A Case of Kinetic *N*- and Equilibrium *C*-Protonation in Strong Acids

By ROGER W. ALDER* and NIGEL C. GOODE
(*School of Chemistry, University of Bristol, Cantock's Close, Bristol* BS8 1TS)

Summary (8-Dimethylamino-1-naphthyl)trimethylammonium tetrafluoroborate undergoes kinetic *N*- and equilibrium *C*-protonation in strong acids; ring deuteriation may involve rate-limiting ring inversion in the non-planar *C*-protonated dication.

THE protonation of weakly basic compounds in strong acids has been extensively studied, especially since the advent of 'super-acids' such as $HSO_3F–SbF_5$. Compounds with alternative protonation sites (*e.g.* phenols and amides) are particularly interesting. In studies of this kind, it is normal practice to add the substrate to the acid at the lowest convenient temperature with efficient mixing in order to minimise side reactions. By this procedure hydrogen ion activity is abruptly increased by 10—20 logarithmic units; in this respect there is a resemblance to the aqueous quenching of a carbanion. With this analogy in mind, it is surprising that little evidence has been produced for kinetically controlled protonations in strong acids. We report a clear case of such behaviour.

The tetrafluoroborate (**1**) is obtained *via* the slow reaction of 1,8-bis(dimethylamino)naphthalene with methyl fluorosulphate,[1] followed by treatment of the non-crystalline fluorosulphate salt with aqueous sodium tetrafluoroborate. The salt (**1**)† dissolves in HSO_3F, CF_3SO_3H, or 98% H_2SO_4 to give (**2**), with ^1H n.m.r. absorption at τ 1·4—2·2 (6H, two overlapping AMX systems), 2·7br (1H, NH), 6·0 (9H), and 6·25 (6H, d, *J* 5 Hz). Absorptions due to (**3**) (see below) are absent and the solutions are stable for weeks at room temperature. In a variety of weaker acids (**1**) behaves differently; 72% $HClO_4$ is particularly revealing. 1 min after mixing (**1**) and $HClO_4$, the spectrum of (**2**) is seen, but after 10 min this is replaced by a new set of absorptions. In addition to 3 aromatic protons (ABX spectrum) and a singlet at τ 6·05 (9H), there are singlets at τ 5·85 and 6·25 (3H each) and absorptions at τ 3·1 (1H, d, *J* 9 Hz, of t, *J* 1·5 Hz), 3·4 (1H, m), and 5·6 (2H, m). The latter set of peaks are reasonably assigned to the –CH=CH–CH_2– group of a *C*-protonated ion, presumably (**3**) or (**4**). We prefer (**3**) on the grounds of the small chemical shift difference between the vinylic protons. Weak absorptions in the *N*-methyl region might be due to 10—20% of (**4**); a ^{13}C n.m.r. spectrum in 74% $D_2SO_4–D_2O$ reveals the presence of *ca.* 10% (**2**) at equilibrium. The fact that solutions of (**1**)

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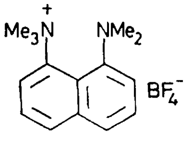
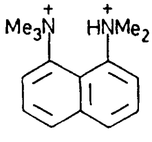
† Satisfactory analytical and spectroscopic data have been obtained for (**1**), although it is difficult to obtain free of traces of the protonated salt (n.m.r.).

in stronger acids are not at equilibrium is revealed by heating them. Thus brief refluxing (15 min, 160 °C) of a solution in CF_3SO_3H converts (**2**) into (**3**).

Further interesting features of the C-protonation of (**1**) are revealed by dissolving it in CF_3CO_2D. The ^1H n.m.r. spectrum shows almost equal concentrations of (**1**) and (**3**) (slow exchange, separate, sharp absorptions). The absorptions due to the allylic system in (**3**) show that, while D^+ has been added at C-2, no exchange of the protons originally present has occurred. 3-H is a double doublet (*J* 9 and 6 Hz). Over a period of days at room temperature 3-H changes first to a doublet (*J* 6 Hz) as 4-H exchanges, and eventually to a singlet when exchange at 2-H is complete. Thus although (**3**) predominates over (**4**) in solution, exchange occurs more rapidly at the *para*-carbon. Redissolving dideuteriated (**1**) in CF_3CO_2H gives a spectrum which shows 3-H as a doublet (*J* 1·5 Hz).



(1)



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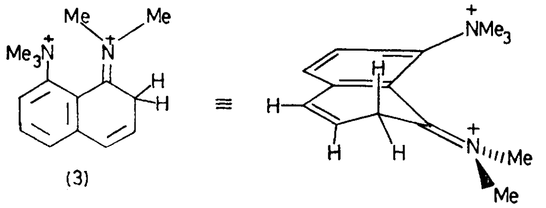

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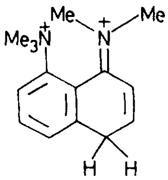

(4)

We interpret these observations in terms of the conformation shown for (**3**) with a non-equivalent CH_2 group ($\nu_{2ax} = ca.\ \nu_{2eq}$, but $J_{2ax,3} = 1{\cdot}5$ Hz, $J_{2eq,3} = 6$ Hz). In the (**1**) $\rightleftharpoons$ (**3**) equilibrium, addition and loss of 2-*ax*-H is rapid on the laboratory time-scale but does not, in itself, lead to exchange. The slow exchange reaction might involve the stereoelectronically poor equatorial deprotonation of (**3**), or rate-limiting ring inversion followed by rapid axial deprotonation. The more rapid exchange at the *para*-carbon is explicable in terms of the latter mechanism, if it is assumed that ring inversion involves temporary loss of immonium ion conjugation. The planar form of (**4**), lacking CN π-overlap is an α-protonated naphthalene and should be more stable than planar (**3**) (β-protonated naphthalene). Thus ring inversion should be easier for (**4**) than (**3**). In 75% H_2SO_4, the n.m.r. signals for the immonium methyl groups of (**3**) remain sharp and distinct at 100 °C.

Benzenium ions are normally assumed to have planar rings and this is borne out by the crystal structure of heptamethylbenzenium tetrachloroaluminate.[2] Although (**3**) is doubtless exceptional, models suggest that mild displacement of C-1 from the C-2—C-6 plane may be inexpensive energetically. Non-planar benzenium ions could play a part in other sterically hindered aromatic substitutions.

(*Received*, 9*th December* 1975; *Com.* 1368.)

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[1] We originally reported that this reaction gave the fluorosulphate of protonated 1,8-bis(dimethylamino)naphthalene (R. W. Alder' P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Comm.*, 1968, 723). Formation of this crystalline product is always a side reaction to methylation, even under scrupulously dry conditions. The formation of protonated salts in highly hindered methylations has been reported by others (Y. Okamoto and K. I. Lee, *J. Amer. Chem. Soc.*, 1975, **97**, 4015 and references therein), but there are several aspects of the present reaction which we still do not understand.

[2] N. C. Baenziger and A. D. Nelson, *J. Amer. Chem. Soc.*, 1968, **90**, 6602.