Hydrogen Randomisation in Pyridine upon Electron Impact

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THE most abundant fragment ion in the 70 ev mass spectrum of pyridine[1] is formed by the loss of hydrogen cyanide in a one-step process from the molecular ion as evidenced by an abundant metastable peak [Figure (a)] at m/e 34·2 (m/e 79 → 52). At a nominal 14 ev, more than 70% of the total ion current due to fragment ions is carried by the $M-$HCN (m/e 52) species. The much less abundant metastable peaks in Figure (a) are consistent with the transitions m/e 78 → 51 (loss of HCN from an $M-1$ ion, calc. m/e 33·4) and m/e 39 → 37 ($C_3H_3^+$ → C_3H^+, calc. m/e 35·1).

2,6-[$^2H_2$]Pyridine (I) was prepared by treatment of pyridine with sodium deuteroxide in deuterium oxide;[2] the isotopic purity established from the low voltage mass spectrum was d_1, 9; d_2, 77; d_3, 14%, and the n.m.r. spectrum showed dideuteration to have occurred almost exclusively in the 2- and 6-positions. The metastable peaks occurring in the m/e 32—37 region of the spectrum of (I) at 70 ev are given in Figure (b). By far the most abundant metastable peaks occur at m/e 36·0 and 34·7 and these correspond to the loss of HCN and DCN, respectively, from 2,6-[$^2H_2$]pyridine. The intensity ratio of these peaks is approximately 3:2, which corresponds to the statistical involvement of the α-, β-, and γ-hydrogens of pyridine in the expulsion of HCN; the loss of HCN does not occur *via* simple rupture of the 1,2- and 5,6-bonds. The metastable peaks at m/e 36·9 and 35·6 arise from the loss of HCN and DCN from the [$^2H_3$]pyridine contaminant (14%), and although their relative abundance cannot be measured accurately, the observed approximate ratios are consistent with a statistical process. The expulsion of HCN and DCN from the [^2H]pyridine contaminant (9%), or from the $M-$H ion of 2,6-[$^2H_2$]pyridine (I) can give to rise the metastable peaks at m/e 35·2 and 33·8, respectively. Randomisation of hydrogens also probably precedes the $C_3H_3^+$ → C_3H^+ reaction observed in the pyridine spectrum, since a low abundance metastable peak is observed at m/e 33·4 for the transition $C_3HD_2^+$ → C_3H^+.†

The behaviour of a monodeuterated pyridine can be evaluated more clearly from the metastable peaks (Figure c) in the spectrum of 2-[$^2H_1$]pyridine

[(II), d_0, 1; d_1, 96; d_2, 3%], prepared by successive treatment of 2-bromopyridine with n-butyl-lithium[3] and deuterium oxide. All the possible
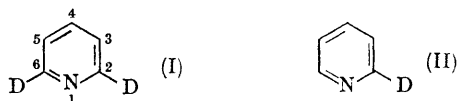
transitions corresponding to the metastable peaks in Figure (a), which could occur after H/D scrambling in (II) are listed in the Table; the relative intensities of the resulting metastable peaks using the observed abundances in the spectrum of
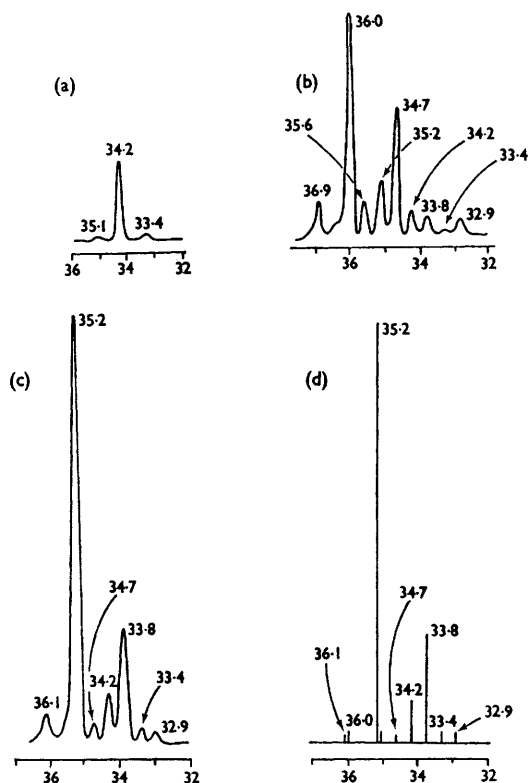
FIGURE

† This metastable peak corresponds to a process of low statistical probability, *e.g.*, the process $C_3H_2D^+$ → C_3H^+ after randomisation of hydrogens and deuteriums in 2,6-[$^2H_2$]pyridine (I) is four times more probable and is partly responsible for the metastable peak at m/e 34·2. Some overlap of metastable peaks occurs and therefore a complete analysis of the less abundant ones is not given. The peak at m/e 32·9 (Figure (b)] establishes the step $M-$D → $M-$D$_2$CN from 2,6-[$^2H_2$]pyridine (I).

pyridine itself have been calculated on the basis of no isotope effect. The calculated spectrum of metastable peaks is given in Figure (d), and agrees well with the observed pattern [Figure (c)].

The present study establishes that the hydrogens of pyridine are randomised prior to the expulsion of

TABLE

Transitions giving rise to metastable peaks in the m/e *32—37 region of the mass spectrum of (II) after* H/D *scrambling*

Transition	Process	Metastable Peak (m/e)
$81 \rightarrow 54$‡	[$^2H_2$]pyridine$-$HCN	36·0
$81 \rightarrow 53$‡	[$^2H_2$]pyridine$-$DCN	34·7
$80 \rightarrow 53$	$M-$HCN	35·2
$80 \rightarrow 52$	$M-$DCN	33·8
$79 \rightarrow 52$	$(M-H)-$HCN	34·2
$79 \rightarrow 51$	$(M-H)-$DCN)	32·9
$78 \rightarrow 51$	$(M-D)-$HCN)	33·4
$39 \rightarrow 37$	$C_3H_3^+ \rightarrow C_3H^+$	35·1
$40 \rightarrow 37$	$C_3H_2D^+ \rightarrow C_3H^+$	34·2
$40 \rightarrow 38$	$C_3H_2D^+ \rightarrow C_3D^+$	36·1

‡ These transitions arise due to the 3% of [$^2H_2$]-contaminant.

HCN from the molecular ion (this is still true even at a nominal 14 ev), and probably also prior to the reactions $(M-H) \rightarrow (M-H)-$HCN and $C_3H_3^+ \rightarrow C_3H^+$. This situation resembles that observed in benzene,[4] where all the major decomposition pathways induced by electron impact are preceded by hydrogen scrambling. Most plausibly, the hydrogen scrambling observed in the benzene case does not involve C–H bond cleavage, but actually randomisation of the carbon atoms *via* structures such as benzvalenes and prismanes, which are known to be generated by photochemical excitation.[4,5] In analogy, it is possible that pyridine is reversibly equilibrated with azaprismane and azabenzvalene structures after excitation upon electron impact, thus resulting in H/D scrambling in partially deuterated pyridines. Although the photochemistry of aza-analogues of benzene has been little investigated, carbon–carbon bond formation probably occurs during the photochemical rearrangement of 4-amino-2,6-dimethylpyrimidine.[6]

[1] "Catalog of Mass Spectral Data", American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburg, Pa., spectrum No. 617.

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[3] H. Gilman and S. M. Spatz, *J. Amer. Chem. Soc.*, 1940, **62**, 446.

[4] K. Jennings, *Z. Naturforsch.*, 1967, **22a**, 454.

[5] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Comm.*, 1966, 593.

[6] K. L. Wierzchowski, D. Shugar, and A. R. Katritzky, *J. Amer. Chem. Soc.*, 1963, **85**, 827; since this manuscript was submitted, it has been reported (F. Lahmani and N. Ivanhoff, *Tetrahedron Letters*, 1967, 3913) that the photochemical conversion of dimethylpyrazines into dimethylpyrimidines occurs in a manner which indicates the formation of dimethyldiazabenzovalenes as intermediates.