Tetrahedron Letters No. 35, pp.3231 - 3232, 1971. Pergamon Press. Printed in Great Britain.

DIRECT AMINATION OF AROMATIC ALDEHYDES: A CORRECTION

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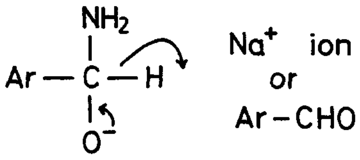
(Received in UK 20 July 1971; Accepted for publication 24 July 1971)

In a previous communication (1) the bi-product arising from O-benzylvanillin, during an acetylenic synthesis with sodamide in liquid ammonia, was wrongly described as O-benzyl-2-aminovanillin by analogy with other nucleophilic substitutions (2). Neither this compound nor the isomeric amide was known but subsequent reactions between simpler aldehydes and sodamide in tetrahydrofuran have shown that alcohols are formed concurrently with the amination products. Evidently the reaction is of the Cannizzaro type: this was first observed by Haller and Bauer (3) in 1909 although it has not otherwise been further studied with amide.

We isolated benzamide (m.p. and mixed m.p. 128°) and benzyl alcohol from the reaction both in ether and tetrahydrofuran and further characterised them by g.l.c. and t.l.c. when they were clearly resolved from samples of o- and p-aminobenzaldehyde. The major product obtained from O-benzylvanillin was the same as that formed in liquid ammonia and was identified as O-benzylvanillamide (m.p. 187-8°); it yielded O-benzylvanillic acid [m.p. 169°, (4)] on acid hydrolysis.

We have no reason to suspect that the mechanism of the Cannizzaro reaction in liquid ammonia differs essentially from that accepted (5). However, the tabulated results show that in this solvent the yield of amide is considerably in excess of the alcohol, probably because of a greater tendency for hydride to be transferred to the metal counter-ion rather than to a molecule of aldehyde.



Product Balance in the Cannizzaro Reaction with Sodamide

Starting Material	% Products*			
	From T.H.F.		From liquid ammonia	
	alcohol	amide	alcohol	amide
benzaldehyde	30	40-45	5	55
_m_-methoxybenzaldehyde	-	-	small	35-40
piperonal	-	-	-	35-40
1-naphthaldehyde	20	35-40	5	45-50

*The remainder was accounted for by recovery.

The reaction described has synthetic advantages for aromatic amides over that employing acid chlorides (e.g. 6).

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