

Tetrazanes as Intermediates in the Oxidation of *N*-Amino-lactams

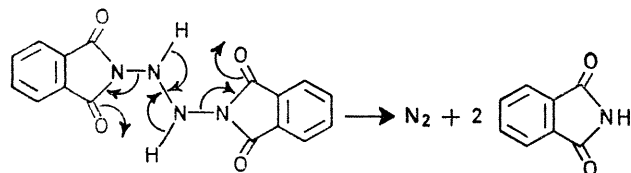
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Summary Tetrazanes (**3**) are obtained by the oxidation of *N*-aminophthalimide (**1**), 1-amino-2-quinolone (**4**), and 1-amino-3-isopropenylbenzimidazolin-2-one (**5**), with iodosobenzene diacetate; they give the parent lactams on mild heating, and the *trans*-tetrazenes on further oxidation.

OXIDATION of *N*-amino-lactams by lead tetra-acetate usually leads to the formation of one or both of two types of products: *trans*-tetrazenes, and the corresponding lactams. For example, oxidation of *N*-aminophthalimide (**1**) by lead tetra-acetate can give the *trans*-tetrazene (**2**), or phthalimide, or both, depending upon the reaction conditions.^{1,2}

Mechanisms for these reactions have not been established. Hoesch and Dreiding² have speculated that phthalimide is formed by the fragmentation of an intermediate tetrazane (Scheme). This mechanism could operate with other



SCHEME

tetrazanes which have an α -carbonyl group. Tetrazanes have also been suggested as intermediates in the more general formation of tetrazenes by the oxidation of 1,1-disubstituted hydrazines,³ but hitherto no 2,3-unsubstituted tetrazanes (**3**) have been isolated and characterised.†

We now report the isolation of such tetrazanes by the oxidation of *N*-aminophthalimide (**1**) and other *N*-amino-lactams (**4**)¹ and (**5**)[†] with iodosobenzene diacetate. The tetrazanes are unstable solids which can explode when heated or scratched. They give the corresponding lactams quantitatively on mild heating (*e.g.* in a solvent at 30–40°) and are converted into the corresponding *trans*-tetrazenes in good yields on further oxidation with lead tetra-acetate or with iodosobenzene diacetate. Thus, tetrazanes are indeed probable intermediates in the oxidation and oxidative deamination of *N*-amino-lactams.

The formation of tetrazanes in these conditions appears to be general for *N*-amino-lactams, but not all are isolable. Thus, 3-amino-2-methyl-quinazolone (**6**) gave a solution

on oxidation of which the i.r. spectrum is consistent with the presence of a tetrazane, but nitrogen was evolved when the

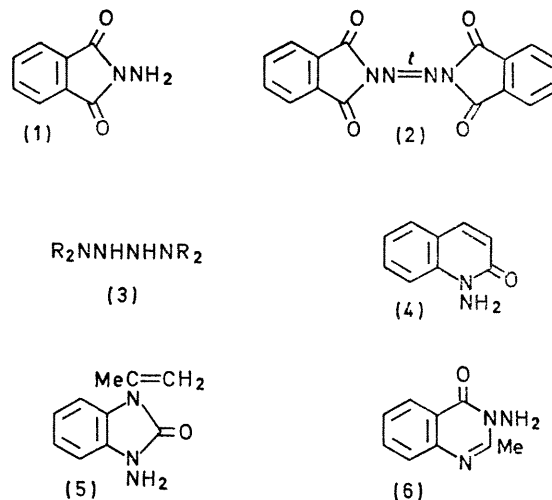
Tetrazanes[‡] from the reaction of *N*-amino-lactams with PhI(OAc)₂^a

<i>N</i> -Amino-lactam	Isolated yield (%) ^b	ν_{\max} N-H (cm ⁻¹) (mull)	Decomp. point
(1)	90	3270	210–212°
(4)	20	3220	130°
(5)	40	3250	86°

^a PhI(OAc)₂ (0.5 mol.) in CH₂Cl₂ was added dropwise to a stirred solution or suspension of the *N*-amino-lactam (1 mol.) in CH₂Cl₂ at 0–10°. The solution was then evaporated to small bulk at 0°.

^b Oxidation to the tetrazane is near-quantitative but the isolated yield depends on solubility and stability of the tetrazane.

solution was concentrated, and only the parent lactam was isolated. *N*-Amino-compounds which have no α -carbonyl group do not give detectable quantities of tetrazanes in



these conditions, however: the oxidations of *N*-aminocarbazole, 1-amino-4-quinolone, and 1-amino-2,3,4,5-tetraphenylpyrrole gave mixtures in which there was no evidence for the presence of tetrazanes.

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† A tetrazane structure has been proposed for an oxidation product of *trans*-1-amino-2,5-diphenylpyrrolidine (C. G. Overberger, M. Valentine, and J.-P. Anselme, *J. Amer. Chem. Soc.*, 1969, **91**, 687), and an iron-tetrazane complex has been isolated (D. Walz and S. Fallab, *Helv. Chim. Acta*, 1960, **43**, 540 and 1961, **44**, 13).

‡ Satisfactory analytical and spectral data have been obtained for all new compounds.

¹ D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *J. Chem. Soc. (C)*, 1970, 576.

² L. Hoesch and A. S. Dreiding, *Chimia (Switz.)*, 1969, **23**, 405.

³ C. G. Overberger, *Record Chem. Progress*, 1960, **21**, 21; C. G. Overberger and L. P. Herin, *J. Org. Chem.*, 1962, **27**, 417.