Stable Carbocations. 198.[1a] 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_3H-SbF_5 (magic acid) in SO_2 or SO_2ClF solution under stable ion conditions. Whereas the formation of oligomeric products was observed at −78 °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 α position to the triple bond, underwent rearrangements to allyl cations after protonation in SO_2 at −20 °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 °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 α-phenyl substituted, have provided indirect evidence for the intermediacy of vinyl cations.[5] Recently, the reaction of α-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.

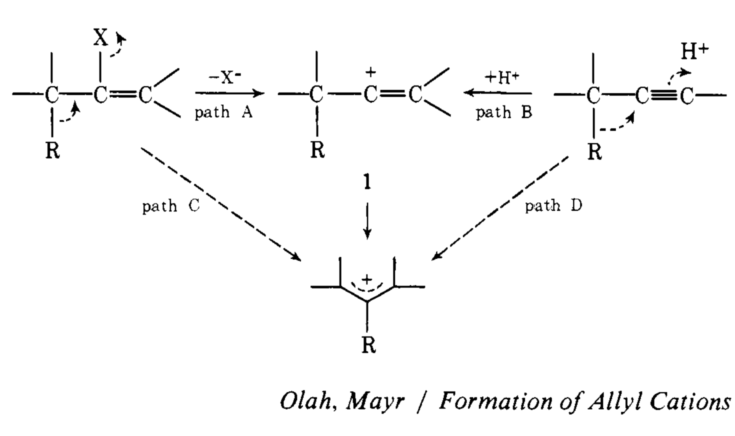
Evidence for alkyl substituted vinyl cations has been obtained from the stereoselective nature of HX additions to allenes and alkynes.[7] Furthermore, skeletal rearrangements, accompanying the solvolysis of some vinyl derivatives and electrophilic attack on alkynes, have been interpreted on the basis of the intermediacy of vinyl cations.[4] 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** → **2**, Scheme I).[8] 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-yl triflate in trifluoroethanol is the only experimental evidence that has been provided for a 1,2-hydrogen migration to a vinylic carbenium center (**1** → **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.[4b]

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_3H at −78 °C yields cyclobutenyl cations[11] and vinyl fluorosulfates.[7] Treating several alkynes with FSO_3H-SbF_5 at −78 °C, we obtained only complex mixtures of unidentified products, probably oligomers. We now wish to report that protonation of alkynes with FSO_3H-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.

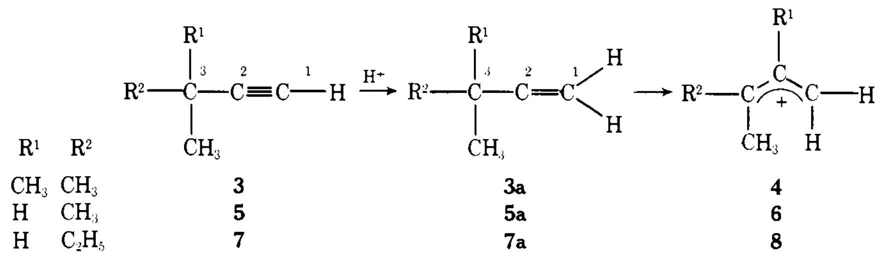
Results

1. 3,3-Dialkyl- and 3-Alkyl-1-alkynes (Scheme II). The addition of a solution of 3,3-dimethyl-1-butyne (**3**) in SO_2 to a $FSO_3H-SbF_5-SO_2$ solution at −78 °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_3H-SbF_5 in SO_2 at −20 °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 °C, was warmed up to room temperature. **4** was identified by its ^1H 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 $FSO_3H-SbF_5-SO_2$ at −20 °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-

Scheme I



Scheme II



sponsible for the observed intramolecular rearrangement. The product compositions in these experiments indicate that the local temperatures present during the addition of the neat alkyne could have been higher than the boiling temperature of the solvent (−10 °C).

Similarly, treatment of **5** with FSO_3H-SbF_5 in SO_2 at −78 °C gave no evidence for the formation of **6**, but conduct of the experiment at higher temperatures, as described for **3**, yielded a pure solution of **6**.[13]

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 δ_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 (δ_C 10.6) and *trans*-butene (δ_C 17.3)[14] indicate that CH_3 is shielding a *cis*-*vic*-CH_3 group by 6.7 ppm relative to a *trans*-*vic*-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 δ_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 δ_C 33.1 were attributable to the *endo*-methyl of **6** the shift difference should increase to approximately 15 ppm in **4**.[15]

In contrast to **4** and **6**, **8** was not obtained quantitatively, but only in 80% yield when **7** was added to FSO_3H-SbF_5 in SO_2 at −20 °C or to FSO_3H-SbF_5 in SO_2ClF at 0 °C. The ^1H NMR spectrum of the allyl cation [1.82 (t, J = 7 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 (δ_C 31.4) which closely corresponds to that of the *endo*-CH_3 of **6** (δ_C 33.1). The 1.7-ppm difference is due to the γ 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^2C^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^3) (Scheme III). Treating 1-butyne (**9**) with FSO_3H-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_3H-SbF_5 in SO_2ClF 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]

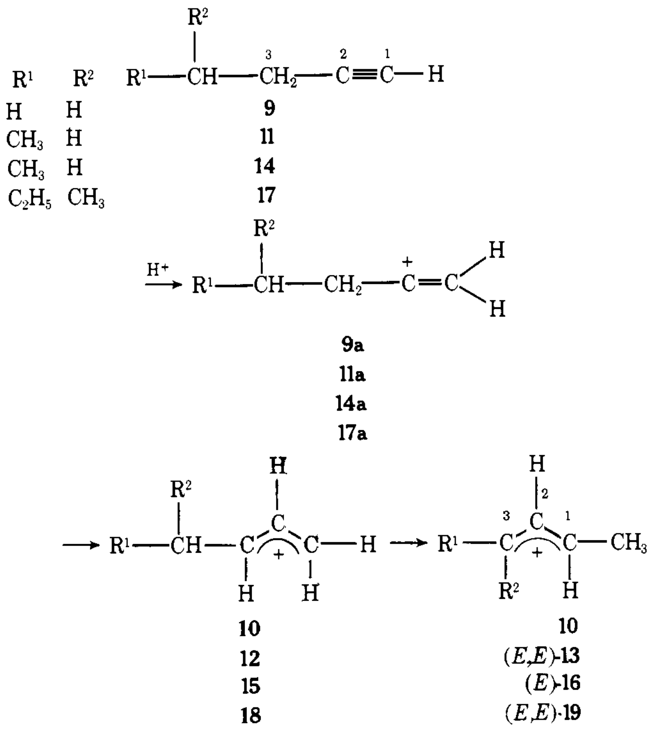
The 2-penten-4-yl cation (**13**) was obtained together with a trace of *tert*-butyl cation when 1-pentyne (**11**) was added to neat FSO_3H-SbF_5 at 0 °C. The ^1H NMR spectrum showed a triplet at δ_H 8.25 (J = 13.5 Hz), which indicated the E,E

Table I. ^{13}C-NMR Data of Allylic Cations[b]

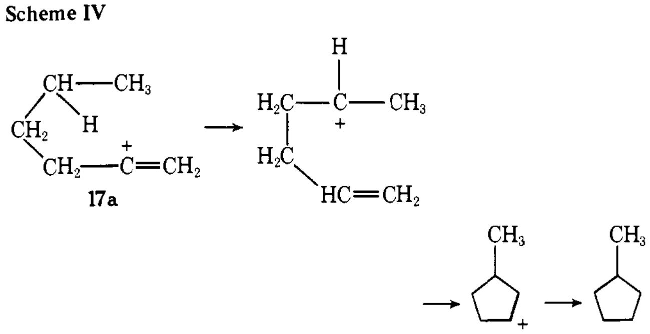
				Substituents (top: exo, bottom: endo)		
	C^1	C^2	C^3	C^1	C^2	C^3
4	171.8 (t)	155.5 (s)	273.2 (s)		18.8 (q, CH_3)	38.4 (q, C_3)
	(166 Hz)					35.4 (q, CH_3)
6	175.0 (t)	146.0 (d)	274.3 (s)			41.4 (q, CH_3)
	(171 Hz)	(177 Hz)				33.1 (q, CH_3)
8	172.5 (t)	144.3 (d)	279.0 (s)			10.6 (q, CH_3), 49.6 (t, CH_2)
	(167 Hz)	(171 Hz)				31.4 (q, CH_3)
13	232.3 (d)	148.3 (d)	232.3 (d)	30.8 (q, CH_3)		30.8 (q, CH_3)
	(164 Hz)	(169 Hz)	(164 Hz)			
(E)-**16**	206.0 (d)	143.9 (d)	251.8 (s)	27.4 (q, CH_3)		37.2 (q, CH_3)
	(165 Hz)	(169 Hz)				29.9 (q, CH_3)
(Z)-**16**	206.6 (d)	141.8 (d)	254.2 (s)			41.1 (q, CH_3)
						35.7 (q, CH_3)
19	231.0 (d)	144.9 (d)	236.2 (d)	30.7 (q, CH_3)		39.1 (t, CH_2), 8.8 (q, CH_3)
	(163 Hz)	(172 Hz)	(166 Hz)			
(E)-**26**	200.5 (d)	151.8 (s)	250.1 (s)	23.6 (q, CH_3)	13.0 (q, CH_3)	34.6 (q, CH_3)
	(161 Hz)					31.5 (q, CH_3)
(Z)-**26**	203.1 (d)	150.8 (s)				38.6 (q, CH_3)
						38.1 (q, CH_3)
(E)-**30**	232.9 (s)	149.7 (s)	238.9 (s)	36.2 (q, CH_3)[a]	17.3 (q, CH_3)	43.1 (d, CH), 19.6 (q, 2 CH)
				35.7 (q, CH_3)[a]		28.6 (q, CH_3)[a]
(Z)-**30**	233.4 (s)	150.9 (s)	240.4 (s)	35.4 (q, CH_3)[a]	19.3 (q, CH_3)	27.3 (q, CH_3)[a]
				34.8 (q, CH_3)[a]		43.1 (d, CH), 20.3 (q, 2 CH)

[a] Specific assignments uncertain. [b] Chemical shifts downfield from external (capillary) Me_4Si.

Scheme III

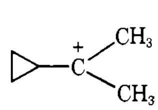


Scheme IV



configuration of **13**.[18] 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.[19] **13** was obtained in less than 40% yield when **11** was added to a solution of FSO_3H-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_3H-SbF_5 in SO_2ClF 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 $FSO_3H-SbF_5-SO_2$ at -20 °C resulted in the additional formation of numerous unidentified oligomeric products.



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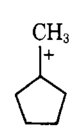

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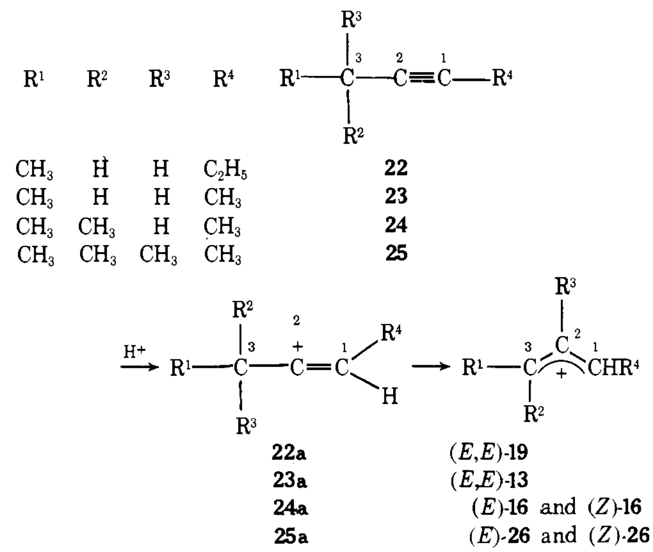
The formation of trace amounts of the 2-hexen-4-yl ion (**19**) has been detected in addition to the 1-methylcyclopentyl cation (**21**) when 1-hexyne (**17**) was added to neat FSO_3H-SbF_5 at room temperature. As in the cases of the other 3-unbranched alkynes **11** and **14**, the addition of 1-hexyne to $FSO_3H-SbF_5-SO_2$ at -20 °C produced also a large amount of oligomeric by-products. The ^1H 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_3H-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**.

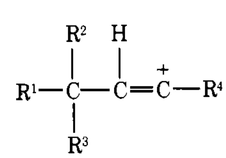
Scheme V



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^3 by 4.7 ppm and shields C^1 by 2.5 ppm. Since the resonance at δ_C 231.0 is shielded by 1.3 ppm relative to the corresponding resonances in (E,E)-**13**, it may be assigned to C^1. C^3, 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 **23–25**. The formulation of the vinyl cations as **23a–25a** (and not as **23b–25b**), which appears arbitrarily at this point, is justified subsequently.

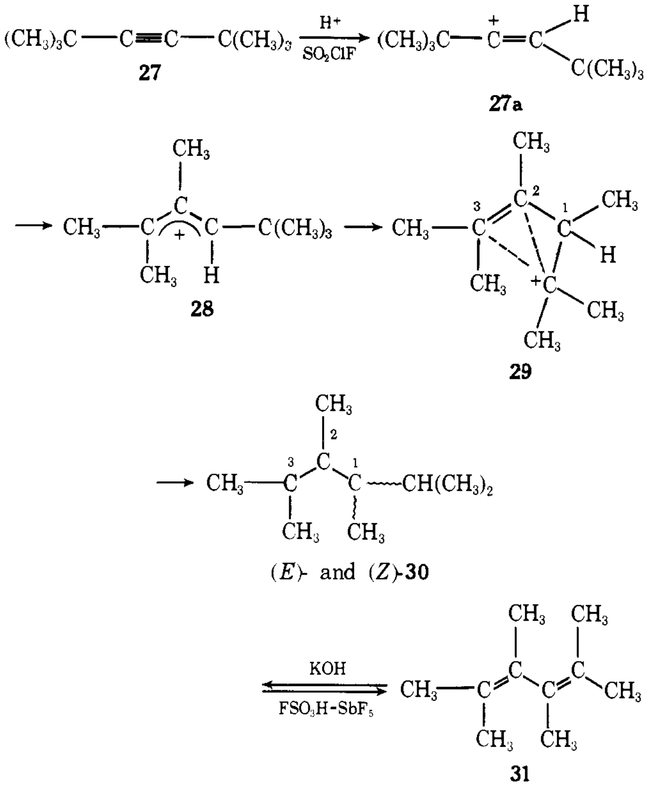


23b–25b

Addition of 3-hexyne (**22**) to FSO_3h-SbF_5 in SO_2 at -20 °C yielded a mixture of products, among which **19** could not be detected. If this alkyne was added dropwise into neat FSO_3H-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



added into a mixture of FSO_3H-SbF_5 in SO_2 at −20 °C. The *E,E* isomer of **13** was, however, obtained in approximately 75% yield when **23** was added to FSO_3H-SbF_5 at room temperature.

16 could be prepared in 80% yield through the dropwise addition of **24** to either a solution of FSO_3H-SbF_5 in SO_2 at −20 °C or neat FSO_3H-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-ol with FSO_3H-SbF_5 in SO_2 at −78 °C. Its ^{1}H NMR spectrum [δ 3.08 (split d, J = 7 Hz, 1-CH_3), 3.31 (s, 2 3-CH_3), 7.73 (d, J = 15 Hz, 2-H), 9.5 (m, 1-H)] was previously reported in the literature.[12,23] In addition to these resonances the product of protonation of **24** showed a broad singlet at δ 3.43 (2 3-CH_3), a doublet at 7.57 (J = 13 Hz, 2-H), and a multiplet at 8.9 (1-H), which were assigned to the (*Z*)-**16** isomer. The 1-CH_3 of (*Z*)-**16** coincides with the related signal of (*E*)-**16.** The presence of a second isomer is also reflected by the ^{13}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 to (*E*)-**16** after the mixture of isomers was heated at 50 °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 ~80% yield when **25** was added to FSO_3H-SbF_5 in SO_2 at −20 °C. The ^{1}H NMR spectrum of the obtained solution was similar to that reported for (*E*)-**26.**[24] While the 1-CH_3 (δ ~3.0) and 3-CH_3 (δ ~3.3) resonances of the stereoisomers overlapped, the singlets at δ 2.49 and 2.60 could be assigned to the 2-CH_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 δ 9.46 and 8.76 necessitated their assignments to (*E*)- and (*Z*)-**26,** respectively.

These structural assignments are verified by the ^{13}C NMR spectrum of the system. The comparison of the methyl shieldings of **4** and **6** shows that 2-methyl shields an *exo*-CH_3 by 3.0 and deshields an *endo*-CH_3 by 2.3 ppm. With these increments the methyl shifts of both isomers of **26** can be estimated utilizing the observed shifts of (*E*)- and (*Z*)-**16.**

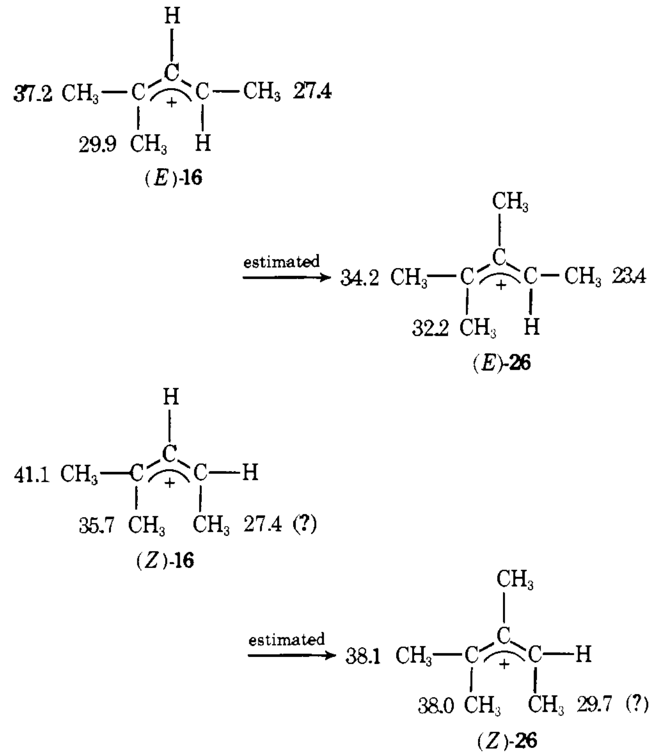


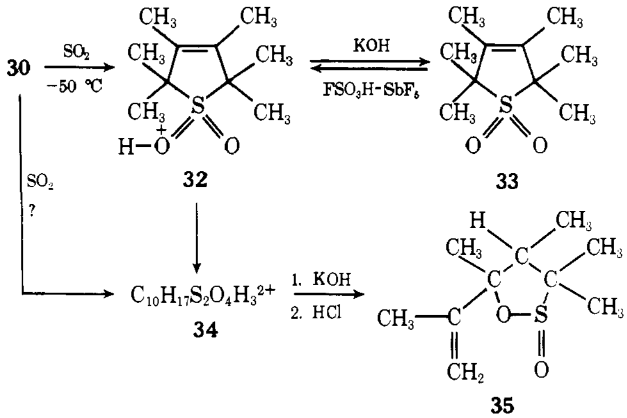
Table I demonstrates that the observed shifts of the major isomer correspond with a maximum deviation of 0.7 ppm to those estimated for (*E*)-**26.** The isomerization of (*Z*)-**26** to (*E*)-**26** at 65 °C (10 min) demonstrates that, also in the presence of a 2-methyl group, the *E* isomer is thermodynamically 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 °C with FSO_3H-SbF_5 in SO_2ClF 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 2.5:1 mixture of (*E*)- and (*Z*)-**30.** The structural assignment of **30** was made on the basis of its ^{13}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}H NMR spectrum [δ 1.43 (d, J = 6–7 Hz, 6 H), 2.37 (s, 3 H), 2.94 (s, 6 H), 3.10 (s, 3 H), 3.6 (m, 1 H)] is similar to that of the pentamethylallyl cation[12] and supports the structural formula **30.**[25]

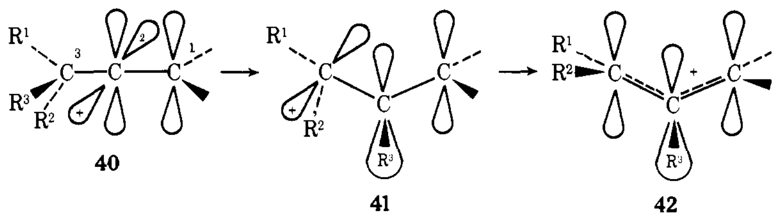
Quenching of **30** with aqueous KOH yielded 2,3,4,5-tetramethyl-2,4-hexadiene, which showed identical spectral parameters with those described in the literature.[26] The protonation of **30** with FSO_3H-SbF_5 in SO_2ClF resulted in the formation of (*E*)- and (*Z*)-**30** in the same ratio as previously obtained from the protonation of **27.** Since the rotational barrier around the C^1C^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 SO_2ClF solution above −30 °C, the coalescence of the 3-CH_3 groups could not be observed.

The stereoisomers of **30** were also the only products when **27** was treated with FSO_3H-SbF_5 in SO_2 at −78 °C. At −50 °C, however, an irreversible change in the NMR spectra of the system was observed. Quenching of this solution with aqueous

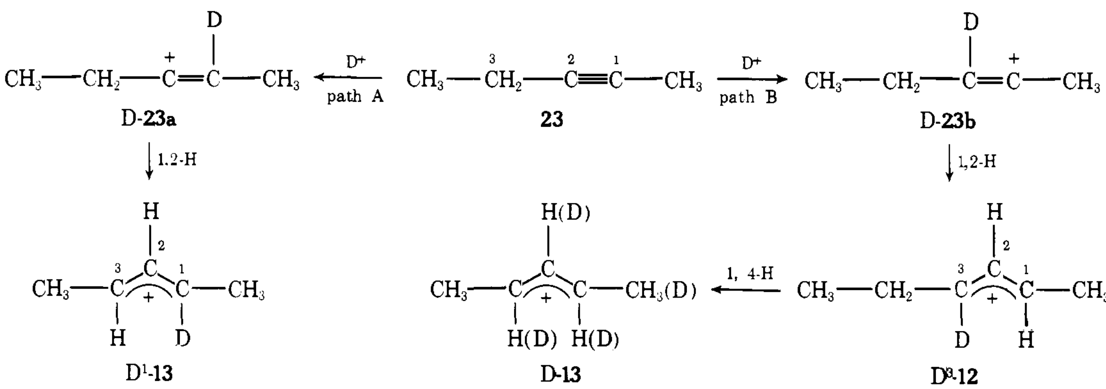
Scheme VII



Scheme VIII



Scheme IX



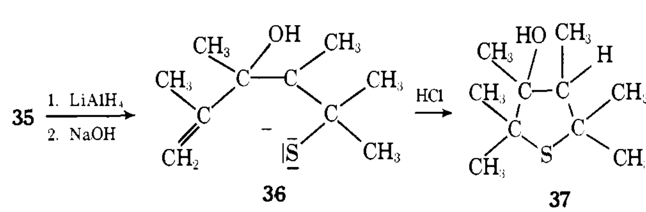
KOH and subsequent extraction with ether yielded 26% of the sulfone **33** (Scheme VII). The symmetry of **33** was reflected in its ^1H NMR and ^{13}C NMR spectra, which consisted of two and four resonances, respectively. After acidification of the remaining aqueous phase, another $C_{10}H_{18}SO_2$ 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**.

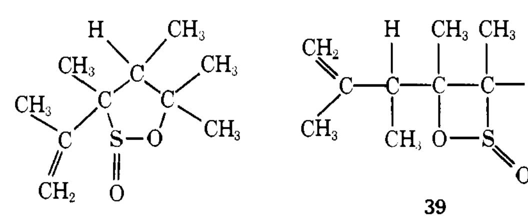
A sulfone structure was excluded by ir spectroscopy, as no absorption was observed in the range of 1350–1310 cm^{-1}.[27] On the other hand, the observed strong absorption at 1130 cm^{-1} is in accord with a cyclic sulfinate.[28] The sulfinate structure is further supported by the ^{13}C NMR spectrum. The singlet at δ_C 72.6 is assigned to the tertiary carbon bound to sulfur and the singlet at δ_C 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.**[29]

33 is protonated on oxygen by FSO_3H-SbF_5 in SO_2ClF solution at −78 °C. **32** was also obtained when **33** was treated with FSO_3H-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_3H-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.**

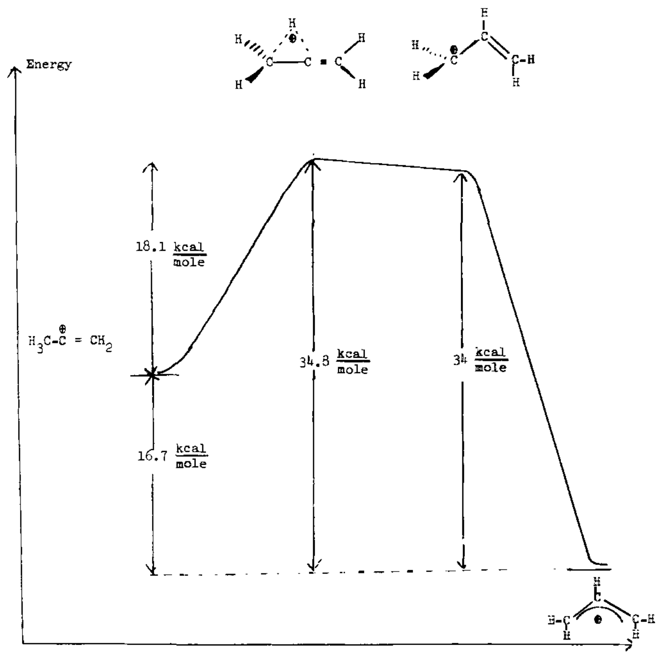


Figure 1. Calculated energy barrier for the rearrangement of 2-propenyl to the allyl cation.[32]

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 (*mono*molecular) or react with an excess of unprotonated alkyne present to give cycloadducts (*bi*molecular) which can undergo further reactions. It is generally observed that bimolecular reactions have more negative activation entropies than monomolecular reactions. Since the rate constant k is proportional to $T \times \exp(\Delta S^{\neq}/R - \Delta H^{\neq}/RT)$, the monomolecular reaction will be accelerated more by raising the temperature. The formation of oligomers, which is generally the sole reaction at −78 °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 °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.[30] 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 the inspection of Scheme VIII.

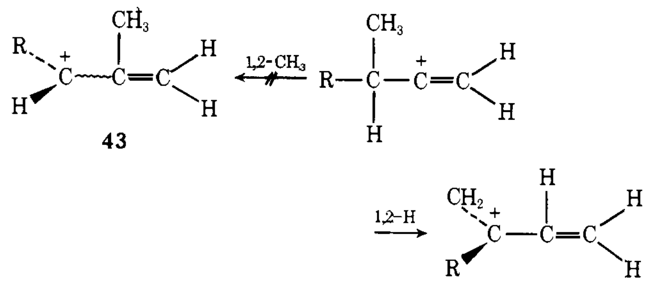
It can be seen that migration of R^3 from C^3 to C^2 initially leads to the formation of a perpendicular allyl cation **41,** which must be rotated 90° around the C^2C^3 bond to yield the planar allyl cation **42.** The transition state of the rearrangement, therefore, does not profit from allylic resonance stabilization, but is rather inductively destabilized by the orthogonal π system of **41.**[31]

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 → 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 β 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, whcch are branched at C^3 (i.e., R^1,R^2 = alkyl), are observed to rearrange to allyl cations in liquid SO_2 (bp −10 °C).

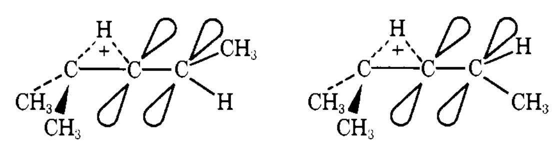
The activation energy is expected to be relatively higher if R^1 = alkyl and R^2 = H. This is reflected by the observation that vinyl cations which are not branched at C^3 rearrange to allyl cations only at higher temperatures, i.e., in boiling SO_2ClF (bp 7 °C) or in FSO_3H-SbF_5 at 20 °C. Furthermore, with the exception of a single structurally unique case,[8e] all such rearrangements, interpreted on the basis of the sequence **40** → **42,** have been observed in systems with R^1,R^2 = alkyl.[8,9]

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.**



43 **44**

The formation of **13** from protonation of **23** can be formulated as arising from two different paths. Mechanism A (Scheme IX) depicts the protonation of the methylated alkynyl carbon C^1 followed by a successive 1,2-H shift to yield the 2-penten-4-yl cation **13.** In contrast, mechanism B implies protonation at C^3 with a subsequent 1,2-hydrogen shift to yield the allylic cation **12,** which has been shown to rearrange to **13** (Scheme III).



45 → (*E*)-**16**; **46** → (*Z*)-**16**

When **23** was treated with FSO_3D-SbF_5, the ^1H NMR spectrum included a doublet at δ 8.25 and a multiplet at δ 10.1 of equal intensities. This spectrum is thus in agreement with the structural formula D^1-**13** and confirms the operation of mechanism A. Mechanism B can be thus excluded, as in this case scrambling of the deuterium label would be expected[17] and the intensity ratio of the allylic protons should be 1:2.

The preference of mechanism A might be a priori expected from our previous energetic considerations, since the 1,2-H shift **23b** → **12** must proceed via a primary carbenium ion.

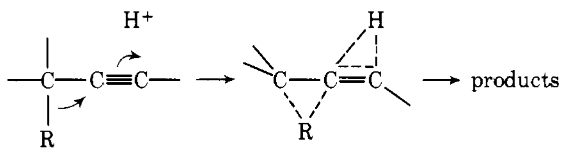
It does seem improbable, however, that **23** is exclusively protonated at C^1. We, therefore, suggest that **23b** can rearrange to **23a** via hydrogen migration across the double bond, such as has been observed in the solvolysis of vinyl triflates.[9,33] The alternative explanation, deprotonation of **23b,** is less probable, since the protonation of the alkynes **3** and **5** has been shown to be irreversible (see below).

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_3D–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.

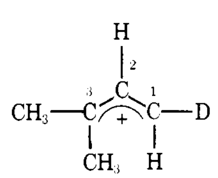
The synchronous reaction of HX with alkynes has been shown to be an anti addition.[34] Consequently, in the case of a concerted mechanism, R should migrate towards the π bond on the opposite side of the approaching proton in such a manner as depicted by the transition state **47.** The concerted mechanism therefore implies that the entering proton should occupy the endo position of the allyl cation.



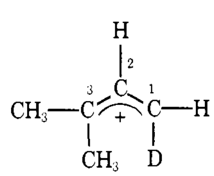
47

In the ^{1}H NMR spectrum of **4** the exo and endo protons at C^1 are differing by 0.56 ppm. Upon treating **3** with FSO_3D–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 δ 8.1–8.3 and 8.4–8.7 of relative intensity of 2:1, respectively. When **5** was treated with FSO_3D–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



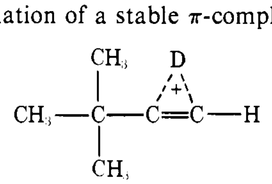
(*E*)-D-**6**



(*Z*)-D-**6**

of (*E*)- and (*Z*)-D-**6,** in which 1-H of the *E* isomer (trans coupling) absorbs at δ 8.5, while the 1-H of the (*Z*)-D-**6** and the 2-H of both isomers absorb at higher field. The previously reported assignment[13] of the deshielded multiplet to H^2, 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 π-complexed species **48,**



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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 C^1C^2 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 C^1C^2 bond in allyl cations increases with decreasing alkyl substitution on C^1. Since we observed that the rotation around the C^1C^2 bond in the cases of **16** and **26** did not occur under the reaction conditions, we also can 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_3D–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_3H and doubly distilled SbF_5. The 1:1 molar ratio was used in all experiments.

Preparation of the Ions. If not otherwise mentioned, FSO_3H–SbF_5 was dissolved in approximately two parts (by volume) SO_2 or SO_2ClF. The solution was cooled to the specified temperature and the neat alkyne (0.1–0.2 equiv) was added dropwise with vigorous vortex stirring. In the case of SO_2 or SO_2ClF 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_3H–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 (41.0 mmol) of FSO_3H–SbF_5 in 10 ml of SO_2ClF at −78 °C. The alkyne solidified immediately in SO_2ClF and was slowly dissolved upon shaking. The solution was then poured into a precooled (−20 °C) solution of 63 g of KOH in 200 ml of water. After filtration, the diene **31** was extracted three 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 0.51 g (27%) of the colorless diene with bp 83–85 °C (85 Torr): ^{1}H NMR ($CDCl_3$) δ 1.52 (br s, 6 H), 1.66 (s, 12 H).

2,2,3,4,5,5-Hexamethyl-2,5-dihydrothiophene 1,1-Dioxide (33). 27 (2.00 g, 14.5 mmol) was added dropwise into a well stirred solution of 12.5 g (39.4 mmol) of FSO_3H–SbF_5 in 8 ml of SO_2 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_2O, 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 crystalline compound. Recrystallization from ether yielded 500 mg of colorless prisms with mp 90–91 °C. Anal. Calcd for $C_{10}H_{18}SO_2$: C, 59.37; H, 8.97; S, 15.85. Found: C, 59.39; H, 8.94; S, 15.60. Ir (KBr) 3000 (m), 2950 (m), 2880 (w), 1460 (m), 1445 (m), 1390 (w), 1290 (s), 1185 (m), 1120 (s), 1095 (s), 715 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, external Me_4Si) δ 1.99 (s, 12 H), 2.30 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 12.3 (q, 3-, 4-CH_3), 23.3 (q, 2-, 5-CH_3), 64.5 (s, C^2, C^5), 133.3 (s, C^3, C^4); mass spectrum (70 eV) *m/e* (relative intensity) 203 (8), 202 (37), 138 (36), 124 (15), 123 (100), 107 (5), 95 (21), 91 (5), 81 (26), 67 (10), 57 (5), 55 (10), 53 (6), 43 (7), 41 (15).

5-Isopropenyl-3,3,4,5-tetramethyl-1,2-oxathiolane 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 provided 110 mg of a mixture which contained mostly **33.** Addition of HCl until a pH of 3.5 was achieved and renewed extraction with two 35-ml portions of ether yielded 1.12 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 $C_{10}H_{18}SO_2$: C, 59.37; H, 8.97; S, 15.85. 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 (s), 798 (s), 775 (s), 725 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (d, J = 7 Hz, 4-CH_3), 1.22, 1.31, 1.41 (three s, 3-CH_3, 3-CH_3, 5-CH_3), 1.88 (dd, J = 1.5 Hz, J = 0.7 Hz, isopropenyl-CH_3), 2.62 (q, J = 7 Hz, 4-H), 4.85 (distorted quintet, J = 1.5 Hz, 1 H, CH_2), 5.02 (br s, 1 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 10.9, 18.4, 21.2, 22.5, 24.8 (q, five CH_3), 45.9 (d, C^4), 72.6 (s, C^3), 102.4 (s, C^5), 111.3 (t, C^7), 151.5 (s, C^6); mass spectrum (70 eV) m/e (relative intensity) 203 (1), 202 (1), 161 (13), 138 (25), 137 (27), 124 (16), 123 (100), 114 (8), 106 (6), 97 (8), 96 (6), 95 (23), 82 (5), 81 (35), 70 (8), 69 (20), 67 (15), 57 (7), 55 (17), 53 (6), 43 (32), 41 (23), 32 (25), 29 (11), 28 (74).

Reduction of 35 with $LiAlH_4$. **35** (1.21 g, 6.00 mmol) was dissolved in 5 ml of dry ether and added to a suspension of 1.30 g of $LiAlH_4$ in 50 ml of ether. The mixture was stirred overnight, then 100 ml of a 10% aqueous NaOH solution was slowly added and the resultant mixture shaken thoroughly. After separation of the organic phase, the aqueous layer was acidified with HCl and extracted three times with a total of 90 ml of ether. After evaporation of the ether 510 mg (45%) of crude 3-hydroxy-2,2,3,4,5,5-hexamethyltetrahydrothiophene was obtained. Distillation (112–117 °C (3 Torr)) and low-temperature recrystallization from ether yielded **39** as a crystalline compound of mp 25 °C (approximately).

Ir (film) 3450 (s), 2960 (s), 2920 (m), 1455 (m), 1365 (m), 1215 (m), 1135 (m), 1115 (m), 1065 (s), 935 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 7 Hz, 4-CH_3), 1.10 (s, CH_3, 3 H), 1.30 (br s, CH_3, 6 H), 1.41 (br s, CH_3, 6 H), 2.01 (s, O-H), 2.18 (q, J = 7 Hz, 4-H); mass spectrum (70 eV) m/e (rel intensity) 189 (10), 188 (73), 119 (14), 115 (32), 114 (77), 99 (100), 86 (13), 75 (75), 74 (52), 72 (21), 71 (23), 70 (73), 59 (14), 57 (10), 55 (16), 43 (70), 41 (26).

Protonation of 33. Crystalline **33** (90 mg) was added to a solution of 4.13 g of FSO_3H–SbF_5 in 3 ml of SO_2ClF. The ^1H NMR spectrum of the resultant solution showed a broad singlet at δ 1.03 and a smaller singlet at δ 1.12; ^{13}C NMR δ 10.5 (q, 3, 4-CH_3), 20.5 (q, 2, 5-CH_3), 70.1 (s, C^2, C^5), 131.8 (s, C^3, C^4).

Protonation of 35. **35** (220 mg) was dissolved in 1 ml of SO_2 and added to 3.02 g of FSO_3H–SbF_5 in 2 ml of SO_2 at −78 °C: ^1H NMR (SO_2) δ 1.42 (d, J = 7 Hz, 3 H), 1.76 (s, 3 H), 1.87 (s, 6 H), 3.23 (q, J = 7 Hz, 1 H), 4.71 (s, 2 H), 6.04 (m, 2 H), 9.24 (s, 1 H), 9.37 (s, 1 H), 9.45 (s, 1 H), the two most deshielded signals coalesce at −20 °C; ^{13}C NMR (SO_2) δ 8.8 (q), 16.4 (q), 20.7 (q), 22.6 (q), 45.0 (d), 55.7 (t), 80.2 (s), 113.3 (s), 127.8 (t), 133.9 (q).

Proton Magnetic Resonance Spectra. ^1H NMR spectra were obtained on a Varian Associates Model A56/60A spectrometer equipped with a variable-temperature probe. External Me_4Si (capillary) was used as a reference for the carbenium ions and internal Me_4Si for the neutral compounds.

Carbon-13 Magnetic Resonance Spectra. The spectrometer used was a Varian Associates Model XL-100 equipped with a broad band decoupler and a variable temperature probe. All shifts are downfield from external (capillary) Me_4Si. Details of the FT ^{13}C NMR conditions were described in detail previously.[35]

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