

## Vinyl Cations in Solvolysis Reactions

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Very few areas of organic chemistry have been so widely explored and thoroughly investigated as reactions that proceed through the formation of carbonium ions. However, most of the work that has been done in this field has been restricted to "normal" trisubstituted carbonium ions (1). On the other hand, com-

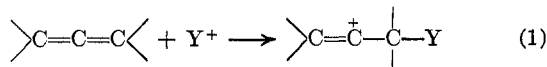


paratively little information is available about an important branch of carbonium ion chemistry that deals with disubstituted (or digonal)<sup>1</sup> carbonium ions.

Vinyl cations (2) are an important part of this branch of carbonium ions.<sup>2</sup> Even so it has not been until recently that "vinyl cations have finally become acceptable members of the reactive intermediate community."<sup>3</sup> Since their acceptance, systematic attempts have been made to obtain more information about reactions in which vinyl cations may be intermediates. Also, considerable work has been done dealing with the geometry and the nature of the bonding in such species.

As yet vinyl cations have not been prepared in solution with lifetimes great enough to permit observation of their spectral properties.<sup>4</sup> Therefore the existence of vinyl cations has not been directly demonstrated. However, evidence for vinyl cations as transitory intermediates has been obtained for an increasing number of reactions. These reactions can be classified into three major groups.

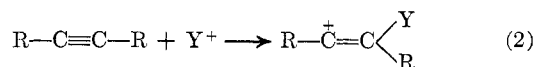
### I. Electrophilic Additions to Allenes (eq 1). Among



reactions in this group are acid-catalyzed hydrations and similar polar additions to allenes.<sup>5</sup> The formation of cyclobutanes,<sup>5</sup> which arise when mineral acids are

added to allenes, has been explained in terms of cyclo-dimerization of intermediate vinyl cations.<sup>6</sup>

### II. Electrophilic Additions to Alkynes (eq 2). These



addition reactions (including hydrations, brominations, and hydrohalogenations) have been studied more thoroughly on a mechanistic basis than have the reactions of group I. On the basis of the resulting kinetic data, vinyl cations have been proposed as intermediates.<sup>7</sup>

A group of recently discovered reactions are those that involve the formation of carbonium ions (during solvolysis) through participation of allenic or acetylenic bonds. Formally, these reactions should be considered as electrophilic additions and so belong to both groups I and II. It has been demonstrated that rearrangement reactions, which occur with participation of double bonds, are not restricted to compounds which possess double bonds in isolated positions.<sup>8</sup> Homoallyl sulfonates (similar in structure to the well-studied homoallyl compounds)<sup>8</sup> rearrange during solvolysis to form alkylcyclopropyl ketones (eq 3) as well as other rearranged products.<sup>8-10</sup> Detailed studies of reaction kinetics by various investigators indicated participation of allenic double bonds in the rate-determining steps.<sup>9-11</sup> The formation of the cyclopropyl

(5) Reviews on addition reactions to allenes: H. Fisher in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964, Chapter 13; A. A. Petrov and A. V. Federova, *Russ. Chem. Rev.*, **33**, 1 (1964); K. Griesbaum, *Angew. Chem. Int. Ed. Engl.*, **5**, 933 (1966); M. V. Mavrov and V. F. Kucherov, *Russ. Chem. Rev.*, **36**, 234 (1967); D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

(6) Review: K. Griesbaum, *Angew. Chem.*, **81**, 966 (1969).

(7) P. E. Peterson and J. E. Duddey, *J. Amer. Chem. Soc.*, **88**, 4990 (1966), and references therein; R. C. Fahey and D. J. Lee, *ibid.*, **89**, 2780 (1967); P. E. Peterson and R. J. Bopp, *ibid.*, **89**, 1284 (1967); D. S. Noyce, M. A. Matesich, and P. E. Peterson, *ibid.*, **89**, 6225 (1967), and references therein; D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020, 1023 (1968).

(8) M. Hanack and H. J. Schneider, *Angew. Chem.*, **79**, 709 (1967); *Angew. Chem. Int. Ed. Engl.*, **6**, 666 (1967).

(9) M. Hanack and J. Häffner, *Tetrahedron Lett.*, 2191 (1964); *Chem. Ber.*, **99**, 1077 (1966); M. Bertrand and M. Santelli, *C. R. Acad. Sci., Ser. C*, **259**, 2251 (1964); **266**, 231 (1968); *Chem. Commun.*, 718 (1968); M. Santelli and M. Bertrand, *Tetrahedron Lett.*, 2511, 2515 (1969).

(10) Th. L. Jacobs and R. S. Macomber, *J. Amer. Chem. Soc.*, **91**, 4824 (1969).

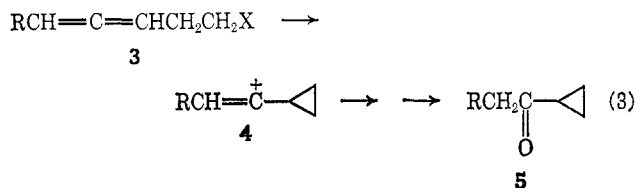
(11) R. S. Bly, A. R. Ballentine, and S. U. Kooock, *ibid.*, **89**, 6993 (1967); R. S. Bly and S. U. Kooock, *ibid.*, **91**, 3292 (1969); M. Santelli and M. Bertrand, *Tetrahedron Lett.*, 3699 (1969).

(1) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964).

(2) Beside vinyl cations other such species would be, e.g., acyl and nitrilium cations, aryl cations, and alkynyl cations; cf. the review on vinyl cations of H. R. Richey, Jr., and J. M. Richey in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., in press.

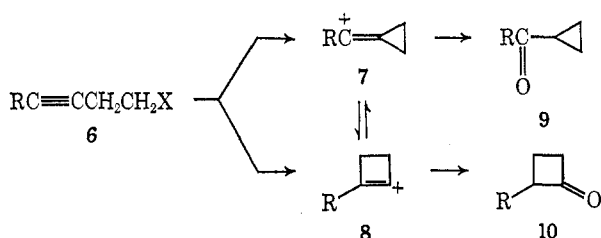
(3) W. M. Jones and D. D. Maness, *J. Amer. Chem. Soc.*, **91**, 4314 (1969).

(4) Cf. H. G. Richey, Jr., J. C. Phillips, and L. E. Rennick, *ibid.*, **87**, 1381 (1965); H. G. Richey, Jr., L. E. Rennick, A. S. Kushner, J. M. Richey, and J. C. Phillips, *ibid.*, **87**, 4017 (1965).



ketone **5** can be explained by the intermediate vinyl cation **4**, stabilized by the neighboring cyclopropane ring.<sup>9,10</sup>

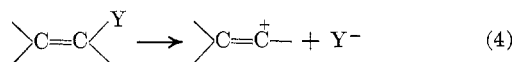
Triple bonds can also participate in the formation of carbonium ions.<sup>12</sup> Homopropargyl compounds (**6**) rearrange during solvolysis to form cyclopropyl ketones (**9**) and cyclobutanones (**10**). These results can be



explained by the intermediate formation of vinyl cations (**7** and **8**).

In addition to the homopropargyl rearrangement, other cases of triple bond participation have been reported.<sup>13</sup> The triple bond can be located even more remotely from the functional carbon atom than in the case of the homopropargyl compounds and still participate in the formation of a carbonium ion. Both vinyl cations and bridged ions have been suggested to explain the resulting cyclic products.<sup>13</sup>

**III. Heterolytic Cleavage of Bonds Attached to Unsaturated (Vinyl) Carbon Atoms (eq 4).** The major



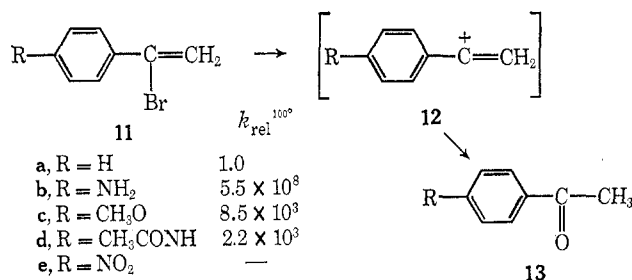
emphasis in this Account is on vinyl cations generated by such heterolytic bond cleavages.

### Solvolysis Reactions of Vinyl Halides

Simple vinyl halides are believed to be highly unreactive in solvolytic processes. Even the presence of silver salts, *e.g.*, silver nitrate,<sup>14</sup> does not seem to facilitate cleavage of the carbon-halogen bond. This lack of reactivity has been attributed to the low stability of vinyl cations and/or to an unusually strong carbon-halogen bond. Stabilization of the carbon-halogen bond can be explained in one of two ways: (a) the bond possesses partial double bond character;<sup>15</sup> or (b) its

$\sigma$  character has been increased due to the change in hybridization of carbon from  $sp^3$  in alkyl halides to  $sp^2$  in vinyl halides.<sup>16</sup> Unfortunately no comprehensive study of the reaction of simple vinyl halides in the presence of silver salts has been made. Only a single report seems to have appeared in the literature. It was shown, however, that no vinyl cation intermediate was involved.<sup>17</sup>

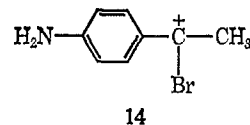
The first attempts to generate vinyl cations in solvolysis reactions were made utilizing vinyl halides in which the potential vinyl cation could be stabilized by an  $\alpha$ -aryl group. Grob and Cseh<sup>1</sup> have shown that



substituted  $\alpha$ -bromostyrenes (**11**) bearing electron-donating substituents in the *para* position of the phenyl ring are easily solvolyzed in 80% aqueous ethanol leading to the corresponding acetophenones (**13**). Compound **11a** leads also to phenylacetylene.

Three mechanisms can be proposed to explain the formation of the acetophenones from vinyl halides: (a) bimolecular elimination of HBr to form an alkyne, followed by addition to the triple bond; (b) addition to the double bond followed by elimination of HBr; and (c) initial formation of an intermediate vinyl cation (**12**). No noticeable change in the reaction rate was observed, however, when the solvolyses were carried out in the presence of triethylamine. This observation was interpreted to mean that neither mechanism a nor mechanism b is in operation.<sup>1</sup> Mechanism c, however, has experimental support. An electron-releasing substituent in the *para* position of the phenyl ring (**11**) tends to enhance the reaction rate greatly. In contrast the electron-withdrawing nitro group causes a striking rate deceleration. These data, coupled with the observation that the reaction rate is increased by a factor of ten when the solvent is changed from 80 to 50% aqueous ethanol, point to unimolecular formation of a vinyl cation (**12**) in the rate-determining step.

Schubert and Barfknecht<sup>18</sup> have studied the solvolysis of  $\alpha$ -bromo-*p*-aminostyrene (**11b**) in acidic media of varying pH. They found that in the region between



(12) M. Hanack, J. Häffner, and I. Herterich, *Tetrahedron Lett.*, 875 (1965); M. Hanack, S. Bocher, K. Hummel, and V. Vött, *ibid.*, 4613 (1968), and references therein; M. Hanack, S. Bocher, K. Hummel, and V. Vött, *Justus Liebigs Ann. Chem.*, in press; J. W. Wilson, *J. Amer. Chem. Soc.*, **91**, 3238 (1969); *cf.* also H. R. Ward and P. D. Sherman, Jr., *ibid.*, **89**, 1962 (1967).

(13) P. E. Peterson and R. J. Kamat, *ibid.*, **91**, 4521 (1969), and references therein; M. Hanack and A. Heumann, *Tetrahedron Lett.*, 5117 (1969).

(14) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1964, Chapter 8.

(15) J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951).

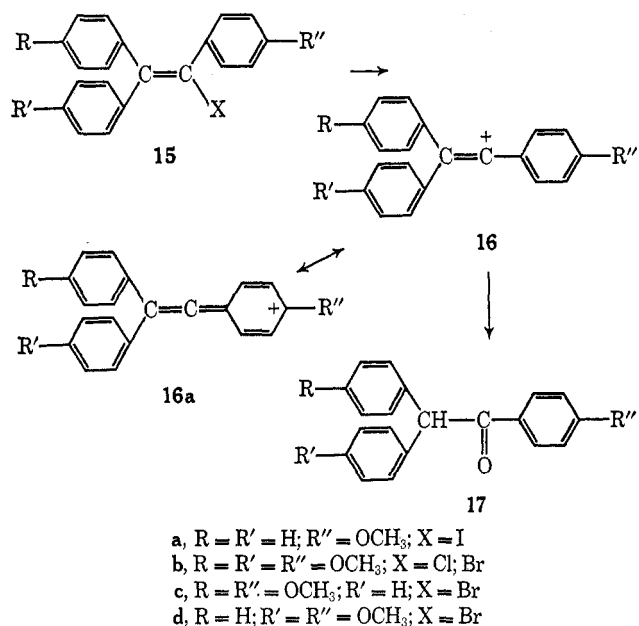
(16) W. Moffit, *Proc. Roy. Soc., Ser. A*, **202**, 548 (1950).

(17) D. Kaufman and L. L. Miller, *J. Org. Chem.*, **34**, 1495 (1969).

(18) W. M. Schubert and G. W. Barfknecht, *J. Amer. Chem. Soc.*, **92**, 207 (1970).

pH 6 and 3, in which the concentration of  $\alpha$ -bromo-*p*-aminostyrene (**11b**) is still predominant, the rate of protonation of **11b** to form intermediate **14** is dependent upon the hydrogen ion concentration. It can be concluded from these results that, under predominantly acidic solvolysis conditions, protonation of the double bond can occur. It should be pointed out that a large discrepancy exists between the reaction rates found by Grob<sup>1</sup> and those found by Schubert.<sup>18</sup>

Another series of  $\alpha$ -arylvinyloxy halides has been more recently investigated. Miller and Kaufman<sup>19</sup> solvolyzed several triaryloxyethylenes (e.g., **15a**) in aqueous dimethylformamide solvent. Substituted benz-



hydriyl phenyl ketones (**17**) were formed in this reaction. Rate data show that the solvolyses are approximately first order in reactant. The reaction rate is not enhanced by added nucleophile but is sensitive to the substituent on the  $\alpha$ -phenyl group. A nearly linear correlation with  $\sigma^+$  substituent constants was found. The  $\rho$  value obtained ( $-3.6$ ) is similar to that found for other reactions involving an intermediate vinyl cation, e.g., the hydration of phenylacetylene. These data are consistent with the formation of a vinyl cation (**16**  $\leftrightarrow$  **16a**) in which the positive charge is delocalized into the phenyl ring.

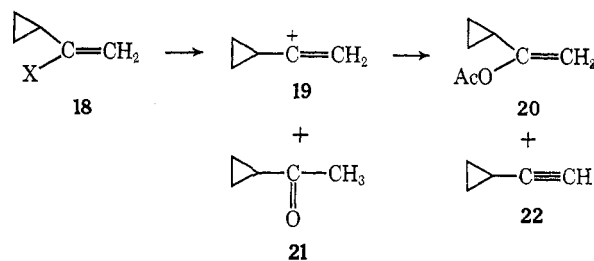
Solvolyzes of triarylvinyloxy halides (**15b**) have been studied by Rappoport and Gal.<sup>20</sup> Their behavior upon solvolysis in 80% aqueous ethanol is again in agreement with the formation of the corresponding vinyl cation. As in the case of triaryloxyethylenes (**15**), solvolyses of the triarylvinyloxy halides are first order in reactant and the major solvolysis products are the corresponding ketones. The rates are independent of the concentration of added sodium hydroxide and only slightly dependent upon the concentration of added *p*-toluenethiolate ion.

The fact that the rates of solvolysis of **15b** increase with increasing solvent polarity lends further support to the formation of an intermediate vinyl cation. However, the Winstein-Grunwald *m* values are lower than would be expected for a pure S<sub>N</sub>1 reaction (*m* = 0.53 for chloride **15b** in 65–80% aqueous ethanol; *m* = 0.34 for the bromide **15b** in 80–90% aqueous ethanol).<sup>20</sup> In 80% aqueous ethanol at 120° the observed rate ratio  $k_{\text{Br}}/k_{\text{Cl}}$  is 58. This ratio is similar to that found for the saturated halides, e.g., *t*-butyl or isopropyl. Solvolyses of the bromide and the chloride **15b** are strongly accelerated by silver salt catalysis.

The stereochemistry of the solvolysis products from vinyl halides, which should lead to a definite proof of the intermediate formation of vinyl cations, was first investigated by Rappoport and Apeloig<sup>21</sup> and by Bergman and Kelsey.<sup>22</sup> Acetolyses of both isomeric di-anisyl-2-phenylvinyl bromides will be considered as an example. The acetolyses were carried out at 120° in the presence of sodium acetate. It was found that either the *cis* (**15c**) or the *trans* vinyl bromide (**15d**) gave the corresponding isomeric *cis-trans* vinyl acetates in a 1:1 ratio. The 1:1 distribution of the *cis* and *trans* acetates was observed after 10% product formation and remained constant throughout the solvolysis. Isomerization of the bromides cannot be responsible for the observed 1:1 ratio of the acetates because the ratios of **15c** to **15d** (beginning with either) are dependent upon the reaction time. Moreover, at equilibrium the ratio of the mole fractions of **15c** and **15d** is 54:46. Isomerization of the vinyl acetates is negligible under solvolysis conditions. The results are in agreement with the intermediacy, in the product-forming step, of a linear sp<sup>2</sup>-hybridized vinyl cation.

Certain phenyl-substituted haloenamines provide another example in which an S<sub>N</sub>1 type solvolysis with the formation of vinyl cations has been suggested.<sup>23</sup>

The first example of an S<sub>N</sub>1 type ionization of a vinyl halide without aromatic substitution at the functional carbon atom was found independently by Bergman and Sherrod<sup>24</sup> and by Hanack and Bässler.<sup>25</sup> It is well documented in the aliphatic series that carbonium ions are strongly stabilized by adjacent cyclopropane rings.<sup>8</sup> That this is also true in the case of vinyl cations has been demonstrated with 1-cyclopropyl-1-haloethylenes (**18**). Both chloride **18** (X = Cl) and



(21) Z. Rappoport and Y. Apeloig, *Proc. Israel J. Chem.*, **7**, 34 (1969); Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, **91**, 6734 (1969).

(22) D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970).

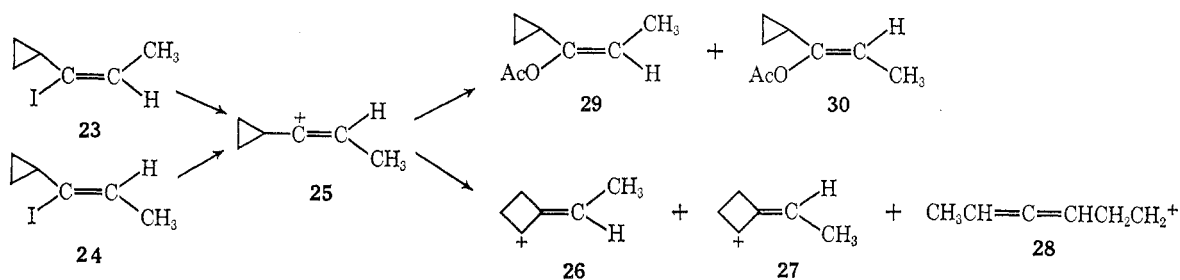
(23) S. J. Huang and M. V. Lessard, *ibid.*, **90**, 2432 (1968).

(24) S. A. Sherrod and R. G. Bergman, *ibid.*, **91**, 2115 (1969).

(25) M. Hanack and T. Bässler, *ibid.*, **91**, 2117 (1969).

(19) L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, **90**, 7282 (1968).

(20) Z. Rappoport and A. Gal, *ibid.*, **91**, 5246 (1969). For an extensive discussion of the *m* values of **15b** and related compounds see Z. Rappoport and Y. Apeloig, submitted for publication.

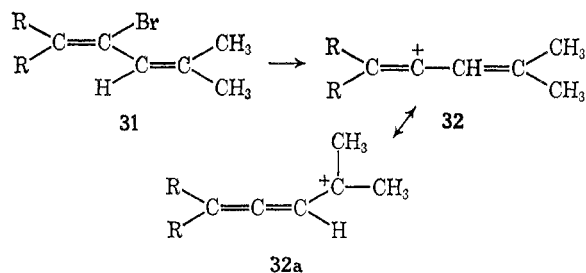


iodide **18** ( $X = \text{I}$ ) react within minutes at room temperature in acetic acid containing silver acetate. Vinyl acetate **20** and ketone **21** are the major products (>80%). Cyclopropylacetylene (**22**) accounts for 15% of the product. Both **18-Cl** and **18-I** are converted to ketone **21** in aqueous methanol buffered with triethylamine, and the conversion occurs in the absence of silver salts at a temperature of 140–160°. The uncatalyzed ionization exhibits good first-order kinetics with negligible change in rate with increasing concentration of triethylamine. The solvolysis of **18-I** in acetic acid-*O-d* in the presence of silver acetate gave no deuterium incorporation in the vinyl acetate **20** formed.<sup>26</sup> Hence a reaction mechanism involving the initial protonation of the double bond is excluded. The results are consistent with the formation of the intermediate vinyl cation **19**, which is stabilized by the neighboring cyclopropane ring.<sup>5</sup> This interpretation is further supported by the nonrearranging tendency of **19**. Rearranged products, *e.g.*, methylenecyclobutyl or 3,4-pentadienyl derivatives, account for less than 5% of the products formed. The unrearranged vinyl cation leads to products that still contain cyclopropane rings, *e.g.*, **20**, **21**, and **22**.

The stereochemistry of the reaction products arising from a cyclopropyl-substituted vinyl cation has been investigated by Bergman and Kelsey<sup>22</sup> using stereoisomeric 1-iodo-1-cyclopropylpropenes (**23** and **24**). Acetolyses of both the *cis* (**23**) and the *trans* isomers (**24**) in the presence of silver acetate at 25° gave as the major products equal amounts of stereoisomeric acetates **29** and **30** (33% of each). Other products include 1-cyclopropylpropyne and rearranged products formed from allylic ions **26** and **27** and from the homoallylic ion **28**. The product distribution was found to be identical starting either with the *cis* (**23**) or with the *trans* iodide (**24**), and it was not affected by the presence of sodium acetate in the reaction medium. These observations point to the conclusion that the products arising from both the *cis* and the *trans* iodides are formed from the same intermediates. The first intermediate is most likely the linear vinyl cation **25**. Due to stabilization by the cyclopropyl group, **25** rearranges only to a minor extent to the allylic ions **26** and **27** and to the homoallylic ion **28**.

The delocalizing ability of allylic double bonds can also be used to stabilize an intermediate vinyl cation.

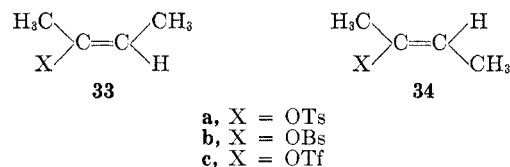
This fact was demonstrated in a study of conjugated



bromodienes of structure **31** by Grob and Spaar.<sup>27</sup> The results of rate and product studies are consistent with the formation of mesomeric vinyl cation  $\text{32} \leftrightarrow \text{32a}$ . Due to steric hindrance between the C-4 methyl group and the bromine atom, the bromodienes **31** react from a nonplanar conformation. A perpendicular orientation of the planes of the double bonds will allow maximum overlap of the orbitals involved in delocalization of the positive charge that develops as the bromide ion leaves. The ground-state conformations of compounds **31** are of the proper geometries for maximum charge delocalization.

### Solvolysis Reactions of Vinyl Sulfonates

The tosylate anion and the brosylate anion have long been the most commonly used leaving groups for the study of solvolysis reactions, but only recently have they been employed in the generation of vinyl cations.<sup>28</sup> Solvolyses of the simple vinyl sulfonates, *e.g.*, 1-cyclohexenyl and *cis*-2-buten-2-yl sulfonates, were first investigated by Peterson and Indelicato.<sup>29</sup> Cyclohexenyl tosylate and **33a** solvolyze in formic acid with the for-



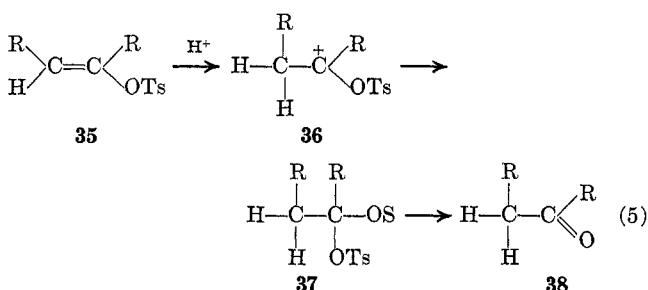
mation of the corresponding ketones, cyclohexanone and 2-butanone, respectively. However, as was shown by kinetic measurements, the products are not formed by a mechanism involving a vinyl cation but by protonation of the double bond and further reaction according to eq 5.

(27) C. A. Grob and R. Spaar, *Tetrahedron Lett.*, 1439 (1969).

(28) For a general method to prepare vinyltosylates and vinylmesylates: N. Frydman, R. Bixon, M. Sprecher, and Y. Mazur, *Chem. Commun.*, 1044 (1969).

(29) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90**, 6515 (1968).

(26) R. G. Bergman and S. A. Sherrod, unpublished results.



In a nonacidic solvent with an ionizing power similar to that of formic acid (50% aqueous methanol), **33a** and **33b** did not react when heated at 59.8° for 18 days.<sup>29</sup> However, **33a,b** and the *trans* isomers **34a,b** were found to react in 50% aqueous methanol at 130°<sup>30</sup> to form mixtures of 2-butyne and 2-butanone. Two important observations were made concerning the two isomers: (1) the *trans* isomer **34a** reacts ten times faster than the *cis* isomer **33a**; (2) 5% of the product from the *trans* isomer is 2-butanone; from the *cis* isomer 28% of the product is 2-butanone. These observations point to a predominantly *trans* coplanar E2 type elimination (with the solvent as the base) for the *trans* compound and increased vinyl cationic character in the solvolysis of the *cis* isomer.<sup>30</sup>

Trifluoromethanesulfonates (triflates)<sup>31,32</sup> are known to be at least 10<sup>4</sup>–10<sup>5</sup> times more reactive under solvolytic conditions<sup>31–33</sup> than the corresponding arenesulfonates. Vinyl triflates, therefore, should be much better precursors than tosylates or brosylates for the generation of vinyl cations.

Stang and Summerville<sup>34</sup> and Jones and Maness<sup>35</sup> prepared, for the first time, acyclic vinyl triflates and investigated their solvolytic reactivities. It was shown that *trans*-2-buten-2-yl triflate (**34c**) solvolyzes in 80% aqueous ethanol at 76° ( $k_{76} = 6.3 \times 10^{-4} \text{ sec}^{-1}$ ) to give dimethylacetylene as the only product. The corresponding *cis* isomer **33c** solvolyzes at 76° ( $k_{76} = 2.3 \times 10^{-5} \text{ sec}^{-1}$ ) to give dimethylacetylene (58%), methylallene (9%), and 2-butanone (33%).<sup>34</sup> The distribution of the products was found to be invariant in the presence of base. An examination of the kinetic data for the solvolyses in 80% aqueous ethanol at different temperatures, coupled with analysis of the reaction products, indicates different reaction mechanisms for isomers **33c** and **34c**. The rate of solvolysis of *trans* isomer **34c** is 40 times that of *cis* isomer **33c**. This suggests that **34c**, due to its favorable geometry, reacts by a concerted elimination mechanism. The *cis* isomer, in which the geometry is unfavorable for concerted elimination, is suggested to react *via* unimolecular ionization with the formation of a vinyl cation intermediate.

(30) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **91**, 6194 (1969).

(31) R. L. Hansen, *J. Org. Chem.*, **30**, 4322 (1965).

(32) The trivial name triflate was suggested by A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*, **90**, 1598 (1968).

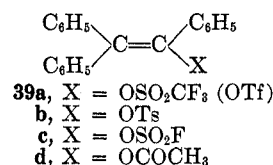
(33) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **91**, 5386 (1969).

(34) P. J. Stang and R. Summerville, *ibid.*, **91**, 4600 (1969).

(35) W. M. Jones and D. D. Maness, *ibid.*, **91**, 4314 (1969).

This view is supported by deuterium isotope effect data. For solvolysis of the deuterio *trans* isomer **34c** ( $\text{H} = \text{D}$ )  $k_{\text{H}}/k_{\text{D}}$  (76°) was found to be 2.09; for the deuterio *cis* isomer **33c** ( $\text{H} = \text{D}$ )  $k_{\text{H}}/k_{\text{D}}$  (100°) was 1.20. The value for the *trans* isomer is consistent with a primary deuterium isotope effect, which indicates bond breaking in the transition state. The value for the *cis* isomer is consistent with a normal  $\beta$ -deuterium isotope effect and thus with the formation of a vinyl cation intermediate.<sup>34</sup>

The higher reactivity of the triflate anion as the leaving group in solvolytic processes is again demonstrated in the solvolysis of triphenylvinyl triflate (**39a**), which undergoes acetolysis about 41,700 times faster than the corresponding tosylate (**39b**).<sup>35</sup> The fluorosulfonate **39c** was also solvolyzed in acetic acid. It showed a



first-order rate constant about three times slower than for the triflate. Triphenylvinyl acetate (**39d**) was the only product formed in acetolyses of **39a** and **39c**. As in the case of the other examples discussed above, a major problem in the study of solvolyses of vinyl triflates is to exclude mechanisms other than heterolytic formation of intermediate vinyl cations.

In addition to an S<sub>N</sub>1 heterolysis, at least four other mechanisms can be written to account for the observed products from solvolyses of the sulfonates **39a–c**:<sup>36</sup> (i) S<sub>N</sub>2 substitution; (ii) acetate addition with subsequent sulfonate elimination; (iii) protonation of the double bond (addition–elimination similar to that shown by Peterson and Indelicato for the formolysis of cyclohexenyl tosylate and **33a**; and (iv) nucleophilic attack at sulfur with cleavage of the sulfur–oxygen bond. Mechanisms i and ii were excluded by the observation that changes in sodium acetate concentration have practically no effect on the solvolysis rate.<sup>36</sup> Mechanism iii is the mechanism most difficult to exclude in favor of the formation of a vinyl cation *via* heterolysis. As can be seen from eq 4, mechanism iii clearly explains the products. However, it was shown that when the solvent was changed from CH<sub>3</sub>COOH to CH<sub>3</sub>COOD there was essentially no change in the rate of solvolysis of **39b** and **39c** (for **39b** at 160.2°,  $k_{\text{CH}_3\text{COOH}}/k_{\text{CH}_3\text{COOD}} = 0.93$ ; for **39c** at 67.5°,  $k_{\text{CH}_3\text{COOH}}/k_{\text{CH}_3\text{COOD}} = 1.04$ ).<sup>36</sup> The absence of a significant solvent isotope effect (which should be present if proton addition to the double bond is the slow step)<sup>37</sup> can be taken as strong evidence against mechanism iii.

Mechanism iv, nucleophilic attack on the sulfur atom of the sulfonate group, can be ruled out for several

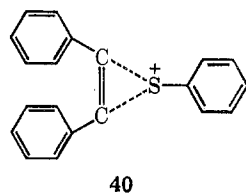
(36) We are indebted to Professor W. M. Jones, University of Florida, for informing us about the experimental details of his investigations and disclosing unpublished discussions of his results.

(37) Cf. D. S. Noyce and R. M. Pollack, *J. Amer. Chem. Soc.*, **91**, 119 (1969).

reasons: by the observation that phenyl triflate and *p*-methoxyphenyl triflate<sup>33</sup> are completely inert to acetic acid (1 week at 200°), and by the observation that acetolysis of **39a** in the presence of  $\alpha, \alpha'$ -ditolylacetophenone gave only triphenylvinyl acetate (**39d**).<sup>36</sup> The latter experiment proved that no acylation of a ketone or its enol, formed by nucleophilic attack on the sulfur atom, takes place. In addition, Bergman<sup>38</sup> has found essentially complete <sup>18</sup>O incorporation in the alcohol product formed when 1-tricycyl triflate was solvolyzed in ethanol-H<sub>2</sub><sup>18</sup>O at 230°.

Determination of the rates of solvolyses of several trianisylvinyl arylsulfonates (**15b**, X = OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Y; Y = *p*-CH<sub>3</sub>O, *p*-CH<sub>3</sub>, H, *p*-Br, *p*-NO<sub>2</sub>, and *o*-NO<sub>2</sub>) in 70% aqueous acetone (75°) gave additional evidence for vinyl cation intermediates in these reactions.<sup>39</sup> From the rates of solvolysis of the different compounds a  $\rho$  value of 1.67 for changes in the leaving group was determined. A rate-determining addition of a proton to the double bond is ruled out since this would require a negative  $\rho$  value for substitution in the leaving group. In addition, the solvolyses of trianisylvinyl tosylate and brosylate (**15b**, X = OTs, OBs) were studied in acetic acid and in deuterioacetic acid. The rate ratios  $k_{\text{CH}_3\text{COOH}}/k_{\text{CH}_3\text{COOD}}$  were determined to be 1.05 and 1.02, respectively. Again, no significant solvent isotope effect was observed.

Modena and his coworkers were among the first to investigate  $\alpha$ -phenyl-substituted vinyl sulfonates.<sup>40</sup> Reactions of 1,2-diaryl-2-arylthiovinyl sulfonates were studied. It was initially thought that a vinyl cation intermediate was involved. However, stereochemical and tracer experiments,<sup>41</sup> as well as rate studies of  $\beta$ -phenylthiovinyl sulfonates in comparison with triphenylvinyl sulfonates,<sup>42</sup> indicated that the  $\beta$ -sulfur atom participates in the reaction and that the cationic intermediate probably is a thiirenium ion (**40**).



40

Investigation of the solvolysis reactions of *cyclic* vinyl sulfonates appears to be especially interesting with respect to the geometry of the intermediate vinyl cations. It has been predicted on the basis of molecular orbital calculations that linear vinyl cations should be more stable than nonlinear ("bent") vinyl cations.<sup>13,43</sup>

(38) R. G. Bergman, unpublished results.

(39) Z. Rappoport and F. Kaspi, unpublished results.

(40) G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968); G. Modena and U. Tonellato, *Chem. Commun.*, 1363 (1968); G. Modena and U. Tonellato, *ibid.*, 1676 (1968).

(41) G. Capozzi, G. Melloni, G. Modena, and U. Tonellato, *ibid.*, 1520 (1969).

(42) G. Modena and U. Tonellato, *Boll. Sci. Fac. Chim. Ind. Bologna*, in press.

(43) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969), and references therein; H. Fischer, K. Hummel, and M. Hanack, *Tetrahedron Lett.*, 2169 (1969).

Recently Stang, Schleyer, and Hanack, independently, have prepared the cyclic vinyl triflates **41–44**.<sup>44</sup> It was possible to obtain these compounds by treating the corresponding ketones with trifluoromethanesulfonic anhydride. A study of the solvolysis rates of cyclic triflates **41–44** in 50% aqueous ethanol at 100°<sup>45</sup> gave the results shown in Chart I, which for comparison also gives the rate of solvolysis of an acyclic triflate (*cis*-2-buten-2-yl triflate).

On solvolysis in aqueous ethanol these cyclic vinyl triflates gave the corresponding ketones as the only product.<sup>45</sup> From the data of Chart I it can be seen that the rates vary greatly—increasing with increasing ring size. The rate of solvolysis of **44** exceeds that of the acyclic model compound. These observations are in agreement with a requirement that a vinyl cation be linear. Although the mechanism of the solvolysis reactions of the cyclic vinyl triflates has not been, as yet, investigated in detail, an addition-elimination process is not very likely. Such a mechanism would not explain the strong effect of ring size on reactivity. Moreover, the measured *m* values for cycloheptenyl (**43**) and cyclooctenyl triflates (**44**) are 0.68 and 0.65, respectively (50–60% aqueous ethanol). These *m* values are in agreement with an S<sub>N</sub>1 process.

Finally a question of major importance will be briefly discussed. From the kinetic data given in the preceding sections and using various models for a comparison of the rates it can be shown that substituted ethylenes undergo solvolysis much slower than saturated reference compounds. Rate differences of 10<sup>4</sup>–10<sup>8</sup> have been estimated<sup>21,29,30,35</sup> between vinyl systems and their saturated counterparts. These differences in reactivity may be attributed to the high energy of the vinyl cation being formed, although it is evident from the data given earlier that the behavior of vinyl cations resembles more closely that which is exhibited by saturated carbonium ions.<sup>46</sup> The reason for the low reactivity of vinyl derivatives has therefore been discussed in terms of reactant stabilization.<sup>19,21,36</sup>


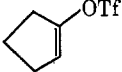
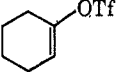
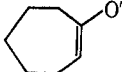
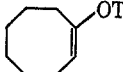
Two types of stabilization have been proposed: (1) partial  $\pi$  character of the bond between the vinyl carbon and the group directly attached to it;<sup>15</sup> and (2) a stronger  $\sigma$  bond between the vinyl carbon and the substituent due to the hybridization state of the vinyl carbon.<sup>16</sup> The validity of assuming reactant stabilization of the vinyl halides by these two effects has been examined using bond lengths, bond dissociation energies, and (electron impact) ionization potentials for saturated organic halides in comparison with vinyl halides.<sup>19,36</sup> The available data are consistent with a stronger carbon-halogen bond in the vinyl halides than in the alkyl halides. The data are rationalized in

(44) T. E. Dueber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. A. Imhoff, P. v. R. Schleyer, K. Hummel, S. Bocher, C. E. Harding, and M. Hanack, *Angew. Chem.*, in press.

(45) R. H. Summerville, W. D. Pfeifer, P. v. R. Schleyer, P. J. Stang, K. Hummel, S. Bocher, and M. Hanack, unpublished results.

(46) Cf. P. E. Peterson and J. E. Duddey, *J. Amer. Chem. Soc.*, **85**, 2865 (1963); P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966).

Chart I

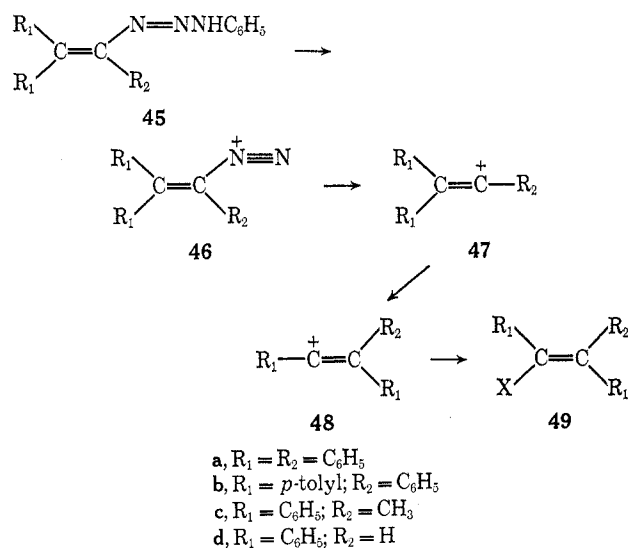
					
$k^{100^\circ}$ (50% C <sub>2</sub> H <sub>5</sub> OH) sec <sup>-1</sup>	$1.77 \times 10^{-3}$	$10^{-7}-10^{-8}$	$1.90 \times 10^{-5}$	$5.8 \times 10^{-4}$	$4.7 \times 10^{-3}$
$k_{rel}$	1.0	$10^{-4}-10^{-5}$	0.011	0.32	2.7

terms of hybridization-type stabilization rather than resonance stabilization for the halogens as well as for other leaving groups (tosylates, triflates).<sup>36</sup> The greater  $\sigma$  character of the bond to the leaving group makes a major contribution to the factors which are responsible for the low solvolytic reactivities of vinyl derivatives. Other factors which may also be responsible for these low reactivities are differences in hyperconjugation, differences in the electronegativity of =CH<sub>2</sub> and -CH<sub>3</sub>, and steric hindrance to backside solvation of the developing vinyl cation.

### Miscellaneous Reactions Involving Vinyl Cations

The formation of vinyl cations by heterolytic bond cleavage has been proposed to occur in reactions other than the solvolyses of vinyl halides and sulfonates. Such reactions are the solvolytic decarboxylation of the potassium salts of *trans*- $\alpha,\beta$ -unsaturated  $\beta$ -halo acids,<sup>47</sup> the deamination of certain vinylamines,<sup>48</sup> and the photolysis of pyrazolenines.<sup>49</sup>

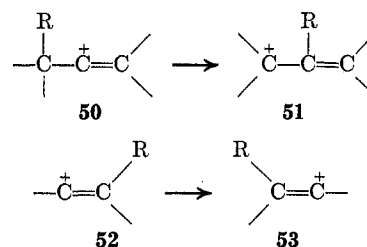
Jones and Miller<sup>50</sup> have found a potentially useful and convenient way to generate vinyldiazonium ions by treating triazenes of structure **45** with acids. The diazonium ion **46** may then lose nitrogen with formation of the corresponding vinyl cation (**47**). In all cases studied the products are those which would be



expected to arise from a vinyl cation intermediate. For example, treatment of **45a** with acetic acid gives triphenylvinyl acetate (**49**, X = OCOCH<sub>3</sub>) in 100% yield. The reactions are accompanied by the rearrangement **47**  $\rightleftharpoons$  **48** which, as predicted on the basis of a vinyl cation mechanism, is suppressed by the addition of potassium acetate. Generation of the less stable vinyl cation **47c** gave almost completely rearranged product.

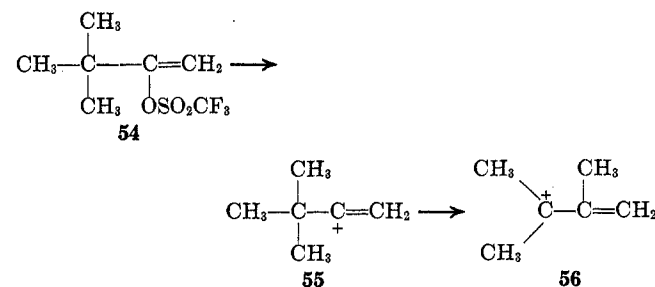
### Rearrangement Reactions Involving Vinyl Cations Generated by Solvolysis

A conclusion as to whether or not vinyl cation intermediates are generated in the solvolyses of vinyl derivatives can be drawn by investigating compounds of a structure such that the intermediate vinyl cation, once formed, can undergo rearrangement. Rearrangements to the double bond (**50**  $\rightarrow$  **51**) and across the double bond (**52**  $\rightarrow$  **53**) are possible. Reactions of the



type **50**  $\rightarrow$  **51** have already been found in the protonation of substituted acetylenes.<sup>51</sup>

Stang, Schleyer, and Hanack independently investigated the solvolysis of *t*-butylvinyl triflate **54**.<sup>52</sup> If the intermediate vinyl cation **55** is formed, it should be able to undergo a 1,2-methyl shift to form the more stable carbonium ion **56**. The products formed when



**54** was solvolyzed in aqueous ethanol buffered with pyridine were indeed the rearranged compounds **57**,

(47) C. A. Grob, J. Csapilla, and G. Cseh, *Helv. Chim. Acta*, **47**, 1590 (1964).

(48) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Amer. Chem. Soc.*, **87**, 863 (1965); D. Y. Curtin, J. A. Kampmeier, and M. L. Farmer, *ibid.*, **87**, 874 (1965).

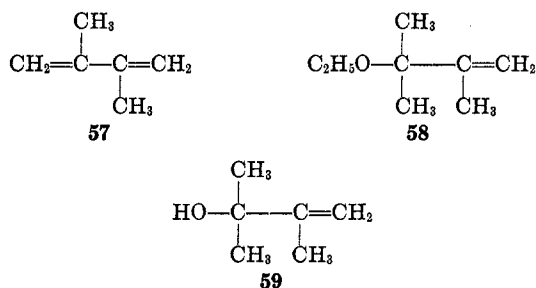
(49) A. C. Day and M. C. Whiting, *J. Chem. Soc. B*, 991 (1967).

(50) W. M. Jones and F. W. Miller, *J. Amer. Chem. Soc.*, **89**, 1960 (1967).

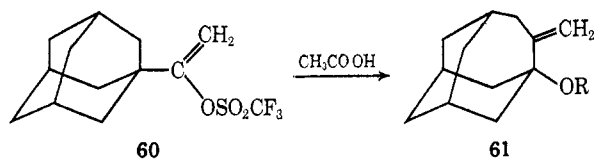
(51) K. Bott, *Tetrahedron Lett.*, 1747 (1969); *Chem. Commun.*, 1349 (1969); T. Sasaki, S. Eguchi, and T. Toru, *ibid.*, 780 (1968); K. Griesbaum and Z. Rehman, *J. Amer. Chem. Soc.*, **92**, 1416 (1970).

(52) A. G. Martinez, M. Hanack, R. H. Summerville, P. v. R. Schleyer, and P. J. Stang, *Angew. Chem.*, **82**, 323 (1970).

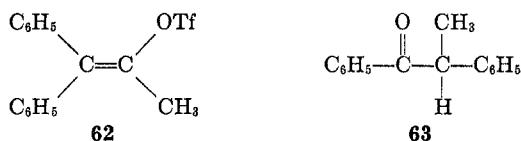
58, and 59. In addition, *t*-butylacetylene and a small



amount of pinacolone were formed. When the reaction was carried out in  $\text{CH}_3\text{COOD}$ , no deuterium incorporation was found in **57**.<sup>53</sup> A rearrangement reaction was also observed when triflate **60** was solvolyzed in various solvents. For example, in trifluoroethanol buffered with lutidine<sup>53</sup> the solvolysis product mixture comprised adamantylacetylene (25%), adamantyl methyl ketone (7%), and the rearranged product **61** ( $\text{R} = \text{CF}_3\text{CH}_2$ ; 69%). Another example has already been mentioned.



Several examples of rearrangement of the type **52**  $\rightarrow$  **53** have been found. When **62** was solvolyzed in 80% ethanol, **63** was formed almost exclusively.<sup>53</sup>

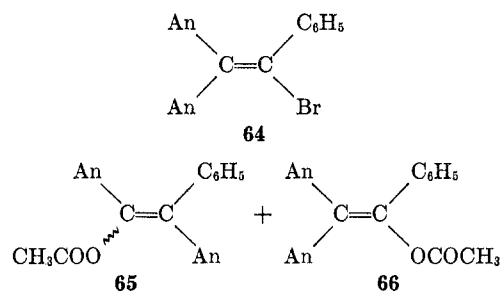


On acetolysis in the presence of silver acetate **64** leads to the rearranged acetate **65** and to the unrearranged acetate **66**.<sup>54</sup> The silver-catalyzed solvolysis of 2-phenylcyclobutenyl bromide (**67**) in aqueous acetonitrile at 100° gave only one product, phenyl cyclopropyl ketone (**70**).<sup>55</sup> The ketone could be formed by

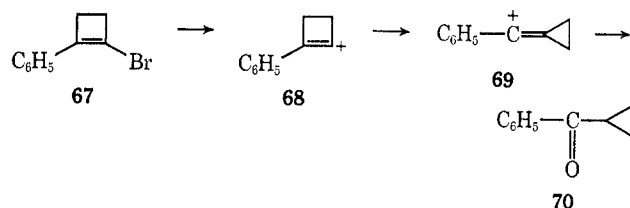
(53) M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *J. Amer. Chem. Soc.*, **92**, 0000 (1970).

(54) Z. Rappoport, personal communication.

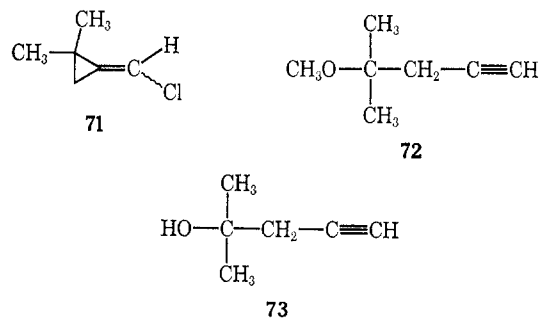
(55) M. Hanack and N. Youssiff, *Tetrahedron Lett.*, in press.



the rearrangement of the initially formed vinyl cation **68** to the more stable cation **69**. An indication of the ease of formation of cyclopropylidene vinyl cations



has been found by solvolysis of dimethylcyclopropylidene chloride (**71**) in aqueous methanol buffered with triethylamine.<sup>56</sup> The solvolysis reaction takes place at 100° to form the acetylenes **72** and **73** as the major products.



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(56) A. Ghenculescu and M. Hanack, *ibid.*, in press.