1,1'AZOBENZIMIDAZOLES

I. M. Nanavyan, A. F. Pozharskii,
and V. V. Kuz'menko

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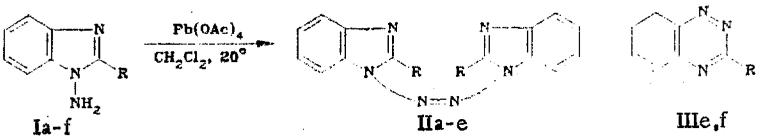
1,1'-Azobenzimidazoles, formally related to the class of tetrazenes, were unknown until recently. It is true that English workers [1] in 1973 obtained salts of 1,1'azobenzimidazoles from salts of 1-amino-3-methylbenzimidazoles using bromino water, but it has not so far proved possible to prepare the base compounds by oxidation of 1-aminobenzimidazoles with, e.g., mercuric oxide [2]. We have now shown that 1,1'-azobenzimidazoles IIa-e are almost always formed when 1-aminobenzimidazoles Ia-e are oxidized with a small excess of lead tetraacetate in methylene chloride.



Ia-f IIa-e IIIe,f

I—III a R=H; b R=CH$_3$; c R=Cl; d R=N(CH$_3$)$_2$; e R=NHCH$_3$; f R=NH$_2$

The best results were obtained for oxidation of 1-amino-2-methyl- and 1-amino-2-chlorobenzimidazole (Ib,c) which gave the tetrazenes IIb,c in 43 and 58% yields with mp 260-262 and 238-239°C respectively (all melting points were determined in sealed capillaries). Oxidation of the unsubstituted amine Ia gave IIa in only 5% yield (mp 261-263°C), the basic product of the reaction being the previously reported [3] 1-acetylbenzimidazole (mp 113°C, $\nu_{C=O}$ 1745 cm^{-1}). Production of tetrazenes IId,e from Id,e was accompanied by significant tarring, the yields being 4-5% with respective melting points of 173-174°C (from benzene/hexane) and 120°C (separated chromatographically because recrystallization proved impossible). The oxidation of Ie also yielded 7.5% of 3-methylamino-1,2,4-benzotriazine (IIIe, mp 189-190°C, from benzene/methanol). It is interesting that oxidation of 1,2-diaminobenzimidazole (If), according to [4] and confirmed by us, leads only to 3-aminobenzotriazine (IIIf) in yields approaching 65-80 %.

Bromine water may also be used as oxidant, giving even better results in certain cases. Addition of bromine water to a solution of amine Ia containing sodium carbonate leads to a 25% yield of tetrazene IIa.

The structures of the tetrazenes IIa-e were determined from IR, UV, PMR, and mass spectroscopic data and by elemental analysis. 1,1'-Azobenzimidazoles were colorless (IIa,b) or slightly yellow (IIc-e) substances, decomposing with ignition in a burner flame. Compounds IIa-c were extremely stable on storing and could be recrystallized from DMF or acetic acid without noticeable decomposition. Tetrazenes IId,e were less stable.

LITERATURE CITED

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