

Short Communication

MASS SPECTROMETRIC INVESTIGATION OF ACETYLENIC COMPOUNDS. PART 29. ON THE GAS PHASE ISOMERIZATION OF PHENYL-SUBSTITUTED ALLYL AND VINYL CATIONS *

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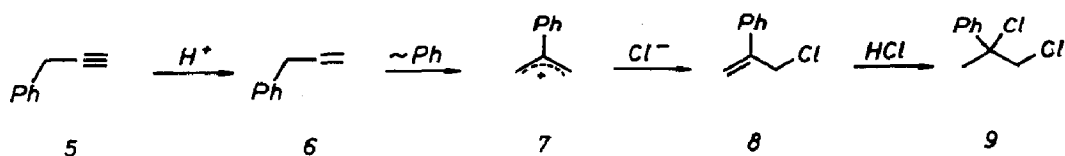
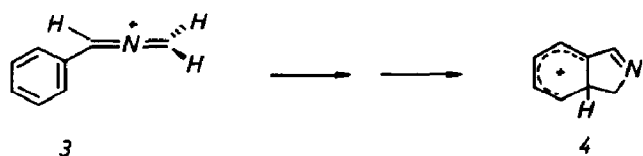
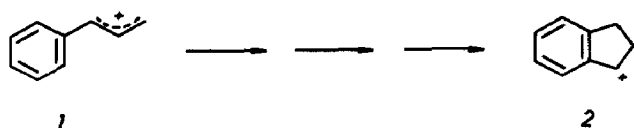
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A large number of stable alkyl-substituted allyl cations has been prepared and investigated in both super-acidic media [2] and in the gas phase [3]. In contrast, very few phenylallyl cations are known as stable species even at low temperature [4]. At first glance, this seems to be surprising since, in most other carbocations, phenyl groups have been shown to exhibit a greater stabilization effect than alkyl groups [5]. However, in contrast to alkylated allyl cations, phenylallyl cations can easily undergo intramolecular cyclization to the corresponding indanyl cations ($1 \rightarrow 2$; Scheme 1) which explains the difficulty in obtaining them as stable species. Similarly, the gas phase chemistry of phenyl-substituted 2-azaallenium ions, **3**, is characterized by intramolecular electrophilic substitution reactions ($3 \rightarrow 4$) [6]. It is also interesting to note that HCl addition to 3-phenylpropyne, **5**, affords 1,2-dichloro-2-phenylpropane [7]. This unexpected result is best explained by a 1,2-phenyl shift to the initially generated vinyl cation ($6 \rightarrow 7$) followed by chlorine capture and eventual addition of a second HCl molecule, thus resulting in the formation of **9** [7]. Combinations of 1,2-shifts and electrophilic substitutions seem to be unknown so far.

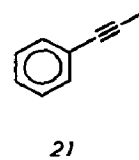
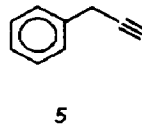
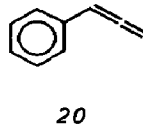
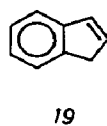
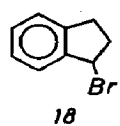
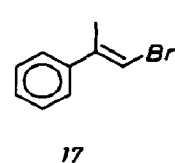
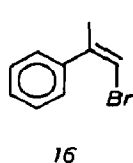
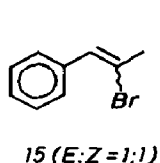
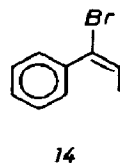
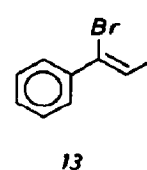
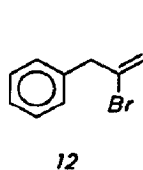
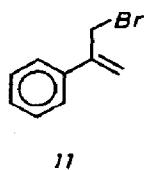
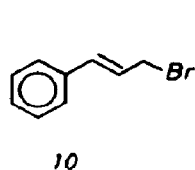
We report here on the gas phase chemistry of various phenyl-substituted allyl and vinyl cations [8], which were initially generated either via dissociative ionization (70 eV electron impact) of appropriately substituted bromohydrocarbons (**10–18**) or by protonation of cyclic olefins, allenes and

* For Part 28, see ref. 1.

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acetylenes, (5, 19–21) under the conditions of chemical ionization. The resulting $C_9H_9^+$ ions (m/z 117) were then subjected to collisional activation (CA) mass spectrometry [9]. All compounds are described in the literature and their syntheses were carried out by routine laboratory methods; purification was achieved by preparative gas chromatography and the structures were confirmed by NMR spectroscopy.



Inspection of the data displayed in Table 1 clearly shows that, within the experimental error, the CA mass spectra of the $C_9H_9^+$ ions are identical except for the ions generated on protonation of 1-phenylpropyne **21** (see m/z 102 and 76). The differences in the CA mass spectra of the $[MH]^+$ ion of **21** are more pronounced when the less exothermic $C_4H_9^+$ is used as Brønsted acid. We conclude that protonation of **21** mainly leads to the 1-phenyl-1-propene-1-yl cation because (i) the species generated should possess an intact methyl group which, on collisional activation, gives rise to the enhanced loss of CH_3 (i.e. formation of m/z 102) and (ii) molecular orbital calculations [8] clearly show that protonation at C-2 would result in the formation of a phenyl-substituted vinyl cation which is significantly more stable than the isomeric cation obtained by protonation of C-1.

TABLE 1

Collisional activation mass spectra of $C_9H_9^+$ ions (m/z 117) generated via dissociative ionization of bromohydrocarbons or protonation of hydrocarbons^{a,b}

Precursor	m/z										
	102	91	89	77	76	75	65	63	51	39	27
10	6.8	36	18	10		6.0	11	17	15	14	2.3
11	7.0	44	19	8.3		6.2	11	18	15	14	2.2
12	6.8	41	18	7.8		6.2	12	18	15	14	2.4
13	7.1	40	18	8.4		6.1	12	17	15	14	2.3
14 EI	6.7	43	19	9.0		6.0	12	18	14	14	2.0
15	7.0	41	18	8.8		5.9	11	18	15	14	2.2
16	6.8	44	19	8.5		6.1	12	18	14	14	2.1
17	6.9	40	19	8.4		6.0	12	18	15	13	2.2
18	6.3	34	18	7.7		6.5	12	18	15	14	2.3
19	5.9	24	18	7.8		6.5	11	19	15	14	2.5
20	7.3	25	17	8.3		6.6	11	18	15	14	2.4
5 Cl/H ₂	6.9	26	18	8.2		6.7	11	18	15	14	2.4
21	11	24	17	7.8	1.3	6.8	8.6	18	14	13	2.2
19	6.3	19	17	7.8		7.0	10	19	16	14	2.6
20	7.9	21	16	11		6.4	10	17	15	14	2.4
5 Cl/i-C ₄ H ₁₀	6.5	22	16	9.4		6.7	10	18	16	15	2.5
21	22	17	13	8.5	7.9	7.2	6.0	13	11	10	1.4

^a Data are expressed as $\Sigma_{27}^{102} = 100\%$. Not included in the normalization are the intensities for the m/z 91 ion which is also generated unimolecularly. The same applies for the fragment ions at m/z 116 and 115 which result from the loss of H and H₂ and whose relative intensities are not included in the table. Very weak signals of poorly reproducible abundance were observed for $C_9H_9^{2+}$, $C_9H_8^{2+}$ and $C_9H_7^{2+}$, respectively.

^b Measurements were carried out in the second field-free region of a Varian MAT 311A mass spectrometer. The data are the average of at least 150 scans.

In contrast, protonation of either **5** and **20** yields an ion whose CA spectrum is similar to that of protonated indene; the CA mass spectrum of protonated **19** is nearly independent of the Brønsted acid employed. We believe that protonation of **19** with $C_4H_9^+$ results exclusively in the formation of the indanyl cation **2** because the differences in proton affinities between *i*- C_4H_8 and **19** are ≤ 30 kJ mole⁻¹ [10]. Thus, we conclude that because the CA mass spectra of all the $C_9H_9^+$ ions are the same (except for **21**), both protonation of **5** and **20** as well as dissociative ionization of **10–18** result in the formation of **2**. This, of course, can only be achieved by both phenyl and hydrogen migrations combined with electrophilic substitution of the phenyl ring within the initially generated allyl- and vinyl-type cations. Although the mechanistic details of these skeletal rearrangements are unknown, we should like to mention that isomerization to indanyl-type ions is unlikely to take place in the molecular ions of **10–19**. This interpretation is supported by kinetic energy release (*T*) measurements (Table 2). It is interesting to note that the *T* values displayed in Table 2 are clustered around specific data depending on the nature of the C–Br bond. The smallest numbers (≤ 22 meV for $T^{0.5}$) are associated with Br loss from allyl-type precursors (**10**, **11** and **18**), intermediate numbers (~ 30 meV) are obtained from precursors **16** and **17** the dissociation of which would result in the initial formation of unstable primary vinyl cations, and the largest *T* values (~ 50 meV) are observed for the dissociation of the molecular ions of **12–15** which would lead to secondary vinyl cations. As the latter are known to be substantially more stable than primary vinyl cations [8], it is obvious that the *T* values cannot simply be explained in terms of an exothermic

TABLE 2

Kinetic energy release ($T^{0.5}$) data for Br loss from the molecular ions of **10–18**^a

Precursor	$T^{0.5}$ (meV)	<i>n</i> values at	
		20% peak height	50% peak height
10	13	2.0	2.0
11	22	1.9	2.1
12	53	1.6	1.7
13	57	1.6	1.7
14	50	1.6	1.8
15	56	1.5	1.8
16	28	1.7	1.8
17	30	1.6	1.7
18	20	1.9	2.0

^a The *T* values were determined by using a ZAB-2F mass spectrometer (second field-free region); data are not corrected for the main ion beam width.

isomerization of the incipient $[M-Br]^+$ ions. More subtle effects, which for the time being are not properly understood, seem to be operative.

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REFERENCES

- 1 G. Depke, M. Hanack, W. Hümmer and H. Schwarz, *Angew. Chem. Int. Ed. Engl.*, 22 (1983) 786.
- 2 N.C. Deno, in G.A. Olah and P.v.R. Schleyer (Eds.), *Carbonium Ions*, Vol. 2, Wiley-Interscience, New York, 1970, Chap. 18.
- 3 W. Franke, C. Wesdemiotis and H. Schwarz, *Z. Naturforsch. Teil B*, 36 (1981) 1315.
- 4 N.C. Deno, C.U. Pittmann, Jr. and J.O. Turner, *J. Am. Chem. Soc.*, 87 (1965) 2155. C.U. Pittmann, Jr. and W.G. Miller, *J. Am. Chem. Soc.*, 95 (1973) 2947. G.A. Olah and R.J. Spear, *J. Am. Chem. Soc.*, 97 (1975) 1539. G.A.G. Asensio and H. Mayr, *J. Org. Chem.*, 43 (1978) 1518.
- 5 G.A. Olah and P.W. Westerman, *J. Am. Chem. Soc.*, 95 (1973) 7530.
- 6 E.-U. Würthwein, H. Halim, H. Schwarz and N.M.M. Nibbering, *Chem. Ber.*, 115 (1982) 2626. J.C. Kleingeld, N.M.M. Nibbering, H. Halim, H. Schwarz and E.-U. Würthwein, *Chem. Ber.*, 116 (1983) 3877.
- 7 K. Vittinghoff and K. Griesbaum, *Tetrahedron Lett.*, (1981) 1889.
- 8 For an excellent presentation on the chemistry of vinyl cations, see P.J. Stang, Z. Rappoport, M. Hanack and L.R. Subramanian, *Vinyl Cations*, Academic Press, New York, 1979. For some aspects of the gas phase chemistry of these species, see Y. Apeloig, W. Franke, Z. Rappoport, H. Schwarz and D. Stahl, *J. Am. Chem. Soc.*, 103 (1981) 2770 and references cited therein.
- 9 For a most recent review on the principle and methodology of CAMS, including many references for its application, see K. Levsen and H. Schwarz, *Q. Rev. Mass Spectrom.*, 2 (1983) 77.
- 10 H.E. Audier, A. Milliet, M. Mruzek, J.P. Denhez, P. Dizabo and C. Schaal, *Can. J. Chem.*, 59 (1981) 968. H. Meot-Ner (Mautner), *J. Am. Chem. Soc.*, 104 (1982) 5.