The Reduction of Nitrilium Salts†

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LITTLE is known about the chemistry of the *N*-alkylnitrilium salts. Meerwein[1] reported the synthesis of *N*-ethylnitrilium fluoborates by reaction of nitriles with triethyloxonium fluoborate and observed that amides were obtained upon hydrolysis with water. We report the reduction of these nitrilium salts to give secondary amines.

A solution of two equivalents of triethyloxonium fluoborate and one equivalent of nitrile in methylene chloride afforded (reflux 24—96 hr.) good yields of *N*-ethylnitrilium fluoborates (I); the yields were conveniently measured by quenching an aliquot with water and analyzing the amide by gas chromatography. Addition of a solution of sodium borohydride in ethanol at 0°, followed by stirring at 25° overnight, led to good conversion of the nitrilium salt into secondary amine (II). The results are summarized in the Table.

In an attempt to stop the reduction at the imine (thus providing a route to the synthesis of aldehydes), the reduction was carried out with sodium borohydride in methanol at −70°. Under these conditions the imino-ether (III) was the only isolable product. Similarly, when the reduction at 0° was stopped after 1 min., the nitrilium salt had been quantitatively converted into the imino-ether (IV). We have found that imino-ethers prepared from amides likewise undergo quantitative conversion into secondary amines under these conditions.[2] Thus it appears that the nitrilium salt is rapidly converted into imino-ether, which undergoes slow reduction to secondary amine.

To effect the reduction directly on the nitrilium salt, we attempted the reduction of *N*-ethylbenzonitrilium fluoroborate (I; $\mathrm{R} = \mathrm{Ph}$) with sodium borohydride in diglyme. After 1 hr. at 0°, the nitrilium salt had been consumed and a new

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$$RC{\equiv}N + Et_3O^+BF_4^- \xrightarrow{CH_2Cl_2} \underset{(I)}{RC{\equiv}N^+Et_3BF_4^-} \xrightarrow[EtOH]{NaBH_4} \underset{(II)}{RCH_2\cdot NHEt_3}$$

$$\begin{tikzcd} & RC(OMe){:}NEt\quad (III) & \\ (I) \arrow[ur, "{NaBH_4,}", "{MeOH,\ -70^\circ}"'] \arrow[dr, "{NaBH_4,\ EtOH}", "{0^\circ,\ 1\ min.}"'] & & \\ & RC(OEt){:}NEt\quad (IV) \arrow[r, "NaBH_4"'] & (II) \end{tikzcd}$$

$$\underset{(I;\, R = Ph)}{PhC{\overset{+}{\equiv}}NEtBF_4^-} \xrightarrow[diglyme]{NaBH_4} \begin{array}{c} PhCH_2\cdot NHEt\quad (V) \\ \downarrow \\ BH_3 \end{array}$$

$$PhCH{=}NEt \xrightarrow[THF]{B_2H_6,} (V)$$

product had appeared. This product (V), isolated in 45% yield, had m.p. 50—52°; molecular weight ($CHCl_3$) 149 ± 2; ν_{max} (Nujol) 3200, 2400, 2300 cm.$^{-1}$; n.m.r.‡ (CCl_4) 68 (3H, t), 158 (2H, m), 208 (1H, quartet), 247 (1H, quartet), 270 (1H, br), and 434 (5H, s) c./sec. The resonances at 208 and 247 c./sec. represented the AB portion of an ABC system with J_{AB} 14, J_{AC} 5, and J_{BC} 3·5 c./sec.; decoupling experiments indicated that these resonances were coupled to the broad resonance centred at 270 c./sec. The mass spectrum confirmed the presence of boron, and elemental analysis supported the empirical formula $C_9H_{16}BN$. We have assigned this compound the amine-borane structure (V).[3] We assume that borohydride transfers one hydride to the nitrilium salt, generating the imine (VI) and diborane; this assumption is supported by the fact that reduction of benzaldehyde *N*-ethylimine (VI) with diborane in tetrahydrofuran leads to (V) in 43% yield. We are currently extending the scope of this novel amine synthesis to include the synthesis and reduction of a variety of *N*-alkylnitrilium salts.

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TABLE

Nitrile	Yield of nitrilium salt (%)	Amine	Yield of amine (%) Anal.[a]	Isolated
PhCN	80	$PhCH_2\cdot NHEt$	75	69
$PhCH_2\cdot CN$ ..	87	$Ph[CH_2]_2\cdot NHEt$	80	72
$Ph_2CH\cdot CN$ ..	59	$Ph_2CH\cdot CH_2\cdot NHEt$ ..	51	49
Bu^nCN ..	93	$Bu^nCH_2\cdot NHEt$	83	76[b]
Bu^sCN ..	96	$Bu^sCH_2\cdot NHEt$	75	70[b]
Bu^tCN ..	89	$Bu^tCH_2\cdot NHEt$	80	74[b]

[a] Determined by gas chromatographic analysis; [b] Isolated as the hydrochloride.

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‡ The n.m.r. spectrum was determined with a Varian Associates A-60 spectrometer and are recorded in c./sec. downfield from tetramethylsilane.

[1] H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Chem. Ber.*, 1956, **89**, 209.

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

[3] We also prepared this compound in 81% yield by reduction of *N*-ethylbenzylamine hydrochloride with sodium borohydride in diglyme, see H. Noth and H. Bayer, *Chem. Ber.*, 1960, **93**, 928.