

Protonated Arenes in the Gas Phase: Xylenium and Related $C_8H_{11}^+$ Ions

D Kuck, G Prior and H F Grützmacher

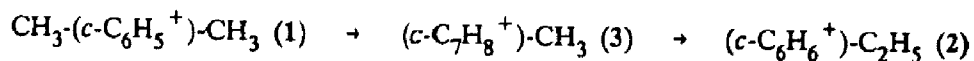
Fakultät für Chemie, Universität Bielefeld, D-4800 Bielefeld 1, FR Germany

D R Müller and W J Richer

CIBA-GEIGY AG, CH-4002 Basel, Switzerland

INTRODUCTION

In the course of our continuing investigations of the chemistry of protonated arenes in the gas phase (Kuck, 1986) we have studied the fragmentation of long-lived xylenium and ethylbenzenium ions (protonated xylene and ethylbenzene, 1 and 2) and methyl-dihydrotropylium ions 3. It is shown that a fraction of ions 1 undergo a skeletal rearrangement by ring expansion-recontraction to isomers 2 via 3, corresponding to the toluenium-dihydrotropylium rearrangement (Kuck, 1985; Williams, 1974). This skeletal isomerization, being unknown for solvated arenium ions (Olah, 1972), occurs also by ion/molecule association of tolyl ions and methane during CID(CH_4) experiments with triple stage quadrupole mass spectrometers.



EXPERIMENTAL

Ions 1-3 and various D- and ^{13}C -labelled analogues were generated by several techniques, including EI induced dissociation of dihydroaromatic precursors (1: methyl 1,4-dimethyl-1,4-dihydrobenzoate, 2: methyl 1-ethyl-1,4-dihydrobenzoate) and CI(*i*-butane) of 7-methylcycloheptatriene in a double-focusing sector instrument (Vacuum Generators ZAB-2F). In addition, ions 1 were generated by CI(CH_4) of the xylenes and the chlorotoluenes (ion/molecule association in the CI source) and from tolyl cations and methane in the rf-only quadrupole of a triple stage quadrupole mass spectrometer (Finnigan MAT TSQ). The fragmentations of the long-lived ions were determined by MIKE as well as high and low energy CID spectrometry with the ZAB and the TSQ instrument, respectively.

RESULTS

As expected from previous work on toluenium ions (Kuck, 1985), long-lived xylenium ions 1 eliminate H_2 and CH_4 , but, surprisingly, they also lose C_2H_4 (Table 1). Loss of C_2H_4 occurs after a slow skeletal isomerization of 1 to 2 via 3, competing with the energy-demanding eliminations of H_2 and CH_4 . This is strongly corroborated by the finding that both metastable ions 2 and ring-expanded isomers 3 expel C_2H_4 exclusively, suggesting 3 as an intermediate.

TABLE 1. Fragmentation of Metastable Ions 1, 2, and 3 (MIKES)

Ion	vs Loss (% Σ) of	H_2	CH_4	C_2H_4
1	$[CH_3-C_6H_5-CH_3]^+$	43.0	46.0	11.0
2	$[C_6H_6-C_2H_5]^+$	1.6	2.4	96.0
3	$[c-C_7H_8-CH_3]^+$	1.4	2.1	96.5

In line with this mechanism, the fragmentation of the α - ^{13}C -ions 1a (Table 2) points to a specific rearrangement of the carbon skeleton, and the analogues 3a and 3b eliminate the label completely. Moreover, the relative amounts of $\text{C}_2(\text{H,D})_4$ expelled from ions 3a and 2b are remarkably similar, proving that C_2H_4 is lost via the ethylbenzenium structure 2 by a non-random hydrogen transfer (cf. Leung, 1977). In contrast, α - CD_3 -xylenium ions 1b exhibit a non-random albeit extensive H/D scrambling, indicating extensive isomerization. However, this pattern can be approximated (Table 2) assuming a fast H ring-walk in the corresponding methyldihydrotropylium intermediates followed by a highly selective ring contraction to the ethylbenzenium rather than to a xylenium structure.

TABLE 2. Ethene Loss (% Σ) from Labelled Metastable Ions (MIKES)

Ion vs m/z	79	80	81	82
1a $^{13}\text{CH}_3\text{-C}_6\text{H}_5\text{-CH}_3^+$	49.6	50.4	-	-
specific[a] (random)	50.0 (25.0)	50.0 (75.0)	-	-
1b $[\text{CD}_3\text{-C}_6\text{H}_5\text{-CH}_3]^+$	13.4	36.3	30.4	20.0
specific[b] (random)	19.0 (2.4)	35.6 (25.5)	25.7 (50.9)	19.7 (21.2)
2a $[\text{C}_6\text{H}_6\text{-CD}_2\text{CH}_3]^+$	85.7	14.3	0.	-
2b $[\text{C}_6\text{H}_6\text{-CH}_2\text{CD}_3]^+$	38.4	61.6	0.	0.
3a $[(\text{c-C}_7\text{H}_8)\text{-CD}_3]^+$	34.4	65.6	0.	0.
3b $[(\text{c-C}_7\text{H}_8)\text{-}^{13}\text{CH}_3]^+$	99.3	0.7	-	-

[a] See text.- [b] Using, as an approximation, the data obtained for ions 2a and 2b.

On the basis of these and previous results (Kuck, 1985) it is suggested that (alkyl)dihydrotropylium ions generally isomerize to the corresponding alkylbenzenium ions.

The elimination of CH_4 from ions 1 is more complex. Several slow isomerization reactions precede this fragmentation, depending on the internal energy of the ions. Besides the ubiquitous hydride ring-walk a slow hydrogen exchange between the ring and the methyl groups is found. In addition to the high energy CID experiments performed with the sector field instrument, the low energy CID data obtained with the TSQ mass spectrometer indicate the occurrence of a methyl ring walk prior to loss of CH_4 . Some selected data are shown in Table 3.

TABLE 3. Methane Loss (% Σ) from Stable and Metastable Xylenium Ions

Ion vs m/z	91	92	93	94
1a MIKES(ZAB)[CID(TSQ)]	44.9 [50.1]	55.1 [49.9]	-	-
specific (random)	50.0 (12.5)	50.0 (87.5)	-	-
1b MIKES(ZAB)[CID(TSQ)]	34.8 [48.7]	9.0 [2.9]	6.8 [3.1]	49.4 [45.3]
specific (random)	50.0 (2.4)	- (25.5)	- (50.9)	50.0 (21.2)

REFERENCES

- Kuck, D., Schneider, J., and Grützmaier, H.-F., *J. Chem. Soc. Perkin Trans. II*, 1985, 689.
- Kuck, D., and Bäther, W., *Org. Mass Spectrom.* 1986, 21, 451.
- Leung, H.-W., and Harrison, A.G., *Org. Mass Spectrom* 1977, 12, 582.
- Olah, G.A., Schlosberg, R.H., Porter, R.D., Mo, Y.K., Kelly, D.P., and Mateescu, G.D., *J. Am. Chem. Soc.* 1972, 94, 2034.
- Olah, G.A., Mo, Y.K., *J. Am. Chem. Soc.* 1972, 94, 9241.
- Williams, D.H., and Hvistendahl, G., *J. Am. Chem. Soc.* 1974, 96, 6755.