl-4,5-dehydropyridazine (**1**) was devised, based on the earlier discovery that benzo-1,2,3-triazines are good sources of benzyne in the vapour phase.[2] 4,5,8-Triphenylpyridazino-[4,5-*d*]triazine (**2**), m.p. 246—248°, was prepared by the



SCHEME 2

sequence outlined in Scheme 2 (Phth=phthalimido). 5-Phenyl-2-phthalimidotetrazole, m.p. 148°, reacted with dibenzoylacetylene in boiling benzene to give 4,5-dibenzoyl-3-phenyl-1-phthalimidopyrazole (69%), m.p. 181°, which, with hydrazine, gave 1-amino-3,4,7-triphenylpyrazolo-[3,4-*d*]pyridazine (87%), m.p. 208°. Oxidation with lead tetra-acetate produced the triazine (**2**) (81%). The mass spectrum of compound (**2**) showed a base peak at *m/e* 202, corresponding to diphenylbutadiyne, and the pyrolysis of the triazine at 420° and 0·01 mmHg gave diphenylbutadiyne

(54%), m.p. and mixed m.p. 86—88°, together with 5-imino-indeno[1,2-*d*]pyridazine (**3**) (17%), m.p. 213—215°, a product formed by the loss of one mole of nitrogen from the triazine.† No pyridazyne dimer was detected.



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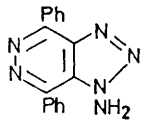

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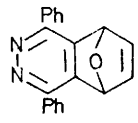
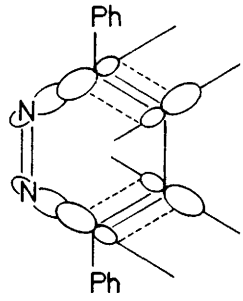


(5)

1-Aminotriazoles are good precursors of dehydroaromatic species. 1-Amino-4,7-diphenyltriazolo[4,5-*d*]pyridazine (**4**) m.p. 182—184°, was prepared from 4,5-dibenzoyl-*v*-triazole[3] by amination with *O*-mesitylsulphonylhydroxylamine,[4] followed by reaction of the 1-aminodibenzoyltriazole with hydrazine. Its oxidation with lead tetra-acetate at room temperature gave neither a dimer nor diphenylbutadiyne, but in the presence of furan an adduct (**5**) (78%), m.p. 245—248°, was obtained. Again, compound (**5**) showed a base peak at *m/e* 202 in the mass spectrum. Its pyrolysis at 550° and 0·01 mmHg gave diphenylbutadiyne (11%) together with a rearrangement product, 5-hydroxy-1,4-diphenylphthalazine (27%). Fragmentation of the adduct (**5**) to give a dehydropyridazine may be compared with the very much more favourable fragmentation of 9,10-dihydro-analogues of (**5**) to give furans and 3,6-di-(2-pyridyl)pyridazine.[5]



(6)

Thus 3,6-diphenyl-4,5-dehydropyridazine is a likely intermediate in the thermal decomposition of compounds (**2**) and (**5**) and in each case it undergoes fragmentation rather than dimerisation. Apart from the thermodynamic stability of the nitrogen being extruded, this reaction is probably facilitated by the very favourable overlap (**6**) of the rear lobes of the C–N σ bonds with the dehydro-orbitals to form the developing acetylenic π bonds.

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† Analogous imines have been observed in the decomposition of some monocyclic 1,2,3-triazines (H. Neunhoeffer, H. D. Vötter, and M. Gais-Mutterer, *Tetrahedron Letters*, 1973, 219).

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