SHORT COMMUNICATION

ELECTRON-IMPACT FRAGMENTATION OF ISOBUTYRONITRILE

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Abstract—The mass spectrum of isobutyronitrile- $2-d_1$ was studied. The results support an earlier proposal of isomerisation of the molecular ion, prior to fragmentation.

IN A RECENT paper¹ the dominant primary reactions of propionitrile under electronimpact were discussed. Our earlier findings with respect to H and HCN elimination from the molecular ion in straight chain aliphatic nitriles² were rationalised by Meyerson and Karabatsos in terms of specific hydrogen migration resulting in an isomerised form of the fragmenting molecular ion. The hydrogen atom lost as HCN comes chiefly from C-2, but that lost as a free atom originates from C-3. The near absence of hydrogen elimination from 2,2-dimethylpropionitrile and the high $[M - H]^+$ intensity in the spectrum of isobutyronitrile, led us to assume that the latter compound preferentially lost hydrogen from C-2.^{3,4} This assumption was also based on the fact that hydrogen elimination from the C-2 position in the isobutyronitrile molecular ion would leave a tertiary carbonium ion, which has an enhanced stability over the corresponding secondary carbonium ion in straight chain nitriles. Contrary to this argument Meyerson and Karabatsos prefer hydrogen elimination from C-3 in the isomerised molecular ion of isobutyronitrile. They explain the near absence of hydrogen elimination from 2,2-dimethylpropionitrile by the inability of the latter to undergo such isomerisation.¹ These authors suggest, however, that elimination of CH₃CN from the latter compound proceeds via a similar isomerised molecular ion, in which a methyl group migrated from C-2 to C-1.⁺

It is not clear however, why this rearranged molecular ion cannot lose a hydrogen atom from one of either C-3 positions to yield an $[M - H]^+$ ion with conjugated double bonds similarly to propionitrile.

In order to trace the origin of the eliminated hydrogen in isobutyronitrile, we studied the mass spectrum of monodeuteroisobutyronitrile, labelled at the C-2 position. The most important peaks are summarised in Table 1; the mass spectrum of the unlabelled compound has been published earlier.³

From these data it is very obvious that the hydrogen lost as a free atom originates almost exclusively from C-3, while in the elimination of HCN only the hydrogen of C-2 is involved. These observations prove that the concept of Meyerson and Karabatsos for the isomerised molecular ion also holds for isobutyronitrile, as these authors suggested.¹

 \dagger In their paper migration of a methyl group from C-3 to C-2 is mentioned; in all probability a C-2 to C-1 migration is intended.

Ion	d_0	d_1
$[C_4H_6N]^+[M - H]$	4	96
$[C_{3}H_{4}N]^{+}[M - CH_{3}]$		100
$[C_3H_3N]^+$	23	77
$[C_{3}H_{2}N]^{+}$	54	46
[C _s HN]+·	68	32
$[C_{s}H_{t}]^{+}\cdot[M - HCN]$	96	4
$[C_{2}H_{4}N]^{+}$	76	24
[C ₈ H ₅]+	51	49
$[C_{2}H_{3}N]^{+} [M - C_{2}H_{4}]$	100	_
[C ₃ H ₃]+	63	37
$[C_{2}H_{4}]^{+}\cdot[M - CH_{3}CN]$	14	86
[CH ₃ N] ⁺	58	42
[C ₀ H ₀]+	53	47
[C.H.]+·	56	44

TABLE 1. ISOTOPIC DISTRIBUTIONS OF SELECTED IONS IN THE SPECTRUM OF ISOBUTYRONITRILE-2- d_1

The deuterium distribution in the $[C_2H_4]^{+}$ ion can be explained analogously for the greater part by elimination of CH₃CN from a molecular ion in which a methyl group has migrated to the C-1 position. This also explains the occurrence of $[C_2H_3N]^+$ ions in only the undeuterated composition.

Therefore the isomerised molecular ion of isobutyronitrile, should be regarded as the precursor of $[C_2H_3N]^+$, instead of the $[C_2H_4N]^+$ ion.³

In the following scheme the deuterium as well as the methyl migration in the molecular ion and the different eliminations are rationalised:



SCHEME 1

The isotopic distribution in $[C_2H_4N]^+$, the third most abundant ion in the mass spectrum, indicates a partial hydrogen scrambling in its precursor ion $[M - H]^+$, before fragmentation. Other fragment ions often originate from more than one precursor ion.³ In such cases it is not possible to calculate their isotopic distributions.

EXPERIMENTAL

Isobutyronitrile-2- d_1 has been prepared starting from isopropyl-2- d_1 -alcohol (>99% deuterium content), purchased from Merck, Sharp & Dohme. The alcohol was brominated with PBr₃ according to the method described by Noller and Dinsmore.⁵ After purification the bromide was dissolved in acetone together with an anion-exchanger (IRA 400) in cyanide form. This mixture was heated for 2 h at 100 °C in a sealed tube, according to Urata.⁶ The nitrile was obtained by distillation. The

spectrum and the isotopic distributions reported in Table 1 were measured with an AEI MS-902 instrument under the following conditions: ion source temperature 150 °C; ion source pressure 2.0×10^{-6} Torr; electron energy 70 eV; resolution (for precise mass measurements) 35000; inlet system temperature 120 °C.

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