The Synthesis of Nitriles from Aldehydes

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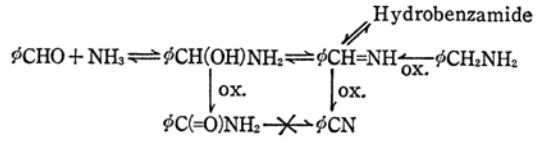
The present authors have been investigating liquid-phase ammoxidation reactions in which an aldehyde with ammonia is oxidized to the corresponding nitrile; in these experiments they have used various kinds of oxidants. The case of iodine[1] and the case of copper compounds with oxygen gas[2] have already been reported.

The authors wish now to report on ammoxidation reactions in which potassium permanganate, manganese dioxide, and silver oxide were used as oxidants. It is very interesting that these three oxidants could oxidize benzaldehyde with ammonia to benzonitrile as well as to benzoic acid and benzamide. It may safely be stated that many kinds of oxidants have the ability to oxidize aldehydes with ammonia to the corresponding nitriles. In fact, Parameswaran *et al.*[3] used lead tetraacetate and Nakagawa *et al.*[4] used nickel peroxide successfully.

It was also found that potassium permanganate oxidized benzylamine to benzonitrile under the reaction conditions adopted by the present authors. It seems that it can be generally stated that no benzonitrile is obtained from benzylamine *via* oxidation by potassium permanganate under usual conditions.[5,6] Other oxidants, however, such as nickel peroxide,[5] iodine pentafluoride[7] and lead tetraacetate,[8] are known to oxidize benzylamine to benzonitrile in relatively good yields.

It is possible that these reactions proceed according to the following scheme:



The fact that no benzonitrile was detected when benzamide was oxidized by manganese dioxide under similar reaction conditions lends support to this scheme.

Some of the results obtained are cited as examples in the table; the typical procedure is illustrated by using the case of the oxidation of benzaldehyde by potassium permanganate.

The authors are now investigating the reaction route and the differences between the various oxidants in the ammoxidation reactions.

The Ammoxidation of Benzaldehyde by Potassium Permanganate. Benzaldehyde, potassium permanganate, and benzene as a solvent were set in an autoclave. After the displacement of the air interior with nitrogen, liquid ammonia was added to the autoclave. The mixture was then magnetically agitated for a desired period at a given temperature. The resultant mixture was treated in the usual manner. The yields of benzoic acid and benzamide were analyzed gravimetrically, while that of benzonitrile was analyzed gas chromatographically. Hydrobenzamide was also detected by means of its infrared spectra.

TABLE

Substrate (0.05 mol)	Oxidant (mol)	Reaction temp., °C	Reaction time, hr	Yields, % φCN	φCOOH	φCONH₂
φCHO	$KMnO_4$ (0.05)	68	4.8	30	38	4
φCHO	MnO_2 (0.18)	70	3.8	27	1	1
φCHO	Ag_2O (0.18)	71	4.5	43	14	3
ϕCH_2NH_2	$KMnO_4$ (0.05)	73	4.8	24	*	*
φCONH₂	MnO_2 (0.18)	70	5.0	*	—	—

* undetectable solvent; benzene 80 m*l* ammonia, 0.55 mol

1) A. Misono, T. Osa and S. Koda, This Bulletin, **39**, 854 (1966).
2) *Ibid.*, **40**, 912 (1967).
3) K. N. Parameswaran and O. M. Friedman, *Chem. Ind.*, **1965**, 988.
4) K. Nakagawa *et al.*, The 19th Annual Meeting of Chem. Soc. Japan, 3N221 (1966).
5) K. Nakagawa and T. Tsuji, *Chem. Pharm. Bull.*, **11**, 296 (1963).
6) H. Shechter, S. S. Rawalay and M. Tubis, *J. Am. Chem. Soc.*, **86**, 1701 (1964).
7) T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).
8) A. Stojiljković, V. Andrejević and M. Lj. Mihailović, *Tetrahedron*, **23**, 721 (1967).