A New Synthesis of Aldehydes *via* Silane Reduction of Nitrilium Ions

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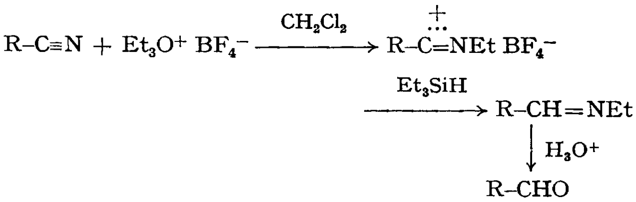
Summary Triethylsilane effectively reduces *N*-alkylnitrilium ions to *N*-alkyl aldimines; subsequent hydrolysis gives aldehydes in good yields.

Because *N*-alkylnitrilium ions are much more activated for nucleophilic attack at carbon than are their parent nitriles, they have begun to receive considerable attention as synthetic intermediates.[1] Thus, although nitriles resist reduction by sodium borohydride, this reagent completely reduces *N*-alkylnitrilium ions to the corresponding secondary amines in high yields.[2] An attempt to halt reduction at the imine stage was reported to be unsuccessful.[2] We report the partial reduction by triethylsilane of *N*-alkylnitrilium ions to *N*-alkylaldimines with subsequent hydrolysis to aldehydes (Scheme).



$$\mathrm{R{-}C{\equiv}N + Et_3O^+\,BF_4^- \xrightarrow{CH_2Cl_2} R{-}\overset{+}{C}{=}NEt\,BF_4^- \xrightarrow{Et_3SiH} R{-}CH{=}NEt \xrightarrow{H_3O^+} R{-}CHO}$$

Scheme

A solution of *N*-ethylnitrilium tetrafluoroborate was prepared from nitrile (1 equiv.) and triethyloxonium tetrafluoroborate (2 equiv.)[3] in dichloromethane according to the method of Borch.[2] The resulting solution was then rapidly added at room temperature to triethylsilane (1·2 equiv.) in dichloromethane. Stirring was continued for 0·5—6 h. Addition of water, followed by steam distillation, afforded the aldehyde in good yield. Representative overall yields of aldehydes, isolated as their 2,4-dinitrophenylhydrazone derivatives on a *ca.* 10 mmole scale, are R = Bu, 71%; $\mathrm{Pr^i}$, 85%; $\mathrm{Bu^t}$, 61%, 1-adamantyl, 83%; cyclopropyl, 79%; $\mathrm{PhCH_2}$, 41%; Ph, 90%; 1-naphthyl, 84%.

The presence of the excess of oxonium salt does not appear to interfere with the reduction step of the sequence. Addition of excess of silane under the normal reaction conditions (*ca.* 1 h) did not appreciably alter the product yields; in fact, unchanged silane could be recovered. The only volatile silicon product which we have observed is triethylfluorosilane.[4] It does not interfere with product isolation.

This method of synthesising aldehydes from nitriles seems to be a general one. It offers advantages over many other methods in its ease, mildness of reaction conditions, and apparent lack of the need for critical temperature regulation to prevent over-reduction. The combination of the use of the mild alkylating agent triethyloxonium tetrafluoroborate and the mild reducing agent triethylsilane may permit the nitrile group to be transformed into the carbaldehyde group even in polyfunctional compounds containing other groups which normally are easily reduced. For example, when *NN*-diethylbenzamide is subjected to the reaction conditions of this synthesis, ethyl benzoate is obtained in 84% yield upon work-up. Although the amide is readily alkylated by the triethyloxonium ion, the resulting carbocation is apparently too stable to be reduced by the silane under these conditions,[5] and instead undergoes hydrolysis to the ester during work-up.

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[1] H. Perst, 'Oxonium Ions in Organic Chemistry,' Verlag Chemie–Academic Press, 1971, pp. 128, 137—138.

[2] R. F. Borch, *Chem. Comm.*, 1968, 442; *J. Org. Chem.*, 1969, **34**, 627.

[3] H. Meerwein, *Org. Syn.*, 1966, **46**, 113.

[4] V. Bažant, V. Chvalovský, and J. Rathouský, 'Organosilicon Compounds,' vol. 2, part 1, Academic Press, New York, 1965, pp. 181—182.

[5] *Cf.* R. F. Borch, *Tetrahedron Letters*, 1968, 61.