ARGENTIC OXIDE OXIDATIONS OF ORGANIC COMPOUNDS

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In a recent note we surveyed the use of silver II picolinate as an oxidising agent (1). These observations were made in connection with some work both in the carbohydrate field and with a study of organic reactions at solid metal electrodes (2). At the surface of the solid silver electrode under the appropriate conditions, and in the absence of complexing agents such as picolinic acid, argentic oxide (AgO) is produced. This oxide, although stoichiometric-ally AgO, appears to be largely identical with that produced by chemical methods, and is a lattice compound of alternate Ag (III) and Ag (I) atoms (3). Its behaviour might consequently be expected to differ from that of the silver (II) state. We therefore surveyed the oxidising activity of the oxide.

After the appearance of our paper, Syper reported some observations (4)* on the use of AgO under acidic conditions.

The conditions employed by Syper were rather severe,* in some cases involving $6\underline{M}$ mineral acid, which rather limits the application of the method to the oxidation of relatively stable molecules, such as aromatic hydrocarbons, and certainly prevents its general application in the carbohydrate and terpene fields. Further, these observations are not relevant to the activity of a silver anode, since in acidic solutions Ag^+ ions are in equilibrium with the electrode ($E^o = 0.799V$. NHE) and it is not therefore feasible to carry out oxidations in acid electrolytes. In our experience such severe conditions are unnecessary for successful oxidations with AgO,** and we have carried out a variety of oxidations in neutral or mildly alkaline conditions.

The reaction is almost invariably a two-electron process, silver metal being obtained as the sole inorganic product. This is readily separated and recovered, simplifying work-up and reducing the cost of the reagent. The oxidation of amino-compounds proceeds very rapidly in mild conditions ($25-70^o$C.) when the materials are stirred together in water. The reaction of

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*Syper comments that our picolinate reactions required basic conditions; in fact these oxidations require neutral conditions. The acidity changes approximately from pH 7 to pH 5 during the course of most reactions.

**Furthermore, AgO decomposes quite rapidly under these conditions with consequent losses in oxidising power.

phosphines and phosphites proceeds even more vigorously (e.g. neat triphenylphosphite and AgO reacted explosively) and again we have usually moderated the reaction by addition of water. Alcohols and aldehydes react readily also, but the relative rates are such that use of the reagent in selective oxidations seems promising.

The products obtained from the amines naturally depend upon the type of amine. Primary amines such as n-butylamine and iso-butylamine give nitrile as the major product, although some ·aldehyde is also obtained. The ratio of aldehyde:nitrile seems to be influenced by the solvent. An amino group attached to a secondary carbon forms the corresponding ketone (e.g. sec-butylamine gives methylethyl ketone); one attached to a tertiary carbon suffers both C-N bond fission and oxidation of the nitrogen moiety. Thus tert-butylamine gives tert-butanol and 2-methyl-2-nitropropane in a 2:1 ratio. Secondary amines, such as dimethylamine are cleaved by the reagent; diethylamine gives acetonitrile and ethanol.

Phosphines, such as triaryl and trialkyl phosphines, are rapidly converted to the phosphine oxide, and trialkylphosphites and triarylphosphites to the corresponding trialkyl and triaryl phosphates. In contrast to the excellent yields of aldehyde obtained by the action of silver picolinate on alcohols (2), AgO converts these compounds to the corresponding carboxylic acids. As would be expected, aldehydes are also rapidly oxidised, again to the appropriate carboxylic acid, aliphatic aldehydes oxidising more readily than aromatic aldehydes. The reagent converts secondary alcohols in good yield to the ketones, the latter being only slowly attacked by the reagent. Again, whereas silver II picolinate cleaves α-amino acids practically quantitatively to the next lower homologous aldehyde (5), the product obtained using AgO as oxidant is the corresponding next lower homologous acid, obtained in only moderate yield.

·The behaviour of the oxidising silver electrode with these compounds is similar in many respects, but some interesting differences have been observed and are under investigation. The oxidation of other materials, such as olefines and acetylenes, is more complex and is also under investigation. Some of the results are summarised in the table. Conditions for these reactions were in general selected rather arbitrarily, and where yields are low, these could doubtless be suitably manipulated to improve yield.

TABLE.

Compound	Main oxidation product, % Yield.*
Benzaldehyde	Benzoic acid, 51.
Anisaldehyde	Anisic acid, 57.
Piperonaldehyde	Piperonylic acid, 30.
n-Hexaldehyde	n-Hexanoic acid, 100.
2-Ethyl butyraldehyde	2-Ethyl butyric acid, 93.
2-Ethyl hexaldehyde	2-Ethyl hexanoic acid, 68.
p-Nitrobenzaldehyde	p-Nitrobenzoic acid, 38.
Veratraldehyde	3,4-Dimethoxybenzoic acid, 47.
Ethanol	Acetic acid, 100.
n-Propanol	Propionic acid, 100.
Butanol-1	n-Butyric acid, 99.
2-Ethylbutanol-1	2-Ethylbutyric acid, 33.
Butanol-2	Ethylmethylketone, 96.
Pentanol-1	n-Pentanoic acid, 100.
3-Methylpentanol-1	3-Methylpentanoic acid, 100.
Hexanol-1	n-Hexanoic acid, 35.
2-Ethylhexanol	2-Ethylhexanoic acid, 100.
Octanol-1	n-Octoic acid, 22.
Borneol	Camphor, 50.
Isoborneol	Camphor, 55.
Benzhydrol	Benzophenone, 70.
p-Nitrobenzyl alcohol	No reaction.
Benzyl alcohol	Benzaldehyde, 12. Benzoic acid , 60.
Anisyl alcohol	Anisaldehyde, 44.
Veratryl alcohol	Veratraldehyde, 50.
Piperonyl alcohol	Piperonaldehyde, 48.
Triphenylphosphine	Triphenylphosphine oxide, 40.
Triphenylphosphite	Triphenylphosphate, 30.
Trihexylphosphite	Trihexylphosphate, 75.
Tridecylphosphite	Tridecylphosphate, 40.
Trilaurylphosphite	Trilaurylphosphate, 60.

*These yields do not represent maximised yields, and could probably be increased where low; in a number of cases yields will vary with reactant ratios, where a second product may be obtained, eg. benzyl alcohol, 2-ethylbutylamine.

TABLE   (Continued)

Benzylamine	Benzaldehyde, 23; Benzonitrile, 77.
2-Ethylhexylamine	2-Ethylhexononitrile, 75.
1-Aminopentane	Pentanonitrile, 87.
DL-Valine	Isobutyric acid, 100.
nor-Valine	Butyric acid, 100.
DL-norLeucine	Pentanoic acid, 49.
DL-isoLeucine	2-Methylbutyric acid, 53.
DL-Leucine	3-Methylbutyric acid, 61.
2-Amino-octoic acid	Heptoic acid, 58.
Phenylglycine	Benzaldehyde, 79.
2-Aminobutyric acid	Propionic acid, 100.

REFERENCES

1. T.G. Clarke and J.B. Lee, Tetrahedron Letters, 415 (1967).

2. T.G. Clarke, N.A. Hampson, J.B. Lee, J.R. Morley, and B. Scanlon, Oxidations involv 1g silver, Can. J. Chem., in the press, parts I and II.

3. V. Sca urin, P.L. Bellon, and A.J. Salkind, J. Electrochem. Soc., 108, 819 (1961).

4. L. Syper, Tetrahedron Letters, 4193 (1967).

5. T.G. Clarke and J.B. Lee, in preparation.