to β–γ transformation rigorously follows the Berry mechanism with O(7) and O(7′) acting as "pivots".

Even though the α–γ and β–γ structures are constitutionally identical, differing only in configuration at Mo(a) and Mo(a′), we have included the γ structure in Figure 2 since it is a fragment of the $Mo_{10}O_{34}{}^{8-}$ and $(Mo_8O_{27}{}^{6-})_\infty$ structures found in the compounds $(NH_4)_8Mo_{10}O_{34}$[12] and $(NH_4)_6Mo_8O_{27}\cdot 4H_2O$,[13] respectively. The formation of these compounds, which occurs in acidified aqueous molybdate solutions, can readily be accounted for by the present mechanistic scheme. If $MoO_4{}^{2-}$ ions attack the Mo(a) and Mo(a′) centered trigonal bipyramids on the O(2)–O(8) and O(2′)–O(8′) edges in the α–γ structure or the O(1)–O(11) and O(1′)–O(11′) edges in the β–γ structure, the $Mo_{10}O_{34}{}^{8-}$ structure is generated. Either analogous attack by hydroxyl ions followed by proton transfer and polycondensation or hydroxyl attack on the O(2)–O(7) and O(2′)–O(7′) edges in the α–γ structure followed by polycondensation leads to the $(Mo_8O_{27}{}^{6-})_\infty$ structure.

These speculations, however, can be rendered meaningful only by experimental data regarding aqueous solution structures. Preliminary infrared spectroscopic data of concentrated aqueous sodium and ammonium molybdate solutions thus far rule out the α-$Mo_8O_{26}{}^{4-}$ structure as a major component at pH 3–4 (see Figure 1h). We are currently measuring infrared, Raman, and ^{17}O NMR spectra of aqueous molybdate species as a function of pH, counterion, temperature, and concentration, and hope to be able to better define their structural and dynamic characteristics.

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References and Notes

(1) The earliest evidence for $Mo_8O_{26}{}^{4-}$ isomerism was presented in an infrared study by M. J. Schwing-Weill and F. Arnaud-Neu, *Bull. Soc. Chim. Fr.*, 853 (1970).

(2) For the structure of α-$Mo_8O_{26}{}^{4-}$ see (a) J. Fuchs and H. Hartl, *Angew. Chem., Int. Ed. Engl.*, **15**, 375 (1976), (b) M. F. Fredrich, V. W. Day, W. Shum, and W. G. Klemperer, American Crystallographic Association, Summer Meeting, 1976, paper M5.

(3) For the structure of β-$Mo_8O_{26}{}^{4-}$ see (a) L. O. Atovmyan and O. N. Krasochka, *J. Struct. Chem.*, **13**, 319 (1972); (b) I. Lindqvist, *Ark. Kemi*, **2**, 349 (1950).

(4) This compound has incorrectly been reported as $[(CH_3)_4N]_2Mo_8O_{25}\cdot 5H_2O$ by J. Fuchs, I. Knöpnadel, and I. Brüdgam, *Z. Naturforsch. B*, **29**, 473 (1974).

(5) We have been unable to reproduce preparations of the anhydrous compounds $[R_4N]_4Mo_8O_{26}$, R = C_2H_5 and C_3H_7, reported by Fuchs et al., in ref 4.

(6) The identical compound was reported by Fuchs et al., in ref 2a and 4.

(7) Satisfactory elemental analyses were obtained for all compounds reported here. Structures were assigned by Raman and infrared spectroscopy.

(8) We do not understand the reasons for this shift in the equilibrium. Selective ion pairing is a possibility, and conductivity measurements in acetonitrile show that **1** behaves as a 3:1 electrolyte and **2** behaves as a 4:1 electrolyte.

(9) Although we have observed the isomerization of **2** in acetonitrile solutions prepared from dried solvent and compound, it is of course impossible to rule out the presence of traces of water. We are currently performing ^{18}O labeling experiments which may rule out a hydrolytic mechanism.

(10) See K. H. Tytko, *Z. Naturforsch. B*, **31**, 737 (1976), and references therein.

(11) J. W. Linnett, *J. Chem. Soc.*, 3796 (1961).

(12) J. Fuchs, H. Hartl, W. D. Hunnius, and S. Mahjour, *Angew. Chem., Int. Ed. Engl.*, **14**, 644 (1975).

(13) I. Böschen, B. Buss, and B. Krebs, *Acta Crystallogr., Sec. B*, **30**, 48 (1974).

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Formation of Ethylenebenzenium and Protonated Benzocyclobutene, but Not α-Phenylethyl, Cations from the Ionization of Gaseous β-Phenylethyl Halides[1,2]

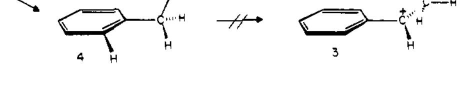
Sir:

Solution ionization and solvolysis studies of a wide variety of β-arylethyl systems have indicated the intermediacy of both ethylenarenium and α-arylethyl ions. The recent definitive study by Olah and Porter[3] of the ionization of β-phenylethyl chloride (**1-Cl**) in superacid medium gives detailed NMR evidence for the formation of the ethylenebenzenium (**2**) and α-phenylethyl (**3**) cations in proportions ranging from 1:2 to 10:1, with the β-ethylphenyl ion (**4**) as the proposed intermediate[3,4] (see Scheme I). Although this medium should minimize solvent effects, we find that the unimolecular decomposition of gaseous **1-Cl** (and n-propylbenzene, **1-CH$_3$**) ions produces negligible amounts of either **2** or **3** as stable (lifetimes $>10^{-5}$ s) ionic products, yielding instead a protonated benzocyclobutene ion (**5**)[6,7] and an unknown ion (X); X appears to be formed by the isomerization of **2** or **5**. In contrast, ionization of β-phenylethyl bromide and iodide (**1-Br, –I**) yields **2** and X.

These conclusions are based on collisional activation (CA) mass spectra[8] of the product ions. A preliminary communication[5] on **1-Br** reported the formation of **2** at low electron energies, but erroneously interpreted the high energy results as evidence for the formation of **3** and **4**. Our present conclusions are based on data obtained from improved CA instrumentation[9] of substantially higher resolution, sensitivity, and precision. The new CA data show no evidence at any ionizing energy for greater loss of $C^\beta H_2$ than $C^\alpha H_2$, which would be expected for **4**.[10] Also the better-resolved CA spectrum of **3** generated from α-phenylethyl bromide shows substantial quantitative differences in comparison to any of the CA spectra of any other of the $C_8H_9{}^+$ isomers studied.[11,12]

Variation of the CA peak abundances (Figure 1) with change of the electron energy used in forming the $C_8H_9{}^+$ ions gives strong evidence that only binary mixtures of $C_8H_9{}^+$ isomers are formed from ionization of **1** with 70 eV electrons; **1-Cl** and **1-CH$_3$** give 20:80 and 40:60 mixtures of **5**:X, respectively, and **1-Br** and **1-I** give 25:75 and 30:70 of (presumably) **2**:X, respectively. The CA spectra of the $C_8H_9{}^+$ ions formed at low energies indicate a single isomer, those from **1-Cl** and **1-CH$_3$** matching closely that from $C_8H_9{}^+$ ions formed by ion source protonation of benzocyclobutene, **5**.[6] No compound could be obtained for the unequivocal generation of **2**, but this appears to be the most logical structure for the $C_8H_9{}^+$ ions formed from **1-Br** and **1-I** at low energies. The equivalence of the α- and β-carbons[8] is consistent with structure **2**, and the value of $[-CH_2]/[-CH_3]$ is far greater than that in the CA spectrum of any other $C_8H_9{}^+$ isomer studied. In fact, the spectra of none of these isomers (o-, m-, and p-methylbenzyl,

Scheme I



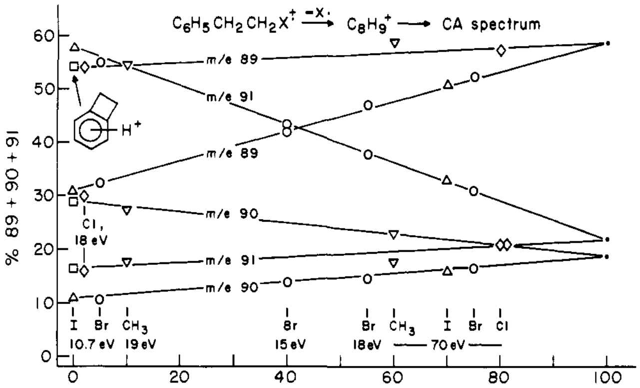


Figure 1. Relative abundances of the *m/e* 89, 90, and 91 peaks in the CA spectra of $C_8H_9^+$ ions produced at various ionizing electron energies from **1-Cl**, **1-CH$_3$**, **1-Br**, **1-I**, and **5**, plotted assuming that only binary mixtures of **2** and X, or of **5** and X, are formed.

methyltropylium, homotropylium, *o*- and *p*-ethylphenyl, and *m*- and *p*-dimethylphenyl)[12] fit any data combination of Figure 1. The CA spectrum of X, although very different than that of **2**, shows the same equivalence of the α- and β-carbons,[10] and thus could instead be **2**. Although $C_8H_9^+$ isomers other than **2** or **5**[6] have this equivalence, an attractive possibility is that X results from the isomerization of excited ions formed initially as either **2** or **5**.[13]

A possible explanation for the rather dramatic difference in behavior of **1-Cl** and **1-CH$_3$** vs. that of **1-Br** and **1-I** is shown in Scheme I. Except for **1-I**, their normal mass spectra show $[C_7H_7^+] \gg [C_8H_9^+]$, presumably because the activation energy for simple cleavage at the β-bond is greater than that at the benzylic α-bond. Thus β-cleavage (loose activated complex) is only competitive at higher energies, where the initially formed **4** ions would have sufficient energy to cyclize to excited **2**[4] or **5** ions which would isomerize to X in $<10^{-5}$ s. The formation of stable **2** and **5** ions in competition with $C_7H_7^+$ at low energies would involve anchimeric assistance,[5,14] formation of **5** possibly favored for the β-loss of Cl and CH_3 because these are smaller groups (so that there is less steric hindrance from the *o*-H atom), and formation of **2** for the β-loss of Br due to the smaller bond dissociation energy. For **1-I**, $[C_7H_7^+]/[C_8H_9^+] = 0.2$; the low energy for direct C–I cleavage could produce **2** ions in this manner which do not isomerize to X, but possibly the large iodine atom interferes with the anchimeric-assisted formation of both **2** and **5**. Further theoretical calculations[4] of the energy and entropy requirements should be helpful in resolving this problem.[15] These results provide a further illustration of the utility of gas phase studies in elucidating reaction pathways under truly nonsolvolytic conditions.

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References and Notes

(1) Collisional Activation and Metastable Ion Characteristics. 52.

(2) Part 51: B. Van de Graaf and F. W. McLafferty, *J. Am. Chem. Soc.*, submitted.

(3) G. A. Olah and R. D. Porter, *J. Am. Chem. Soc.*, **93**, 6877 (1971), and references cited therein.

(4) W. J. Hehre, *J. Am. Chem. Soc.*, **94**, 5919 (1972); Dr. Hehre's constructive scepticism of our evidence[5] for the stability of **4** was an important incentive for these further studies.

(5) N. M. M. Nibbering, T. Nishishita, C. C. Van de Sande, and F. W. McLafferty, *J. Am. Chem. Soc.*, **96**, 5668 (1974).

(6) Benzocyclobutene protonated at any ring position should undergo rapid interconversion between the possible arenium isomers, which are designated here generally as **5**. Protonated 5,8-dimethyltetralin undergoes rapid equilibration between two equivalent forms: D. M. Brouwer, C. MacLean, and E. L. Mackor, *Discuss. Faraday Soc.*, **39**, 121 (1965).

(7) Olah suggested the possible formation of **5** from **1-Cl**, but found no evidence for this.[3]

(8) F. W. McLafferty, P. F. Bente, III, R. Kornfeld, S.-C. Tsai, and I. Howe, *J. Am. Chem. Soc.*, **95**, 2120 (1973); F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente, III, S.-C. Tsai, and H. D. R. Schuddemage, *ibid.*, **95**, 3886 (1973).

(9) T. Wachs, C. C. Van de Sande, P. F. Bente, III, P. P. Dymerski, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, accepted; measurements were made on a reversed-geometry double-focusing mass spectrometer, ion accelerating potential 7.8 kV.[1] The data are computer averaged composites of at least 15 separate scans. The $C_8H_9^+$ ions from $C_6H_5CHBrCH_3$ show CA peaks at *m/e* 89, 90, and 91 of 51%, 29%, and 20%. Labeled compounds were made by standard procedures (isotopic enrichments: ^2H, >99%; ^{13}C, 90%).

(10) The CA spectra of **1-Br-α,α-d_2** and **β,β-d_2**, and of **1-Br-α-^{13}C** and **-β-^{13}C**, are identical (±1% absolute) at ionizing electron energies of 10.7, 12, 14.7, 17.7, and 70 eV, and show that the α- and β-carbons are mainly involved in the losses of CH_2, CH_3, and CH_4.

(11) The CA spectrum of **3** does have an *m/e* 91 peak; formation of this peak is unusual in requiring ~20 eV activation energy, shifting it to lower masses by ~0.5 units in the earlier study so that it was not recognizably resolved from the larger *m/e* 90. The doubled ion accelerating voltage of this study not only increases the resolution but halves the mass shift from the 20 eV kinetic energy loss. The CA spectrum of $C_8H_9^+$ ions from **3-β-^{13}C** shows that none of its CH_2 loss involves the β-carbon; that of **3-α-^2H** shows that $\lesssim 17\%$ (less because some H scrambling occurs) involves the α-carbon. However, that of **1-Br** shows ~90% of the CH_2 loss involves the α- and β-carbons, indicating the formation of $\lesssim 12\%$ **3**.

(12) A detailed study of 13 $C_8H_9^+$ isomers has been made: C. Köppel, C. C. Van de Sande, N. M. M. Nibbering, T. Nishishita, and F. W. McLafferty, *J. Am. Chem. Soc.*, in press.

(13) X could be the *exo*-cyclopropanonorbornenyl ion; the CA spectrum of the $C_8H_9^+$ ions from 5-methylenenorbornene correspond to a 1:2 mixture of X and methyltropylium ions, although a mixture of the latter, **3**, and methylbenzyl also fits within experimental error.

(14) Ionization efficiency data for **1-Cl** and **1-Br** show appreciable $C_8H_9^+$ formation near the appearance potential for $C_7H_7^+$.

(15) The α- and β-methyl-β-phenylethyl chlorides show very similar behavior, producing $C_9H_{11}^+$ ions giving identical CA spectra. The isomer produced at low electron energies could be the homolog of **2** or **5**: an additional isomer is indicated at high energies.

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