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Dissociative Ionization of Aryl-Substituted Vinyl Bromides in the Gas Phase: Experimental and Computational Evidence for the Formation of Stable α-Arylvinyl Cations both by Direct Means and Spontaneous Exothermic Isomerization of Unstable Isomeric Ions

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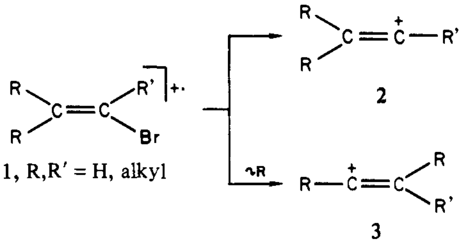
Abstract: The kinetic energy release T which accompanies the Br· loss from ionized (E)- and (Z)-β-bromostyrenes (**5** and **6**) in the gas phase is higher by 0.7 ± 0.03 kcal mol^{-1} than that from the molecular ion of α-bromostyrene (**4**). Together with both collisional activation (CA) spectra and MO calculations this is interpreted as evidence for the direct formation of the α-phenylvinyl cation **7** from **4**$^{+\cdot}$ and exothermic isomerization of the incipient [M − Br]$^+$ species formed from **5**$^{+\cdot}$ and **6**$^{+\cdot}$. Except for collision-induced CH$_2$ loss, the CA spectra of the C$_8$H$_7^+$ ions formed from **4**$^{+\cdot}$, **5**$^{+\cdot}$, and **6**$^{+\cdot}$ and by chemical ionization of phenylacetylene are nearly identical. In the collision-induced methylene loss from the C$_8$H$_7^+$ ions derived from α- and β-^{13}C-labeled **4** and **5**, C$_\alpha$ contributes 21.5% and C$_\beta$ 78.7% starting from **4**, but C$_\alpha$ contributes 29.9% starting from **5**, indicating a partial degenerate isomerization prior to the CH$_2$ loss. The various possible cationic intermediates from the dissociative ionization of **4**–**6** and the pathways connecting them were investigated computationally by MINDO/3 and ab initio methods. Only **7** and the phenyl-bridged ion **9** are stable species, while the β-phenylvinyl cation **11** rearranges without activation energy via the hydrogen-bridged ion **10** to **7**. The corrected STO-3G calculated relative energies in kcal mol^{-1} are (**7**) 0, (**9**) 16, (**10**) 25, and (**11**) 42. The calculated barriers for the **11** → **9** and the **7** → **9** rearrangements are 4.4 and 32 kcal mol^{-1}. MINDO/3 calculations show that p-OH and p-Me substituents have little effect on the energy differences between the α-aryl and the aryl-bridged vinyl cations. The T values associated with Br· loss from M$^{+\cdot}$ of (E)-β-bromo-2,6-, -2,5-, and -3,5-dimethylstyrenes are on the average 0.43 kcal mol^{-1} higher than from the α-bromo analogues, indicating a similar isomerization to the more stable α-arylvinyl cations. The T value for Br· loss from M$^{+\cdot}$ of 2,2-dianisyl-1-phenylvinyl bromide (**25**) is 0.23 kcal mol^{-1} higher than that for M$^{+\cdot}$ of (E)- and (Z)-1,2-dianisyl-2-phenylvinyl bromides (**23** and **24**). Similar results are obtained for the 2,2-dianisyl-1-tolylvinyl and (Z)-1,2-dianisyl-2-tolylvinyl bromides (**27** and **26**). Exothermic isomerization of the α-phenyl and α-tolylvinyl cations to the α-anisylvinyl cations **28** and **29** is corroborated by CA spectra of the [M − Br]$^+$ ions. The loss of the An$_2$C$^{+\cdot}$ fragment from these ions is ascribed to a competition between the direct, collision-induced high-energy dissociation of **28** and **29**, with a β-aryl rearrangement prior to decomposition. Similarities and differences between the reactions of the vinyl cations in the gas and the condensed phase are discussed.

Many intrinsic properties of ions can be examined advantageously in the gas phase.[2] For example, the number and structures of ionic species capable of existing in significant minima on the potential energy surface can be revealed by collisional activation (CA) mass spectrometry.[3] Complementary information may be obtained from the kinetic energy release, T, which accompanies unimolecular dissociation of a metastable ion of interest.[2a,b,3d,4] The shape of these metastable peaks constitutes a "direct picture" of what happens when dissociation takes place. As has been shown for several systems, when ions lose a neutral X (X = Br·, CO, CH$_2$O, or H$_2$O) to form a carbenium ion R$^+$, exothermic isomerization of the incipient caton is indicated by an increase in the kinetic energy release, ΔT.[4,5] This increase which can be coveniently measured for metastable ion decompositions (ion lifetime ca. 10^{-5} s), occurring in one of the field-free regions of a double-focusing mass spectrometer, arises because part of the potential energy liberated upon exothermic isomerization of the incipient cation is partitioned into the bond which is finally broken in the dissociation step. Such data are not accessible from solution experiments since collisions lead to a rapid dissipation of any released kinetic energy. Moreover, intermolecular reactions may occur even at low temperature in condensed phase, preventing in many cases the detection of stable ionic species.[6]

Scheme I



1, R,R' = H, alkyl

2

3

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Table I. Kinetic Energy Release (*T*) For ^{79}Br· Loss from Ionized α- and β-Bromostyrenes and Triarylvinyl Bromides[a]

compd	*T*, kcal mol^{-1}	compd	*T*, kcal mol^{-1}	Δ*T*
4	0.51	5	1.23	0.72, *T*(5) − *T*(4)
		6	1.18	0.67, *T*(6) − *T*(4)
13	0.38	14	0.78	0.40, *T*(14) − *T*(13)
15	0.60	16	1.03	0.43, *T*(16) − *T*(15)
17	0.83	18	1.28	0.45, *T*(18) − *T*(17)
23	0.97	25	1.20	0.23, *T*(25) − *T*(23)
24	0.96			0.24, *T*(25) − *T*(24)
26	0.95	27	1.17	0.22, *T*(27) − *T*(26)

[a] The kinetic energy release data were derived from the metastable peak width at half-height with the use of Beynon's equation.[11d] The spectra were recorded employing the MIKES methodology.[11]

The existence of vinyl cations as intermediates in solvolysis reactions or electrophilic additions to allenyl or triple bonds in solution is now well established.[7] However, direct spectroscopic evidence for their existence in solution was achieved only in a very limited number of cases.[8] Experimental data for *gaseous* vinyl cations is more limited,[4b,9] but their energies and structures can only be obtained by MO calculations. A large number of substituted vinyl cations have already been investigated computationally.[10]

In this paper we report results of gas-phase experiments on the dissociative ionization of α- and β-aryl-substituted vinyl bromides (1). The solvolysis of these compounds was investigated extensively.[7i,m] Under electron impact the vinyl bromides form the vinyl cations; and we demonstrate that cleavage of the C–Br bond in $1^{+\cdot}$ does not always give the skeletally unrearranged ion **2**. Depending on the α-substituent R′, the unimolecular loss of Br from ionized **1** may be accompanied by migration of R across the double bond to give the rearranged ion **3** (Scheme I). This study is supplemented by both ab initio and MINDO/3 calculations. The gas-phase results are briefly compared with the solvolysis-rearrangement data in solution.

Scheme II

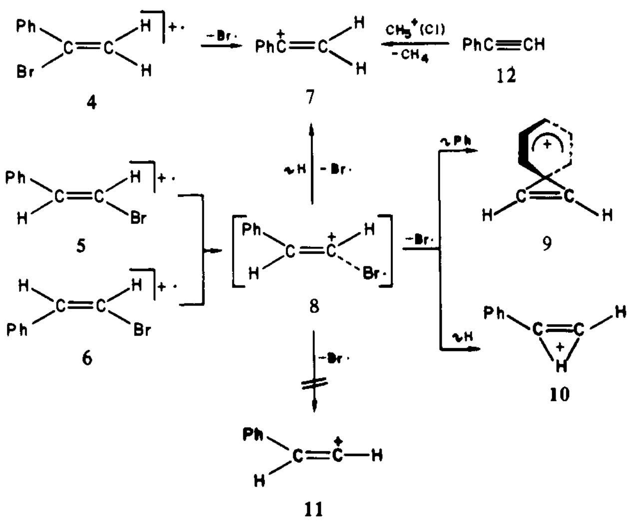

Table II. CA Spectra of the $C_8H_7^+$ Ions Formed from Several Precursors[a]

fragment ions	*m/z*	$C_8H_7^+$ precursor: PhC(Br)=CH$_2^{+\cdot}$ (4)	$C_8H_7^+$ precursor: (*E*)-PhCH=CHBr$^{+\cdot}$ (5)[b]	$C_8H_7^+$ precursor: PhC≡CH (12) + CH$_5^+$
$C_8H_n^+$	102	(247)	(200)	(250)
	101	12	12	12
	89	4.8	2.7	4.8
	88	0.5	0.5	0.5
$C_7H_n^+$	87	2.6	2.5	2.5
	86	1.2	1.0	1.1
	85	0.4	0.4	0.4
	77	(115)	(142)	(117)
$C_6H_n^+$	76	(31)	(32)	(34)
	75	14	15	14
	74	9.9	11	10
	64	0.4	0.4	0.4
$C_5H_n^+$	63	8.2	8.6	8.3
	62	4.3	4.5	4.4
	61	1.6	1.6	1.6
	53	0.5	0.4	0.5
	52	4.8	5.0	4.9
$C_4H_n^+$	51	15	15	15
	50	15	14	15
	49	1.4	1.5	1.5
	39	1.9	1.7	1.8
$C_3H_n^+$	38	1.1	1.0	1.1
	37	0.9	0.7	0.9
$C_2H_n^+$	27	0.2	0.2	0.2
	26	0.2	0.2	0.2

[a] The spectra were recorded with use of the "linked B/E scan" technique.[13] The relative abundances are given in percent and are normalized to a total of 100 units over the *m/z* range 26–102. Excluded from the normalization procedure are those fragment ions which are also formed unimolecularly and whose relative intensity may be dependent upon the energy distribution function.[3] The data for these fragments are given in parentheses. [b] The CA spectrum of the [M − Br]$^+$ ion from 6 is identical with that for 5, except that the intensity of the *m/z* 89 ion is 3.3%.

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(6) The case of the 2-adamantyl cation can be taken as an example. The only adamantyl cation detected so far in solution is the 1-adamantyl cation; there is no experimental indication for the existence of 2-adamantyl cation despite a substantial barrier for the isomerization 2-adamantyl → 1-adamantyl cation. In the gas phase, however, both species were recently identified as stable cations. See: (a) Wesdemiotis, C.; Schilling, M.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.*, **1979**, *18*, 950. (b) Houriet, R.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 951.

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Table III. Collision-Induced $^{13}CH_2$ Loss from $[M-Br]^+$ Ions Formed from ^{13}C-Labeled α- and β-Bromostyrenes 4 and 5

	PhBr-$^{13}C=CH_2$ (α-^{13}C)-4	PhBr-$C={}^{13}CH_2$ (β-^{13}C)-4	PhH-$^{13}C=CHBr$ (α-^{13}C)-5	PhH-$C={}^{13}CHBr$ (β-^{13}C)-5
$^{13}CH_2$ loss[a]	20.3	74.9	28.3	66.6
% methylene loss from the side chain	95.2		94.9	
% contribution of				
C_α	21.3		29.9	
C_β	78.7		70.1	

[a] Expressed in percent of $({}^{13}CH_2/{}^{13}CH_2 + {}^{12}CH_2)$ loss. The ^{13}C incorporation in the molecular ion is 91%. A correction for the contributions of the remaining unlabeled 9% of the $[M-Br]^+$ ions to CH_2 loss is not necessary in the MIKES method.[11]

Results and Discussion

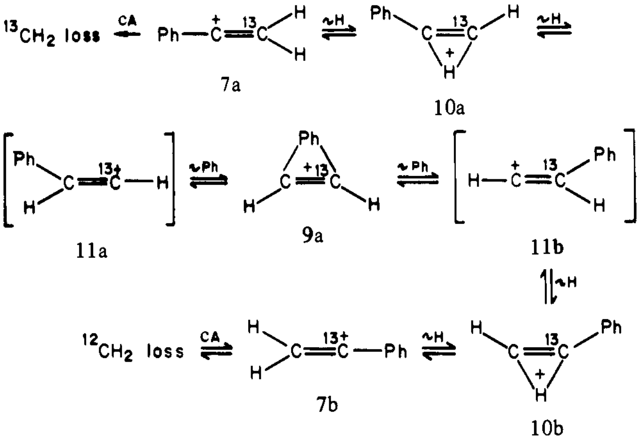
α- and β-Bromostyrenes. The values of the kinetic energy release (*T*) which accompanies Br· loss from ionized α-bromostyrene (4) and (*E*)- and (*Z*)-β-bromostyrenes (5 and 6, respectively) are given in Table I.

The differences in the *T* values rule out an equilibration of the molecular ions of α- and β-bromostyrenes prior to Br· loss. The loss of Br· from $4^{+}\cdot$ is characterized by a significantly smaller kinetic energy release than the analogous dissociations of $5^{+}\cdot$ and $6^{+}\cdot$ which show broader metastable peaks. Consequently, in line with theory and the current interpretation of kinetic energy release values,[2a,b,3d,4,5] the molecular ion of 4 undergoes simple C–Br bond cleavage to the α-phenylvinyl cation 7. In contrast, the substantially larger *T* values ($\Delta T = 0.72$ and 0.67 kcal mol^{-1}, respectively) associated with Br· elimination from $5^{+}\cdot$ and $6^{+}\cdot$ compared with $4^{+}\cdot$ suggest that this process is accompanied by an exothermic isomerization of the dissociating $[M-Br]^+$ β-bromostyrene cation radical **8** to more stable cations(s). Possible structures for this cation are the α-phenylvinyl cation **7**, the bridged species **9** and **10**, and the β-phenylvinyl cation **11** (Scheme II). However, the increase in the kinetic energy release, the following collisional activation (CA) data, and MO calculations rule out the formation of a stable β-phenylvinyl cation (**11**). The MO calculations (see below) appear to exclude the intervention of the hydrogen-bridged cation **10**, which is found to collapse without activation energy to **7**.[12]

The ΔT values for the dissociative ionization of **5** and **6** do not give direct information on the structure(s) of the rearranged $C_8H_7^+$ cations(s). This is achieved by CA spectroscopy[3] and by studying suitably ^{13}C-labeled precursors. Relevant CA data for the $C_8H_7^+$ ions generated from $4^{+}\cdot$ and $5^{+}\cdot$ are given in Table II.

Table II shows that except for the *m*/*z* fragment which corresponds to collision-induced CH_2 loss from $C_8H_7^+$, the CA spectra of the $[M-Br]^+$ ions formed from $4^{+}\cdot$ and $5^{+}\cdot$ by dissociative ionization, as well as that of the $C_8H_7^+$ ion formed by protonation of phenylacetylene **12** with CH_5^+ (chemical ionization (CI)[14]), are essentially identical. These results suggest that the gas-phase protonation of **12** gives exclusively the α-phenylvinyl cation **7**, which is also formed directly from $4^{+}\cdot$. Furthermore, a large fraction of the incipient $[M-Br]^+$ ions (**8**) generated from $5^{+}\cdot$ and $6^{+}\cdot$ must rearrange to **7**. From the small, but reproducible, intensity differences for collision-induced CH_2 loss from $C_8H_7^+$ (4.8 ± 0.5% for **4** and **12** compared with 2.7 ± 0.4% and 3.3 ± 0.4% for **5** and **6**, respectively), the following conclusions can be drawn: 44 ± 10% of the ion **8** formed from $5^{+}\cdot$ and 31 ± 10% starting from $6^{+}\cdot$ rearrange to an additional stable structure which may be **9** (as suggested by the calculations) or **10**. From a structural point of view, elimination of CH_2 from either **9** or **10** is less likely than from **7**, as observed.[15]

Scheme III



Investigation of the side-chain ^{13}C-labeled analogues of **4** and **5** (Table III) leads to several conclusions. (a) Approximately 95% of the total CH_2 loss from the $[M-Br]^+$ ions involves the side-chain carbons for both α- and β-bromostyrenes. (b) C_α and C_β contribute to a different extent to the CH_2 formation, suggesting that they do not become structurally equivalent during or prior to the decomposition. Consequently, both a single symmetric structure, e.g., **9** and a complete degenerate isomerization of **7** prior to the CH_2 loss can be ruled out for the $[M-Br]^+$ ions from **4** and **5** (and probably also from **6**). Hence, the CH_2 loss from $C_8H_7^+$ differs from the analogous collision-induced decomposition of the $C_8H_9^+$ cation formed upon dissociative ionization of ^{13}C-labeled β-phenylethyl bromide. This reaction reveals the equivalence of the two side-chain atoms, indicating the intermediacy of an ethylenebenzenium ion.[15g] (c) The individual contributions of C_α and C_β to the CH_2 loss differ slightly for the α- and β-bromostyrenes, thus corroborating the results and the interpretation of the CA spectra. In particular, C_α contributes 21.3% and C_β contributes 78.7% to the CH_2 loss from the $[M-Br]^+$ ions which are derived from **4**. The collision-induced $C_\alpha H_2$ loss indicates that direct CH_2 loss from **7a** and/or **7b** is likely to be accompanied or preceded by a *partial* degenerate isomerization of **7**. A competition between direct methylene loss from **7a** and degenerate isomerization prior to decomposition is depicted in Scheme III, where **9a**, **10a**, **10b**, **11a**, and **11b** are either intermediates or transition states. MINDO/3 calculation (see below), show, however, that a lower energy path is available for the

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(12) A lower stability of **11**, compared with **7**, was already deduced from solvolysis studies of **5**; see ref 7 m and Lee, C. C.; Ko, E. C. F. *J. Org. Chem.* **1975**, *40*, 2132.

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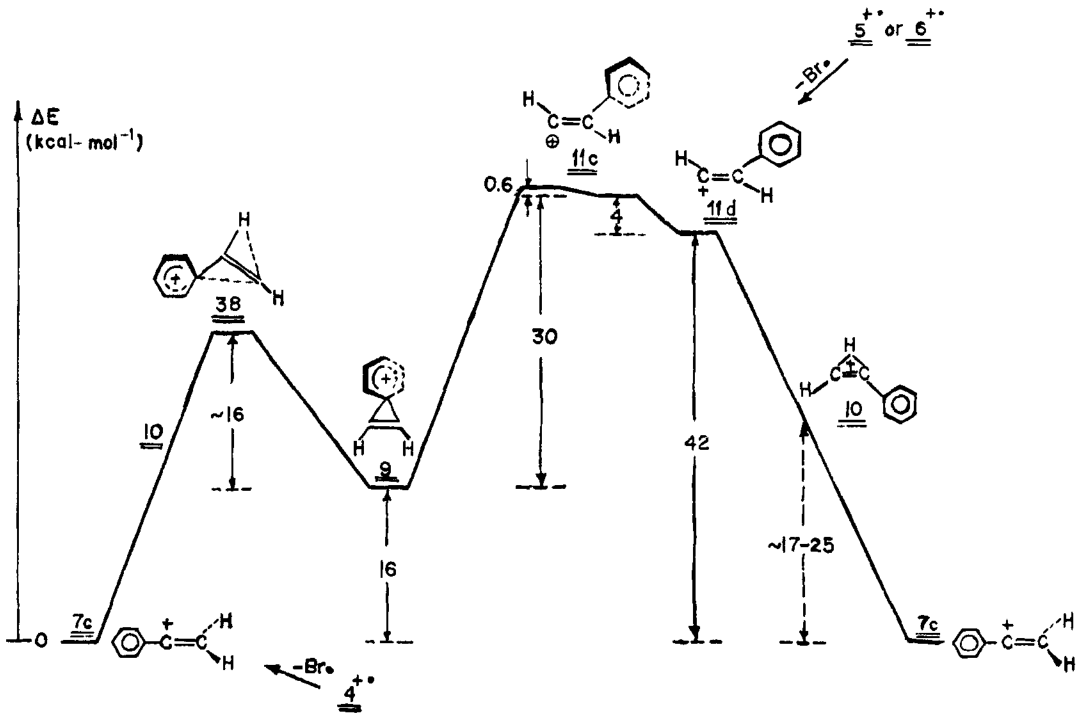
Scheme IV

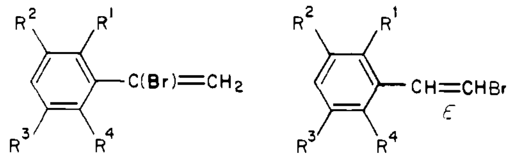


degenerate isomerization of 7 (Scheme IV). The partial rearrangement of the more stable ion **7a** to the less stable species **9a** is consistent with the observation that the collision-induced formation of m/z 89 is a high-energy reaction. Preliminary experiments demonstrate that the energy loss, i.e., the energy deposited as excitation energy of the $[M - Br]^+$ ion during the inelastic collision with the neutral gases,[11d] is ca. 26 eV. Our MO calculations give an activation energy of ca. 32 kcal mol^{-1} for the degenerate isomerization of 7, whereas the formal cleavage of the C_α–C_β bond of 7 during the direct CH_2 elimination should require much more energy. However, the latter route is entropically favored over the multistep rearrangements which are characterized by tight transition states. The preference of entropically favored processes hold particularly for reactions of ions with substantial excess energy,[2a,b,3,11c,d,16] i.e., for ions which are collisionally activated. From the data in Table III we calculate that ca. 57% of the α-phenylvinyl cation **7** eliminates CH_2 directly, whereas the remaining 43% undergoes a **7a** $\rightleftharpoons$ **7b** isomerization prior to collision-induced decomposition.

(d) The side-chain contributions of the α- and β-carbon atoms to the $^{12}CH_2/^{13}CH_2$ losses depend on the precursor structure. When $\mathbf{5}^{+\cdot}$ is the precursor, the relative contribution of C_α is 8.6% (29.9% vs. 21.3%) higher than that from $\mathbf{4}^{+\cdot}$. Together with the T values and the CA data this oservation is consistent with decomposition of the ion **8** from **5** mainly to **7** and partially to the phenyl-bridged cation **9**. Methylene is then eliminated as described in Scheme III but the increased amount of $C_\alpha H_2$ loss requires that, in addition to **7**, an ion of higher symmetry, i.e., **9**, has to be formed. A direct decomposition of **8** to **10** or **7** (via **10**) is inconsistent with the ^{13}C-labeling experiments and with the MO results. However, since (i) 57% of ion **7** eliminates CH_2 directly and 43% undergoes a degenerate isomerization **7a** $\rightleftharpoons$ **7b** prior to collision-induced dissociation and (ii) ~44% of ion **8** rearranged to **9** from which CH_2 loss is likely to occur after the rearrangement **9** → **7**, the calculated value for $^{13}CH_2$ loss from (β-^{13}C)-**5** is ca. 69%. This value is in good agreement with the experimentally derived value of 66.6%.

The above interpretation is corroborated by the results of MO calculations (see below) which are presented schematically in Scheme IV.[17] Among the computed cationic structures only **7** and **9** are found to be stable, **7** being by far the most stable (by 16 kcal mol^{-1}).[17] The isomeric β-phenylvinyl cation **11** and the hydrogen-bridged cation **10** do not exist in a potential minimum. On full optimization **11** isomerizes spontaneously to **7** via **10**, but a barrier of 4.4 kcal mol^{-1} must be surpassed before **11** can rearrange to **9**. The dissociative ionization of **5** and **6** is therefore expected to lead mainly to **7**.[17] The degenerate isomerization of **7** proceeds preferentially via **9** with an activation energy of ca. 32 kcal mol^{-1}.

Aryl-Substituted α- and β-Bromostyrenes. The generality of the exothermic isomerization of the ions derived from β-bromostyrene is shown in a study of the kinetic energy release associated with the dissociative ionization of the pairs α- and (E)-β-bromo-2,6-dimethylstyrenes (**13** and **14**), the 2,5-dimethyl analogues **15** and **16**, and the 3,5-dimethyl analogs **17** and **18**.



13, $R^1 = R^4 = Me$, $R^2 = R^3 = H$ 14
15, $R^1 = R^3 = Me$, $R^2 = R^4 = H$ 16
17, $R^2 = R^3 = Me$, $R^1 = R^4 = H$ 18

Table I shows that Br· elimination from the molecular ions of the α-bromostyrenes **14**, **16**, and **18** is always associated with larger T values than those for the molecular ions of the corresponding β-bromo isomers **13**, **15**, and **17**. Thus, in *analogy* with the unsubstituted bromostyrenes, the direct formation of the substituted β-arylvinyl cations **22** (Scheme V) is less likely than a rearrangement to a more stable isomeric cation. The near constancy of the ΔT values for each pair of isomers suggests that the

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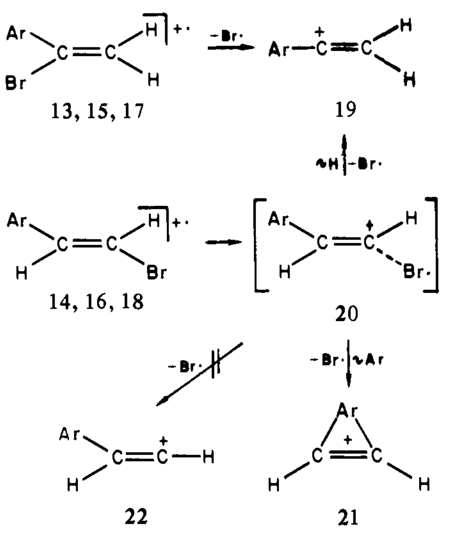
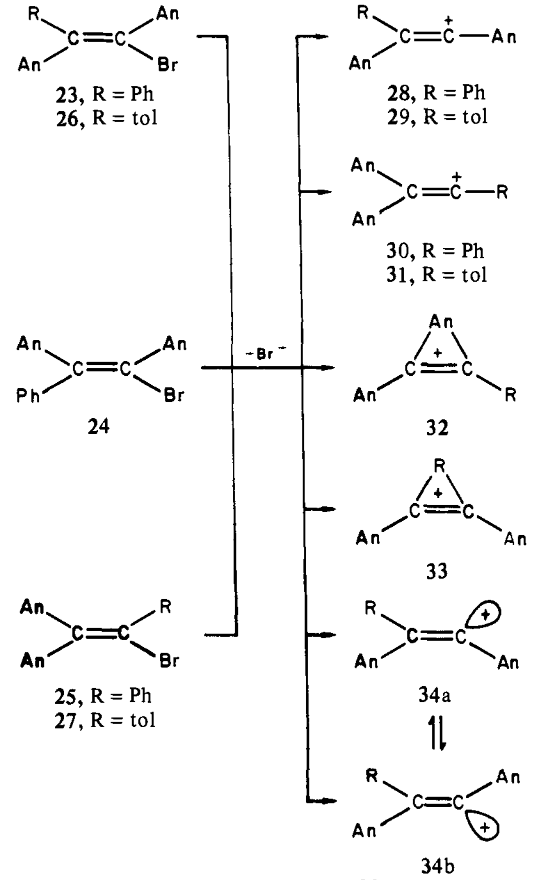
[16] Williams, D. H.; Howe, 1. "Principles of Organic Mass Spectrometry"; McGraw-Hill: London, 1972.

[17] The energies of **10**, **11c**, and **11d** in Scheme IV refer to hypothetical assumed geometries. In the discussion we assume that in the dissociative ionization of **5** and **6** the point of entry to the cationic energy surface is at structure **11d**, where the phenyl ring retains (as in **5** and **6**) coplanarity with the HC═CH group. It is reasonable that partial bridging by hydrogen is achieved even before the Br· dissociates completely. In this case the entry point to Scheme IV is lower in energy than that of **11d**. The barrier of 4.4 kcal mole^{-1} given for the **11d** → **9** rearrangement is therefore a lower limit for the additional energy needed for the **5** (or **6**) → **9** reaction compared with the **5** (or **6**) → **7c** reaction.

Scheme V



Scheme VI



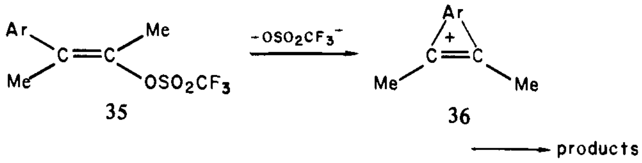
An = p-MeOC$_6$H$_4$ tol = p-MeC$_6$H$_4$

amount of potential energy liberated as translational energy upon isomerization of the dissociating [M − Br]$^+$ ion **20** to the α-arylvinyl cation **19** and/or the bridged ion **21** (Scheme 5) is approximately 0.43 kcal mol^{-1} for all the three isomeric dimethylphenyl derivatives.

A quantitative interpretation of the substituent effects on T values is presently not available. However, the increase of the values in the order 2,6-dimethyl < 2,5-dimethyl < 3,5-dimethyl may indicate the operation of a steric effect. The much higher solvolysis rate of **13** compared with **4** was attributed to its ground-state destabilization due to the orthogonality of the sterically hindered phenyl ring and the vinyl π-system and to the increased overlap between the incipient vacant p orbital at C$_\alpha$ and the phenyl ring in the transition state.[18] The operation of similar effects in the gas-phase dissociative ionization of **13**–**18** may indirectly affect the excess energy available in the transition state of the dissociation step, which itself partially determines the magnitude of T. However, the order of T values also follows the electronic stabilization of the ions.

Triarylvinyl Bromides. The gas-phase dissociative ionization of the substituted triarylvinyl bromides **23**–**27** was also studied. Their solvolysis in solution to the triarylvinyl cations had been studied in detail. The competition between capture of the ions by the solvent and β-aryl rearrangement depends on the nature of the aryl group R. When R = Ph both the substituted α-phenylvinyl cation **30** can be formed from **23**–**25** (Scheme VI). Capture of the rearranged ion **28** was observed with several nucleophiles;[19a–j] i.e., the ionization rearrangement **25** → **30** → **28** is faster than capture of **30** by nucleophiles.[19c,d] Solvolysis of the β-tolyl derivative **26** gave only capture products of the α-anisylvinyl cation **29**, but **27** gave products from both **29** and **31** in 60% EtOH.[19k]

No evidence for the long-lived aryl-bridged triarylvinyl cation **32** or **33** in solution is available, although there is strong evidence for the intermediacy of the aryl-bridged ion **36** in the solvolysis of (E)-3-aryl-2-buten-2-yl trifluoromethanesulfonate (**35**).[20]



We investigated two problems in the gas phase: (a) the stability of the pairs of isomeric ions **28**/**30** and **29**/**31** and (b) the possibility that the ionization of the geometrical isomers **23** and **24** leads initially to the isomeric bent ions **34a** and **34b** which rapidly equilibrate (Scheme VI). A rapidly equilibrating mixture of **34a** and **34b** is not easily distinguishable from **28**,[21] although the bent structure is unlikely both on energetic grounds[22] and from studies of cyclic vinyl trifluoromethanesulfonates.[23]

The kinetic energy release values associated with Br· loss from ionized **23**–**27** are given in Table I. Again, the T and ΔT values argue that an isomerization at the stage of the molecular ions is extremely unlikely.[24] The increase in ΔT values in comparing **25** with **23** and **24** suggests that the gaseous [M − Br]$^+$ ion **30**, formed from **25**, does not exist in a potential well, but it is difficult to reconcile the differences with a direct formation of bent vinyl cations **34a** or **34b** (R = Ph). The increase in ΔT can be best accounted for by exothermic isomerization of the decomposing [M − Br]$^+$ ion to **28** which can also be formed directly from ionized **23** and **24**. However, the data are also compatible with an exothermic isomerization of the incipient [M − Br]$^+$ ion to another

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[18] (a) Yates, K.; Périé, J. J. *J. Org. Chem.* **1974**, *39*, 1902. (b) Yates, K.; Madrapilias, G. *Ibid.* **1980**, *45*, 3892.

[19] (a) Rappoport, Z.; Apeloig, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6734; (b) *Tetrahedron Lett.* **1970**, 1817; **1970**, 1845. (c) Rappoport, Z.; Gal, A.; Houminer, Y. *Ibid.* **1973**, 641. (d) Rappoport, Z.; Houminer, Y. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1506. (e) Rappoport, Z.; Kaspi, J.; Apeloig, Y. *J. Am. Chem. Soc.* **1974**, *96*, 2612. (f) Rappoport, Z.; Apeloig, Y. *Ibid.* **1975**, *97*, 821, 836. (g) Houminer, Y.; Noy, E.; Rappoport, Z. *Ibid.* **1976**, *98*, 5632. (h) Rappoport, Z.; Schnabel, I.; Greenzaid, P. *Ibid.* **1976**, *98*, 604. (j) van Ginkel, F. I. M.; Hartmann, E. R.; Lodder, G.; Greenblatt, J.; Rappoport, Z. *Ibid.* **1980**, *102*, 7514. (k) Rappoport, Z.; Houminer, Y.; Aviv, M., unpublished results. (l) Lee, C. C. In "Isotopes in Organic Chemistry. Isotopes in Cationic Reactions"; Buncel, E. and Lee, C. C., Eds.; Elsevier: Amsterdam, 1980; Vol. 5 Chapter 1.

[20] Stang, P. J.; Dueber, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 2683, 2686, **1977**; *99*, 2602.

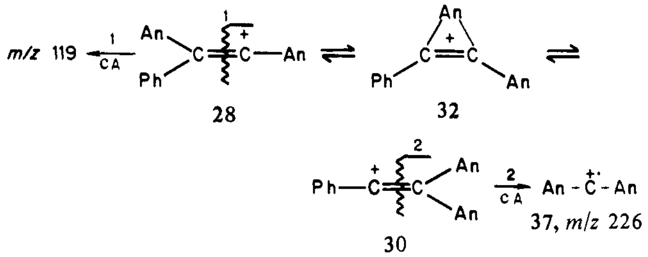
[21] Kelsey, D. R.; Bergmann, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 228.

[22] Sustmann, R.; Williams, J. E.; Dewar, M. J. S.; Allen, L. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 5350. Hopkinson, A. C.; Yates, H.; Csizmadia, I. G. *J. Chem. Phys.* **1971**, *55*, 3835.

[23] Pfeifer, W. D.; Bahn, C. A.; Schleyer, P. v. R.; Bocher, S.; Harding, C. E.; Hummell, K.; Hanack, M.; Stang, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 1513.

[24] This conclusion refers to a skeletal rearrangement of M$^{+\cdot}$ and not to the formation of the same [M − Br]$^+$ ion from **23** and **24**.

Scheme VII



more stable structure, e.g., the aryl-bridged cation **32**, provided that it is more stable than **28**.[25] Similarly, the higher T value obtained for dissociation of ionized **27** compared with that of **26** is consistent with the formation of the stable substituted β-tolylvinyl cation **29**, whereas **31** is not likely to be formed as a stable species.

If the $[M - Br]^+$ ions from the pairs of ionized bromides **23** and **25**, or **26** and **27** do indeed have identical structures, i.e., **28** and **29**, the CA spectra of these ions formed from both precursors must be identical. This is indeed the case with regard both to the decomposition products and to their respective relative abundances.[26]

So that the possibility could be ruled out that the excess energy due to the use of 70-eV ionizing electrons leads to an isomerization of the $[M - Br]^+$ ions after Br· loss from $M^{+\cdot}$, CA spectra were taken at ionizing energies close to the threshold energy for the $[M - Br]^+$ ion formation. The spectra taken at a nominal electron energy of ca. 10 and 70 eV are identical. Consequently, the formation of a mixture of interconverting isomers separated by a significant potential barrier can be excluded,[3,27] and each family of gaseous $[M - Br]^+$ ions should possess a single structure. We believe that **28** and **29** are the species formed upon dissociative ionization of **23**–**25** and of **26** and **27**, respectively.

Part of the collision-induced fragments of the $[M - Br]^+$ ion (m/z 315) obtained from **23**–**25** are given below in terms of the percent of the total ion fragment formation: m/z 300 (12%), 284 (11%), 268 (10%), 238 (15%), 226 (16%), and 119 (1.8%). The collision-induced losses of Me·, MeO·, Me· + MeOH, and Ph· (giving m/z 300, 284, 268, and 238, respectively) can take place from either **28** to **30**. However, the fragments at m/z 226 and 119 seem to arise from structurally different species, seemingly indicating the existence of at least two stable $[M - Br]^+$ ions. Obviously, m/z 226 ($An_2C^{+\cdot}$?) cannot be formed directly from **28**, whereas the formation of m/z 119 (AnC^+?) as well as the interpretation of the T values are compatible only with structure **28**. We suggest that direct collision-induced dissociations of **28** compete with a rearrangement occuring after the CA. As discussed above for the CH_2 loss from the substituted phenylvinyl cations, these and other direct dissociations involving cleavage of the C_α–C_β bond can be regarded as high-energy reactions. In contrast, the rearrangements across the double bond require lower activation energies, as found in solution.[7m] Thus, part of the collisionally activated $[M - Br]^+$ ion **28** rearranges to **30** prior to direct dissociation to m/z 119. The rearranged product gives the m/z 226 fragment whose tentative structure is that of an ionized dianisylcarbene **37** (Scheme VII).[28] The alternative, that **30** is exclusively formed as a single stable structure from **25** is compatible neither with the CA spectra nor with the T values. Similar arguments, especially the insensitivity of the CA spectra to the ionizing energy, exclude a rapidly equilibrating mixture of ions **28** and **30**.[27] Although a dissociative ionization of the precursors **23**–**25** to give exclusively the anisyl-bridged cation **32** cannot be ruled out on the basis of the CA spectra alone, it is inconsistent with the MO calculations and the ΔT differences which indicate an exothermic isomerization of **30**.

The CA spectra of the $[M - Br]^+$ ions from **26** and **27** are also identical with and insensitive to the ionizing energy. The most abundant fragments are m/z 314 (21%), 298 (14%), 282 (11%), 252 (9%), and 238 (11%) which are homologues of fragments discussed for the dissociation of **28**, and 226 (10%), 119 (2%), and 103 (1%). The formation of m/z 226 and 119 is analogous to the processes described in Scheme VII (tol replacing Ph), whereas m/z 103 can be formed from **31** in analogy to the cleavage of **30**. Consequently, both the T values (Table I) and the CA spectra are best compatible with Br· loss from both $\mathbf{26}^{+\cdot}$ and $\mathbf{27}^{+\cdot}$ to give an $[M - Br]^+$ ion with structure **29**.

Comparison of Gas-Phase and Solvolysis Data. Several aspects of the gas-phase and the solvolysis reactions which generate the same vinyl cations could be compared. The present gas-phase data corroborates results observed in solution on the structure and the relative stabilities of isomeric ions.

The solvolytically generated α-arylvinyl cations from α-halostyrenes form phenylacetylene in solution[18,29] while its radical ion is generated in the gas phase. This is only a formal analogy since the gas-phase reaction involves the expulsion of H· whereas in solution H^+ is eliminated. Moreover, in solution the solvent or an added base is involved in the elimination.[29b]

Primary vinyl cations are usually unstable. α-Unsubstituted-β-arylvinyl cations are not formed in solution, and the solvolytically generated α-arylvinyl cations are stable toward rearrangement.[18,29] The possibility of the degenerate rearrangement **7a** $\rightleftharpoons$ **7b** (Scheme III) was never investigated in solution but it is unlikely due to the high-energy requirements and the lack of a driving force.[12] Although the formation of acetophenone from the solvolysis of **5** and **6** was interpreted as due to a **5** (or **6**) → **11** → **7** sequence,[12] it is highly likely that the reaction proceeds by a different mechanism.[30] Consequently, the similarity between the reactions in both media is limited to the fact that **7** is much more stable than **11**, and if **11** is formed at all, it spontaneously rearranges to **7**. However, the excess energy available to the gas-phase ions after collisional activation is sufficient to lead to some scrambling of C_α and C_α via the high-energy **7** $\rightleftharpoons$ **11** or, more likely, **7** $\rightleftharpoons$ **9** routes.

A similar situation prevails with the triarylvinyl cations. Solvolysis of **23**–**25** under a variety of conditions gives only a mixture of the (E)- and (Z)-α-anisylvinyl products;[19a-j] i.e., ion **28** is so much more stable than **30** that the rearrangement **30** (from **25**) → **28** in solution is faster than the reaction of **30** with any nucleophile present.[19c,d] Obviously, β-anisyl rearrangement in **28** formed from **23** and **24** was not observed.[19g] The acetolysis of the tolyl derivatives **26** and **27** gave only products derived from the ion **29**, but in 60% EtOH the rearrangement of **31** to **29** is slower than its capture by the solvent. Consequently, in the solvolysis of **27**, products derived from both ion **29** and **31** were formed.[19k]

The gas-phase data are similar in indicating that the α-anisylvinyl cations **28** and **29** are the species formed either for direct means or via rearrangement of the substituent across the double bond. However, the partial "antithermodynamic" rearrangements **28** $\rightleftharpoons$ **30** and **29** $\rightleftharpoons$ **31** of the collisionally-activated ions prior to decomposition have no parallel in solution. This can be due to the fact that capture of the ion by the solvent before rearrangement in solution is a low-energy process whereas the collision-induced fragmentations probably require high activation energies. An analogy to the gas-phase data is found, however, in solution chemistry of structurally related energetic sp^2-hybridized ions

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[25] Reliable calculations on the relative stabilities of triarylvinyl cations such as **28** and **32** are presently prohibitively expensive.

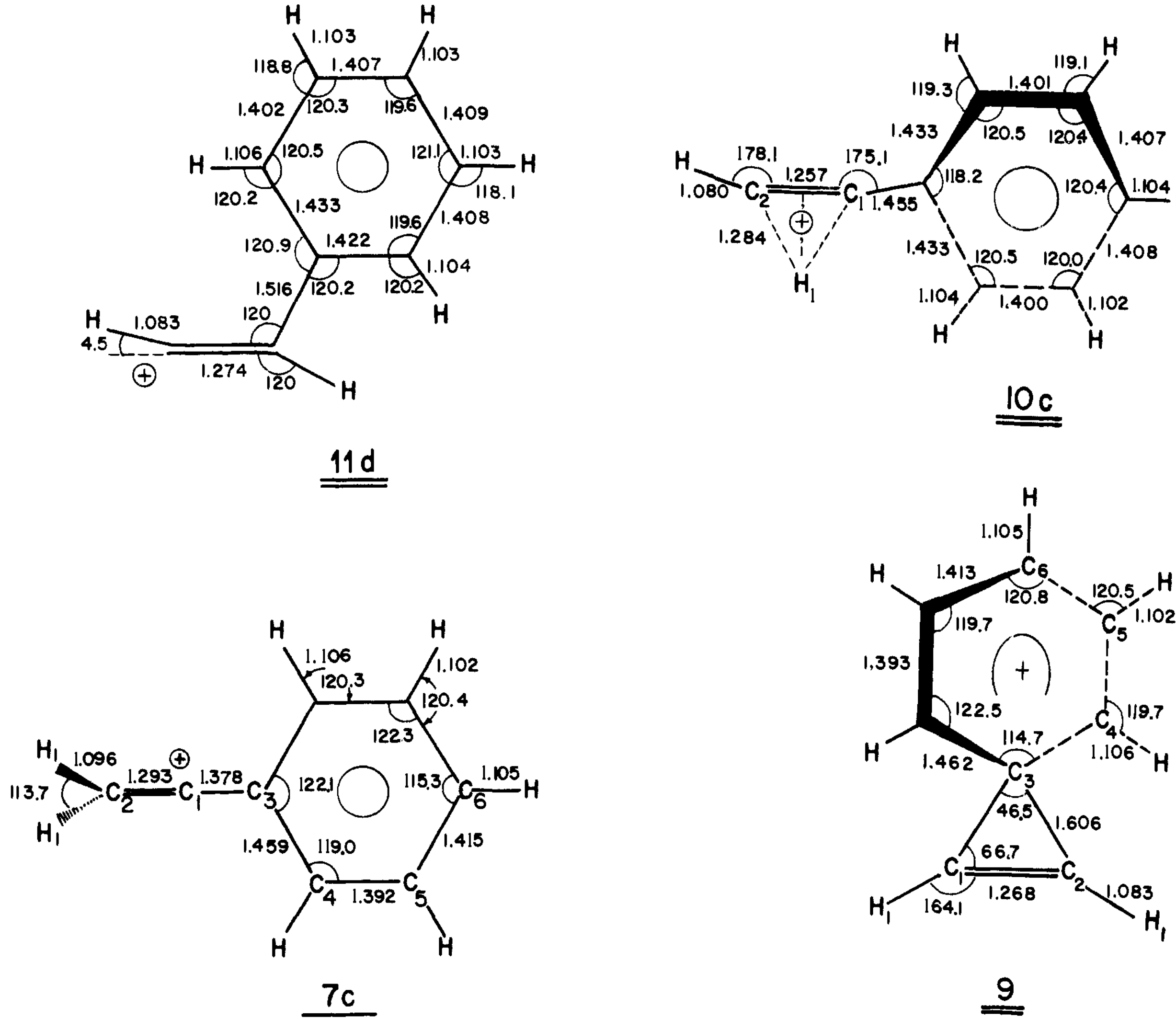
[26] For the sake of brevity, we report only the data of those collision-induced signals which are either very abundant or diagnostically useful for assignment of the structure of the $[M - Br]^+$ ion. The full data can be obtained on request from the authors.

[27] For isomeric ions separated by significant potential barriers, it has been shown convincingly (e.g., ref 15g) that CA spectra are quite sensitive to the ionizing energy.

[28] The "hot" 1-anisyl-2,2-diphenylethyl cation (Ph_2CHC^+HAn) formed by deamination gives 0.9% rearrangement of a β-phenyl group to the substituted cation $PhC^+HCHPhAn$: McCall, M. J.; Townsed, J. M.; Bonner, W. A. *J. Am. Chem. Soc.* **1975**, *97*, 2743.

[29] (a) Grob, C. A.; Cseh, G. *Helv. Chim. Acta* **1964**, *47*, 194. (b) Grob, C. A.; Pfaendler, H. R. *Ibid.* **1971**, *54*, 2060. (c) Rappoport, Z.; Shulman, P.; Thuval (Shoolman), M. *J. Am. Chem. Soc.* **1978**, *100*, 7041.

[30] Jäckel, H. P.; Hanack, M. *Chem. Ber.* **1977**, *110*, 199. Reference 7m, p 461.



11d

10c

7c

9

Figure 1.

which are formed in deamination.[28]

Solvolysis of **23** and **24** under various conditions gives indentical mixtures of the (*E*)- and the (*Z*)-1,2-dianisyl-2-phenylvinyl derivatives,[19a,f] arguing for the formation of an identical linear sp-hybridized α-arylvinyl cation from both precursors. However, a rapid interconversion of isomeric bent triarylvinyl cations which is faster than the capture process cannot be excluded. The gas-phase results, which show the same *T* value for Br· loss from $\mathbf{23}^{+\cdot}$ and $\mathbf{24}^{+\cdot}$ and the same energy-insensitive CA spectra for the resulting $[M - Br]^+$ ions are more consistent with the suggestion that the same linear cation is obtained.

Whereas the solvolysis rates of structurally different precursors such as **4**, **13**, and **25** are used as a probe for the relative stabilities of the derived ions in solution, the present understanding of the gas-phase reactions does not enable the use of absolute *T* values as a similar probe. However, the increase in the *T* values for the formation of the family of isomeric ions derived from **13**, **15**, and **17**, respectively, is consistent with the expected increased stabilization of the transition state for the $M^+ \rightarrow [M - Br]^+$ process due to enhanced electron donation by the *o*- compared with a *m*-methyl group. A similar effect of *o*- and *p*-methyl groups on relative solvolysis rates was observed in solution.[18]

Molecular Orbital Calculations. Quantum mechanical calculations can provide insight into the experimental results. Theoretical calculations are usually performed for isolated molecules and gas-phase experiments are therefore well suited for comparison. Our recent study of the $C_4H_5^+$ cations[9f,10d] is one example which demonstrates the advantages of a combined experimental–theoretical investigation of gas-phase problems. We use here both the semiempirical MINDO/3 method[31] and standard ab initio methods[32] with the minimal STO-3G basis set.[33] Both methods are reliable in predicting relative energies of isomeric cations.[34] A combination of the MINDO/3 and the ab initio methods provides an effective procedure for studying relatively large systems such as $C_8H_7^+$. MINDO/3 provides a fast and reliable method for geometry optimizations.[31] These optimized geometries are then used in the ab initio calculations for obtaining more accurate relative energies.[35]

We have studied computationally possible structures of the $C_8H_7^+$ cations which might be generated in the ionization of α- and β-bromostyrenes. These include the α-phenylvinyl cation (**7**)[36] the β-phenylvinyl cation (**11**) the phenyl-bridged vinyl cation (**9**),[37]

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[31] Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307.

[32] The Gaussian-70 series of programs were used: Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M.; Pople, J. A. Program No. 236, Quantum Chemistry Program Exchange (*QCPE*), Indiana University, Bloomington, Indiana.

[33] Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, 51, 2657.

[34] For reviews see: (a) Hehre, W. J. In "Application of Electronic Structure Theory"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 4, pp 277–331. (b) Radom, L.; Poppinger, D.; Haddon, R. C. *Carbonium Ions* **1976**, *5*, 2303–2426.

[35] (a) Recent studies (Köhler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479; **1978**, *100*, 5279 and references therein) suggest that this strategy is useful for calculating carbocations.

[36] STO-3G calculations with partial geometry optimization were reported previously.[10a]

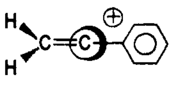
Table IV. Calculated Heats of Formation (MINDO/3, kcal mol^{-1}), Total Energies (STO-3G, hartrees), and Relative Energies (kcal mol^{-1}) of the Phenylvinyl Cations 7, 9, 10, and 11

	MINDO/3		STO-3G^{a,b}	
cation^a	ΔH_f^0	rel energy	tot energy	rel energy
7c^c	232.0	0.0	−303.01238	0.0
7d^d	243.7	11.7	−302.96714	28.4
9	257.3	25.3 (17)^f	−302.97413	24.0 (16)^f
10c^c	248.8	16.8	−302.93559^e	48.2 (25)^f
10d^d	249.6	17.6		
11c^c	267.0	35.0	−302.93892	46.1
11d^d	270.5	38.5	−302.94496	42.3

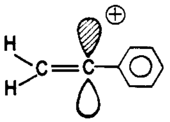
^{a} Using the MINDO/3 optimized geometries (Figure 1). The optimized structures of 10d and 11c which are very similar to those of 10c and 11d were omitted from Figure 1 (7d is omitted for simplicity). ^{b} All the C-H bond lengths are assumed to be 1.08 Å except for 10c, where the bond lengths to the bridging hydrogen are reoptimized at STO-3G. ^{c} The benzene ring is perpendicular to the $C_1C_2H_1$ plane. ^{d} The benzene ring is in the plane defined by $C_1C_2H_1$. ^{e} With partial optimization of the C_1-C_2 and the C_1-H_1 (and C_2-H_1) bond lengths (C_1-C_2 = 1.233 Å, C_1-H_1 = C_2-H_1 = 1.327 Å). Computed energy at the MINDO/3 optimized geometry (with C-H = 1.08 Å) is −302.929 91 hartrees. ^{f} "Corrected", see text. See also ref 44.

and the hydrogen-bridged cation **10**. Full geometry optimizations[38] were carried out with the MINDO/3 method. Single-point calculations at the MINDO/3 optimized geometries[39] were then performed with the use of the STO-3G basis set.[32,33] The calculated geometries of the carbocations are reported in Figure 1; heats of formation (MINDO/3), total energies (STO-3G), and relative energies are given in Table IV. Two local minima are found on the phenylvinyl cation potential energy surface; the α-phenylvinyl cation, **7**, and the phenyl-bridged vinylcation, **9**. Both the β-phenylvinyl cation **11** and the hydrogen-bridged phenylvinyl cation **10** collapse without activation energy to **7** (MINDO/3). The energies which are reported in Table IV for **10** and **11** refer to arbitrarily constrained structures. In **11** the $C_1C_2H_2$ and the C_1C_2-phenyl bond angles are fixed at 120°, while in **10** the bridging hydrogen is held at equal distances from C_1 and C_2 (Figure 1). The most stable cation is the perpendicular α-phenyl vinyl cation **7c**, which benefits from conjugation between the formally empty $2p(C^+)$ orbital and the phenyl ring.[10a] The all-planar ion **7d**, where such conjugation is excluded, is 28.4 kcal mol^{-1} (STO-3G) less stable. The phenyl-bridged **9** is 24.0 kcal mol^{-1} (STO-3G; 25.3 kcal mol^{-1} at MINDO/3) less stable than **7**. The hypothetical β-phenylvinyl cation **11** is considerably higher in energy (by 35–42 kcal mol^{-1}; Table IV) and can rearrange exothermically to either **7** or **9**.

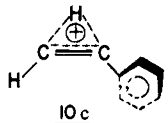
The two computational methods disagree on the identity of the most stable conformer of **11**. According to STO-3G the all-planar cation **11d** is more stable than the perpendicular rotamer **11c** by 3.8 kcal mol^{-1}. According to MINDO/3, however, **11c** is more stable than **11d** by 3.5 kcal mol^{-1} (Table IV). We prefer to use the ab initio results. Since the β-bromostyrenes are probably planar[40a] the phenyl ring must rotate by 90° during the ionization process before rearrangement to **9** can occur. The barrier to the rearrangement of **11d** to **9** is 4.4 kcal mol^{-1} at STO-3G,[40b] significantly higher than the **11c** → **9** carrier of 0.6 kcal mol^{-1} predicted by MINDO/3.[17]



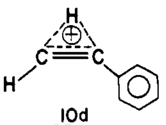
7c



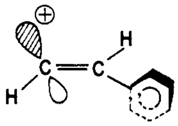
7d



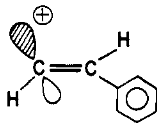
10c



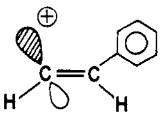
10d



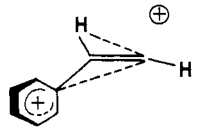
11c



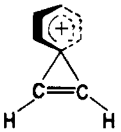
11d



11e



38



9

Our calculations use relatively simple levels of theory,[41] and the results should be examined with caution. Previous experience shows that the calculated relative energies of isomeric acylic cations such as **7** and **11** remain nearly constant when the basis set is varied.[34] However, in comparing isomeric cyclic and acyclic molecules[34,42] or classical and nonclassical structures,[10d,35,43] the use of a large basis set (including polarization functions) and the inclusion of electron correlation are crucial for calculating accurately energy differences. Based on experience with smaller cations, we estimate that the STO-3G energies of **9** and **10** have to be lowered relative to that of **7** (or **11**) by ≃8 and ≃23 kcal mol^{-1}, respectively.[10d,35,43] With MINDO/3 no correction is needed for **10**, but the energy of **9** has to be lowered by ≃8 kcal mol^{-1} relative to **7**.[35,44] We conclude that **7** is more stable than **9** by 16–17 kcal mol^{-1}, than **10** by 17–25 kcal mol^{-1}, and than **11** by 42 kcal mol^{-1} (see Table IV and Scheme IV).[45]

We have also investigated by MINDO/3 possible routes for the rearrangement of **7** to **9** which may account for the partial degenerate rearrangement of **7a** to **7b** prior to collision induced methylene loss. One possible route, **7a** ⇄ **10a** ⇄ **11a** ⇄ **9a** ⇄

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(37) (a) Previous extended Hückel[37b] and MINDO/2[37c] calculations have concentrated on the possibility of stabilizing a tetracoordinate planar carbon. Recent STO-3G calculations have shown, however, that the tetrahedral **9** is by 102 kcal mol^{-1} more stable than the planar form:[37d] (b) Hoffmann, R.; Alder, R. G.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. (c) Schoeller, W. *J. Chem. Soc., Chem. Commun.* **1974**, 872. (d) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419.

(38) Except where restrictions had to be imposed, see discussion.

(39) C-H bond lengths are calculated with MINDO/3 to be systematically longer, by 0.02–0.03 Å, than with STO-3G. In the STO-3G calculations we have therefore used a standard C–H bond length of 1.08 Å for all hydrogens. In **10**, the bond lengths to the bridging hydrogen were optimized also at STO-3G (see Figure 1).

(40) (a) The planar conformation of styrene is more stable than the perpendicular conformation by 4.4 kcal mol^{-1} (STO-3G): Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 1496. (b) This is the sum of the 3,8 kcal mol^{-1} barrier for rotation of **11d** to **11c**, and the activation energy of 0.6 kcal mol^{-1} (MINDO/3) for the **11c** → **9** rearrangement.

(41) The time needed to perform a single calculation is proportional to n^4 (n = number of basis functions). Calculations at the next higher theoretical level, e.g., the 4-31G and 6-31G* basis sets, are ~15 and ~80 times, respectively, slower than the STO-3G calculations. On our IBM 370/168 computer single point calculations of $C_8H_7^+$ would require ~1.5 and ~8 h at 4-31G and 6-31G*, respectively.

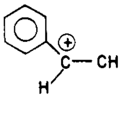
(42) E.g., Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.

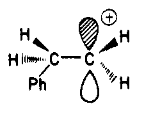
(43) (a) Weber, J.; McLean, A. D. *J. Am. Chem. Soc.* **1976**, *98*, 875. (b) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R., *Ibid.* **1973**, *95*, 6531. (c) Weber, J.; Yoshimine, M.; McLean, A. D. *J. Chem. Phys.* **1976**, *64*, 4159.

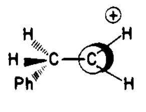
(44) In contrast to STO-3G, MINDO/3 reproduces correctly the relative energies of open and of H-bridged structures (e.g., $C_2H_3^+$),[35] resulting in a large difference in the calculated energies of **10** relative to **7** between the two methods. Correction of the STO-3G result by 23 kcal mol^{-1} (see text) brings the results to the two methods to a closer agreement. We prefer to use the "corrected STO-3G" values over the MINDO/3 results.[35]

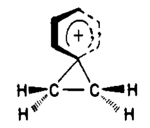
11b ⇄ **10b** ⇄ **7b** (Scheme III), requires 46 kcal mol^{-1} (STO-3G; 36 kcal mol^{-1} at MINDO/3). The calculations reveal a lower energy path. A synchronous migration of the β-hydrogen and the α-phenyl group leads to a doubly-bridged structure **38**, which collapses directly to **9** (Scheme IV). Structure **38**, which represents the transition state for the **7** ⇄ **9** rearrangement (Scheme IV), lies 32 kcal mol^{-1} higher in energy than **7**. This represents the upper limit for the activation energy of the **7a** ⇄ **7b** rearrangement (Scheme III) since MINDO/3 probably underestimates the stability of **38** by some 5–10 kcal mol^{-1}.[35] Our conclusions regarding the relative energies of the $C_8H_7^+$ cations and the energy paths which connect them are summarized in Scheme IV.[45]

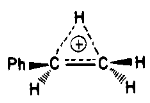
A comparison of our calculations with those for the analogous saturated phenylethyl cations[46] is of interest. The α-substituted cation **39** is the most stable isomer also among the phenylethyl cations.[46] The β-substituted phenylethyl cation, which is the most stable in the orthogonal perpendicular conformation, **40**, is by 41.6 kcal mol^{-1} (STO-3G) less stable than **39**. The energy differences between **39** and **40** and **7** and **11** are similar. The bridged **41** is only 6.2 kcal mol^{-1} (STO-3G) less stable than **39**. Taking into account the deficiencies of the basis set, we estimate that **39** and **41** are actually of comparable stability. The energy separation between the α-phenylvinyl cation **7** and the phenyl-bridged ion **9** is much higher. The energy gained upon bridging is much smaller for the β-vinylic cations (i.e., $\Delta E(\mathbf{11}-\mathbf{9})$ = 18.3 kcal mol^{-1}) than for the corresponding saturated cations ($\Delta E(\mathbf{40}-\mathbf{41})$ = 35.4 kcal mol^{-1}). This reluctance of the vinylic cations to bridge results mainly from higher ring strain. Structure **9** contains a cyclopropene ring while **41** contains a cyclopropane ring. The additional strain of cyclopropene compared with cyclopropane is estimated in eq 1.[47] At STO-3G, $\Delta E(1)$ = −20.6 kcal mol^{-1}, accounting


39


40


40a

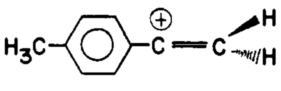

41

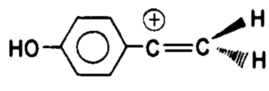

42

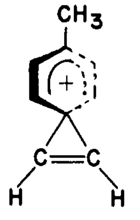
$$\text{c-}C_3H_4 + C_2H_6 \rightarrow \text{c-}C_3H_6 + C_2H_4 \qquad (1)$$

for the stability difference between **9** and **41**.

In contrast to the vinylic series where a barrier separates **11** and **9**, **40** collapses spontaneously to the bridged ion **41**. Furthermore, **11** rearranges without activation to **7**, but a significant barrier separates **40** and **39**.[48] In **40**, rotation by 60° around the C–C$^+$ bond to **40a** must precede hydrogen bridging (**42**) and rearrangement to the more stable ion **39**.[48] In the vinyl cation **11**, on the other hand, the 2p (C$^+$) orbital and the β-hydrogens are confined to the same plane, and bridging occurs spontaneously. In conclusion, despite the overall similarity, the $C_8H_7^+$ and the $C_8H_9^+$ cations should behave differently. The β-phenylvinyl cation **11** is expected to rearrange primarily to the α-substituted cation **7**, while the β-phenylethyl cation **40**, is predicted to collapse to the bridged ion **41**. These theoretical predictions are verified experimentally (compare our results with those reported in ref 15g).


43, H_f° = 223.1 KCAL·MOL^{-1}


44, H_f° = 164.9 KCAL·MOL^{-1}


45, H_f° = 248.6 KCAL·MOL^{-1}

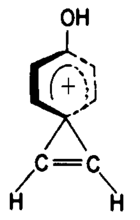
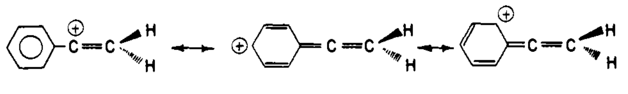

46, H_f° = 191.4 KCAL·MOL^{-1}

Figure 2.

Some of the structural details of the phenylvinyl cations are of interest. The α-phenylvinyl cation adopts the linear perpendicular conformation **7c** in which overlap between the cationic 2p (C$^+$) orbital and the benzene's π electrons is maximal.[10a] The short C_1–C_3 bond length of 1.378 Å results. The C_3–C_4 and the C_5–C_6 bonds are considerably lengthened relative to benzene (1.39 Å). As expected,[10a,49] the C_3–C_4 bonds (1.459 Å) are longer than the C_5–C_6 bonds (1.415 Å). The significant contribution of the allenic resonance hybrids **7e** and **7f** is apparent. Similar structural changes were reported for the analogues benzyl cation.[49]


7c **7e** **7f**

The cyclopropene ring in the phenyl-bridged cation **9** is distorted: the C_1–C_2 bond is shortened (1.268 Å) relative to cyclopropene (1.317 Å) while the C_1–C_3 and C_2–C_3 bonds are lengthened considerably (1.606 Å; 1.481 Å in cyclopropene). As a result the $C_1C_3C_2$ bond angle in **9** shrinks to 46.50°. As in **7** the benzenic C_3–C_4 and C_5–C_6 bonds are longer than the C_4–C_5 bonds. The structure of the bridged ethylenebenzenium cation **41** is similar except that the C_1–C_2 bond (1.400 Å) is longer.[46] In contrast to the linear parent $HC^+{=}CH_2$,[34,43a,c] the α-hydrogen in **11** is bent by 4.5°. Bending of the α-hydrogen stabilizes the cation by maximizing hyperconjugation between the 2p (C$^+$) orbital and the adjacent bonds. The trans isomer **11d** is more stable than the cis isomer **11e**[50b] because C–C hyperconjugation is more stabilizing than C–H hyperconjugation[10b] and because overlap is larger when the interacting orbitals are antiperiplanar.[50b] Bending at the vinylic center occurs also in other unsymmetrically substituted β-vinyl cations such as $HC^+{=}CHOH$[51a] and $HC^+{=}CHF$.[51b] These cations however, adopt the cis arrangement[51] because C–O and C–F bonds are poorer hyperconjugating groups than the C–H bond.[10b]

Economical constraints restrain us from studying theoretically all the cations which were investigated experimentally in this work. However, we have carried out MINDO/3 calculations for the *p*-methyl (**43**) and the *p*-hydroxy (**44**) α-substituted phenylvinyl

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(45) The somewhat different conclusions which are reported in ref 7m, pages 20 and 395 are based on preliminary STO-3G calculations which are assumed geometries, and the deficiancies of the STO-3G basis set were not taken into account.

(46) (a) Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 5919. (b) Reference 34a, page 324.

(47) Deficiencies of the computational method tend to cancel out in isodesmic reactions (e.g., eq 1).[34]

(48) The hydrogen-bridged **42** was not studied previously. Hehre's results[46] and preliminary calculations in our laboratory suggest a barrier of ~6 kcal mol^{-1} for the **40** → **39** rearrangement.

(49) Hehre, W. J. *Acc. Chem. Res.* **1975**, *8*, 369.

(50) (a) The same applies to **11c** where the α-hydrogen is bent by 7.4°. (b) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*.

(51) (a) Csizmadia, I. G.; Bernardi, F.; Lucchini, V.; Modena, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 542; (b) Csizmadia, I. G.; Lucchini, V.; Modena, G. *Theor. Chim. Acta* **1975**, *39*, 51.

cations and for the corresponding aryl-bridged cations **45** and **46**. We find (Figure 2) that these substituents have little effect on the relative stabilities of these isomeric cations. The **7–9**, **43–45**, and **44–46** energy separations are 25.3, 25.5, and 26.5 kcal mol^{-1}, respectively. The α-substituents are expected to stabilize the β-phenylvinyl cation **11** less than the α-phenylvinyl cation **7**.[10a–c] The energy separations between the α- and the β-isomers (or between the α- and the bridged isomers) are expected to be larger in the substituted phenylvinyl cations than in the present system. The substituted systems[52] are therefore expected to behave similarly to the bromostyrenes.

Experimental Section

General Procedures. The collisional activation (CA)[3] spectra were obtained with the use of either a ZAB-2F or a Varian MAT 311A double-focusing mass spectrometer, in which ions pass through the magnetic field (B) before entering the electric field (E). The collision cell was differentially pumped and situated in front of the energy resolving slit. Depending on the volatility, samples were either introduced via the heated gas inlet system or by use of a direct insertion mode. The source temperature was 150–180 °C, the uncorrected ionizing energy of the electron beam 70 eV and 10 eV, and the accelerating voltages were 8 (ZAB-2F) and 3 kV (MAT 311A), respectively. The magnetic and electric fields were adjusted to transmit exclusively the [M − Br]$^+$ ions. Helium was then introduced into the collision cell via a variable leak until the precursor ion abundance decreased to $^1/_3$ of its original value due to scattering and decomposition. CA spectra were then obtained either by scanning the electrostatic sector potential (MIKES methodology[11]) or by a simultaneous scanning of the magnetic and electric fields (linked B/E scan[13]). The data were taken on line to a PDP 11 computer or directly recorded on an XY recorder and normalized to the sum of the fragment ion intensities. Only peak heights were measured, and the abundances were not corrected for reduced multiplier response. The CA spectra are mean values of at least three (and at most five) measurements. The reproducibility was ±3 - ±10% depending on the abundance of the precursors. The kinetic energy release (T) measurements for unimolecular ^{79}Br· loss from the molecular ions were obtained with use of the ZAB-2F instrument and applying the MIKES technique. The T values were derived from the half-widths of the metastable peaks by using Beynon's equation[11d] and are the mean values of at least three scans. The energy resolution ($E/\Delta E$) of the instrument was from 2000 to 2500; corrections were applied for the widths of the main beam.

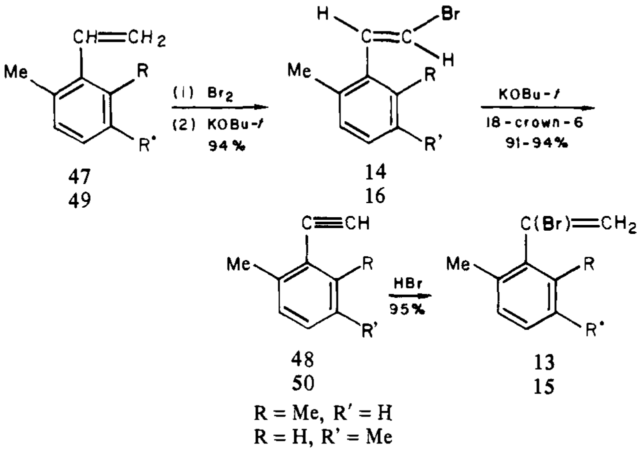
^{1}H NMR spectra were recorded on Varian EM 390 and Bruker WH 270 instruments; chemical shifts are reported in δ units downfield from internal Me$_4$Si. Preparative GC was performed on a Hewlett-Packard 5750 equipped with a thermal conductivity detector with helium as the carrier gas. The column mostly used is 4 mm × 3 m glass column packed with 5% UCCW-982 on chromosorb G, AW, AMCS (100/120 mesh). The boiling points given are uncorrected. All compounds mentioned in the mass spectrometric part of the paper were purified by GC.

Materials. **α-Bromostyrene (4)**,[53] **(*E*)- and (*Z*)-β-bromostyrenes (5** and **6)**,[54] **(*Z*)- and (*E*)-1,2-dianisyl-2-phenylvinyl bromides (23** and **24)**,[19a] and **2,2-dianisyl-1-phenylvinyl bromide (25)**[19d,55] were described previously and synthesized by the literature methods. The synthesis of **(*Z*)-1,2-dianisyl-2-tolylvinyl bromide (26)** and of **2,2-dianisyl-1-tolylvinyl bromide (27)** will be described elsewhere.[19k]

The ^{13}C-labeled α- and β-bromostyrenes (α-^{13}C)-**4**, (β-^{13}C)-**4**, (α-^{13}C)-**5**, and (β-^{13}C)-**5** were synthesized according to literature methods for the unlabeled compounds. They were characterized by ^{1}H NMR and by comparison of the GC retention times with those of the unlabeled samples.

(α-^{13}C) **Benzoic acid** was prepared from phenyllithium and ^{13}CO$_2$ (^{13}C enrichment 91%) in 92.5% yield. It was then converted[56] to (α-^{13}C) **benzyl bromide** in 82% yield; δ(CCl$_4$) 4.4 (d, 2 H, J = 152 Hz), 7.28 (m, 5 H). (α-^{13}C)**Benzyl cyanide** was prepared from the bromide in 90% yield by reacting it with NaCN in 90% EtOH; δ(CCl$_4$) 3.64 (d, 2 H, J = 134 Hz), 7.3 (m, 5 H). Treatment of the cyanide with KOH/H$_2$O/EtOH gave potassium (2-^{13}C)-phenyl acetate from which **(2-^{13}C)-phenylacetic acid** was obtained in an overall 90.4% yield; δ(CDCl$_3$) 3.62 (d, 2 H, J = 129 Hz), 7.3 (m, 5 H), 9.0 (s, 1 H). The acid was converted by a literature method[57] to **(2-^{13}C)-2-phenylethyl bromide** in 82.5% yield; δ(CCl$_4$) 3.13 (dt, 2 H, J = 131 and 7.5 Hz). Dehydrobromination with diazabicycloundecene (DBU)[58] gave 72% of **(α-^{13}C)-styrene:** δ(CCl$_4$) 5.05–5.2 (m, 1 H), 5.5–5.8 (m, 1 H), 6.62 (ddd, 1 H, J = 153; 17 and 11 Hz), 7.25 (m, 5 H). Bromination followed by dehydrobromination with KOBu-*t* gave a 9:1 mixture of **(α-^{13}C)-α-bromostyrene** [(α-^{13}C)-**4**] and **(*E*)-(α-^{13}C)-β-bromostyrene** [(β-^{13}C)-**5**] in 93% yield. The mixture was separated by preparative GC. (α-^{13}C)-**4**: δ(270 MHz, CDCl$_3$) 5.78 (dd, 1 H, J = 6.5 and 2 Hz), 6.12 (dd, 1 H, J = 5 and 2 Hz), 7.35 (m, 3 H), 7.6 (m, 2 H). (α-^{13}C-**5**) was identified by use of analytical GC.

Scheme **VIII**



(1-^{13}C)-Phenylacetic acid was prepared from benzylmagnesium bromide and ^{13}CO$_2$ in 66% yield; δ(CCl$_4$) 3.55 (d, 2 H, J = 7.5 Hz), 7.2 (s, 5 H), 11.05 (s, 1 H). The acid was converted to **(1-^{13}C)-2-phenylethyl bromide** in an overall 91% yield by LiAlH$_4$ reduction, tosylation of the alcohol, and replacement of the tosylate with LiBr; δ(CCl$_4$) 3.11 (q, 2 H, 2 H, J = 7.5 Hz), 3.48 (dt, 2 H, J = 153 and 7.5 Hz), 7.18 (m, 5 H). Dehydrobromination with DBU gave 78% of **(β-^{13}C)styrene**; δ(270 MHz, CDCl$_3$) 5.35 (ddd, 1 H, J = 160 Hz; 11 and 1 Hz), 5.75 (ddd, 1 H, J = 153 Hz, 17.5, and 1 Hz), 6.83 (dd, 1 H, J = 17.5 and 11 Hz), 7.2–7.45 (m, 5 H). Bromination, followed by KOBu-*t* dehydrobromination gave a 9:1 mixture of *(β-^{13}C)-α-bromostyrene* [(β-^{13}C)-**4**] and *(E)-(β-^{13}C)-β-bromostyrene* [(β-^{13}C)-**5**] in 86% yield. This mixture was separated by preparative GC and the compounds were identified by GC retention times and ^{1}H NMR: (β-^{13}C)-**4** δ(270 MHz, CDCl$_3$) 5.78 (dd, 1 H, J = 167 and 2 Hz), 6.12 (dd, 1 H, J = 159 and 2 Hz), 7.35 (m, 3 H), 7.6 (m, 2 H); (β-^{13}C)-**5** δ(270 MHz, CDCl$_3$) 6.77 (dd, 1 H, J = 191 and 14 Hz), 7.11 (dd, 1 H, J = 16 and 14 Hz, ABX system), 7.3 (m, 5 H).

(*E*)-β-(2,6-Dimethylphenyl)vinyl bromide (14) was obtained in 95% yield by bromination–dehydrobromination of 2,6-dimethylstyrene **47**. **14**: δ(CCl$_4$) 2.27 (s, 6 H), 6.2 (d, 1 H, J = 14 Hz), 6.95 (s, 3 H), 7.06 (d, 1 H, 14 Hz); MS M$^{+\cdot}$ m/z 212/210 (20%), 131 (100); colorless liquid; bp 85–90 °C (0.1 torr). Treatment of **14** with KOBu-*t* in the presence of catalytic amounts of 18-crown-6 ether[59] gave 93.8% of **(2,6-dimethylphenyl)acetylene (48)**: δ(CCl$_4$) 2.42 (s, 6 H), 3.36 (s, 1 H), 6.95 (m, 3 H); MS M$^{+\cdot}$ m/z 130 (56%), 115 (100); colorless liquid; bp 95–100 °C (15 torr). Addition of gaseous HBr[29c] to a solution of **48** in CHCl$_3$ gave 95.5% of pure **α-(2,6-dimethylphenyl)vinyl bromide (13)**: δ(CCl$_4$) 2.32 (s, 6 H), 5.64 (d, 1 H, J = 1 Hz), 5.9 (d, 1 H, J = 1 Hz), 6.95 (m, 3 H); colorless liquid; bp 86–91 °C (0.1 torr); MS M$^{+\cdot}$ m/z 212/210 (14%), 131 (100).

α-(2,5-Dimethylphenyl)vinyl bromide (15) and **(*E*)-β-(2,5-dimethylphenyl)vinyl bromide (16)** were synthesized similarly to **13** and **14** from the styrene **49** via the acetylene **50** (scheme VIII). **15**: δ(CCl$_4$) 2.29 (s, 3 H), 2.33 (s, 3 H), 5.65 (d, 1 H, J = 1 Hz), 5.79 (d, 1 H, J = 1 Hz), 6.98 (m, 3 H); colorless liquid; bp 90 °C (0.1 torr); MS M$^{+\cdot}$ m/z 212/210 (22%), 131 (100). **16**: δ(CCl$_4$) 2.27 (s, 6 H), 6.5 (d, 1 H, J = 14 Hz), 6.9 (s, 2 H), 7.02 (s, 1 H), 7.2 (d, 1 H, J = 14 Hz); MS M$^{+\cdot}$ m/z 212/210 (31%), 131 (100); colorless liquid; bp 88 °C (0.1 torr). **(2,5-Dimethylphenyl)acetylene (50)**: δ(CCl$_4$) 2.25 (s, 6 H), 3.02 (s, 1 H), 6.98 (s, 2 H), 7.18 (s, 1 H); MS M$^{+\cdot}$ m/z 130 (91%), 115 (100); colorless liquid; bp 95–100 °C (15 torr).

α-(3,5-Dimethylphenyl)vinyl bromide (17) and **(*E*)-β-(3,5-dimethylphenyl)vinyl bromide (18)** were prepared in 91% yield as a 7:3 mixture

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(52) The cations derived from the polysubstituted bromostyrenes **13–18** (i.e., **19**, **21**, and **22**) are closely related to **43** and **45**. The *p*-hydroxy substituent in **44** and **46** is used as a model for a *p*-methoxy substituent. The effect of adding aryl groups at the double bond as in **28–34** could not be studied.

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by adding Br_2 to 3,5-dimethylstyrene, followed by dehydrobromination. The colorless liquids were separated by preparative GC. **17**: $\delta(CCl_4)$ 2.3 (s, 6 H), 5.62 (d, 1 H, $J = 1$ Hz), 5.98 (d, 1 H, $J = 1$ Hz), 6.98 (s, 1 H), 7.1 (s, 2 H); MS $M^{+\cdot}$ m/z 212/210 (35%), 131 (100). **18**: $\delta(CCl_4)$ 2.3 (s, 6 H), 6.63 (d, 1 H, $J = 14$ Hz), 6.84 (s, 3 H), 6.98 (d, 1 H, $J = 14$ Hz); MS $M^{+\cdot}$ m/z 212/210 (40%), 131 (100).

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Template Effects. 3.[1] The Quantitative Determination of the Catalytic Effects of Alkali and Alkaline Earth Cations in the Formation of Benzo-18-crown-6 in Methanol Solution

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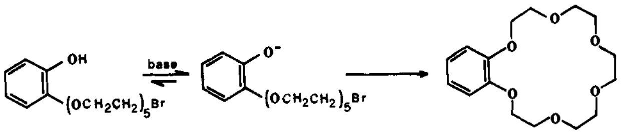
Abstract: Cyclization of the conjugate base of *o*-hydroxyphenyl 3,6,9,12-tetraoxa-14-bromotetradecyl ether to benzo-18-crown-6 in methanol solution has been found to be strongly and specifically accelerated by added alkali and alkaline earth bromides. The observed accelerations range from 13.2 for Cs^+ to a spectacular 540 for Sr^{2+}. The reported data refer to conditions in which the rate is independent of cation concentration, thus providing for the first time a quantitative determination of the template effect of added cations in the formation of a macrocyclic polydentate ligand. The different catalytic abilities as observed for the different cations are tentatively discussed in terms of a combination between proximity of the reactive ends in the bifunctional precursor complexed around the metal ion, and chemical factors arising from the extent of interaction of the cation with the nucleophilic oxide ion.

The study of interactions between alkali and alkaline earth cations with a variety of ligands has developed rapidly in the past decade as a subject of interdisciplinary nature.[2] It is now increasingly appreciated that coordinative interactions of alkali and alkaline earth cations may have a deep influence on a variety of chemical phenomena, among which is the course of many organic reactions. Remarkable examples of these effects may be found in the findings that alkali and alkaline earth cations may strongly facilitate the ease of formation of crown ethers.[1,3] The high yields obtained without high dilution led several authors to suggest that the metal ion acts as a template, i.e., organizes the crown's precursor around the metal ion itself in a conformation similar to that of the crown formed. Kinetic evidence of the template effect of some alkali and alkaline earth cations has been reported by us[4] for the base-promoted cyclization of *o*-hydroxyphenyl 3,6,9,12-tetraoxa-14-bromotetradecyl ether (AH) to benzo-18-crown-6 (B18C6) in water solution (Scheme I). The observed effect was explained as due to the greater reactivity of A^-M^{z+} as compared to that of free A^-. The reactivities of the associated forms could not be determined because of the failure to observe saturation kinetics even at the highest attainable cation concentrations, which indicated that conversion of A^- to A^-M^{z+} was far from being complete. Thus, the assessment of the catalytic effectiveness of the different cations was not possible in water solution. We have now obtained definite evidence that this goal can be achieved working in methanol solution, where interactions of cations with polyether ligands are known to be much stronger than in water.[5] The results of such an investigation are reported herein.

Scheme I



AH **A⁻** **B18C6**

Results and Discussion

The kinetics of cyclization of AH were carried out spectrophotometrically[4] on very dilute substrate ($\sim 3 \times 10^{-4}$ M) in order to suppress polymerization. $MeOEt_4N$ was added as the base to generate the anion A^-. Because of the low acidity of AH, excess $MeOEt_4N$ was required to promote extensive dissociation. For instance, in the presence of 0.08 M base the degree of dissociation was 0.88 (Table I). The amount of base to obtain a given extent of dissociation was significantly lowered by the presence of 0.05–0.1 M sodium, potassium, and cesium bromides. A significantly greater acidity-enhancing effect was brought out by added 0.001–0.003 M calcium, strontium, and barium bromides, which permitted AH to be quantitatively neutralized by an equivalent amount of base. This observation is indicative of strong interactions of the A^-M^{z+} type with the alkali cations and, even more so, with the alkaline earth cations.[6]

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