

Formal 1,1-Elimination of Hydrogen Cyanide from *o*-Nitrobenzyl Cyanide under Electron Impact

By A. Kalir and E. Sali, Department of Organic Chemistry, Tel Aviv University Medical School, Israel Institute for Biological Research, Ness-Ziona, Israel
Asher Mandelbaum,* Israel Institute of Technology, Haifa, Israel

The elimination of HCN from the molecular ion of *o*-nitrobenzyl cyanide under electron impact is shown by deuterium labelling to take place with the abstraction of one of the benzylic hydrogens. This is the first case of a specific 1,1-elimination. *o*-Nitrobenzyl chloride and *o*-nitrobenzyl alcohol do not undergo similar eliminations.

THE electron-impact-induced eliminations of molecules of HX from organic molecular ions RX^{*+} ($X = OH, OCOR, HNCOR, \text{halogen, CN, etc.}$) are usually 1,2,^{1a,e} 1,3,^{1b} 1,4,^{1c} and 1,5^{1d} eliminations. The preferred site of abstraction of the hydrogen atom has been shown to be dependent on the nature of the group X,² on the stereochemical features of the system R,^{2,3} and also on the original chemical environment of the abstracted hydrogen atom.^{2,4} The eliminations are believed to take place *via* cyclic transition states, which usually are of five, six, or seven members.² To the best of our knowledge a specific 1,1-elimination of HX has not been reported hitherto.[†]

† In the reported cases where 1,1-eliminations seem to occur, they are non-specific processes, which take place after hydrogen scrambling over the system.^{5a,b} One such process is the elimination of hydrogen cyanide from benzyl cyanide and from the isomeric *o*-, *m*-, and *p*-cyanobenzyl cyanides. These compounds were investigated with the aid of extensive labelling, and it has been concluded that the loss of hydrogen cyanide occurred after an almost complete randomisation of all hydrogen atoms.^{5a,b} Thus a part of the $[M - HCN]^+$ ions can be considered as formally arising from a 1,1-elimination, but it does not seem likely that this is really the case.

Another case, mentioned in passing, is [2,2-²H₂]propionitrile which gave rise to C₂H₃D⁺ ion under electron impact.^{5b} It is possible, however, that the C₂H₃D⁺ ion is formed by the loss of CN radical from $[M - D]^+$ ion. Weak metastable peaks for the transitions 55 → 28 and 54 → 28 were detected in the case of unlabelled propionitrile, but precise mass measurement of the *m/e* 28 ion showed two components C₂H₄⁺ and CH₂N⁺.^{5b,c}

A true 1,1-elimination does not seem to be an easy decomposition route of an organic gas-phase ion, since the large distance between the non-bonded atoms H and X would hinder the formation of the necessary three-membered cyclic transition state. We describe here the first case where a specific 1,1-elimination occurs, but it is shown that it does not take place by a simple one-step mechanism involving the intermediacy of a three-membered transition state.

¹ H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967: (a) pp. 185, 344, 435; (b) pp. 111, 186, 436; (c) pp. 98, 436; (d) S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, 1966, **88**, 56; W. Carpenter, A. M. Duffield, and C. Djerassi, *Chem. Comm.*, 1967, 1023; (e) Th. H. Kinstle, P. J. Ihrig, and E. J. Goettert, *J. Amer. Chem. Soc.*, 1970, **92**, 1780; I. Howe and D. H. Williams, *Chem. Comm.*, 1971, 1195.

² M. M. Green and R. B. Roy, *J. Amer. Chem. Soc.*, 1970, **92**, 6368; M. M. Green, R. J. Cook, J. M. Schwab, and R. B. Roy, *ibid.*, p. 3076; J. Deutsch and A. Mandelbaum, *ibid.*, p. 4288; E. Gil-Av, J. H. Leftin, A. Mandelbaum, and S. Weinstein, *Org. Mass Spectrometry*, 1970, **4**, 475.

³ S. Meyerson and A. W. Weitkamp, *Org. Mass Spectrometry*, 1968, **1**, 659.

⁴ S. Meyerson, paper presented at the International Conference on Mass Spectrometry, Brussels, 1970.

⁵ (a) R. S. Ward and D. H. Williams, *J. Org. Chem.*, 1969, **34**, 3373; (b) T. A. Molenaar-Langeveld, N. M. M. Nibbering, and Th. J. de Boer, *Org. Mass Spectrometry*, 1971, **5**, 725.

⁶ (a) S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, 1964, **86**, 2555; (b) Dr. S. Meyerson, personal communication; (c) W. Heerma, J. J. de Ridder, and G. Dijkstra, *Org. Mass Spectrometry*, 1969, **2**, 1103.

We found that the elimination of HCN gives rise to one of the most abundant ions in the mass spectrum of *o*-nitrobenzyl cyanide (1) (m/e 135, 78% of the most

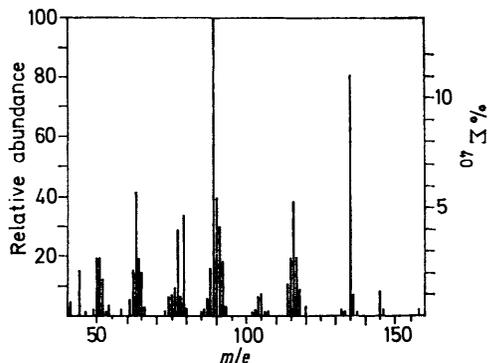


FIGURE 1 Mass spectrum of *o*-nitrobenzyl cyanide

abundant ion, $\% \Sigma_{40}$ 11.1). A metastable peak at m/e 112.5 (calc. 112.5) indicates that HCN is lost as a single entity. This ion is absent from the mass spectrum of the *para*-isomer. In order to determine the origin of the hydrogen atom involved in the elimination of HCN we measured the mass spectrum of $[\alpha\alpha\text{-}^2\text{H}_2]o$ -nitrobenzyl cyanide. In contrast to benzyl cyanide and the isomeric cyanobenzyl cyanides^{5,6} (including the *ortho*-isomer), the elimination from *o*-nitrobenzyl cyanide takes place exclusively ($99 \pm 1\%$) with the abstraction of one of the benzylic hydrogens. The high site specificity is retained when the energy of ionization is lowered to 15 eV (nominal). Practically no randomisation occurs before the elimination from the metastable molecular ion, and consequently an intense metastable peak is detected at m/e 112.9.

The fact that this fragmentation takes place only in the *ortho*-isomer suggests that the nitro-group plays an

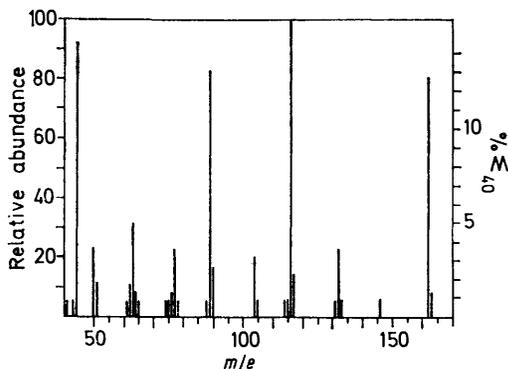


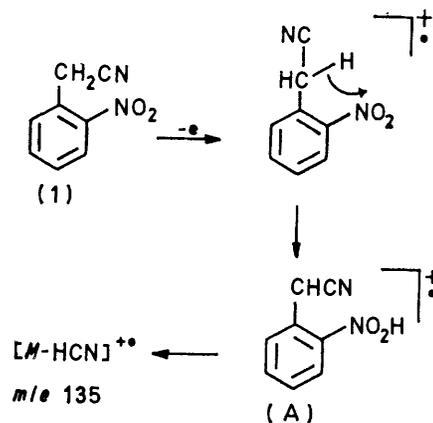
FIGURE 2 Mass spectrum of *p*-nitrobenzyl cyanide

important role in this elimination. The site specificity is reminiscent of the known behaviour of *ortho*-nitro-

⁷ G. E. Robinson, E. B. Thomas, and J. M. Vernon, *J. Chem. Soc. (B)*, 1971, 1273.

arenes containing benzylic hydrogens, which lose a hydroxyl radical under electron impact after migration of one of the benzylic (almost exclusively⁷) hydrogen atoms.⁸ It can be assumed that the elimination of HCN from *o*-nitrobenzyl cyanide is a two-step process. Initially one of the benzylic hydrogen atoms migrates to the nitro-group to form intermediate (A), and then the elimination of HCN involving the above-mentioned hydrogen atom can take place *via* a cyclic transition state, possibly with further isomerisation of the resulting ion. This seems to be another case of a two-step fragmentation process under electron impact, some of which have recently been reported.⁹ A similar elimination has been found to be negligible in *o*-nitrobenzyl chloride which gives rise instead to an abundant m/e 136 $[M - Cl]^+$ ion.

Another compound which was suspected of giving rise to 1,1-elimination was *o*-nitrobenzyl alcohol which



has been reported to eliminate H_2O under electron impact.^{5a,8} Deuterium labelling showed that the hydroxy hydrogen atom participates in this elimination, and the origin of the other hydrogen atom is at the benzylic position. The authors suggested two mechanisms, in both of which it was assumed that the oxygen atom of the eliminated H_2O originates from the nitro-group.⁸ In analogy with the elimination of HCN from *o*-nitrobenzyl cyanide another mechanism could be suggested, namely α -elimination of H_2O from the alcohol part of the molecule.

Labelling with ^{18}O was employed to distinguish between the possibilities. *o*-Nitrobenzyl alcohol labelled with ^{18}O at the hydroxy-group gave rise to $[M - \text{H}_2\text{O}]^+$ ion which contained almost all the ^{18}O . Therefore the elimination of the H_2O from the molecular ion of *o*-nitrobenzyl alcohol involves the oxygen of the nitro-group,

⁸ (a) S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, 1966, **88**, 4794; (b) J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc. (B)*, 1966, 396; (c) F. Benoit and J. L. Holmes, *Org. Mass Spectrometry*, 1970, **3**, 993.

⁹ J. S. Smith and F. W. McLafferty, *Org. Mass Spectrometry*, 1971, **5**, 483; P. R. Briggs, T. W. Shannon, and P. Vouros, *ibid.*, p. 545.

as assumed by previous authors,⁸ and practically no 1,1-elimination occurs in this case.

A formal 1,1-elimination of ethanol occurring in two steps has been suggested recently.¹⁰

EXPERIMENTAL

The mass spectra were measured with an Atlas CH4 mass spectrometer fitted with a TO-4 ion source. The samples were introduced both through the heated inlet system (at 150 °C) and by the direct inlet system (without heating).

o- and *p*-Nitrobenzyl cyanides were prepared from the corresponding bromides and a suspension of NaCN and HCN in dimethyl sulphoxide.¹¹

[α -²H₂]*o*-Nitrobenzyl Cyanide.—Deuteriofluoroacetic acid

¹⁰ A. W. J. D. Dekkers, N. M. M. Nibbering, and W. N. Speckamp, *Tetrahedron*, 1972, **28**, 1829.

(1.52 g) was added slowly to a cooled stirred suspension of sodium cyanide (1.0 g) in [²H₆]dimethyl sulphoxide (5 ml). A solution of *o*-nitrobenzyl bromide (1.45 g) in [²H₆]dimethyl sulphoxide (4 ml) was added to the suspension, and the mixture was stirred for 2 h and left overnight. D₂O (5 ml) was added, the resulting solid precipitate filtered off and recrystallised from MeOD (yield 450 mg). It had m.p. 82 °C.

o-Nitrobenzyl [¹⁸O]Alcohol.—*o*-Nitrobenzyl bromide (82 mg), potassium carbonate (54 mg), and H₂¹⁸O (1 g) (supplied by Yeda, Rehovoth, containing 62.8% ¹⁸O and 0.279% ¹⁷O) were heated at 80 °C in a stoppered 5 ml flask for 6 h. After cooling the solid material was filtered off and used without further purification (35 mg); m.p. 70—72 °C.

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¹¹ A. Kalir and E. Sali, Abstracts of the 41st Annual Meeting of the Israel Chem. Soc., October 1971, p. 209.