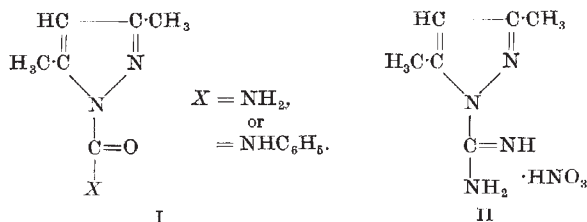
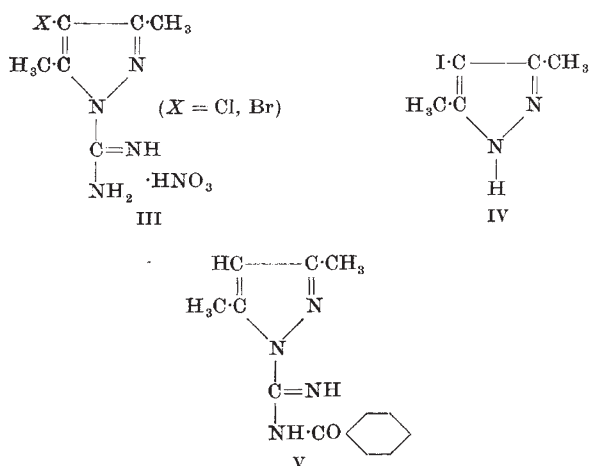


Carbamidine-substituted Pyrazoles

THE ease with which 1-substituted pyrazoles may be converted into the free imino compounds varies with the nature of the 1-substituent and the reacting substance. Thus, 1,3,5-trimethyl pyrazole may be nitrated¹ and 1-phenyl pyrazole reduced to the pyrazoline² without loss of the N-methyl or N-phenyl groups respectively. On the other hand, pyrazoles of the 1-carbamyl or 1-phenylcarbamyl type, (I), derived from the acyl hydrazides, semicarbazide³ and 4-phenylsemicarbazide⁴, are much less stable and readily give the free imino derivatives.



Aminoguanidine, although of the acyl hydrazide class, has shown differences from semicarbazide in many respects. It possesses considerably stronger basic powers. It yields imino-triazenes with aromatic β -diketones, whereas semicarbazide forms osazones⁵ and its azide, guanyl azide, can be cyclized to a 5-substituted tetrazole, although, under similar conditions, carbamyl azide does not give this reaction⁶. Our investigation extends the comparison of the acyl hydrazides to the pyrazole series and deals with the stability and reactivity of the carbamidine type prepared by Thiele⁷. 3,5-Dimethyl 1-carbamidine nitrate pyrazole (II) has been investigated as typical of the class. It is more stable than the related carbamides, approaching that of compounds of the 1-aryl or 1-alkyl type. It reacts with chlorine and bromine, giving the 4-chloro and 4-bromo derivatives respectively (III). With iodine, 'deguanylation' as well as substitution takes place, the product obtained being 4-iodo, 3,5-dimethyl pyrazole (IV).



An anomalous action with iodine is also observed in the halogenation of the N-benzoyl-carbamidine pyrazole (V). With this substance, 4-chloro- and 4-bromo-substituted compounds are readily formed, whereas iodine (or methyl iodide) yields a compound,

free of halogen, with an empirical formula C_4H_4NO . Incidentally, this similarity of action between iodine and methyl iodide is not observed with the carbamidine pyrazole.

Attempted hydrazinolysis of the carbamidine pyrazole yields unexpected results. During the reaction, acetyl acetone and 3,5-dimethyl pyrazole may be detected in the escaping vapours. The residue consists mainly of aminoguanidine nitrate. With an excess of hydrazine hydrate (4 moles), triamino-guanidine nitrate is the main product. The benzoyl-substituted-carbamidine pyrazole, under similar conditions, is unchanged by hydrazine hydrate. This is the first recorded example that we have been able to find of ring fission in the pyrazole series by hydrazine hydrate. It is analogous to the replacement by hydrazine hydrate of aminoguanidine⁸ or biamino-guanidine⁹ from their benzal derivatives, and to the displacement of hydroxylamine from the *iso*-oxazoles by treatment with hydrazines¹⁰.

3,5-Dimethyl 1-carbamidine nitrate pyrazole has been characterized by its benzoyl and *p*-toluenesulphonyl chloride derivatives, as well as by the formation of stable picrates, flavianates and chloroplatinates. The free base has also been obtained in a pure, crystalline form. In some respects the carbamidine pyrazole is very resistant to chemical action; for example, refluxing with acetic anhydride in glacial acetic acid, or heating at 50° C. (for 2 hr.) with an equimolar quantity of fuming nitric acid does not appreciably affect it. The presence of sulphuric acid during nitration produces deguanylation, however, the product being 3,5-dimethyl 4-nitro pyrazole. Sulphuric acid alone, under certain conditions, also causes fission of the carbamidine group. Other reagents, for example, boiling concentrated aqueous potassium hydroxide or sodium and ethyl alcohol, can also bring about the same result.

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² Balbiano, *Gazz. chim. ital.*, **18**, 358 (1888).

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⁴ Wheeler and Norton, *J. Amer. Chem. Soc.*, **50**, 2488 (1928).

⁵ Thiele and Bihau, *Ann.*, **302**, 299 (1898). Thiele and Strange, *Ann.*, **283**, 27 (1894). De, *Quart. J. Ind. Chem. Soc.*, **4**, 183 (1927).

⁶ Hantzsch and Vagt, *Ann.*, **314**, 339 (1906).

⁷ Thiele and Dralle, *Ann.*, **302**, 275 (1898). See also De and Rakshit, *J. Ind. Chem. Soc.*, **13**, 509 (1936).

⁸ O'Connor, Horgan and Reilly, *J. App. Chem.*, **1**, 91 (1951).

⁹ Scott, F. L., and O'Sullivan, D. A. (unpublished work).

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Adsorption of Water Vapour on Solid Surfaces

In their recent communication¹, Dr. F. P. Bowden and Mr. W. R. Throssell reported conclusive quantitative evidence against the view at one time widely held that metal surfaces invariably adsorb water vapour strongly from air at high relative humidities. In my work of some years ago on the gravimetric determination of thin oxide films, more especially those formed at room temperatures, no attempt to