New Method for the Conversion of Tertiary Aromatic Amides into Aldehydes

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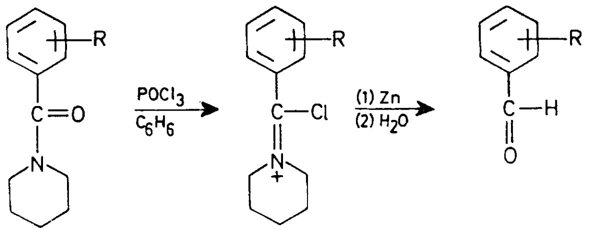
Summary The reaction of Vilsmeier complexes of tertiary aromatic amides with zinc affords the corresponding aldehydes in high yields.

Recently we have described some new selective procedures for the reduction of primary, secondary, and tertiary amides involving the intermediate generation of Vilsmeier complexes of amides which were reduced to the corresponding amines with sodium borohydride[1] or zinc–ethanol.[2] The enamine tautomers of such Vilsmeier complexes have been used to achieve selective functionalization at carbon atoms which are α to amide carbonyl groups.[3]

We now report a new mild procedure for the conversion of tertiary aromatic amides into aldehydes. A typical reaction involves treatment of the aromatic amide with $POCl_3$ in refluxing benzene for 15 min. The resulting Vilsmeier complex is cooled to 25 °C and treated with Zn dust for about 5 min. Work-up in an aqueous medium affords the corresponding aldehydes in high yields.



Table

Amide R	Reagents/mol (a) $POCl_3$	Reagents/mol (b) Zn	Time/min (a) $POCl_3$	Time/min (b) Zn	Yields/ %
o-Cl	2	5	20	5	95
p-Cl	2·5	6	15	5	97
o-Br	2·5	6	20	5	87
m-Br	2·2	6	10	4	90
H	2·5	5	15	4	95

With primary and secondary amides, the procedure afforded either the corresponding amines or higher molecular weight products formed by intermolecular reactions.

This procedure offers an attractive method of converting tertiary amides into aldehydes and appears to possess significant advantages in terms of selectivity and yields over other known procedures[4] for effecting such conversions.

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[1] Atta-ur-Rahman, A. Basha, N. Waheed, and S. Ahmed, *Tetrahedron Letters*, 1976, 219.

[2] A. Basha and Atta-ur-Rahman, *Experientia*, submitted for publication.

[3] Atta-ur-Rahman, A. Basha, and V. U. Ahmad, *Experientia*, in the press.

[4] I. T. Harrison and S. Harrison, 'Compendium of Organic Synthetic Methods,' vol. I, Wiley-Interscience, New York, 1971, p. 148.