Preparation of Alkyl and Benzyl Fluorides from the Corresponding Primary Amines

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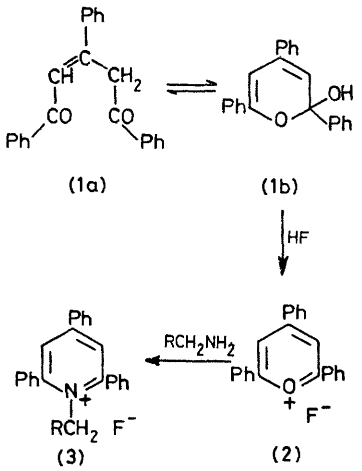
Summary Primary alkyl and benzyl amines are converted by 2,4,6-triphenylpyrylium fluoride into the corresponding pyridinium fluorides which thermolyse smoothly at 100—130 °C to give alkyl and benzyl fluorides, the latter in yields of 60—70%, the former in somewhat lower yields.

THE Schiemann conversion of primary aromatic amines into aryl fluorides by pyrolysis of the corresponding diazonium tetrafluoroborates has been widely applied.[1] No comparable method previously existed for the conversion of aliphatic amines into fluorides: we here report that this gap in synthetic methodology has now been filled. In connection with our work on the nucleophilic displacement of *N*-alkyl groups from 2,4,6-triphenylpyridinium salts,[2] we demonstrated that pyrolysis of such tetrafluoroborates under well defined conditions[3] does give poor yields of benzyl fluorides, but they are contaminated with the corresponding hydrocarbons indicating a radical mechanism and the method is not synthetically attractive. However, we have now discovered that pyrolysis of pyridinium fluorides proceeds smoothly.

The 2,4,6-triphenylpyrylium pseudo-base (**1b**) reacts with 40% aqueous hydrogen fluoride to give the stable pyrylium fluoride (**2**) (≥90%), m.p. 112 °C. Under carefully defined conditions involving the continuous removal of water by azeotroping out with benzene–ethanol, the fluoride (**2**) reacts readily with a variety of alkyl and benzyl primary amines to give the corresponding pyridinium fluorides (**3**) as stable crystalline solids. In this way we prepared 1-n-heptyl-, 1-n-octyl-, 1-n-undecyl-, 1-allyl-, 1-(2-pyridyl)-, and 1-phenyl-2,4,6-triphenylpyridinium fluoride together with the corresponding 1,1′-tetramethylene-, 1,1′-pentamethylene-, and 1,1′-hexamethylenebis-(2,4,6-triphenylpyridinium) fluorides (average yield 82%).†



The melting points of the pyridinium fluorides (**3**) lie in the range 80—120 °C and on heating to just above melting the *N*-alkyl and *N*-benzyl derivatives decompose smoothly to give the corresponding fluorides. The benzyl fluorides obtained (yields, 62% unsubstituted, 65% *p*-chloro, 61% 2,4-dichloro, and 67% *o*-chloro) were of ≥95% purity as determined by ^{1}H n.m.r. spectroscopy. The alkyl fluorides and difluorides usually contained *ca.* 10% of olefin as shown by ^{1}H n.m.r. and g.l.c. data (yields, 65% n-heptyl, 48% n-octyl, 37% 3-hydroxypropyl, 40% tetramethylenebis-, 43% pentamethylenebis-, and 45% hexamethylenebis-fluoride). It is essential that the triphenylpyridinium fluorides be quite dry before pyrolysis (one week *in vacuo*); pyrolysis of 1-aryl derivatives failed and the cyclohexyl compound gave mainly cyclohexene.

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† Correct elemental analyses were obtained for all new compounds.

[1] A. Roe, *Org. Reactions*, 1949, **5**, 193.

[2] See, *inter alia*, N. F. Eweiss, A. R. Katritzky, P.-L. Nie, and C. A. Ramsden, *Synthesis*, 1977, 634; J. B. Bapat, R. J. Blade, A. J. Boulton, J. Epsztajn, A. R. Katritzky, J. Lewis, P. Molina-Buendia, P.-L. Nie, and C. A. Ramsden, *Tetrahedron Letters*, 1976, 2691.

[3] See, *e.g.*, A. Chermprapai, M.Sc. Thesis, University of East Anglia, 1978.