Stable Carbocations. 198,\(^1\)a Formation of Allyl Cations via Protonation of Alkynes in Magic Acid Solution. Evidence for 1,2-Hydrogen and Alkyl Shifts in the Intermediate Vinyl Cations

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Abstract: A series of 12 alkynes has been protonated with FSO\(_3\)H-SbF\(_5\) (magic acid) in SO\(_2\) or SO\(_2\)CIF solution under stable ion conditions. Whereas the formation of oligomeric products was observed at \(-78^\circ\)C, allyl cations were formed in high yields at higher temperatures. In many cases this way of preparing allyl cations is superior to other methods. While alkynes, which are branched in the a position to the triple bond, underwent rearrangements to allyl cations after protonation in SO\(_2\) at \(-20^\circ\)C, the corresponding reactions of the unbranched systems demanded higher temperatures. Only the sterically crowded di-tert-butylacetylene rearranged to stereoisomeric allyl cations upon protonation even at \(-78^\circ\)C. The nonequilibrium nature of the protonation step and the intermediacy of vinyl cations was demonstrated by deuterium labeling.

Whereas trivalent alkyl cations have been recognized as reactive intermediates since Ingold's definition of SN1 reactions\(^2\) and have been extensively studied as long lived species within the last 15 years,\(^3\) evidence for the existence of vinyl cations\(^4\) has proved to be more elusive. Indeed, the low reactivity of vinyl halides under SN1 conditions has suggested that vinyl cations are not formed as reactive intermediates. During the last ten years, however, extensive studies on the solvolysis of vinyl derivatives, the plurality of which have been \(\alpha\)-phenyl substituted, have provided indirect evidence for the intermediacy of vinyl cations.\(^5\) Recently, the reaction of \(\alpha\)-aryl vinyl fluorides with SbF\(_5\) has been reported to yield vinyl cations as stable species in low nucleophilic media by both Hanack\(^6a\) and Masamune.\(^6b\) Discrepancies of results and the question of whether real vinyl cations were indeed observed, however, remain to be resolved.

Evidence for alkyl substituted vinyl cations has been obtained from the stereoselective nature of HX additions to allenes and alkynes.\(^7\) Furthermore, skeletal rearrangements, accompanying the solvolysis of some vinyl derivatives and electrophilic attack on alkynes, have been interpreted on the basis of the intermediacy of vinyl cations.\(^8\) In contrast to the large number of 1,2-alkyl migrations observed in alkyl cations, there were only isolated reports on 1,2-alkyl shifts occurring in vinyl cations (i.e., 1 \(\rightarrow\) 2, Scheme I).\(^9\) Moreover, while 1,2-hydrogen shifts are extremely fast in simple carbenium ions, the formation of a small amount of 3-(2,2,2-trifluoroethoxy)-3-methyl-1-butene in the solvolysis of 3-methyl-1-buten-2-y1 triflate in trifluoroethanol is the only experimental evidence that has been provided for a 1,2-hydrogen migration to a vinylic carbenium center (1 \(\rightarrow\) 2, R = H).\(^9\) Though the reaction paths via vinyl cations (A and B, Scheme I) seem to be probable, synchronous ionization and alkyl (hydrogen) migration (C and D, Scheme I) have not been rigorously excluded in any of these cases.\(^10\)

The formation of allyl cations from vinyl cations has not been detected under stable ion conditions.\(^10\) In our previous work it has been observed that the protonation of several alkynes with FSO\(_3\)H at \(-78^\circ\)C yields cyclobutenyl cations\(^11\) and vinyl fluorosulfates.\(^7\) Treating several alkynes with FSO\(_3\)H-SbF\(_5\) at \(-78^\circ\)C, we obtained only complex mixtures of unidentified products, probably oligomers. We now wish to report that protonation of alkynes with FSO\(_3\)H-SbF\(_5\) at more elevated temperatures results in the predominant formation of the related allyl cations. Moreover, unequivocal evidence has been obtained for these transformations proceeding through the intermediacy of vinyl cations.

Results

1. 3,3-Dialkyl- and 3-Alkyl-1-alkynes (Scheme II). The addition of a solution of 3,3-dimethyl-1-butene (3) in SO\(_2\) to a FSO\(_3\)H-SbF\(_5\)-SO\(_2\) solution at \(-78^\circ\)C yielded a complex mixture of unidentifiable products, among which the allylic cation 4 could not be detected. If, however, the neat alkyne 3 was added dropwise into a solution of FSO\(_3\)H-SbF\(_5\) in SO\(_2\) at \(-20^\circ\)C, quantitative formation of 4 was observed. Kinetic control of product formation was demonstrated by the observation that 4 was not obtained when the sample, prepared at \(-78^\circ\)C, was warmed up to room temperature. 4 was identified by its \(^1\)H NMR spectrum, which showed the same temperature dependence as reported earlier.\(^12\) The \(^13\)C NMR spectrum of 4 will be discussed in comparison with 6. The slow addition of the alkyne 3 dissolved in SO\(_2\) to FSO\(_3\)H-SbF\(_5\)-SO\(_2\) at \(-20^\circ\)C resulted in the formation of only a small amount of 4 besides oligomeric products. We therefore conclude that local heating accompanying the addition of the neat alkyne is re-

\[\begin{align*}
\text{C}_2H_5 & \rightarrow \text{C}_2H_3\text{C}_2H_4 \rightarrow \text{C}_2H_3\text{C}_2H_2\text{C}_2H_5 \\
\text{X} & \rightarrow \text{X}^+ \rightarrow \text{X}^+ \rightarrow \text{X}^+ \\
\text{C} & \rightarrow \text{C}^+ \rightarrow \text{C}^+ \rightarrow \text{C}^+ \\
\text{R} & \rightarrow \text{R}^- \rightarrow \text{R}^- \rightarrow \text{R}^-
\end{align*}\]
The allylic resonances in the $^{13}$C NMR spectrum of 6 (Table I) were assigned on the basis of their multiplicities in the off resonance proton coupled spectrum. The assignments of the $\delta_C$ 33.1 and 41.4 signals to the endo- and exo-CH$_3$ in 6, respectively, were made upon comparison of these shifts with the methyl shifts in 4, the sp$^3$ carbon resonances in cis-butene ($\delta_C$ 10.6) and trans-butene ($\delta_C$ 17.3) indicate that CH$_3$ is shielding a cis-CH$_3$ group by 6.7 ppm relative to the trans-CH$_3$ group. Consequently, the replacement of the 2-H by methyl in 6 (i.e., formation of 4) would be expected to shield the exo-methyl by 6.7 ppm relative to the endo-methyl. Hence, if the $\delta_C$ 41.4 resonance were attributable to the exo-methyl carbon of 6, the 8.3-ppm shift difference between the methyl resonances in 6 should decrease to 1.6 ppm in 4, which is close to the observed value of 3.0 ppm. In contrast, if the resonance at $\delta_C$ 33.1 were attributable to the endo-methyl of 6 the shift difference should increase to approximately 15 ppm in 4.

In contrast to 4 and 6, 8 was not obtained quantitatively, but only in 80% yield when 7 was added to FSO$_3$H-SbF$_5$ in SO$_2$ at $-20$ °C or to FSO$_3$H-SbF$_5$ in SO$_2$ClF at 0 °C. The $^1$H NMR spectrum of the allyl cation [1.82 (t, $J$ = 6 Hz, CH$_3$), 3.77 (br s, CH$_3$), 4.09 (mc, CH$_2$), 8.1-8.5, 8.5-8.8 (m, 3 allyl H)] is similar to that of 6. The $^{13}$C NMR spectrum allowed assignment of the structure to (E)-8 on the basis of the 3-CH$_3$ resonance ($\delta_C$ 31.4) which closely corresponds to that of the endo-CH$_3$ of 6 ($\delta_C$ 33.1). The 1.7-ppm difference is due to the $\gamma$ effect of the additional CH$_3$ group in 8.$^{16}$ The absence of a second isomer of 8 cannot be due to rapid rotation around the C$_2$C$_3$ bond, since the rotational barrier is expected to be similar to that in 6, in which both methyl carbons absorb at different resonances. The reason must be the higher thermodynamic stability of the E isomer with the bulkier ethyl in the exo position. It is possible, however, that 10-15% of the Z isomer remained undetected by our analytical methods.

### 2. 1-Alkynes (unbranched at C$_2$) (Scheme III).

Treating 1-butyne (9) with FSO$_3$H-SbF$_5$ under varying conditions did not yield the butenyl cation 10, most probably because of competing cycloaddition reactions at low temperatures and decomposition of 10 at more elevated temperatures. The 1-buten-3-yl cation, prepared from 3-buten-2-ol by reaction with FSO$_3$H-SbF$_5$ in SO$_2$ClF at $-78$ °C, was observed to decompose above $-20$ °C.$^{17}$

The monosubstituted allyl cations 12, 15, and 18, which are expected to be the initial rearrangement products of the vinyl cations 11a, 14a, and 17a, respectively, were not observed, as they underwent 1,4-hydrogen shifts giving the cations 13, 16, and 19, respectively.$^{17}$

The 2-penten-4-yl cation (13) was obtained together with a trace of tert-butylic cation when 1-pentyne (11) was added to neat FSO$_3$H-SbF$_5$ at 0 °C. The $^1$H NMR spectrum showed a triplet at $\delta_H$ 8.25 ($J$ = 13.5 Hz), which indicated the E,E

### Table I. $^{13}$C-NMR Data of Allylic Cations$^b$

<table>
<thead>
<tr>
<th></th>
<th>C$^1$</th>
<th>C$^2$</th>
<th>C$^3$</th>
<th>C$^1$</th>
<th>C$^2$</th>
<th>C$^3$</th>
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<tr>
<td>4</td>
<td>171.8 (t)</td>
<td>155.5 (s)</td>
<td>273.2 (s)</td>
<td>18.8 (q, CH$_3$)</td>
<td>38.4 (q, C$_3$)</td>
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<td>6</td>
<td>170.0 (t)</td>
<td>146.0 (d)</td>
<td>274.3 (s)</td>
<td>35.4 (q, CH$_3$)</td>
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<td>8</td>
<td>172.5 (t)</td>
<td>144.3 (d)</td>
<td>279.0 (s)</td>
<td>41.4 (q, CH$_3$)</td>
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<tr>
<td>13</td>
<td>232.3 (d)</td>
<td>148.3 (d)</td>
<td>232.3 (d)</td>
<td>30.8 (q, CH$_3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(E)-16</td>
<td>206.0 (d)</td>
<td>143.9 (d)</td>
<td>251.8 (s)</td>
<td>10.6 (q, CH$_3$), 49.6 (t, CH$_2$)</td>
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<tr>
<td>(Z)-16</td>
<td>206.6 (d)</td>
<td>141.8 (d)</td>
<td>254.2 (s)</td>
<td>31.4 (q, CH$_3$)</td>
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<td>19</td>
<td>231.0 (d)</td>
<td>144.9 (d)</td>
<td>236.2 (d)</td>
<td>30.7 (q, CH$_3$)</td>
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<td>(E)-26</td>
<td>200.5 (d)</td>
<td>151.8 (s)</td>
<td>250.1 (s)</td>
<td>39.1 (t, CH$_2$), 8.8 (q, CH$_3$)</td>
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<td>(Z)-26</td>
<td>203.1 (d)</td>
<td>150.8 (s)</td>
<td>23.6 (q, CH$_3$)</td>
<td>13.0 (q, CH$_3$)</td>
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<tr>
<td>(E)-30</td>
<td>232.9 (s)</td>
<td>149.7 (s)</td>
<td>238.9 (s)</td>
<td>36.2 (q, CH$_3$)$^a$</td>
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<tr>
<td>(Z)-30</td>
<td>233.4 (s)</td>
<td>150.9 (s)</td>
<td>240.4 (s)</td>
<td>17.3 (q, CH$_3$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Specific assignments uncertain. $^b$ Chemical shifts downfield from external (capillary) Me$_4$Si.
configuration of 13. The C$_2v$ symmetry is also reflected in the $^{13}$C NMR spectrum, which shows three resonances at δ$_C$ 30.8, 148.3, and 232.3 ppm when 11 was added to a solution of FSO$_3$H-SbF$_5$ in SO$_2$ at -20 °C in the same way as described for the preparation of 4, 6, and 8. The by-products did not contain the α-methylcyclopropylcarbinyl cation, which has been shown to be an intermediate of the rearrangement 12 - 13.\(^{17}\)

When 14 was added to a solution of FSO$_3$H-SbF$_5$ in SO$_2$ClIF at 0 °C the main product was the dimethylcyclopropylcarbinyl cation 20, which may be formed from 15.\(^{17}\) At 0 °C 20 rearranged slowly to (E)-16, which was obtained in approximately 80% yield after 1 h. The stereochemical assignment to the E isomer was possible by comparison with (Z)-16, which was observed as a by-product when 24 was treated with magic acid (see below). As before, the addition of 14 to FSO$_3$H-SbF$_5$-SO$_2$ at -20 °C resulted in the additional formation of numerous unidentified oligomeric products.

The formation of trace amounts of the 2-hexen-4-yl ion (19) has been detected in addition to the 1-methylcyclopentyl cation (21) when 1-hexyne (17) was added to neat FSO$_3$H-SbF$_5$ at room temperature. As in the cases of the other 3-unbranched alkynes 11 and 14, the addition of 1-hexyne to FSO$_3$H-SbF$_5$-SO$_2$ at -20 °C produced also a large amount of oligomeric by-products. The $^1$H NMR\(^{20}\) and $^{13}$C NMR\(^{21}\) spectra of 21 were in accord with literature reports. The presence of 19 was shown by independent synthesis (from 4-hexen-3-ol and FSO$_3$H-SbF$_5$ in SO$_2$ at -78 °C) with subsequent comparison of the $^{13}$C NMR spectra. The E,E configuration of 19 was concluded from the triplet splitting of the 2-H ($J$ = 13 Hz), analogous to that observed in (E,E)-13.

The carbon NMR assignments in 19 were based upon the comparison of 6 with 8. Replacement of one methyl in 6 by ethyl (i.e., formation of 8) deshields C by 4.7 ppm and shields C by 2.5 ppm. Since the resonance at δ$_C$ 231.0 is shifted by 1.3 ppm relative to the corresponding resonances in (E,E)-13, it may be assigned to C, C, the carbon assigned to the resonance at δ$_C$ 236.2, is deshielded by 3.9 ppm relative to (E,E)-13, also in accord with expectation.

The formation of 21 may similarly be explained by an initial 1,2-hydrogen shift in the vinyl cation 17a, since 18 has been observed to rearrange to 21,\(^{17}\) An alternative mechanism, implying 1,5-hydrogen abstraction in the vinyl cation (Scheme IV), can, however, not be excluded.\(^{22}\)

3. Dialkylacetylenes (Scheme V). Whereas the protonation of monosubstituted acetylenes can always be expected to occur at the unsubstituted alkynyl carbon to yield the more stable vinyl cation, the site of attack may not be predicted a priori in the unsymmetrically substituted dialkylacetylenes. The formulation of the vinyl cations as \(\text{C}_{2v}\) may similarly be explained by an initial 1,2-hydrogen shift in the vinyl cation 17a, since 18 has been observed to rearrange to 21,\(^{17}\) An alternative mechanism, implying 1,5-hydrogen abstraction in the vinyl cation (Scheme IV), can, however, not be excluded.\(^{22}\)

Addition of 3-hexyne (22) to FSO$_3$H-SbF$_5$ in SO$_2$ at -20 °C yielded a mixture of products, among which 19 could not be detected. If this alkynyl was added dropwise into neat FSO$_3$H-SbF$_5$ precooled to 0 °C, a solution containing ~70% 19 was obtained, which also contained a small amount of tert-butyl cation and some polymeric products.

The cation 13 was not detected when 2-pentyne (23) was
Scheme VI

\[ (\text{CH}_3)_2C\equiv C\equiv C(\text{CH}_3)_2 + \text{H}^+ \rightarrow (\text{CH}_3)_2C\equiv C\equiv C(\text{CH}_3)_2^+ \]

The comparison of the methyl resonances the product of protonation of 13 could be assigned to the 2-CH\text{\textsubscript{3}} previously reported in the literature. 2,23 In addition to these resonances the product of protonation of \( \text{FSO}_3\text{H-SbF}_5 \) in \( \text{SO}_2 \) at \(-20^\circ\text{C}\) or neat \( \text{FSO}_3\text{H-SbF}_5 \) at room temperature. In both cases \((E)\) and \((Z)\)-16 were formed in a ratio of 2:1. The \( E \) isomer was identical with the product obtained from protonation of 14. It was independently synthesized from reaction of 4-methyl-3-penten-2-01 with \( \text{FSO}_3\text{H-SbF}_5 \) in \( \text{SO}_2 \) at \(-78^\circ\text{C}\). Its \(^1\text{H NMR} \) spectrum [\( \delta \ 3.08 \) (split d, \( J = 13 \text{ Hz} \), 1-CH\text{\textsubscript{3}}), 3.31 (s, 2-3-CH\text{\textsubscript{3}}), 7.73 (d, \( J = 15 \text{ Hz} \), 2-H)], 9.5 (m, 1-H)] was previously reported in the literature. 1,22 In addition to these resonances the product of protonation of 24 showed a broad singlet at \( \delta 3.43 \) (2-3-CH\text{\textsubscript{3}}), a doublet at 7.57 (\( J = 13 \text{ Hz} \), 2-H), and a multiplet at 8.9 (1-H)], which were assigned to the \((Z)\)-16 isomer. The 1-CH\text{\textsubscript{3}} of \( (Z)\)-16 coincides with the related signal of \((E)\)-16. The presence of a second isomer is also reflected by the \(^{13}\text{C NMR} \) spectrum, since each allylic resonance of \((E)\)-16 is accompanied by a corresponding smaller resonance of the \( Z \) isomer (Table I).

\((Z)\)-16 completely isomerized (E)-16 after the mixture of isomers was heated at 50 \( ^\circ\text{C} \) for 10 min. Kinetic control of the initially formed products was thus demonstrated.

A 2:1 mixture of \((E)\)-26 and \((Z)\)-26 was obtained in \( \sim 80\% \) yield when 25 was added to \( \text{FSO}_3\text{H-SbF}_5 \) in \( \text{SO}_2 \) at \(-20^\circ\text{C} \). The \(^1\text{H NMR} \) spectrum of the obtained solution was similar to that reported for \((E)\)-26. 24 While the 1-CH\text{\textsubscript{3}} (\( \delta \sim 3.0 \)) and 3-CH\text{\textsubscript{3}} (\( \delta \sim 3.3 \)) resonances of the stereoisomers overlapped, the singlets at \( \delta 2.49 \) and 2.60 could be assigned to the 2-CH\text{\textsubscript{3}} of the \( E \) and \( Z \) isomer, respectively. As the shielding effect of 1-methyl on the 2-methyl can be expected to be greater in \((E)\)-26, the structural assignment of the two isomers is possible. The relative intensities of the quartets at \( \delta 9.46 \) and 8.76 necessitated their assignments to \((E)\)- and \((Z)\)-26, respectively.

These structural assignments are verified by the \(^{13}\text{C NMR} \) spectrum of the system. The comparison of the methyl

Table I demonstrates that the observed shifts of the major isomer correspond with a maximum deviation of 0.7 ppm to those estimated for \((E)\)-26. The isomerization of \((Z)\)-26 to \((E)\)-26 at 65 \( ^\circ\text{C} \) (10 min) demonstrates that, also in the presence of a 2-methyl group, the \( E \) isomer is thermodynamically favored.

4. Di-tert-butylacetylene (Scheme VI). In contrast to the previously discussed systems, the sterically crowded di-tert-butylacetylene (27) could be protonated at \(-78^\circ\text{C} \) with \( \text{FSO}_3\text{H-SbF}_5 \) in \( \text{SO}_2\text{ClF} \) to yield allyl cations quantitatively. Ion 28, which would result from a 1,2-methyl shift in the vinyl cation 27a, was not observed, however. 28 Rearranges, probably via the homoallylic ion 29,23 to the observed 2:5 mixture of \((E)\)- and \((Z)\)-30. The structural assignment of 30 was made on the basis of its \(^{13}\text{C NMR} \) spectrum, which displayed three allylic resonances (singlets) and five separate methyl groups, one of which had a relative intensity of two. The \(^1\text{H NMR} \) spectrum [\( \delta 1.43 \) (d, \( J = 6.7 \text{ Hz} \), 6 H), 2.37 (6, 3 H), 2.94 (3, 6 H), 3.10 (6, 3 H), 3.6 (m, 1 H)] is similar to that of the pentamethylyallyl cation 12 and supports the structural formula 30.25

Quenching of 30 with aqueous KOH yielded 2,3,4,5-tetramethyl-2,4-hexadiene, which showed identical spectral parameters with those described in the literature. 26 The protonation of 30 with \( \text{FSO}_3\text{H-SbF}_5 \) in \( \text{SO}_2\text{ClF} \) resulted in the formation of \((E)\)- and \((Z)\)-30 in the same ratio as previously obtained from the protonation of 27. Since the rotational barrier around the C-C\text{\textsubscript{2}} bond of 30 can be expected to be of the order of 13 kcal/mol,12 the observed mixture of isomers reflects the differing thermodynamic stabilities of \((E)\)- and \((Z)\)-30. As 30 decomposed in \( \text{SO}_2\text{ClF} \) solution above \(-30^\circ\text{C} \), the coalescence of the 3-CH\text{\textsubscript{3}} groups could not be observed.

The stereoisomers of 30 were also the only products when 27 was treated with \( \text{FSO}_3\text{H-SbF}_5 \) in \( \text{SO}_2 \) at \(-78^\circ\text{C} \). At \(-50^\circ\text{C} \), however, an irreversible change in the NMR spectra of the system was observed. Quenching of this solution with aqueous
Scheme VII

KOH and subsequent extraction with ether yielded 26% of the sulfone 33 (Scheme VII). The symmetry of 33 was reflected in its $^1H$ NMR and $^{13}C$ NMR spectra, which consisted of two and four resonances, respectively. After acidification of the remaining aqueous phase, another CloH$_3$SO$_2$ isomer was isolated in 38% yield. It is insoluble in KOH and shows four CH$_3$ singlets, a CH$_3$ attached to CH, and a =CH$_2$ group in its $^1H$ NMR spectrum, which satisfies the structural formulation 35.

A sulfone structure was excluded by IR spectroscopy, as no absorption was observed in the range of 1350–1310 cm$^{-1}$. On the other hand, the observed strong absorption at 1130 cm$^{-1}$ is in accord with a cyclic sulfinate. The sulfinate structure is further supported by the $^{13}C$ NMR spectrum. The singlet at δc 72.6 is assigned to the tertiary carbon bound to sulfur and the singlet at δc 102.4 to a tertiary carbon coordinated to oxygen. If both of these carbons were bound to sulfur, the observed shift difference of 30 ppm could not be readily explained.

The LiAlH$_4$ reduction of 35 yields the tetrahydrothiophene derivative 37. Its formation excludes structures of the type 38. Structure 39, containing a four-membered ring, cannot be excluded. It would be expected, however, that 39 would eliminate SO$_2$ during the course of distillation. It is on the basis of these considerations that we prefer the structural formulation 35.

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**Scheme VIII**

**Scheme IX**

33 is protonated on oxygen by FSO$_3$H–SbF$_5$ in SO$_2$ClF solution at −78 °C. 32 was also obtained when 33 was treated with FSO$_3$H–SbF$_5$ in SO$_2$ at −78 °C. Within 1 h at −20 °C 32 was completely converted to 34. Identical NMR spectra of 34 were obtained when 35 was treated with FSO$_3$H–SbF$_5$ at −78 °C. Because the resonances attributable to 32 and 34 were also observed in the spectrum which was obtained upon warming 30 in SO$_2$ to −50 °C, these two ions are regarded as the sources of 33 and 35.
Discussion

The formation of allyl cations via protonation of alkynyl precursors has been shown to be the result of kinetic and not thermodynamic control. A vinyl cation may either rearrange to an allylic ion (monomolecular) or react with an excess of unprotonated alkyne present to give cycloaducts (bimolecular) which can undergo further reactions. It is generally observed that bimolecular reactions have more negative activation entropies than monomolecular reactions. Since the rate constant is proportional to \( T \times \exp(\Delta S^\# / R - \Delta H^\# / RT) \), the monomolecular reaction will be accelerated more by raising the temperature. The formation of oligomers, which is generally the sole reaction at \(-78^\circ\text{C}\), can therefore be reduced or even eliminated at more elevated temperatures.

Only in the case of the di-tert-butylacetylene are steric repulsions inhibiting bimolecular reactions and intramolecular rearrangements are preferred even at \(-78^\circ\text{C}\). The fact that in all other systems bimolecular reactions are more favorable indicates that a considerable activation barrier is present, which retards 1,2-hydrogen or alkyl shifts in vinyl cations. On first consideration this seems to be somewhat surprising, as 1,2-hydrogen shifts are known to occur in alkyl cations very readily, frequently with an activation barrier of less than 3-4 kcal/mol. Moreover, the thermodynamic driving force for these rearrangements is expected to be greater in vinyl cations. The origin of the increased barrier of 1,2-hydrogen and alkyl shifts in vinyl cations does, however, become apparent upon consideration of Scheme VIII.

It can be seen that migration of \( R^3 \) from \( C^2 \) to \( C^3 \) initially leads to the formation of a perpendicular allyl cation \( 41 \), which must be rotated \( 90^\circ \) around the \( C^2C^3 \) bond to yield the planar allyl cation \( 42 \). The transition state of the rearrangement, therefore, does not profit from allylic resonance stabilization, but is rather inductively destabilized by the orthogonal \( \pi \) system of \( 41 \).

Pople, Schleyer, and co-workers have calculated the energies of the isomeric \( C_3H_5^+ \) ions.\(^{32} \) Their results, which have been obtained at the 6-31G\(^*\) level, provide the energy profile of the vinyl cation \( \rightarrow \) allyl cation rearrangement (Figure 1). As it is known that the 6-31G\(^*\) method overestimates ring strain, the actual barrier for the rearrangement should be lower than the 18 kcal/mol calculated.

\( 41 \) is expected to be stabilized considerably if \( R^1 \) and \( R^2 \) are alkyl substituents. Since the stabilization of \( 40 \) by the effect of the alkyl groups should be much less important, the activation barrier should become considerably lower in such a case than in the parent system that is shown in Figure 1. As a consequence, vinyl cations, which are branched at \( C^1 \) (i.e., \( R^1, R^2 = \text{alkyl} \)), are observed to rearrange to allyl cations in liquid SO\(_2\) (bp \(-10^\circ\text{C}\)).

The activation energy is expected to be relatively higher if \( R^1 = \text{alkyl} \) and \( R^2 = \text{H} \). This is reflected by the observation that vinyl cations which are not branched at \( C^2 \) rearrange to allyl cations only at higher temperatures, i.e., in boiling SO\(_2\)CF\(_2\) (bp \(7^\circ\text{C}\)) or in FS\(_2\)H-SbF\(_5\) at \(20^\circ\text{C} \). Furthermore, with the exception of a single structurally unique case, all such rearrangements, interpreted on the basis of the sequence \( 40 \rightarrow 42 \), have been observed in systems with \( R^3, R^2 = \text{alkyl} \).

The observation that hydrogen possesses a greater migratory aptitude in these systems than methyl may be readily rationalized on the basis of the greater thermodynamic stability of the tertiary cation \( 44 \) relative to the secondary cation \( 43 \).

\begin{align*}
\text{Discussion} \\
\text{Figure 1. Calculated energy barrier for the rearrangement of 2-propenyl to the allyl cation.}^{32}
\end{align*}
Analogously, 26 was exclusively formed from 25a and not from 25b as demonstrated by the absence of an allylic hydrogen in the $^1$H NMR spectrum when 26 was treated with FSO$_3$D-SbF$_5$.

Further evidence that the mechanism via 23b-25b is not the primary reaction path is obtained from the observation that protonation of 24 yields a mixture of (E) and (Z)-16. This result may be rationalized by the expectation that in the transition states 45 and 46 the different stabilities of the products would not yet be experienced. If the reaction, however, would proceed via 24b and 15, the exclusive formation of (E)-16 would be expected (see Scheme III).

Throughout the previous discussion we have anticipated that protonation of the investigated alkynes results in the formation of vinyl cations, which then rearrange to the allylic ions (path B, Scheme I). However, the alternative explanation, in which a concerted ionization and alkyl (hydrogen) migration (path D, Scheme I) takes place, has not yet been excluded.

The synchronous reaction of HX with alkynes has been shown to be an anti addition. Consequently, in the case of a concerted mechanism, R should migrate towards the endo position of the allyl cation.

In the $^1$H NMR spectrum of 4 the exo and endo protons at C1 are differing by 0.56 ppm. Upon treating 3 with FSO$_3$D-SbF$_5$, we obtained a spectrum which still shows both allylic hydrogens in a 1:1 ratio. However, their intensity, relative to the methyl protons, is decreased by a factor of 2. This spectrum is in accord with monodeuterated 4, in which the deuterium label is equally distributed between the exo and endo positions.

The 100-MHz $^1$H NMR spectrum of 6 shows multiplets at $\delta$ 8.1-8.3 and 8.4-8.7 of relative intensity of 2:1, respectively. When 5 was treated with FSO$_3$D-SbF$_5$, a doublet (J = 17 Hz) was observed instead of the deshielded multiplet and the intensity ratio became 3:1. This is in accord with a 1:1 mixture of (E)- and (Z)-6, in which 1-H of the E isomer (trans coupling) absorbs at $\delta$ 8.5, while the 1-H of the (Z)-6 and the 2-H of both isomers absorb at higher field. The previously reported assignment$^{13}$ of the deshielded multiplet to H$_2^1$, therefore, has to be revised.

Since, in the case of a concerted mechanism, deuterium should be observed exclusively in the endo position, we consider these results as clear evidence for the intermediacy of vinyl cations. The formation of a stable $\pi$-complexed species 48, which undergoes R migration, would lead to the same results as the concerted mechanism and can therefore also be excluded. These experiments, however, do not allow one to conclude that the vinyl cations 3a and 5a are linear species. The equilibration of two bent or two bridged ions would also lead to the observed deuterium scrambling and would not contradict the experimental results.

The crucial question, of course, is whether the deuterium scrambling can occur subsequent to the migration of R. The rotational barrier of the C1C2 bond in 4 and 6 is expected to be higher than in the parent (unsubstituted) allyl cation, which has been calculated to be 34 kcal/mol$^{32}$ (Figure 1). Moreover, experimental data demonstrate that the rotational barrier of the C1C2 bond in allyl cations increases with decreasing alkyl substitution on C1. Since we observed that the rotation around the C1C2 bond in the cases of 16 and 26 did not occur under the reaction conditions, we can also exclude the rotation around this bond in 4 and 6.

The incorporation of only one deuterium atom when 3 and 5 were treated with FSO$_3$D-SbF$_5$ finally demonstrates that the protonation of alkynes is not an equilibrium process.

Experimental Section

All alkynes were commercially available in >97% purity (Farchan Chemicals, Chemical Samples). Magic acid used was prepared from triply distilled FSO$_3$H and doubly distilled SbF$_5$. The 1:1 molar ratio was used in all experiments.

Preparation of the Ions. If not otherwise mentioned, FSO$_3$H-SbF$_5$ was dissolved in approximately two parts (by volume) SO$_2$ or SO$_2$CIF. The solution was cooled to the specified temperature and the neat alkyn (0.1-0.2 equiv) was added dropwise with vigorous vortex stirring. In the case of SO$_2$ or SO$_2$CIF solutions, the temperature was controlled by a low-temperature bath or by evaporation of the solvent (−10°C and 7°C, respectively). If the alkynes were added to neat FSO$_3$H-SbF$_5$, the solutions were cooled by a water or ice bath.

2.3.4.5-Tetramethyl-2,4-hexadiene (31). 27 (1.92 g, 13.9 mmol) was added dropwise to a solution of 13.0 g of FS$_3$H-SbF$_5$ in 10 ml of SO$_2$CIF at −78°C. The alkynyl solidified immediately in SO$_2$CIF and was slowly dissolved upon shaking. The solution was then poured into a cooled (−20°C) solution of 63 g of KOH in 200 ml of water. After filtration, the diene 31 was extracted five times with a total of 200 ml of water. After filtration, the diene 31 was extracted three times with a total of 200 ml of ether. The organic layer was dried over MgSO$_4$, the ether fractionated off, and the residue distilled to give 31.

2.3.4.5-Hexamethyl-2,5-dihydrothiophene (1,1-Dioxide (33). 27 (1.92 g, 13.9 mmol) was added dropwise to a well-stirred solution of 12.5 g (39.4 mmol) of FSO$_3$H-SbF$_5$ in 8 ml of SO$_2$CIF at −78°C. The mixture was kept for 1 h at −25°C and poured into a solution of 43.5 g of KOH in 100 ml of H$_2$O, which was precooled to −30°C. The aqueous solution was extracted with 30, 30, and 10 ml of ether. After drying over MgSO$_4$, the ether was evaporated to yield 750 mg (26%) of a colorless liquid with bp 97-100°C (1.2 Torr). Anal. Calcd for C$_{15}$H$_{18}$S$_2$: C, 59.37; H, 8.97.

2.3.4.5,6-Tetramethyl-1,2-oxathioline-2-Oxide (35). After extraction of 33, the KOH solution was acidified with concentrated HCl to pH 6. Extraction with two 35-ml portions of ether yielded 110 mg of a mixture which contained mostly 33. Addition of HCl to a pH of 5.4 was achieved and renewed extraction with two 35-ml portions of ether yielded 1.2 g (38%) of crude 35. Distillation provided 730 mg (25%) of a colorless liquid with bp 97-100°C (1.2 Torr). Anal. Calcd for C$_{15}$H$_{18}$S$_2$: C, 59.37; H, 8.97. Found: C, 59.17; H, 9.01; S, 15.76. IR (film) 3090 (w), 2990 (s), 2900 (sh), 1635 (m), 1460 (m), 1380 (m), 1130 (s), 1100 (m), 910 (m), 865 (m).