

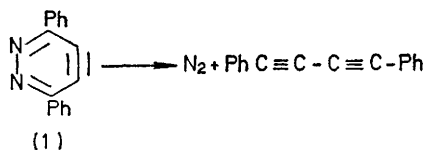
## Fragmentation of 3,6-Diphenyl-4,5-dehydropyridazine to Diphenylbutadiyne

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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

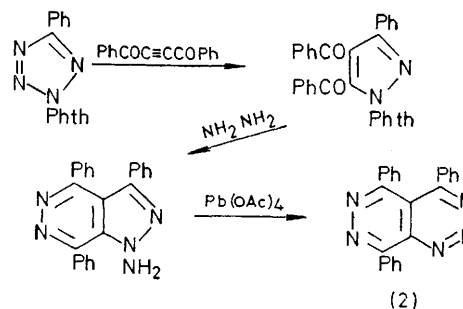


SCHEME 1

system.<sup>1</sup> The difference has been ascribed to differences in bond energies and resonance energies, totalling about 38 kcal mol<sup>-1</sup>, 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-

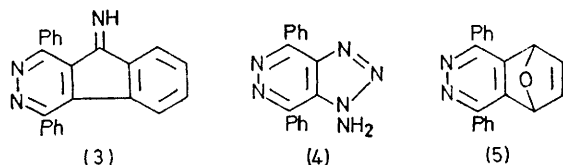
dehydropyridazine (**1**) was devised, based on the earlier discovery that benzo-1,2,3-triazines are good sources of benzyne in the vapour phase.<sup>2</sup> 4,5,8-Triphenylpyridazino-[4,5-*d*]triazine (**2**), m.p. 246–248°, was prepared by the



SCHEME 2

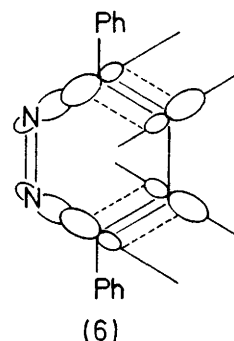
sequence outlined in Scheme 2 (Phth=phthalimido). 5-Phenyl-2-phthalimidotetrazole, m.p. 148°, reacted with dibenzoylacetylene in boiling benzene to give 4,5-dibenzoyl-3-phenyl-1-phthalimidopyrazole (69%), m.p. 181°, which, with hydrazine, gave 1-amino-3,4,7-triphenylpyrazolo-[3,4-*d*]pyridazine (87%), 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 pyridazine dimer was detected.



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<sup>3</sup> by amination with *O*-mesitylsulfonylhydroxylamine,<sup>4</sup> 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.<sup>5</sup>



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  $\sigma$  bonds with the dehydro-orbitals to form the developing acetylenic  $\pi$  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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<sup>3</sup> J. J. Looker, *J. Org. Chem.*, 1965, **30**, 638.

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<sup>5</sup> W. S. Wilson and R. N. Warrener, *J.C.S. Chem. Comm.*, 1972, 211.