Gas Phase Reactions of Protonated 1,3-Diphenylpropyne and Some Isomeric [C₁₅H₁₃]⁺ Ions

Gas Phase Reactions of Protonated 1,3-Diphenylpropyne and Some Isomeric $[C_{15}H_{13}]^+$ Ions

Wolfgang Bäther, Dietmar Kuck and Hans-Fr. Grützmacher†

Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse, D-4800 Bielefeld 1, FRG

Metastable (3-phenyl-2-propynyl)benzenium ions, generated by electron impact induced fragmentation from the appropriately substituted 1,4-dihydrobenzoic acid, react by loss of ˙CH₃ and C₆H₆. The study of deuterated derivatives reveals that hydrogen/deuterium exchanges involving all hydrogen and deuterium atoms precede the fragmentations. The results suggest a skeletal rearrangement by electrophilic ring-closure reactions giving rise to protonated phenylindene and protonated 9,10-methano-9,10-dihydroanthracene prior to the elimination of C₆H₆ and ˙CH₃, respectively. A study of isomeric $[C_{15}H_{13}]^+$ ions by collision-induced decomposition and by deuterium labelling shows that these ions interconvert by hydrogen migrations and skeletal rearrangements.

Previous studies[1,2] have shown that a fast interannular proton transfer occurs in ring-protonated α,ω-diphenylalkanes a which can be generated in a mass spectrometer by chemical ionization (CI) of α,ω-diphenylalkanes 1 (Scheme 1, route a) and by electron impact (EI) induced fragmentation of ω-phenylalkyl-1,4-dihydrobenzoic acids 2 (Scheme 1, route b), respectively. This proton transfer between both phenyl groups can be detected by the elimination of the isotopomers of benzene from metastable ions[3] in the first field-free region (1st FFR) and the second field-free region (2nd FFR) of a VG ZAB-2F mass spectrometer using compounds specifically labelled on one of the phenyl groups.
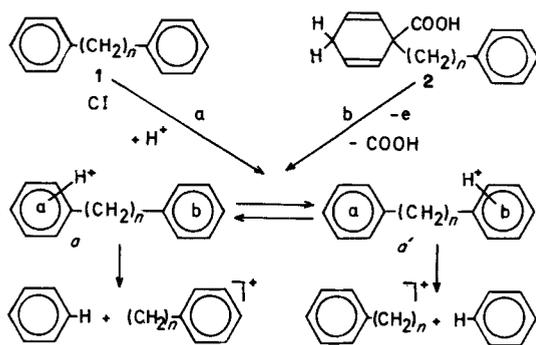
Scheme 1

In ω-phenylalkylbenzenium ions a with $2 < n < 20$, a complete mixing ('scrambling') of the 11 ring-protons occurs prior to fragmentation of the metastable ions, indicating that the rate of the H/D exchange reaction is at least 20 times faster than the elimination reaction.[2]

It has been shown that the proton transfer is inhibited in (trans-4-benzyl-cyclohex-1-yl)benzenium ions

† Author to whom correspondence should be addressed.

because the two phenyl groups can hardly approach each other.[2]

A similar steric effect is expected for the proton exchange reactions of protonated 1,4-diphenylbutyne and protonated 1,3-diphenylpropyne in which the two phenyl groups are kept apart by the alkynyl groups. However, the mass spectrometric reactions, especially of (3-phenyl-2-propynyl)benzenium ions (b), show effects which must be due to skeletal rearrangements in addition to proton exchange reactions. Here, we report the results of a study of these reactions of $[C_{15}H_{13}]^+$ ions.

RESULTS AND DISCUSSION

(3-Phenyl-2-propynyl)benzenium ions (b), of m/z 193 and specifically protonated at one of the phenyl groups, arise in the EI mass spectrum (see Fig. 1) of 1-(3-phenyl-2-propynyl)-1,4-dihydrobenzoic acid (3) by loss of the ˙COOH radical. The EI-induced decomposition of this compound as deduced from an investigation of metastable ions is shown in Scheme 2. In contrast to the 70 eV EI mass spectrum, the abundances of the ions m/z 116 and m/z 115 are very small in the mass-analysed ion kinetic energy (MIKE) spectrum[4] of the molecular ions of 3. The main reaction path of the metastable molecular ions is the loss of ˙COOH and the formation of (3-phenyl-2-propynyl) benzenium ions (b).

The MIKE spectrum of ions b (Fig. 2) shows peaks for the loss of H˙ (m/z 192), ˙CH₃ (m/z 178), C₂H₄/C₂H₅ (m/z 165/164) and C₆H₆ (m/z 115) from metastable ions in the 2nd FFR. The same reactions occur with similar relative rates in the 1st FFR as shown by a B/E linked-scan spectrum[5] of ions b. The deuterated ions b₁ and b₂, specifically labelled at the original phenyl group and at the methylene group of
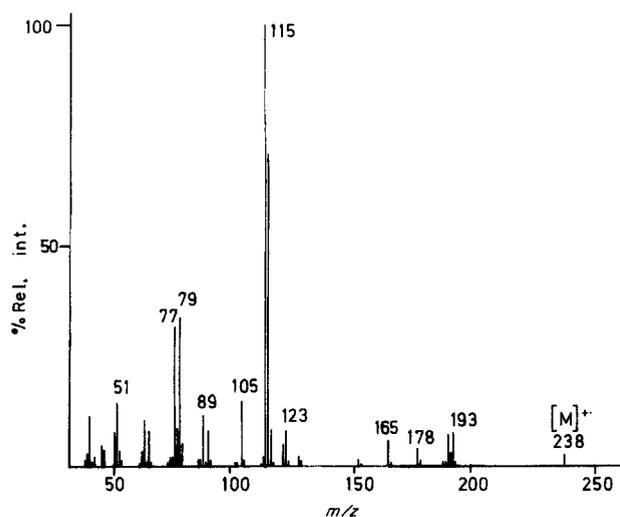
Figure 1. 70 eV mass spectrum of 1-(3-phenyl-2-propynyl)-1,4-dihydrobenzoic acid (3).

the carbon bridge, respectively (Scheme 3), lose all possible isotopomers of methyl and benzene in the 1st FFR and 2nd FFR. However, while these results indicate extensive H/D exchange reactions in metastable b_1 and b_2 ions the data of Table 1 show clearly that *complete scrambling* over all positions at the phenyl groups or of all hydrogen atoms *does not take place.*

The reactions of metastable (3-phenyl-2-propynyl)benzenium ions (*b*) differ from those of ω-phenylalkylbenzenium ions (a)[1,2] in three aspects: (i) Elimination of a C_6H_6 molecule dominates the fragmentation of ions *a* while ions *b* lose preferentially a ˙CH_3 radical. (ii) The hydrogen migrations occur in ions *a* only between the two rings whereas in ions *b* the hydrogen atoms of the bridge also participate in the hydrogen exchange. (iii) In contrast to ions *a* the hydrogen exchange in ions *b* does not result in a statistical distribution of the label over all ring-positions.

Nevertheless, the data of Table 1 prove that *both*
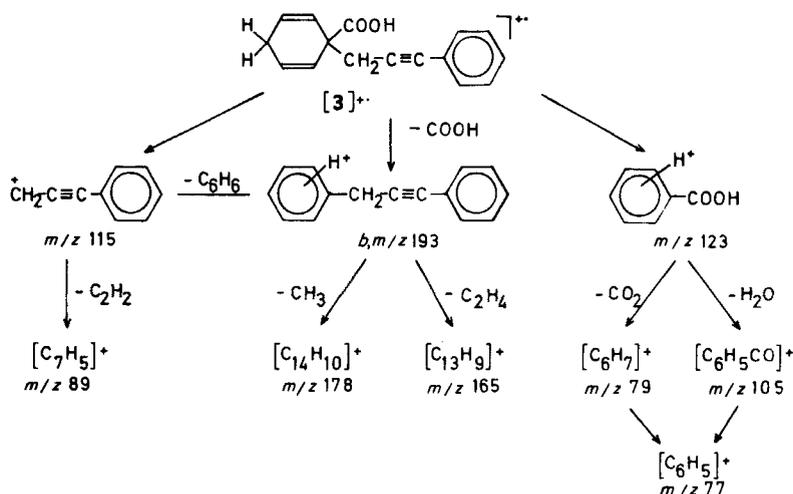
Scheme 2
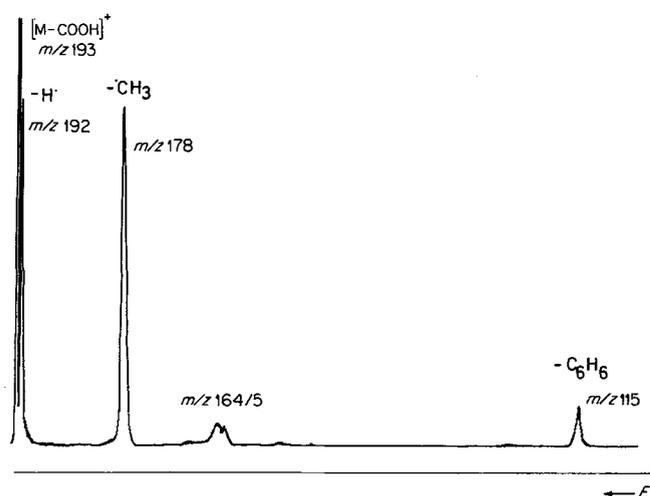

Figure 2. MIKE spectrum of (3-phenyl-2-propynyl)-1-benzenium ions *b* (from 3).

phenyl groups have become equivalent prior to the elimination of benzene. These results clearly indicate other rearrangement reactions besides hydrogen migration and can be accounted for by the reaction sequences shown in Schemes 4 and 5.
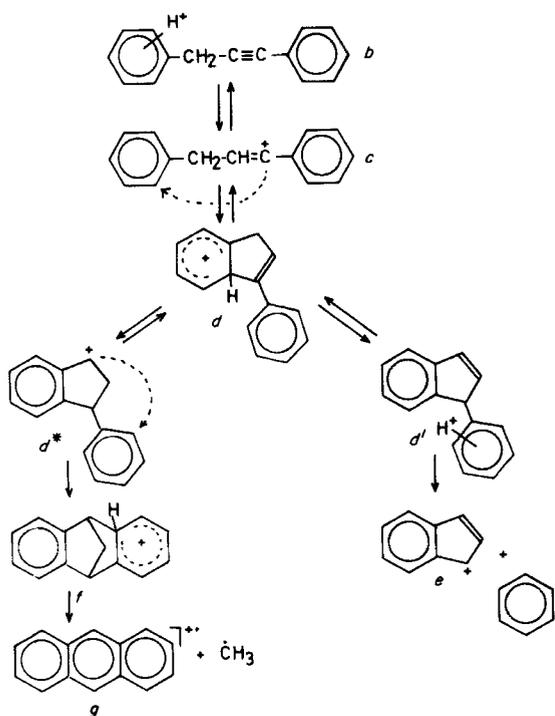
The first step in the rearrangement of ion *b* is a proton transfer to the central carbon atom (C(2))
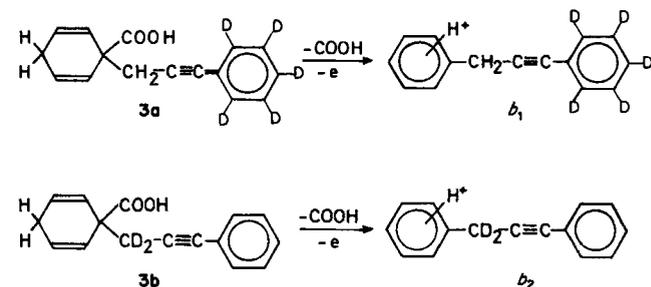
Scheme 3

Table 1. Relative abundances for the loss of isotopomers of benzene and methyl radical from metastable ions b_1 and b_2

Ion		$-C_6H_6$	$-C_6H_5D$	$-C_6H_4D_2$	$-C_6H_3D_3$	$-C_6H_2D_4$	$-C_6HD_5$	$-CH_3$	$-CH_2D$	$-CHD_2$	$-CD_3$
b_1	1st FFR	15	21	18	16	15	15	40	44	14	2
	2nd FFR	12	19	17	16	16	20	42	46	12	—
	Calc. for 6H/5D	0.2	6.5	32.5	43.3	16.2	1.3	12.1	45.4	36.4	6.1
	Calc. for 8H/5D	1.3	16.3	40.8	32.6	8.2	0.5	19.6	48.9	28.0	3.5
b_2	1st FFR	53	33	14	—	—	—	50	39	11	—
	2nd FFR	54	38	8	—	—	—	50	42	8	—
	Calc. for 11H/2D	26.9	53.9	19.2	—	—	—	57.7	38.5	3.8	1

Scheme 4

which is the most basic position of the hydrocarbon.[6] Formation of c from b is exothermic by about 69 kJ mol^{-1} (see Table 2 for the estimated heats of formation of relevant $[C_{15}H_{13}]^+$ ions). Electrophilic attack of the vinyl ion on the phenyl group[7] generates a protonated phenylindene ion d in which migration of the proton gives rise to d', d^* and other isomers prior
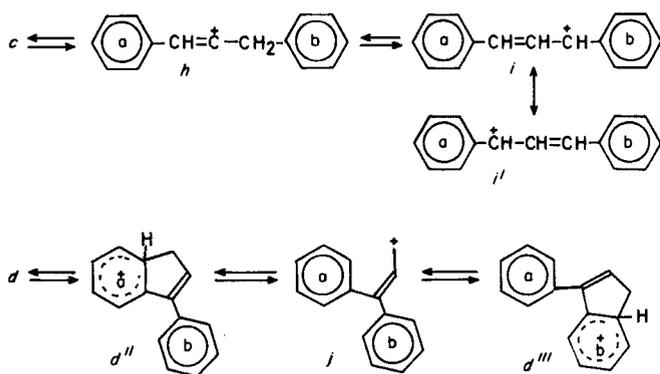
Scheme 5

to loss of a benzene molecule and formation of an indenyl ion e.[8,9a] A second intramolecular electrophilic substitution of the 3-phenylindanyl ion d^* leads to a protonated 9,10-methano-9,10-dihydro-anthracene ion f which decomposes to ionized anthracene g by loss of a methyl radical. Hence, the competition between loss of C_6H_6 and loss of CH_3 from metastable ions b can be explained by the formation of the stable product ions e and g. The heats of formation of the key intermediates of both fragmentation reactions, i.e. the protonated phenylindenes $d-d^*$ and the protonated 9,10-methano-9,10-dihydro-anthracene f, respectively, are below that of the educt ion b (Table 2) so that these intermediate ions are formed with excess energy, facilitating hydrogen exchange reactions via ions $d-d^*$.

A preceding hydrogen migration within the vinyl ion c gives rise to the 1,3-diphenylallyl ion i in which both phenyl groups are in equivalent positions because of the resonance structures[11] ($i \leftrightarrow i'$, Scheme 5). Thus, this hydrogen migration makes the phenyl groups equivalent prior to the ring closure to ion d. A second mechanism which equilibrates the phenyl groups after the ring-closure reaction consists of the hydrogen migration $d \rightarrow d''$ (Scheme 5) and the ring-opening/ring-closure reaction $d'' \rightarrow d'''$, via the 1,1-diphenylallyl ion j. A similar mechanism has been proposed for a phenyl migration in the phenyl-2-azaallyl cation.[9b]

The validity of the rearrangement reactions of $[C_{15}H_{13}]^+$ ions suggested in Schemes 4 and 5 can be tested by generating the various isomeric $[C_{15}H_{13}]^+$ ions independently. Assuming no isomerization prior to the fragmentations, the ions c, d^*, h and i are formed by the electron impact induced fragmentations shown in Scheme 6 from the precursors 4–7. Similarly, protonation of 8 and 9 in a chemical ionization experiment gives rise to ions $d\ddagger$ and f or their tautomers, respectively. The MIKE spectra of $[C_{15}H_{13}]^+$ ions generated by the reactions of Scheme 6 contain signals due to the losses of $\cdot H$, $\cdot CH_3$ and C_6H_6 which have also been observed for metastable ions b (Table 3).

Thus, all metastable $[C_{15}H_{13}]^+$ ions decompose by the same fragmentations. However, the relative abundances of the resulting fragment ions are different, and most of the $[C_{15}H_{13}]^+$ ions eliminate more C_6H_6 than does b. This can be attributed to differences in the excess energy of the $[C_{15}H_{13}]^+$ ions of different origins. The effect of different excess energies is clearly indicated by the different MIKE spectra of ions d^* and $d\ddagger$ which have been generated by electron impact induced fragmentation of 7 and by gas phase

Table 2. Estimated heats of formation, ΔH_f, of ions given in Schemes 4 and 5

Ion	$\Delta H_f(\text{kJ mol}^{-1})$
b	1139[b]
c	1070[c]
d[a]	~970[d]
d*	959[e]
e	1000[f,10e]
f	~960[g]
g	954[f,10d]
h	1133[h]
i	<1059[i]

[a] And tautomers. <1059[j]

[b] From ΔH_f ($C_6H_5CH_2C\equiv CC_6H_5$) = 426 kJ mol^{-1} (by increments[10a]) and PA ($C_6H_5CH_2C\equiv CC_6H_5$) = $PA(n\text{-}C_4H_7C_6H_5)$ = 815 kJ mol^{-1}.[10b]

[c] By isodesmic reaction using $\Delta H_f(C_6H_5C\equiv CH)$ = 327 kJ mol^{-1},[10d] $\Delta H_f(C_6H_5\overset{+}{C} = CH_2)$ = 971 kJ mol^{-1}[10b] and $\Delta H_f(C_6H_5CH_2C\equiv CC_6H_5)$ = 426 kJ mol^{-1}.[10a]

[d] From ΔH_f (3-phenylindene) = 256 kJ mol^{-1} (by increments[10a]; and PA(3-phenylindene) = PA(o-xylene) = 817 kJ mol^{-1}.[10b]

[e] By isodesmic reaction using $\Delta H_f(C_6H_5CH = CH_2)$ = 147 kJ mol^{-1},[10a] $\Delta H_f(C_6H_5\overset{+}{C}HCH_3)$ = 837 kJ mol^{-1}[10b] and ΔH_f (1-phenylindene) = 269 kJ mol^{-1} (by increments[10a]).

[f] With $\Delta H_f(C_6H_6)$ = 83 kJ mol^{-1}[10a] and $\Delta H_f(CH_3)$ = 142 kJ mol^{-1}[10a] the combined ΔH_fs of the fragmentation products are $(e + C_6H_6)$ = 1083 kJ mol^{-1} and $(g + CH_3)$ = 1096 kJ mol^{-1}, respectively.

[g] From ΔH_f(9,10-methano-9,10-dihydroanthracene) = 249 kJ mol^{-1} (by increments[10a]) and PA(o-xylene) = 817 kJ mol^{-1}.[10b]

[h] By isodesmic reaction using $\Delta H_f(CH_3CH = \overset{+}{C}CH_3)$ = 913 kJ mol^{-1},[10b] $\Delta H_f(C_6H_5CH_3)$ = 50 kJ mol^{-1},[10d] $\Delta H_f(C_2H_4)$ = 52 kJ mol^{-1},[10d] ΔH_f $(C_6H_5CH = CH_2)$ = 147 kJ mol^{-1}[10d] and $\Delta H_f(CH_4)$ = −75 kJ mol^{-1}.[10d]

[i] By isodesmic reaction using $\Delta H_f(C_6H_5\overset{+}{C}HCH_3)$ = 837 kJ mol^{-1},[10b] $\Delta H_f(C_6H_5CH = CH_2)$ = 147 kJ mol^{-1}[10a] and $\Delta H_f(CH_4)$ = −75 kJ mol^{-1}.[10d] The calculated value is an upper limit because of an additional stabilization by the vinyl group.
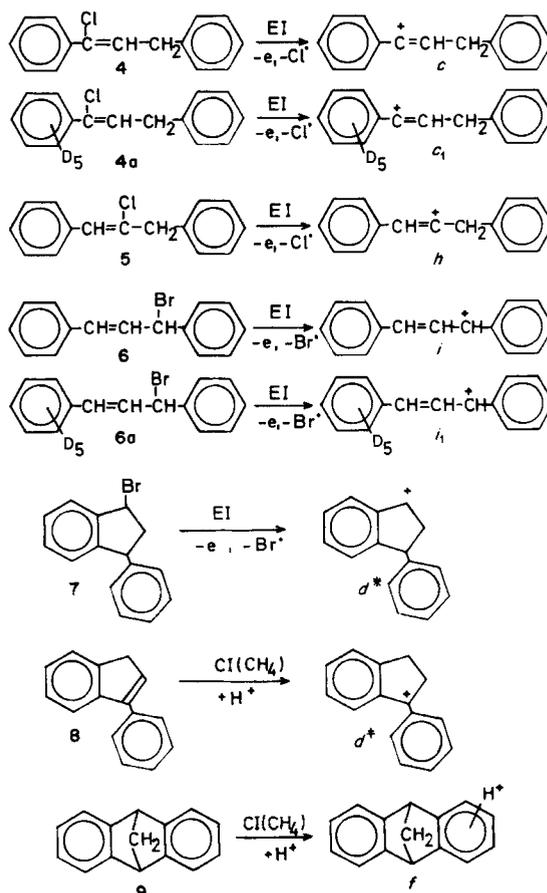
protonation of **8**, respectively (Scheme 6). Ions d^* and $d\ddagger$ interconvert by allowed hydride shifts and, hence, would be expected to give the same MIKE spectra. Similarly, the vinyl ions c and h interconvert by an allowed 1,2-hydride shift, but in spite of the expected equilibration between both structures the MIKE spectra of c and h are different (Table 3).

In agreement with this explanation the peak pattern produced by collisional induced decomposition (CID) of metastable $[C_{15}H_{13}]^+$ ions $c, d^*, d\ddagger, f, h$ and i (Scheme 6) in the CID/MIKE spectra are identical within the limits of error (Table 4).†

Although this result indicates an interconversion of the isomeric $[C_{15}H_{13}]^+$ ions according to the Schemes 4 and 5 *after collisional activation*, the isomerization reactions are obviously slow processes in metastable

† The loss of ·CH_3 and C_6H_6 from metastable $[C_{15}H_{13}]^+$ ions also occurs by CID which can be separated from the corresponding unimolecular reactions by applying a voltage to the collision cell. The intensity ratio −·CH_3/−C_6H_6 for the CID process is constant for ions $b, c, d', d\ddagger, f, h$ and i, in contrast to the behaviour of these ions during unimolecular fragmentations (Table 3).

Scheme 6

$[C_{15}H_{13}]^+$ ions because the H/D exchanges in the deuterated b_1 and b_2 ions have not reached the statistical distribution (Table 1). A similar effect is observed in the MIKE spectra of the deuterated vinyl ions c_1 and allyl ions i_1 (Scheme 6). Again the elimination of all isotopomers of methyl and benzene occurs, but the intensity distribution observed for the reactions of metastable ions in the 2nd FFR is far from the statistical values (Table 5).

It is of interest to note that the distribution of deuterium label in the reaction products of metastable ions c_1 and i_1 (Table 5) is identical, but different from that of metastable ions b_1 (table 1). A rapid equilibration $c \rightleftharpoons h \rightleftharpoons i$ (Scheme 5) puts both phenyl groups into identical positions. The subsequent reaction via ring closure to ions d and d' followed by elimination

Table 3. MIKE spectra of some $[C_{15}H_{13}]^+$ ions (Scheme 6)

Ion	−H·	−·CH₃	−C₆H₆
b	29	57	14
c	22	33	45
d*	24	47	29
d‡	30	56	14
f	25	50	25
h	17	33	50
i	42	26	32

Table 4. CID/MIKE spectra of some $[C_{15}H_{13}]^+$ ions (Scheme 6)[a]

Ion	$-H_2$	$-2 \times H_2$	$-CH_4$	$-C_2H_4$	$-C_3H_6$	$-C_4H_8$	$-C_5H_8$
b	44	14	6	22	7	5	2
c	46	15	5	20	7	5	2
d*	48	15	5	15	10	5	2
d‡[b]	~45	~15	~5	20	~10	~5	~1
f	34	11	1	25	16	8	3
h	45	16	5	20	8	4	2
i[b]	~35	~15	~5	~20	~15	~5	<5

[a] In % of total CID; error ±5%. The signals for loss of ·CH_3 and C_6H_6 are not included in the table.
[b] Large error because of very low intensity.

Table 5. Relative abundances for the loss of isotopomers of benzene and methyl in the MIKE spectra of ions c_1 and i_1

Ion	$-C_6H_6$	$-C_6H_5D$	$-C_6H_4D_2$	$-C_6H_3D_3$	$-C_6H_2D_4$	$-D_6HD_5$	$-CH_3$	$-CH_2D$	$-CHD_2$	$-CD_3$
c_1	6	23	13	9	12	37	22	59	18	1
i_1	7	25	11	9	11	37	22	57	19	2
Calc. for 8H/5D	1.6	16.3	40.8	32.6	8.2	0.5	19.6	48.9	28.0	3.5

of a benzene molecule without additional hydrogen migrations in the intermediate ions gives rise to the loss of C_6H_5D and C_6HD_5, respectively. This corresponds to the maxima of the intensity distribution for benzene elimination from metastable b_1, c_1 and i_1, but the distribution is more peaked for the latter two ions. This result shows that the isomerization $c \rightleftarrows h \rightleftarrows i$ by 1,2-hydride shifts is fast, and that there is less excess energy available for hydrogen migrations in the ions $c(c_1)$ and $i(i_1)$ formed by EI-induced fragmentation from the halides **4(4a)** and **6(6a)** than in those ions formed by an exothermic hydrogen migration from ions $b(b_1)$. The same conclusion follows from an analysis of the intensity distribution for the loss of the isotopomers of the methyl group. The formation of f (Scheme 4) from an equilibrium mixture $c \rightleftarrows h \rightleftarrows i$ via d and d^* without much hydrogen migration between both aromatic groups would result mainly in the loss of CH_2D in the case of the pentadeuterated ions which, indeed, is observed for the fragmentation of metastable ions c_1 and i_1. Therefore, the hydrogen migrations between the aromatic moieties of the protonated 1-phenylindene ions $d-d^*$ are slow compared to further fragmentations. This result is corroborated by the observation of a slow H/D exchange in protonated pentadeuterodiphenylmethane ions,[12] in contrast to the behaviour of the higher homologues of the ω-phenylalkylbenzenium ions.[2]

EXPERIMENTAL

Mass spectrometry

The mass spectrometric measurements were performed with a double focusing mass spectrometer VG-ZAB-2F equipped with a combined EI/CI ion source

using the following experimental conditions:

EI Electron energy, 70 eV; electron trap current, 50 μA; ion source temperature, c. 180 °C, accelerating voltage, 6 kV.

CI. Reagent gas, CH_4; electron energy, 100 eV; electron emission current, 100 μA, ion source temperature, c. 180 °C, accelerating voltage, 6 kV.

The reactions of metastable ions in the 1st FFR and 2nd FFR of this instrument were studied in the usual manner. CID/MIKE spectra were obtained by introducing He into the collision chamber of the 2nd FFR.

Synthesis of compounds

1-(3-Phenyl-2-propyn)-1,4-dihydrobenzoic acid (3). 3-Phenyl-2-propynyl bromide (b.p. 115–117 °C/12 Torr) was obtained in 48% yield from the corresponding alcohol by reaction with $Br_2/(C_6H_5)_3P$ in CCl_4.[13] Reductive alkylation of benzoic acid[2] by this bromide in liquid NH_3 yields **3**. M.p.: 115–116 °C; ^{1}H-NMR ($CDCl_3$): δ 10.68 (s, 1H), δ 7.17–7.35 (m, 5H), δ 5.94 (s, d, 4H), δ 2.80 (s, 2H), δ 2.69 (t, 2H).

Deuterated 1-(3-phenyl-2-propyn)-1,4-dihydrobenzoic acids (3a and 3b). The deuterated dihydrobenzoic acids **3a** and **3b** were synthesized by the same procedures as **3** using the appropriately labelled bromides. These bromides were obtained from the corresponding propinols. 3-Phenyl-d_5-2-propin-1-ol was prepared as follows: Phenyl-d_5-ethin was prepared from benzaldehyde-d_5 by a Wittig reaction with $(C_6H_3)_3\overset{+}{P}CH_3Br^-$ and addition of Br_2 to the resulting styrene-d_5 followed by base-catalysed elimination of HBr. Reaction of phenyl-d_5-ethin with EtMgBr followed by addition of CH_2O resulted in the 3-phenyl-d_5-2-propin-1-ol in a total yield of 19%. ^{1}H-NMR

showed no signals due to ^1H at the phenyl group. 3-Phenyl-2-propin-1-ol-1-d_2 was obtained from phenylpropiolic acid methyl ester by reduction with LiAlD$_4$ in ether (80%).

1-Chloro-1,3-diphenyl-1-propene (4), 3-bromo-1,3-diphenyl-1-propene (6)[15] and 9,10-dihydro-9,4-methanoanthracene (9)[16] were obtained as described in the literature. The corresponding phenyl-d_5-derivatives **4a** and **6a** were prepared by using C$_6$D$_5$MgBr during the synthesis.

2-Chloro-1,3-diphenyl-1-propene (5) (b.p. 134 °C/0.1 Torr) was obtained by reaction of PCl$_5$ with 1,3-diphenylacetone in benzene in 33% yield.

Acknowledgement

REFERENCES

1. D. Kuck, W. Bäther and H. F. Grützmacher, *J. Am. Chem. Soc.* **101**, 7154 (1979).
2. W. Bäther, D. Kuck and H. F. Grützmacher, *Org. Mass Spectrom.* **20**, 589 (1985).
3. For the mechanism of this benzene elimination, see W. Bäther and H. F. Grützmacher, *Int. J. Mass Spectrom. Ion Proc.*, in press.
4. R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, Amsterdam (1973).
5. K. R. Jennings, in *High Performance Mass Spectrometry: Chemical Application*, ed. by M. L. Gross, p. 3, ACS Symposium Series 70, American Chemical Society, Washington DC (1978).
6. (a) G. Melloni, G. Modena and U. Tonellato, *Acc. Chem. Res.* **14**, 227 (1981); (b) J. Catalan and M. Yanez, *J. Chem. Soc., Perkin Trans. 2* 1627 (1979).
7. Related electrophilic cyclization reactions are known from reactions in solution, see D. M. Dytnerski, K. Ranganayakulu, B. P. Singh and T. S. Sorensen, *Can. J. Chem.* **60**, 2933 (1982).
8. This reaction corresponds to the well-known dealkylation of protonated phenylalkanes, see (a) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.* **88**, 2621 (1966); (b) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.* **89**, 1047 (1967).
9. (a) The formation of indanyl ions from phenylalkenyl ions has been observed recently by H. Franke, W. Franke, H. Schwarz and H. Terlouw, *Int. J. Mass Spectrom. Ion Proc.* **57**, 233 (1984); (b) E. U. Würthwein, H. Halim, H. Schwarz and N. M. M. Nibbering, *Chem. Ber.* **115**, 2626 (1982).
10. (a) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Waugen, H. E. O'Neal, A. S. Rodgers, R. Shaw and R. Walsh, *Chem. Rev.* **69**, 279 (1969); (b) D. H. Aue and M. T. Bowers, in *Gas Phase Ion Chemistry*, ed. by M. T. Bowers, Vol. 2, Chapt. 9, Academic Press, New York (1979); (c) G. Bouchoux and J. Dagaut, *Org. Mass Spectrom.* **17**, 151 (1982); (d) H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data* **6**, Suppl. 1 (1977); (e) Y. Apeloig, W. Franke, Z. Rappoport, H. Schwarz and D. Stahl, *J. Am. Chem. Soc.* **103**, 2770 (1981).
11. In contrast to $c \rightleftharpoons h \rightleftharpoons i$ an interconversion of unsubstituted metastable allyl and 2-propenyl ions by 1,2-hydride shifts has not been observed: P. C. Burgers, J. L. Holmes, A. A. Mommers and J. E. Szulejko, *Org. Mass Spectrom.* **18**, 596 (1983).
12. D. Kuck, unpublished data.
13. L. Horner, H. Oediger and H. Hoffman, *Justus Liebigs Ann. Chem.* **626**, 26 (1959).
14. A. Zaki and Y. Iskander, *J. Chem. Soc.* 68 (1943)
15. R. Lespieau and R. Wakeman, *Bull. Soc. Chim. Fr.* **51**, 384 (1932).
16. W. R. Vaughan and M. Yoshimine, *J. Org. Chem.* **22**, 7 (1957).