

**Acknowledgment.** The authors wish to thank the National Research Council of Canada and the University of Alberta for their generous support of this work. One of the authors (D.D.T.) is also grateful to the administration of the University of St. Andrews and the Faculty of the Department of Chemistry at St. Andrews for their hospitality during the period in which this manuscript was prepared.

## References and Notes

- (1) Part 8. D. D. Tanner, T. Pace, and T. Ochiai, *Can. J. Chem.*, **53**, 2202 (1975).
- (2) (a) Postdoctoral Fellow, University of Alberta, 1971–1972; (b) Postdoctoral Fellow, University of Alberta, 1972; (c) Postdoctoral Fellow, University of Alberta, 1972–1973. (d) Taken in part from the Ph.D. Thesis of T. Pace, University of Alberta, 1975.
- (3) M. S. Kharasch, W. S. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **20**, 1430 (1955).
- (4) P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).
- (5) W. Thaler, *J. Am. Chem. Soc.*, **85**, 2607 (1963).
- (6) D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Am. Chem. Soc.*, **91**, 7398 (1969).
- (7) D. S. Ashton, J. M. Tedder, and J. C. Walton, *Chem. Commun.*, 1487 (1971).
- (8) D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *J. Am. Chem. Soc.*, **93**, 4802 (1971).
- (9) D. D. Tanner, M. W. Mosher, N. C. Das, and E. V. Blackburn, *J. Am. Chem. Soc.*, **93**, 5846 (1971).
- (10) C. Ronneau, J. Scumillian, P. Dejalive, and A. Bruylants, *Tetrahedron Lett.*, 317 (1972).
- (11) D. D. Tanner, Y. Kosugi, E. V. Blackburn, and T. Ruo, *Tetrahedron Lett.*, 2413 (1976).
- (12) J. G. Traynham, E. E. Green, Y. S. Lee, F. Schweinsberg, and C. E. Low, *J. Am. Chem. Soc.*, **94**, 6552 (1972).
- (13) P. S. Skell and K. J. Shea, *J. Am. Chem. Soc.*, **94**, 6550 (1972).
- (14) D. D. Tanner, J. E. Rowe, T. Pace, and Y. Kosugi, *J. Am. Chem. Soc.*, **95**, 4705 (1973).
- (15) W. Thaler, "Methods in Free-Radical Chemistry", Vol. 2, E. S. Huyser, Ed., Marcel Dekker, New York, N.Y., 1969, p 201.
- (16) D. D. Tanner, T. Pace, and T. Ochiai, *J. Am. Chem. Soc.*, **97**, 6162 (1975).
- (17) K. Ody, A. Nechvatal, and J. Tedder, *J. Chem. Soc., Perkin Trans. 2*, 521 (1976).
- (18) P. S. Skell and K. J. Shea, "Free Radicals", Vol. 2, J. K. Kochl, Ed., Wiley, New York, N.Y., 1973.
- (19) S. J. Cristol, M. A. Imhoff, and D. C. Lewis, *J. Org. Chem.*, **35**, 1722 (1970).
- (20) J. H. Hargis and P. B. Shelvin, *J. Chem. Soc., Chem. Commun.*, 179 (1973).
- (21) (a) R. V. Lloyd, D. E. Wood, and M. T. Rogers, *J. Am. Chem. Soc.*, **96**, 7130 (1974); (b) R. V. Lloyd and D. E. Wood, *J. Am. Chem. Soc.*, **97**, 5986 (1975).
- (22) D. D. Tanner, T. Pace, and T. Ochiai, *J. Am. Chem. Soc.*, **97**, 4303 (1975).
- (23) J. C. Conly, *J. Am. Chem. Soc.*, **75**, 1148 (1953).
- (24) R. C. Weast, Ed., "Handbook of Chemistry and Physics", 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969.
- (25) V. F. Willie, K. Dirr, and H. Kerber, *Justus Liebigs Ann. Chem.*, **591**, 177 (1955).
- (26) C. F. H. Allen and S. Converse, "Organic Syntheses", Collect. Vol. 1, Wiley, New York, N.Y., 1951, p. 226.
- (27) H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography", Varian Aerograph, Berkeley, Calif., 1969.
- (28) G. H. Cady, *Inorg. Synth.*, **5**, 156 (1957).
- (29) K. Bieman, "Mass Spectrometry, Applications to Organic Chemistry", McGraw-Hill, New York, N.Y., 1962.

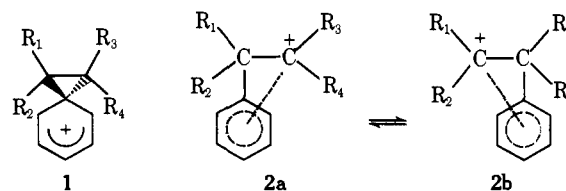
## Rearrangement of Ethylenebenzenium Ions to $\alpha$ -Phenylethyl (Styryl) Cations. Determination of the Relative Energies of the $\sigma$ -Bridged Ethylenebenzenium Ion, the Open-Chain 2-Phenylethyl Cation, and the $\alpha$ -Styryl Cation<sup>1</sup>

George A. Olah,\* Robert J. Spear,<sup>2a</sup> and David A. Forsyth<sup>2b</sup>

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received July 22, 1975

**Abstract:** 2-Chloroethylbenzene (3-H) is initially ring protonated by HF-SbF<sub>5</sub> (1:1) in SO<sub>2</sub>ClF, but upon standing at -78 °C, an irreversible reaction occurs to form the ethylenebenzenium ion (4-H). The subsequent quantitative rearrangement of 4-H to the  $\alpha$ -styryl cation (5-H) was followed by <sup>1</sup>H NMR spectroscopy; for this reaction  $E_a = 13$  kcal/mol,  $\log A = 13.6$ . 5-H is stable even at elevated temperatures and does not rearrange to the methyltropylium ion. The analogous rearrangement of 4-OMe to 5-OMe was also observed, using *p*-(2-chloroethyl)methoxybenzene as the precursor. The relative energy of the  $\sigma$ -bridged 4-H and the open-chain 2-phenylethyl cation (8-H) are discussed in terms of these results. Carbon-13 chemical shifts are discussed in relation to the structure and charge distribution of these, and related, carbocations.

The solvolytic behavior of  $\beta$ -arylalkyl systems has been one of the most studied and most controversial topics of modern physical organic chemistry.<sup>3</sup> The original proposal by Cram<sup>3a</sup> that the intermediates in these reactions were  $\sigma$ -bridged ethylenebenzenium (phenonium)<sup>4</sup> ions (**1**) was criticized by Brown,<sup>3b,c</sup> who suggested that the experimental data could alternatively be rationalized in terms of weakly  $\pi$ -bridged, rapidly equilibrating ions (**2a**, **2b**). Further solvolytic studies led to the conclusion by Brown that a continuous spectrum of ions exists, from open to completely bridged ions, depending upon solvent and substitution in the ions.<sup>5</sup> It has also been suggested from studies of isotope effects that the initial intermediates in the aryl-assisted pathways are unsymmetrically bridged ions, which may subsequently collapse to ethylenearenium ions (**1**).<sup>3d,6,7</sup> The behavior of 2-arylethyl systems



is possibly the most diverse of all the  $\beta$ -arylalkyl systems. Competition between the aryl-assisted and solvent-assisted pathways, which characterize many of the  $\beta$ -arylalkyl solvolyses, is finely balanced.<sup>3d,8</sup>

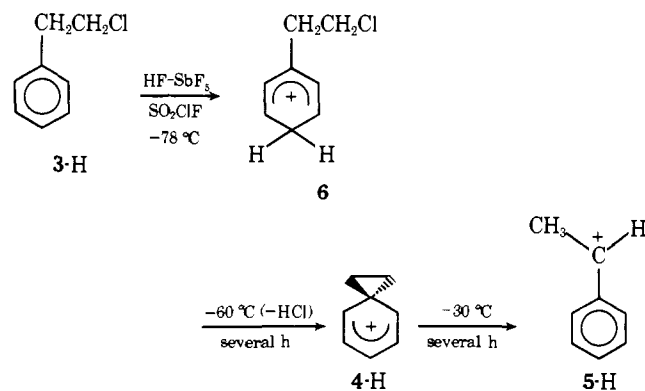
A number of studies aimed at resolving the structure of the intermediate ions from  $\beta$ -arylalkyl precursors by examining these systems under stable ion conditions have been published.

It is not always possible to probe the structure of initial intermediates which may be important under solvolytic conditions because of possible subsequent conversions to more stable carbocation structures. Nevertheless, under stable ion conditions,  $\beta$ -arylethyl derivatives yield ions which were unequivocally determined by NMR studies to have the  $\sigma$ -bridged ethylenebenzenium ion structure rather than equilibrating open or  $\pi$ -bridged forms.<sup>9-11</sup> Theoretical studies also indicate a preference for the  $\sigma$ -bridged ion. Hehre has reported STO-3G calculations on the parent ethylenebenzenium ion (**1**) which predict the symmetrical  $\sigma$ -bridged structure to be more stable than the most stable open form.<sup>12</sup> An earlier MO study demonstrated that the EHT and CNDO/2 methods are quantitatively unreliable for structures containing the cyclopropane ring, but an estimate was made indicating that the bridged ethylenebenzenium ion was favored over the open form.<sup>13</sup>

We have currently been reexamining the ionization of 2-chloroethylbenzene (**3-H**) under stable ion conditions. Previous attempts to study this system have been hindered by the extreme sensitivity to polymerization and the (apparently competing) formation of the  $\alpha$ -styryl cation (**5-H**) in the ionization process.<sup>9</sup> We have developed novel experimental conditions which allow the ethylenebenzenium ion (**4-H**) to be obtained free of any other products. Most importantly, we have observed the conversion of the ethylenebenzenium ion to the isomeric  $\alpha$ -styryl cation in quantitative yield. Previously, it was reported that ethylenebenzenium and methylcarbenium ions were formed by separate pathways with no interconversion of the two types.<sup>9</sup> The rearrangement most likely involves the open-chain 2-phenylethyl cation as a higher-energy intermediate. Thus, a kinetic study yields data on the relative energies of the  $\sigma$ -bridged and open forms in the phenylethyl system. For comparison, the ionization behavior of *p*-(2-chloroethyl) methoxybenzene (**3-OMe**) has also been studied. The <sup>13</sup>C NMR chemical shifts, summarized in Table I, are discussed in terms of the structure and charge distribution in these and related carbocations.

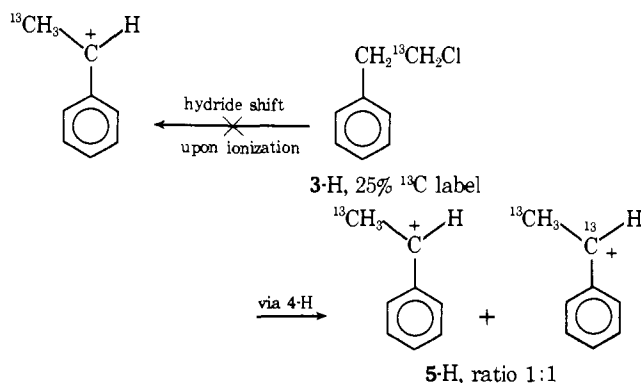
## Results and Discussion

**Preparation of Ions and Their Rearrangements.** Addition of a solution of 2-chloroethylbenzene (**3-H**) in SO<sub>2</sub>ClF to a solution of HF-SbF<sub>5</sub> (1:1) in SO<sub>2</sub>ClF at -78 °C initially results in ring protonation to yield the *p*-2-chloroethylbenzenium ion (**6**, Table I). **6** exhibits <sup>1</sup>H NMR spectra characteristic of monoalkylbenzenium ions;<sup>14</sup> at temperatures below -90 °C, the static *p*-alkylbenzenium ion can be frozen out, but at higher temperatures rapid intramolecular hydrogen shifts lead to broadening and eventual coalescence of the peaks in the <sup>1</sup>H NMR spectrum corresponding to all of the protons bound to the ring. If the solution of **6** is stored at -78 °C for several days, an irreversible reaction occurs to form the ethylenebenzenium ion (**4-H**, Table I). At -60 °C, the reaction is considerably faster, taking only a few hours for complete conversion to **4-H**. Some  $\alpha$ -styryl cation (**5-H**) is also usually



observed to form. If the solution of **4-H** is allowed to rise in temperature, no change occurs in the <sup>1</sup>H NMR spectrum until -30 °C, where a slow, quantitative formation of **5-H** is observed. The half-life of this reaction is 155 min at -27 °C. A typical experimental sequence is depicted in Figure 1a-e, while the <sup>13</sup>C NMR spectrum of **4-H** and **5-H** are shown in Figure 2a and 2b.

Solutions prepared in the manner described above are free of polymeric impurities, implying that the polymerization reactions which hampered earlier studies<sup>9</sup> were due to reaction of the ions with non-ionized precursor and not due to inherent instabilities of the ions. The small concentration of **5-H** formed from **6** at -60 °C (Figure 1c) was shown, by ionizing **3-H** containing 25% <sup>13</sup>C label at C(2) of the side chain, *not* to be due to a competing hydride-shift mechanism occurring before formation of **4-H**. At the low conversion levels to **5-H** at -60 °C, the label was shown by <sup>13</sup>C NMR spectroscopy to be equally distributed at C<sup>+</sup> and CH<sub>3</sub> in **5-H**, showing that the reaction must proceed via **4-H**.<sup>15</sup> The reaction itself is probably due to local overheating during the addition of **3-H** to the acid, since further conversion of **4-H** to **5-H** after all of **6** has been consumed is negligible at -60 °C. As expected, complete



conversion of **4-H** to **5-H** at -10 °C distributes the label equally at C<sup>+</sup> and CH<sub>3</sub> in **5-H**.

It should be noted that  $\beta$ -phenylethyl derivatives, when solvolyzed under normal conditions, yield no products originating from the styryl cation (**5-H**) except for the "hot" carbocations formed by deaminative acetolysis of 2-phenylethylamine.<sup>3d</sup> In this latter reaction, 18% of the products are derived from **5-H**, but <sup>14</sup>C labeling studies showed that **5-H** was not derived from **4-H** in this reaction.<sup>3d</sup>

For comparison, we have also studied the behavior of *p*-(2-chloroethyl)methoxybenzene (**3-OMe**) under stable ion conditions. The methoxyl group should stabilize the resulting *p*-methoxyethylenebenzenium ion (**4-OMe**) relative to **4-H**. However, when **3-OMe** is treated with HF-SbF<sub>5</sub> in SO<sub>2</sub>ClF at -78 °C, **4-OMe** can only be observed as a transient species

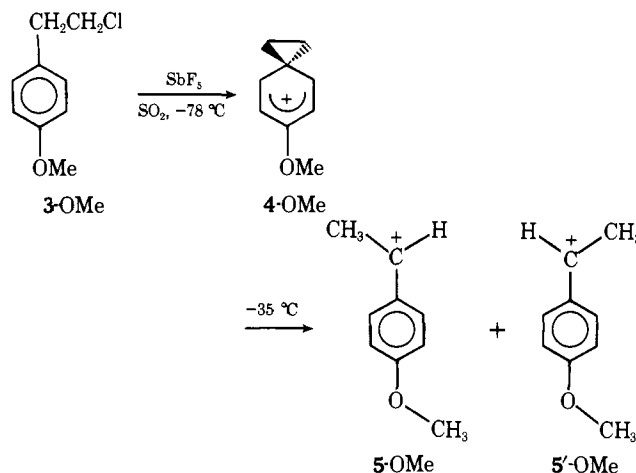
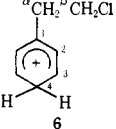
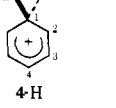
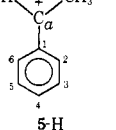
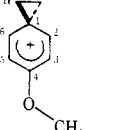
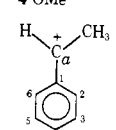
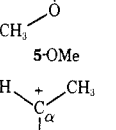
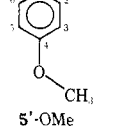
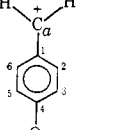
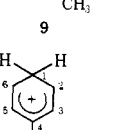
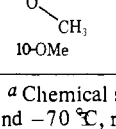


Table I.  $^{13}\text{C}$  NMR Data<sup>a</sup> for the Ethylenebenzenium Ions,  $\alpha$ -Styryl Cations, and Related Carbocationic Species

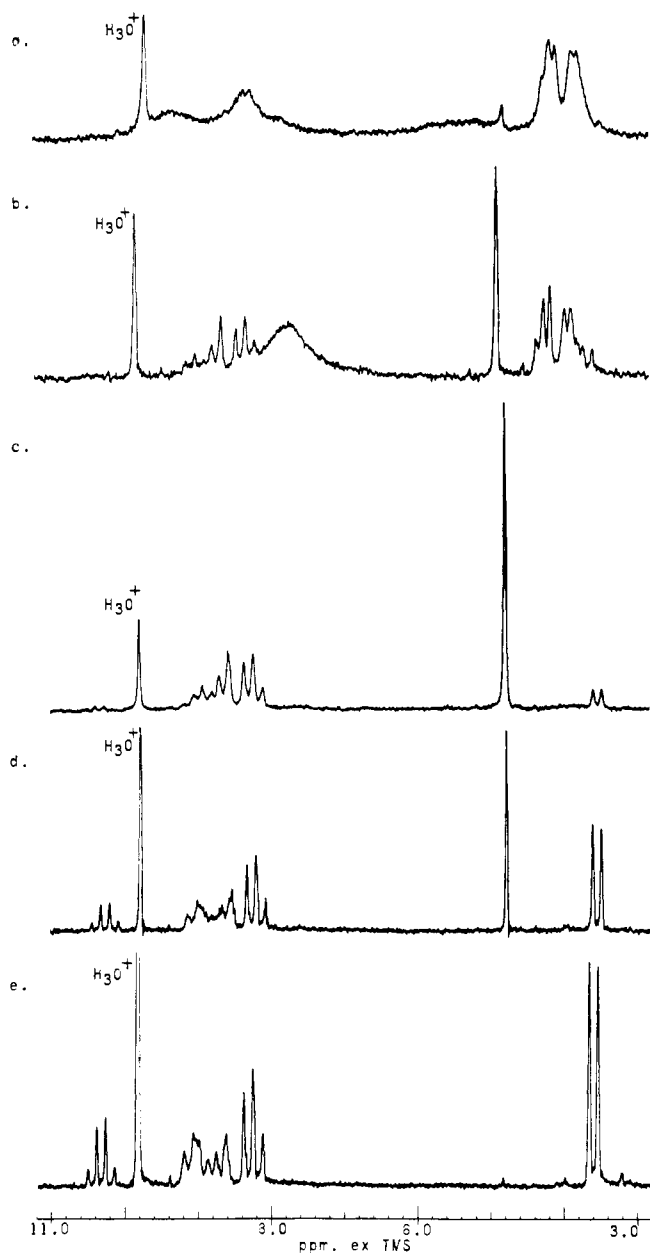
Ion	C(1)	C(2), C(6)	C(3), C(5)	C(4)	C $_{\alpha}$	Additional	
	<i>b</i>	197.7	136.8	181.2	48.9	43.2	$\beta\text{CH}_2$ , 40.7 <sup>d</sup>
	<i>c</i>	68.8	171.8	133.4	155.4	60.7	
	<i>e</i>	68.9	$^1J_{\text{CH}} = 173.5$ 171.9	$^1J_{\text{CG}} = 173.8$ 133.4	$^1J_{\text{CH}} = 168.3$ 154.9	$^1J_{\text{CH}} = 178.4$ 60.7	
	<i>c</i>	142.4	C(2), 143.8 $^1J_{\text{CH}} = 169.4$ C(6), 155.3 <sup>g</sup>	C(3), 134.3 <sup>f</sup> $^1J_{\text{CH}} = 174.7$ C(5), 133.9 <sup>f</sup> $^1J_{\text{CH}} = 174.7$	162.0 <sup>g</sup>	229.8 $^1J_{\text{CH}} = 159.7$	CH <sub>3</sub> , 27.2 $^1J_{\text{CH}} = 130.7$
	<i>e</i>	141.5	C(2), 143.6 C(6), 155.1	133.8	161.6	230.4	CH <sub>3</sub> , 27.4
	<i>e</i>	49.25	171.2 (br)	121.0 (br)	183.1	41.2 $^1J_{\text{CH}} = 176.2$	OCH <sub>3</sub> , 59.35 $^1J_{\text{CH}} = 149.9$
	<i>h</i>	135.9	C(2), 142.5 C(6), 157.3	C(3), 125.0 C(5), 116.2	185.3	195.5	OCH <sub>3</sub> , 60.1 CH <sub>3</sub> , 21.1
	<i>h</i>	135.9	C(2), 147.1 C(6), 152.5	C(3), 117.6 C(5), 123.5	185.3	195.5	OCH <sub>3</sub> , 60.1 CH <sub>3</sub> , 21.1
	<i>h</i>	139.9	C(2), 156.6 C(6), 151.4	C(3), 118.6 C(5), 125.9	188.2	148.8	OCH <sub>3</sub> , 61.5
	<i>i</i>	39.9 $^1J_{\text{CH}} = 125.9$	C(2), 175.1 <sup>g</sup> C(6), 168.4 <sup>g</sup>	C(3), 120.7 $^1J_{\text{CH}} = 173.4$ C(5), 126.7 $^1J_{\text{CH}} = 174.6$	191.9		OCH <sub>3</sub> , 62.2 $^1J_{\text{CH}} = 152.8$

<sup>a</sup> Chemical shifts are in parts per million from external (capillary) Me<sub>4</sub>Si; coupling constants are in hertz. <sup>b,c</sup> In HF-SbF<sub>5</sub>-SO<sub>2</sub>ClF at -90 and -70 °C, respectively. <sup>d</sup> Assignment confirmed from  $^{13}\text{C}$  labeled precursor. <sup>e</sup> In SbF<sub>5</sub>-SO<sub>2</sub> at -80 °C. <sup>f</sup> Alternate assignment possible. <sup>g</sup>  $^1J_{\text{CH}}$  could not be determined accurately due to partial overlap of signals. <sup>h</sup> In SbF<sub>5</sub>-SO<sub>2</sub>ClF at -80 °C. <sup>i</sup> In FSO<sub>3</sub>H-SO<sub>2</sub>ClF at -40 °C.

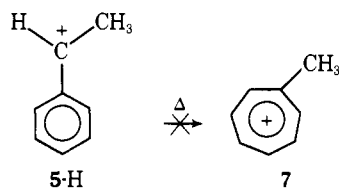
which rapidly rearranges to the isomeric *p*-methoxystyryl cations **5**-OMe and **5'**-OMe at -78 °C. **4**-OMe can be prepared using SbF<sub>5</sub> in S<sub>2</sub>, as reported previously.<sup>9</sup> The subsequent rearrangement, under these conditions, is slow below -70 °C, but can be readily followed by  $^1\text{H}$  NMR spectroscopy at higher temperatures. At -35 °C, the half-life of the reaction is  $24 \pm 1$  min. The facile rearrangement of **4**-OMe in HF-SbF<sub>5</sub> can be rationalized as involving protonation of the methoxyl group and subsequent destabilization of **4**-OMe. HF-SbF<sub>5</sub> is a sufficiently strong acid to protonate a wide range of aromatic

methoxyl groups, yielding dicationic species in some instances.<sup>16</sup>

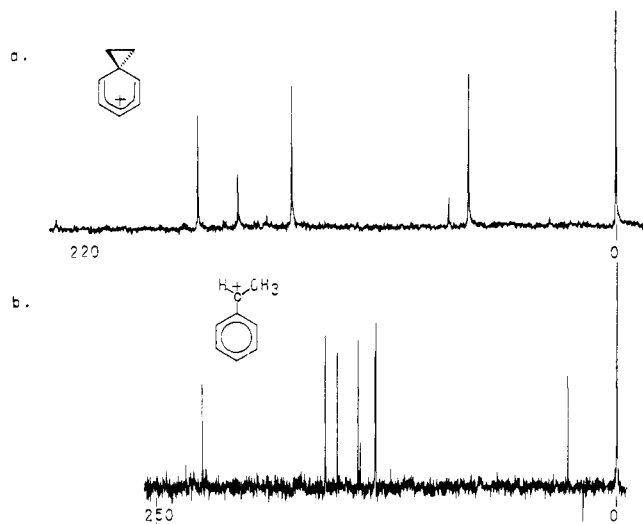
The behavior of **5**-H at elevated temperatures is also of interest because of the possibility for rearrangement to the methyltropylium ion (**7**). Winstein and co-workers<sup>17</sup> observed the formation of the tropylium ion and substituted tropylium ions from thermal rearrangement of norbornadien-7-yl cations. Although earlier mass spectral studies suggested that the conversion of benzyl cations to tropylium ions was an extremely facile process,<sup>18</sup> recent studies using ion cyclotron resonance



**Figure 1.**  $^1\text{H}$  NMR spectra obtained from 2-chloroethylbenzene (**3-H**) in  $\text{HF-SbF}_5\text{-SO}_2\text{ClF}$  at  $-78\text{ }^\circ\text{C}$ . (a) The *p*-2-chloroethylbenzenium ion (**6**) at  $-90\text{ }^\circ\text{C}$ ; the broadness is due to hydrogen migration which has not been completely frozen out. (b) The solution of **6** after 20 min at  $-60\text{ }^\circ\text{C}$ , showing the partial formation of the ethylenebenzenium ion (**4-H**). Note that hydrogen migration in the aromatic ring of **6** is now rapid, leading to the broad absorption at  $\delta$  7.5–8.2. (c) The spectrum of **4-H** after complete conversion from **6**. The small doublet at  $\delta$  3.6 is from the  $\alpha$ -styryl cation (**5-H**). (d) The solution in c after heating at  $-20\text{ }^\circ\text{C}$  for 100 min, showing the conversion of **4-H** to **5-H**. (e) **5-H** after complete conversion.



have shown that interconversion does not occur.<sup>19</sup> Solutions of **5-H** are remarkably stable and can be heated in a sealed tube at  $60\text{ }^\circ\text{C}$  for days without noticeable decomposition. Ultimately polymeric materials do form, but **7** is never detectable in solution. Presumably, the conversion of a benzylic cation into a



**Figure 2.** (a) The  $^{13}\text{C}$  NMR spectrum of the ethylenebenzenium ion (**4-H**). (b) The  $^{13}\text{C}$  NMR spectrum of the  $\alpha$ -styryl cation (**5-H**). Note these spectra are at differing sweep widths; a small amount of **5-H** can be detected in the spectrum of **4-H**.

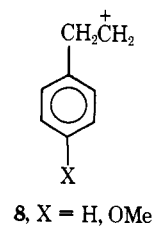
tropylium ion in solution is prohibitively energetic and any rearrangements which do yield tropylium ions cannot involve benzylic cation intermediates.

**Structure of the Ions and Their Relative Energies.** The  $^{13}\text{C}$  NMR data for **4-H** and **4-OMe** (Table I) are completely consistent with the symmetrical  $\sigma$ -bridged structures.<sup>9,20</sup> The most unequivocal data are the high-field shifts of the spiro carbon (C(1)) compared to the deshielded position of ipso aromatic carbons,<sup>21a</sup> and the cyclopropyl-like  $\sigma$  carbons with their characteristically large  $^1J_{\text{CH}}$  values;<sup>21b</sup> neither can be rationalized in terms of equilibrating open or  $\pi$ -bridged ions.

The rearrangement of **4-H** to **5-H** and **4-OMe** to **5-OMe** is extremely interesting.

By analogy with studies by Poulter and Winstein<sup>22</sup> on ring opening of cyclopropylcarbinyl cations the conversion of **4-H** to **5-H** must proceed via the open-chain 2-phenylethyl cation **8**. Cyclopropane protonation in the ethylenebenzenium ion would lead to a dicationic intermediate, which is improbable, particularly in view of the quoted work by Winstein.<sup>22</sup> Although the  $^{13}\text{C}$  NMR data cannot rule out very small contributions from **8** to the ground-state structure of **4**, it is also reasonable to assume that **8** corresponds to a high-energy intermediate in the transformation of **4** to **5**. Such a scheme is depicted in Figure 3. We have accordingly determined the activation energy ( $E_a$ ) for the transformation of **4-H** to **5-H** by determining the rate of rearrangement by  $^1\text{H}$  NMR spectra in the temperature range  $-27$  to  $-5\text{ }^\circ\text{C}$ ; a value of 13 kcal/mol,  $\log A = 13.6$ , was obtained.

If **8-H** is a local energy minimum on the reaction profile (Figure 3), the energy difference between **4-H** and **8-H** will



closely approximate  $E_a$ , thereby placing an upper energy limit of 13.0 kcal/mol between **4-H** and **8-H** in this superacid solution. This can be compared to the 35.4 kcal/mol difference calculated between the open and bridged ions in the gas phase in STO-3G calculations by Hehre.<sup>12</sup> Hehre indicated that with

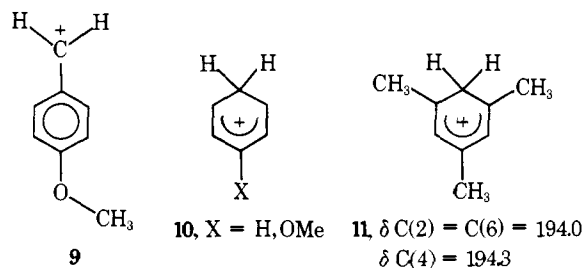


Figure 3. A reaction profile for the conversion of the ethylenebenzenium ion (4-H) to the  $\alpha$ -styryl cation (5-H) via the intermediate 2-phenylethyl cation (8).

further geometric optimization and an extended basis set, the difference between open-chain and bridged forms was likely to be 20–25 kcal/mol. An earlier theoretical estimate of the energy difference was 1–4 kcal/mol, based on EHT and CNDO calculations and an experimental energy difference for the corresponding radical species.<sup>13</sup>

Substitution at  $C_\alpha$  or  $C_\beta$  by groups which are able to supply electron density by inductive or resonance donation should markedly lower the energy of the open ions (cf. 8) relative to the corresponding bridged ions (cf. 4). The obvious conclusion regarding the relative energies of 4-H and 8-H (<13 kcal/mol difference) is that the open ions could be more stable than the corresponding bridged ions from some suitably substituted  $\beta$ -phenylalkyl derivatives. Indeed, previous studies on the 2,3-dimethyl-3-phenyl-2-butyl system suggest that equilibrating ions are formed under stable ion conditions.<sup>9,23</sup> We are currently examining, under stable ion conditions, some derivatives of 3-H, where  $C_\alpha$  and  $C_\beta$  are substituted by methyl groups in the anticipation that the energy relationship between the open-chain and bridged ions can be further elucidated.

**Charge Distributions.** The <sup>13</sup>C spectra reported in Figure 1 allow some conclusions to be drawn regarding relative charge distributions in benzenium ions, ethylenebenzenium ions, and benzylic cations. Conclusions about charge distributions from <sup>13</sup>C chemical shifts should be made with care, but shifts of carbon atoms of the same hybridization and substitution pattern and at positions remote from the site of changes in structure appear to reliably reflect charge densities.<sup>24</sup> The <sup>13</sup>C chemical shifts of C(4) in 4-H appears at higher field than C(4) in 5-H, which suggests that more positive charge is delocalized into the ring  $\pi$  system in the  $\alpha$ -styryl cation than in the ethylenebenzenium ion. Even greater charge delocalization would be expected in a primary benzylic ion and the shift of C(4) in the *p*-methoxybenzyl cation 9 is in agreement with this ex-



pectation when compared with the C(4) shifts in 4-OMe and 5-OMe. Further evidence suggesting greater charge delocalization into the  $\pi$  system in the benzylic ions relative to the ethylenebenzenium ions can be seen by the fact that methoxyl rotation in ion 4-OMe is fast enough to give broad coalesced peaks for the carbons ortho and meta to the methoxyl substituent. The faster methoxyl rotation at  $-78$  °C in 4-OMe indicates lesser electron demand on the methoxyl group and hence less charge development at C(4).

From the chemical shift of C(4) in 10-OMe (Table I), benzenium ions produced by protonation of the aromatic ring appear to have more charge delocalized into the ring system than even a primary benzylic ion. The substantial difference in chemical shifts at C(4) in the benzenium ion 10-OMe and the structurally similar ethylenebenzenium ion 4-OMe can be rationalized on the basis of the well-known ability of a cyclopropyl group to delocalize positive charge. That the cyclopropyl group plays an important role in delocalizing charge can be seen by comparing the chemical shifts of the cyclopropyl carbons in 4-H to the much more shielded cyclopropyl carbons in 4-OMe, in which the methoxyl group lessens the need for charge stabilization by the cyclopropyl group. Unfortunately, it is not possible to compare the <sup>13</sup>C shifts for 4-H with those for 10-H, since all attempts to obtain a <sup>13</sup>C spectrum of the completely frozen-out (static) ion 10-H have so far been unsuccessful.<sup>25</sup>

The closest analogy to 10-H is the mesitylenium ion (11), where the carbon-13 shifts of C(2) = C(6) and C(4) are nearly coincident.<sup>26</sup> In contrast, the C(2) = C(6) resonances in 4-H are strongly deshielded from C(4), and this represents another example of the deshielding of a charge-bearing carbon resonance induced by a directly attached cyclopropyl group.<sup>21</sup> The <sup>13</sup>C NMR spectra of 9 and 10-OMe are characterized by large chemical-shift differences between both the carbon pairs C(3)  $\neq$  C(5) and C(2)  $\neq$  C(6). The corresponding proton chemical shifts also show large (on the <sup>1</sup>H NMR scale) chemical-shift differences between H(3) and H(5) and H(2) and H(6).<sup>16,28</sup> The chemical-shift difference between C(3) and C(5) is due to the  $\gamma$ -substituent effect<sup>24</sup> from the frozen-out methoxyl methyl group, which shields the syn carbon C(3) relative to C(5), the anti carbon (Table I). A further example of the  $\gamma$ -substituent effect can be seen in the  $\alpha$ -styryl cation (5-H), where C(2), the carbon syn to the methyl group, is shielded by 11.5 ppm over C(6). Note, however, the near equivalence of C(3) and C(5) in 5-H ( $\Delta\delta = 0.4$  ppm) in contrast to the chemical-shift differences between C(2) and C(6) in 9 and 10-OMe, which are comparable to the  $\gamma$ -substituent effect induced difference between C(3) and C(5).

The reason for the chemical-shift differences between these carbons meta to the methoxyl group is not immediately obvious. If it is a result of charge polarization, it is not reproduced by semiempirical calculations, nor is the  $\gamma$ -substituent effect reproduced.<sup>24</sup> Further studies using more sophisticated theoretical methods, such as *ab initio*, may be helpful in resolving this question. As a result of this, the relative assignment of C(2) and C(6) in 9 and 10-OMe and the major and minor isomers 5-OMe and 5'-OMe, shown in Table I, cannot be made with any certainty.

## Experimental Section

2-Chloroethylbenzene, *p*-methoxyphenylethanol, and anisole were commercial samples. *p*-(2-Chloroethyl)methoxybenzene and 2-chloroethylbenzene, 25% <sup>13</sup>C labeled at C(2) of the side chain, were available from a previous study.<sup>9</sup> All materials were purified before use; fluorosulfuric acid was doubly and SbF<sub>5</sub> triply distilled before use. HF-SbF<sub>5</sub> was an equimolar solution prepared by addition of anhydrous HF to SbF<sub>5</sub>.

**Preparation of Ions.** The 2-chloroethylbenzenium ion (6) was prepared by dropwise addition of 2-chloroethylbenzene (3-H) (200

mg) in  $\text{SO}_2\text{ClF}$  (1 ml) to a 1:3 (by volume) solution of  $\text{HF-SbF}_5$  in  $\text{SO}_2\text{ClF}$  (2.5 ml) at  $-78^\circ\text{C}$ . Vigorous shaking and cooling were maintained during addition. Conversion of **6** to the ethylenebenzenium ion (**4-H**) was carried out either by allowing the solution of **6** to stand at  $-78^\circ\text{C}$  for several days or at  $-60^\circ\text{C}$  for several hours (cf. Figure 1). The styryl cation (**5-H**) was formed from **4-H** by warming to  $-20$  to  $-10^\circ\text{C}$ .

The *p*-methoxyethylenebenzenium ion (**4-OMe**) was prepared by addition of *p*-(2-chloroethyl)methoxybenzene (**3-OMe**) in  $\text{SO}_2$  at  $-78^\circ\text{C}$  to  $\text{SbF}_5$  in  $\text{SO}_2$  at  $-78^\circ\text{C}$ . Conversion of **4-OMe** to the *p*-methoxystyryl cations (**5-OMe**, **5'-OMe**) was achieved after several hours at  $-40$  to  $-30^\circ\text{C}$ . The *p*-methoxybenzyl cation and *p*-methoxybenzenium ion<sup>16</sup> were prepared as described previously.

**Nuclear Magnetic Resonance Spectra.**  $^1\text{H}$  NMR spectra were obtained using a Varian Associates Model A56/60 spectrometer equipped with a variable temperature probe. The temperatures reported were the thermostat settings on the temperature controller, which was calibrated by direct insertion of a thermometer to within  $10^\circ\text{C}$  of the actual temperature. More accurate temperature determinations were made in the kinetic studies (see below). Chemical shifts were measured from external (capillary)  $\text{Me}_4\text{Si}$ .

$^{13}\text{C}$  NMR spectra were obtained using a Varian Associates Model XL-100 spectrometer equipped with a broad band decoupler, variable temperature probe, and interfaced with a Varian 620-L computer operating with 8192 digital points. Chemical shifts were measured from the  $^{13}\text{C}$  signal of 5%  $^{13}\text{C}$ -enriched  $\text{Me}_4\text{Si}$  contained in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube. Coupling constants were obtained directly from the spectra recorded in the gyro-gate mode.

**$^{13}\text{C}$  Labeling Study.** The ionization of **3-H** containing 25%  $^{13}\text{C}$  at C(2) of the side chain was carried out to determine the position of the label in **5-H**. The initial conditions were the same as used to generate **4-H** from **3-H** at  $-60^\circ\text{C}$  in the absence of label. The small amount of **5-H** formed along with **4-H** showed equal enhancement of the  $\text{C}^+$  and  $\text{CH}_3$  resonances in the  $^{13}\text{C}$  NMR spectrum due to the  $^{13}\text{C}$  enrichment, thus indicating complete scrambling. Also, the resonance for the equivalent ethylene carbons in **4-H** was enhanced in labeled **4-H**. The  $^{13}\text{C}$ - $^{13}\text{C}$  coupling between the spiro carbon and the ethylene carbon in **4-H** could not be determined because of the insufficient strength of the label and the splitting in the expected doublet is probably less than 10 Hz ( $J_{\text{CC}}$  for cyclopropane is predicted to be  $\sim 10$  Hz).<sup>21b</sup> Complete conversion of labeled **4-H** to **5-H** also gave scrambled label in **5-H**, as indicated by the enhancements of the  $\text{C}^+$  and  $\text{CH}_3$  resonances in the  $^{13}\text{C}$  spectrum. Accurate confirmation of the scrambling by  $^1\text{H}$  NMR spectroscopy was impossible because of the small size of the  $^{13}\text{C}$  satellites. For instance, the  $\text{CH}_3$  doublet is split into a doublet of doublets by the  $\sim 12\%$   $^{13}\text{C}$  content in the  $\text{CH}_3$  group, so that each satellite doublet is only  $\sim 6\%$  as large as the central doublet.

**Kinetic Measurements.** The rate of conversion of **4-H** to **5-H** was measured at  $-26.6$  and  $-5.4^\circ\text{C}$ , respectively, by  $^1\text{H}$  NMR spectroscopy. The temperatures were measured before and after the rate determinations using the peak separation in methanol as the temperature probe. No changes in the temperatures were observed. The method gives temperatures accurate to about  $\pm 1^\circ\text{C}$ . Rates were measured by following the integrated loss of intensity of the ethylene singlet in **4-H** through about 2 half-lives. Quantitative conversion to **5-H** was indicated by the corresponding increase in intensity of the  $\text{C}^+-\text{H}$  and  $\text{CH}_3$  peaks of **5-H**. The first-order rate constants were  $7.46 \times 10^{-5} \text{ s}^{-1}$  at  $26.6^\circ\text{C}$  and  $5.77 \times 10^{-4} \text{ s}^{-1}$  at  $-5.4^\circ\text{C}$ . From the Arrhenius equation,  $E_a = 12.7 \text{ kcal/mol}$  and  $\log A = 13.6$ .

**Acknowledgment.** Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

## References and Notes

- (1) Stable Carbocations. 195. Part 194: D. A. Forsyth, R. J. Spear, and G. A. Olah, *J. Am. Chem. Soc.*, **98**, 2512 (1976).
- (2) (a) Postdoctoral Research Associate, 1973-1975; (b) National Institutes of Health Postdoctoral Fellow, 1974-1975.
- (3) For major reviews on the solvolytic behavior of  $\beta$ -arylalkyl systems, see (a) D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964); (b) H. C. Brown, *Chem. Soc., Spec. Publ.*, No. 16, 1 (1962); (c) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965); (d) C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer in "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 27.
- (4) Following the nomenclature proposed by G. A. Olah, *J. Am. Chem. Soc.*, **94**, 808 (1972), ions of this type are termed ethylenebenzenium rather than the original "phenonium".
- (5) For Brown's more recent viewpoint, see the discussion in ref 3d and (a) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Am. Chem. Soc.*, **89**, 370 (1967); (b) H. C. Brown and C. J. Kim, *J. Am. Chem. Soc.*, **90**, 2082 (1968).
- (6) W. H. Saunders, Jr., S. Asperger, and D. H. Edison, *J. Am. Chem. Soc.*, **80**, 2421 (1958).
- (7) (a) S. L. Loukas, M. R. Velkou, and G. A. Gregoricu, *Chem. Commun.*, 1199 (1969); 251 (1970); (b) S. L. Loukas, F. S. Varveri, M. R. Velkou, and G. A. Gregoriou, *Tetrahedron Lett.*, 1803 (1971).
- (8) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5244 (1970).
- (9) G. A. Olah and R. D. Porter, *J. Am. Chem. Soc.*, **93**, 6877 (1971), and earlier literature cited therein.
- (10) L. Ebersson and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3506 (1965).
- (11) J. A. Manner, J. A. Cook, Jr., and B. G. Ramsey, *J. Org. Chem.*, **39**, 1199 (1974).
- (12) W. J. Hehre, *J. Am. Chem. Soc.*, **94**, 5919 (1972).
- (13) E. I. Snyder, *J. Am. Chem. Soc.*, **92**, 7529 (1970). Figure 1 of Snyder's paper indicates a difference between open and bridged forms greater than 40 kcal/mol from directly calculated energies in the CNDO method; however, the energy difference for the same system listed in Table I is found to be 119.4 kcal/mol by converting from a. u.
- (14) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Am. Chem. Soc.*, **94**, 2034 (1972), and earlier literature cited therein.
- (15) The previous conclusion<sup>13</sup> that **5-H** was formed by a competing hydride-shift mechanism was based upon the reported observation, via  $^{13}\text{C}$  satellites in the  $^1\text{H}$  NMR spectrum derived from the 25%  $^{13}\text{C}$  labeled precursor **3-H**, that the  $^{13}\text{C}$  label remained exclusively at the  $\text{CH}_3$  group in **5-H**. Despite the claimed accuracy, we found it impossible to accurately determine the relative label positions from the  $^1\text{H}$  NMR spectrum, even in a spectrum as clean as Figure 1e.
- (16) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 353, 2212 (1973).
- (17) M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6350, 6352, 6354 (1967).
- (18) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions", F. W. McLafferty, Ed., Academic Press, New York, N.Y., 1963, pp 516-519, and literature cited therein.
- (19) R. C. Dunbar, *J. Am. Chem. Soc.*, **97**, 1382 (1975), and literature cited therein.
- (20) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).
- (21) (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, Chapter 5; (b) Chapter 10.
- (22) C. D. Poulter and S. Winstein, *J. Am. Chem. Soc.*, **91**, 3649 (1969).
- (23) G. A. Olah, M. B. Comisarow, and C. J. Kim, *J. Am. Chem. Soc.*, **91**, 1458 (1969).
- (24) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3419 (1975), and references cited therein.
- (25) G. A. Olah and D. A. Forsyth, unpublished results.
- (26) G. A. Olah, R. J. Spear, G. Messina, and P. W. Westerman, *J. Am. Chem. Soc.*, **97**, 4051 (1975).
- (27) G. A. Olah and R. J. Spear, *J. Am. Chem. Soc.*, **97**, 1539 (1975), and references cited therein.
- (28) G. A. Olah, R. D. Porter, C. L. Jewell, and A. M. White, *J. Am. Chem. Soc.*, **94**, 2044 (1972).