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A NEW SYNTHESIS OF 1- AND 2-AMINO PHENAZINES

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THE preparation of phenazine dyes by the oxidation of mixtures of aromatic amines is assumed to take place through the intermediate formation of indamines. 2-Aminoindamines do indeed undergo ready cyclization to yield 2-aminophenazines,[1,2] probably by a similar mechanism to that involved in the ready addition of aromatic amines to quinones.[3] Although Nietski _et al._[4] prepared 2-amino-, 2,7-diamino- and 2-amino-7-hydroxy-phenazine by the oxidation of 2,4'-diamino-, 2,4,4'-triamino- and 2,4'-diamino-4'-hydroxy-diphenylamine respectively with manganese dioxide, it is somewhat surprising that this type of reaction has not been more extensively used for the synthesis of simpler phenazines, particularly since it might be expected to give the products in relatively high yield in contrast to most of the available methods for phenazine synthesis.

Failure to synthesize 2-amino-6-methoxyphenazine by the oxidation of 2,4'-diamino-6-methoxydiphenylamine with inorganic reagents led us to

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[1] Ullman and Gnaedinger, _Ber. Dtsch. Chem. Ges._ **45**, 3437 (1912).

[2] Cohen and Crabtree, _J. Chem. Soc._ **119**, 2055 (1921).

[3] Pearson _et al._, _Heterocyclic Compounds_ (Edited by Elderfield) Vol. 6, Chap. 14; John Wiley, New York (1957).

[4] Nietski _et al._, _Ber. Dtsch. Chem. Ges._ **23**, 1852 (1890); **28**, 2969 (1895).

attempt the reaction using organic nitro compounds as oxidizing agents. Refluxing the diphenylamine in nitrobenzene gave a 40% yield of the required phenazine (m.p. 278 - 281°; C, 69.3; H, 5.1; N, 18.3%. $C_{13}H_{11}ON_3$ requires C, 69.3; H, 4.9; N, 18.65%). The same technique applied to 2,4'-diaminodiphenylamine gave a 50-60% yield of pure 2-aminophenazine.

Amino and methoxy groups in the 2' position are usually eliminated on oxidation of 2-aminodiphenylamines (see ref. 3). Although 2,2'-diaminodiphenylamine gave phenazine quantitatively with ferric chloride,[5] our method gave a 50% yield of 1-aminophenazine, identical with a sample prepared by Cookson's synthesis.[6]

That the reaction mechanism involves the participation of the 2' or 4' substituent is shown by the low yields of phenazines obtained when the method was applied to diphenylamines in which such substituents were lacking; e.g. 2,4-diaminodiphenylamine gave only a 5% yield of 2-aminophenazine, and 2-aminodiphenylamine only a trace of phenazine. The mechanism must therefore be different from that involved in the production of carbazole by heating 2-aminodiphenyl with organic nitro compounds.[7] A mechanism involving quinone imines as intermediates, such as that generally proposed for the oxidative cyclization of 2-aminodiphenylamines is possible but is difficult to reconcile with the production of 2-amino-8-methoxyphenazine (m.p. 217-220°; C, 68.5; H, 5.1; N, 18.35. $C_{13}H_{11}ON_3$ requires C, 69.3; H, 4.9; N, 18.65%) in 64% yield from

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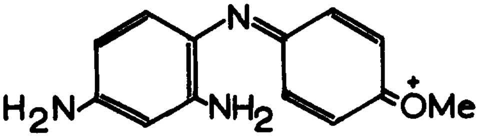
[5] Tomlinson, J. Chem. Soc. 158 (1939).

[6] Cookson, J. Chem. Soc. 1328 (1953).

[7] Weinmayr, U.S.P. 2, 351, 171 of June 13, 1944.

2,4-diamino-4'-methoxydiphenylamine unless a quinonoid cation of type I is assumed as an intermediate in the oxidation.



The 2' methoxy isomer, on the other hand, gave only a small yield of 1-aminophenazine, the elimination of the methoxy group in this instance being in marked contrast to the retention of a 2'-amino group.

It seems possible that this method can be applied generally to the synthesis of 1- and 2-aminophenazines as well as to phenazines with some other substituents in the 1- and 2-positions. These possibilities and the mechanism of the reaction are being explored and full details will be reported later.

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