Correction of the Structure of Iodonitroimidazole and its *N*-Methyl Derivatives

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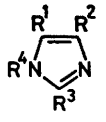
Summary Iodonitroimidazole and its *N*-methyl derivatives which have previously been considered to have structures (**2**), (**3**), and (**4**), have been shown to possess the structures (**5**), (**6**), and (**7**) respectively.

DURING the development of synthetic routes to some novel substituted nitroimidazoles, we used published methods purporting to proceed *via* (**1**) and (**2**) to give (**3**).[1,2] However, the compounds we obtained by nucleophilic substitution reactions on (**3**) were isomeric with the desired compounds. This was shown by an *X*-ray crystallographic examination of one of the target compounds and mass spectral and n.m.r. evaluation of both series of compounds.†

We now report that the iodonitroimidazole and its *N*-methyl derivatives, to which the structures (**2**), (**3**), and (**4**) have hitherto been assigned, in fact possess the structures (**5**), (**6**), and (**7**) respectively.

Iodination of 2-deuterioimidazole[3] under the conditions originally described by Pauly[1,4] gave di-iodoimidazole in which all the original deuterium was retained. The deuterium in this compound was back-exchanged by refluxing with water for 20 h; the material thus obtained was identical in all respects to the di-iodoimidazole prepared from undeuteriated imidazole.

Thus, Pauly's assignment of structure (**1**) to this compound was incorrect, and the structure is in fact (**8**). Pauly[5] deduced the structure (**1**) by arguing that, since the monoiodoimidazole obtained by sodium sulphite reduction of di-iodoimidazole gave, on bromination, a dibromoiodoimidazole which was not identical to the unambiguously synthesised isomer (**9**) (m.p.[5] 181 °C), it must be 2-iodo imidazole,[6] and therefore di-iodoimidazole has structure (**1**). We have found that the dibromoiodoimidazole prepared by Pauly (m.p.[5] 215 °C) gives, after neutralisation with aqueous sodium hydroxide (1 equiv.), material of m.p. 186—187 °C; n.m.r. [$(CD_3)_2SO$]: δ 7.88 (1H, s); *m/e* (electron impact) 272 and 274. We therefore assign the structure (**10**) to the latter compound and suggest that Pauly's dibromoiodoimidazole is the hydrobromide of (**10**).



	R^1	R^2	R^3	R^4
(**1**)	I	H	I	H
(**2**)	NO_2	H	I	H
(**3**)	NO_2	H	I	Me
(**4**)	H	NO_2	I	Me
(**5**)	NO_2	I	H	H
(**6**)	NO_2	I	H	Me
(**7**)	I	NO_2	H	Me
(**8**)	I	I	H	H
(**9**)	Br	I	Br	H
(**10**)	Br	I	H	H

Reaction of 2-iodo-1-methylimidazole[7] (2 g) with a nitrating mixture of concentrated nitric acid (10 ml) and concentrated sulphuric acid (20 ml; added last, with cooling) for 3 h at room temperature gave authentic 2-iodo-1-methyl-4-nitroimidazole (730 mg; 30%), m.p.

† These results will be reported elsewhere.

243—244 °C [m.p. of 1:1 mixture with (**7**) 198 °C; m.p.[1] of (**7**) 240 °C]; n.m.r. [$(CD_3)_2SO$]: δ 8·44 (1H, s) and 3·62 (3H, s) [n.m.r. spectrum of (**7**) in $(CD_3)_2SO$: δ 8·20 (1H, s) and 3·72 (3H, s)].

In view of the above findings, the structural assignments of a number of reported derivatives[1,8] of (**5**), (**6**), and (**7**) require appropriate revision. In addition, the structures assigned to several other halogenonitroimidazoles,[2,9] by virtue of their interconversion with (**5**) or its derivatives, should now be considered uncertain.

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