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MASS SPECTROMETRY OF ARALKYL COMPOUNDS WITH A FUNCTIONAL GROUP—V

THE CYANOTROPYLIUM ION FROM BENZYLCYANIDE

N. M. M. NIBBERING and TH. J. DE BOER
University of Amsterdam, Laboratory for Organic Chemistry, Nieuwe Achtergracht 129

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Abstract—Mass spectra of benzylcyanide and its α-d_2, *ortho*-d_2 and *para*-d_1 analogues suggest a cyanotropylium structure for the $(P-1)^+$-ion.

INTRODUCTION

IN A preceding paper[1] it has been shown that the molecular ion of 2-phenyl-1-nitroethane loses successively a molecule of water and an O atom, yielding a species C_8H_7N possibly resembling benzylcyanide. This species then eliminates HCN in a process, which was supposed to involve participation of an *ortho*-H atom from the aromatic ring.

$$C_6H_5CH_2CH_2NO_2^{+\cdot} \xrightarrow[-O]{-H_2O} C_8H_7N^+ \; (C_6H_5CH_2CN^+?) \xrightarrow{-HCN} C_7H_6^{+\cdot}$$

To test this point of view we have synthesized the *ortho*-d_2 analogue from 2-phenyl-1-nitroethane. The mass spectrum of this compound, however, revealed a random participation of all hydrogen atoms from the C_8H_7N species in the HCN loss.

This prompted us to study the mass spectral behaviour of benzylcyanide itself. This compound loses preferentially HCN, as already noted by Biemann[2] in a study of the unlabeled compound. Deuterium exchange between benzylcyanide and a deuterated carrier in a GLC-column has been studied by Senn *et al.*[3] Although mass spectrometry was used to determine the deuterium incorporation in benzylcyanide, no attention was paid to the fragmentation mechanism.

RESULTS AND DISCUSSION

The spectra of benzylcyanide and its α-d_2, *ortho*-d_2 and *para*-d_1 analogues are presented in Figs 1 to 4. Those from the α-d_2 and *ortho*-d_2 compounds are strikingly similar, which suggests a rearrangement of the corresponding molecular ions to a common precursor.

Table 1 shows the mass region *m/e* 116 to *m/e* 120 for undeuterated benzylcyanide and its α-d_2, *ortho*-d_2 and *para*-d_1 analogues. In the columns, headed "obs.", the observed relative abundances are recorded. The columns, headed "corr.", are obtained after corrections for naturally occurring ^{13}C, ^{15}N and for isotopic impurities (Experimental).

In the correction for the presence of d_1 molecules in the α-d_2 and *ortho*-d_2 cyanides it has been assumed that these lose an H and a D atom in the statistical ratio 6:1, as a first approximation.

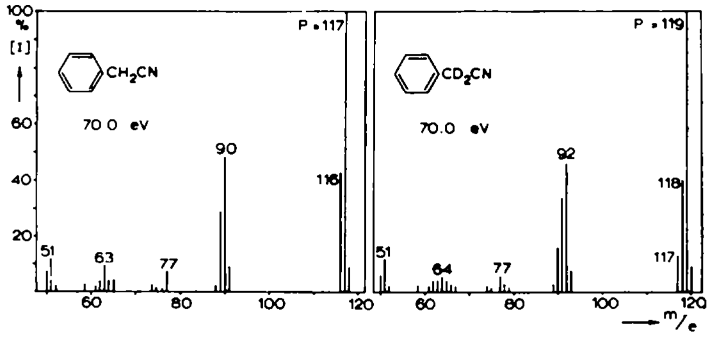


FIG. 1.   FIG. 2.

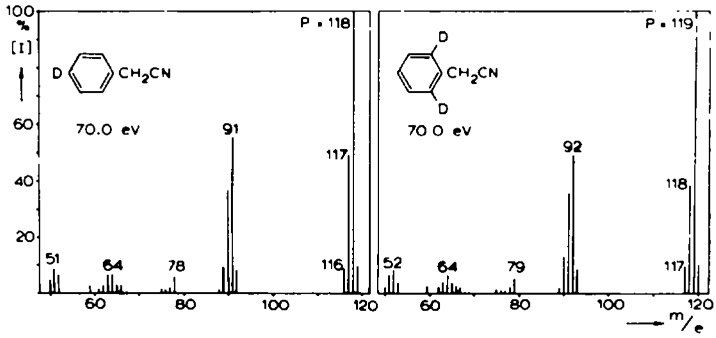


FIG. 3.   FIG. 4.

FIGS. 1–4. Mass spectra of benzylcyanide and its α-d_2, *para*-d_1 and *ortho*-d_2 analogues.

TABLE 1. PARTIAL MASS SPECTRA OF BENZYLCYANIDE AND ITS α-d_2, *ortho*-d_2 AND *para*-d_1 ANALOGUES AT 70·0 eV

Relative abundances with respect to parent ion (= 100)

m/e	d_0		α-d_2		*ortho*-d_2		*para*-d_1	
	Obs.	Corr.	Obs.	Corr.	Obs.	Corr.	Obs.	Corr.
120	—	—	9·00	0·17	10·84	2·07	—	—
119	—	—	100·00	100·00	100·00	100·00	9·92	0·28
118	9·26	0·48	39·48	30·53	38·77	34·58	100·00	100·00
117	100·00	100·00	13·33	9·94	10·45	8·25	49·23	38·94
116	42·70	44·35	1·03	0·31	1·08	0·46	8·96	3·99
115	0·86	0·89	—	—	—	—	0·84	0·74

Following the directions of Meyer,[4] we may calculate from this Table the isotope effect *i*, expressing the favoured loss of H over D, and the preference for loss of the α-hydrogens to the ring hydrogens, expressed as *p*:

$$\begin{aligned} \alpha\text{-d}_2\text{: loss D/loss H} &= 2p/5i = 9{\cdot}94/30{\cdot}53 = 0{\cdot}33 \\ \textit{ortho}\text{-d}_2\text{: loss D/loss H} &= 2/(2pi + 3i) = 8{\cdot}25/34{\cdot}58 = 0{\cdot}24 \\ \textit{para}\text{-d}_1\text{: loss D/loss H} &= 1/(2pi + 4i) = 3{\cdot}99/38{\cdot}94 = 0{\cdot}10 \end{aligned}$$

Solution of these equations gives $i = 1{\cdot}52$ and $p = 1{\cdot}25$.

These numbers are strikingly similar to those found for toluene viz. $i = 1{\cdot}58$ and $p = 1{\cdot}32$.[4]

We may state, therefore, that the scrambling of the H atoms in the molecular ion of benzylcyanide is analogous to that suggested for toluene.

It may be noted that the d_1 molecules from the α-d_2 and *ortho*-d_2 samples have been assumed to lose an H and a D atom in the statistical ratio 6:1 (see above).

With $i = 1{\cdot}52$ and $p = 1{\cdot}25$, however, this ratio becomes $(5i + pi):p = 7{\cdot}60:1$ and $(4i + 2pi):1 = 9{\cdot}88:1$ for the d_1 molecules from the α-d_2 and *ortho*-d_2 samples, respectively. Taking this into account, the following corrected values for the relative abundances of the mass region *m/e* 117 to *m/e* 119 and for the ratios loss D/loss H from the α-d_2 and *ortho*-d_2 benzylcyanides are obtained:

TABLE 2

Relative abundances with respect to parent ion (= 100)			loss D/loss H	
m/e	α-d_2	*ortho*-d_2	α-d_2	*ortho*-d_2
119	100·00	100·00	$\frac{9{\cdot}83}{30{\cdot}53} = 0{\cdot}32$	$\frac{8{\cdot}14}{34{\cdot}58} = 0{\cdot}24$
118	30·53	34·58		
117	9·83	8·14		

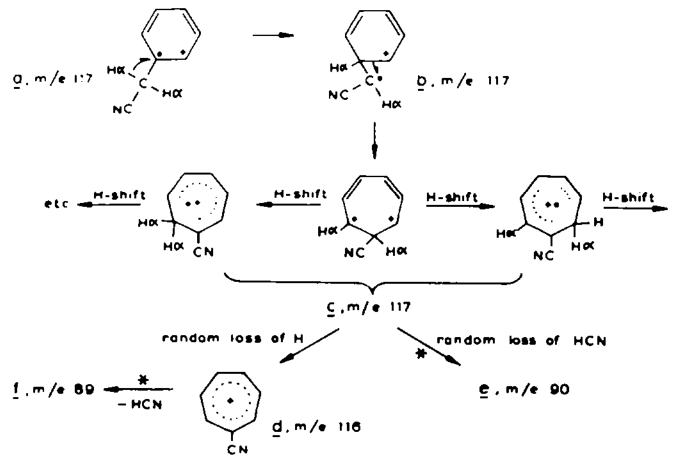
These ratios are similar to those calculated above, so that the values for i and p do not change by this correction.

Thus, analogous to toluene[4] an H atom is lost from an incompletely scrambled molecular ion of benzylcyanide, yielding the cyanotropylium ion. This structure has been proposed also for the $(P\text{-}1)^+$-ions from the *ortho*-, *meta*- and *para*-tolunitriles,[5] because of the similarity of the mass spectra from these compounds.[6]

Although there is a strong resemblance of benzylcyanide to toluene in the behaviour upon electron impact, it is not necessary to adopt the mechanism of ring expansion, proposed for toluene.[4] Furthermore, the statement that an H shift between non-equivalent adjacent positions in the 7-membered ring structure, suggested for the molecular ion from *p*-methylethylbenzene, is very slow compared to the rate of H shift between equivalent positions,[4] seems to be inapplicable to ion *c* from benzylcyanide (Scheme A).

An alternative mechanism for ring expansion is presented in Scheme A (sequence $a \rightarrow b \rightarrow c$). Scrambling of the hydrogens in ion *c* may proceed *via* a series of consecutive 1–2 shifts of H, as proposed for toluene[4] and observed in the photoisomerization of cycloheptatriene,[7] and/or successive 1–5 shifts of H, observed in the thermal isomerization of unsubstituted and substituted cycloheptatrienes.[8]

SCHEME A



Finally, a HCN molecule is eliminated from the parent ion as well as from the (parent-1)-ion of benzylcyanide after an extensive scrambling of the H atoms in the molecular ion (Scheme A, sequences *c* → *e* and *c* → *d* → *f*, respectively). This is supported by the corresponding diffuse peaks, found in the spectra (Appendix, reaction Nos. 1 and 2, respectively). The detailed structures of the resulting ions *e* and *f* remain uncertain.

EXPERIMENTAL

Mass spectra were obtained with an A.E.I. MS2H- and an A.E.I. MS9 mass spectrometer. Samples were introduced through a heated (Gallium) inlet system at 150°. The spectra from both instruments were essentially the same. The *m/e*- and the m_2/m_1-values for diffuse peaks have been measured on the MS9 instrument (Appendix), as described earlier.[9]

All the samples were purified by preparative gas chromatography with a Wilkens Aerograph A-90-P instrument. The applied columns were a 2·5 m/6 mm with 30% PEG 2000 for the undeuterated benzylcyanide and its *ortho*-d_2 and *para*-d_1 analogues (column temp 158°: retention time 68·5 min) and a 2 m/6 mm with 20% Silicone Rubber SE-52 for the α-d_2 compound (column temp 150°; retention time 18·5 min). The supporting material was kieselguhr and He gas was used as carrier gas.

The deuterium content of the samples was measured by Mass Spectrometry, using such a low ionization energy, that in the parent mass region from the spectrum of the undeuterated benzylcyanide the molecular ion peak remained only. The results of these measurements are collected in Table 3.

TABLE 3. MEASUREMENTS OF DEUTERIUM CONTENT (%) OF DEUTERATED BENZYLCYANIDES AT 10·0 eV; ACCURACY LIMIT 0·1%

	α-d_2	*ortho*-d_2	*para*-d_1
d_2	91·4	94·9	—
d_1	8·3	4·4	89·9
d_0	0·3	0·7	10·1

APPENDIX. DIFFUSE PEAKS, OBSERVED IN THE MASS SPECTRA OF SITE-SPECIFICALLY DEUTERATED $C_6H_5\overset{*}{C}H_2CN$

Reaction	Metastable transitions	d_0		α-d_2		*ortho*-d_2		*para*-d_1		Calc.	
No.		m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1	m^*	m_2/m_1
1	$C_8H_7N^+ \rightarrow C_7H_6^+ + HCN$	69·21	0·769	—	—	—	—	—	—	69·27	0·769
1	$C_8H_5D_2N^+ \rightarrow C_7H_4D_2^+ + HCN$	—	—	71·09	0·772	71·10	0·772	—	—	71·18	0·773
1	$C_8H_5D_2N^+ \rightarrow C_7H_5D^+ + DCN$	—	—	69·57	0·767	69·57	0·766	—	—	69·63	0·765
1	$C_8H_6DN^+ \rightarrow C_7H_5D^+ + HCN$	—	—	—	—	—	—	70·15	0·770	70·22	0·771
1	$C_8H_6DN^+ \rightarrow C_7H_6^+ + DCN$	—	—	—	—	—	—	68·62	0·767	68·68	0·763
2	$C_8H_6N^+ \rightarrow C_7H_5^+ + HCN$	68·26	0·767	—	—	—	—	—	—	68·32	0·767
2	$C_8H_4D_2N^+ \rightarrow C_7H_3D_2^+ + HCN$	—	—	70·15	0·767	70·15	0·766	—	—	70·22	0·771
2	$C_8H_4D_2N^+ \rightarrow C_7H_4D^+ + DCN$	—	—	68·63	0·766	68·63	0·764	—	—	68·68	0·763
2	$C_8H_5DN^+ \rightarrow C_7H_4D^+ + HCN$	—	—	—	—	—	—	69·21	0·767	69·27	0·769
2	$C_8H_5DN^+ \rightarrow C_7H_5^+ + DCN$	—	—	—	—	—	—	67·68	0·764	67·73	0·761

Preparation of the α-d_2 *analogue from benzylcyanide.* 4 g of $C_6H_5CH_2CN$, 300 mg K_2CO_3 and 25 g D_2O were stirred for 70 hr at a temp of 90° in a closed glass vessel. The exchanged product was then extracted with dry ether, the ether soln dried over $MgSO_4$ and the ether removed. From the NMR spectrum of the crude product it appeared that the methylene group was deuterated to the extent of 96·5%. This was purified by GLC, as described above.

Preparations of the ortho-d_2 *and* para-d_1 *analogues from benzylcyanide.* These were synthesized from the corresponding benzylchlorides, the preparations of which have been described previously.[9] A mixture of 3·5 g chloride, 2·2 g NaCN, 25 mg NaI and 20 ml dry acetone was stirred and refluxed for 20 hr.[10] After reaction the acetone was removed, some water added and the benzylcyanide extracted with ether. After drying of the ether soln over $MgSO_4$ and removal of the ether, the residue was distilled *in vacuo*, yielding benzylcyanide with b.p. 98°/7–8 mm. This was purified by GLC, as described above.

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