Organic and Biological Chemistry

Generation and Rearrangements of the 1-Cyclopropylvinyl Cation. A Comparison of the Intermediates Formed upon Ionization of 1-Cyclopropyl-1-iodoethylene and 3,4-Pentadien-1-yl Iodide[1a]

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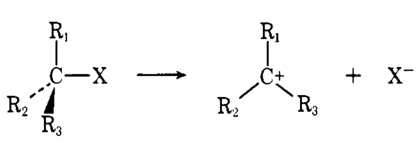
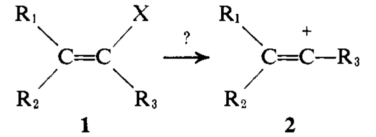
Abstract: Evidence is presented that 1-cyclopropyl-1-iodoethylene (**13**) undergoes both silver-catalyzed and uncatalyzed solvolysis *via* the initial formation of the 1-cyclopropylvinyl cation (**14**). This ion appears to be stabilized by delocalization of charge from the ionization center into the cyclopropane ring. The products of ionization of **13** have been compared with those from 3,4-pentadien-1-yl iodide (**34**); both distributions are very similar when the ionizations are carried out under closely similar conditions, and it is therefore probable that vinyl cation **14** is the first intermediate formed in the ionization of **34** as well. Although its major fate appears to be direct reaction with solvent, cation **14** undergoes some rearrangement; temperature dependence studies indicate that this rearrangement is an activated process, and product studies suggest that the rearrangement initially generates an unsymmetrical 2-methylenecyclobutyl carbonium ion.

The study of solvolytic displacement reactions has over the years provided chemists with much fundamental information about the structure and behavior of carbonium ions, as well as the role played by the solvent in the generation and destruction of such ions.[2] However, it was apparent when we initiated the work described in this paper that nearly all detailed studies which had been carried out on carbonium ion systems involved ions with three ligands, *i.e.*, sp^2 hybridized or "aliphatic" ions (**1**). It is for such ions that a generalized reaction scheme involving a spectrum of intermediates from intimate ion pairs to free ions has been developed.[3]

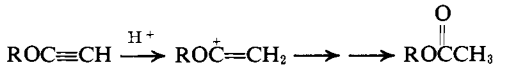
One of the most powerful ways to study a carbonium ion reaction is to examine the effect of varying the environment of the process or the structure of the substrate on the reaction course. Owing to the restriction of most studies to sp^2 ions, structure variation usually involves changing the nature of one of the ligands (R_1, R_2, or R_3 in **1**). However, important information about such ion processes could also in principle be obtained by making a structural change at the ionization center. This would represent direct modification of the precise point at which displacement occurs, and might serve to perturb greatly almost any of the reaction steps, even those involving movement of atoms relatively remote from the reaction site (*e.g.*, in the solvation shell). We therefore decided to attempt the study of processes which might cause ionization of vinyl derivatives, thereby generating "vinyl cations" (**2**). Such intermediates have only two ligands and might therefore be expected to be sp, rather than sp^2, hybridized in their lowest energy configurations.





1 **2**

The focus of our interest on the solvolytic displacement reaction required that we have a method of directly generating vinyl cations by ionization of vinyl derivatives. This presented a problem; at the beginning of this study there were very few reports of reactions of vinyl derivatives in the literature which appeared to proceed by initial ionization to vinyl cations. In a number of instances, however, vinyl cations had apparently been generated by other methods. As early as 1944, for example, Jacobs and Searles proposed[4] cation **4** as an intermediate in the acid-catalyzed hydra-



$$\underset{\mathbf{3}}{\mathrm{ROC{\equiv}CH}} \xrightarrow{H^+} \underset{\mathbf{4}}{\mathrm{RO\overset{+}{C}{=}CH_2}} \longrightarrow \longrightarrow \mathrm{RO\overset{O}{\overset{\|}{C}}CH_3}$$

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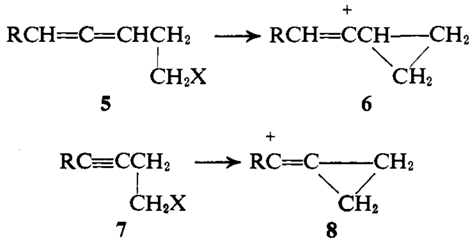
(1) (a) A preliminary account of this work has been reported: S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 2115 (1969); (b) National Science Foundation Predoctoral Fellow, 1967–present; (c) Alfred P. Sloan Foundation Fellow, 1970–1972; Camille and Henry Dreyfus Teacher–Scholar Grant Awardee, 1970–1975.

(2) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

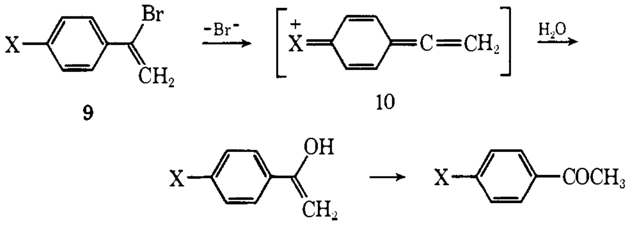
(3) For leading references, see (a) D. Bethell and V. Gold, "Carbonium Ions: An Introduction," Academic Press, London, 1967; (b) V. J. Shiner, Jr., M. W. Rapp, and H. R. Pinnick, *J. Amer. Chem. Soc.*, **92**, 232 (1970); (c) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362 (1969); (d) H. L. Goering and E. C. Linsay, *ibid.*, **91**, 7435 (1969), and earlier papers; (e) I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969).

(4) T. L. Jacobs and S. Searles, Jr., *J. Amer. Chem. Soc.*, **66**, 686 (1944).

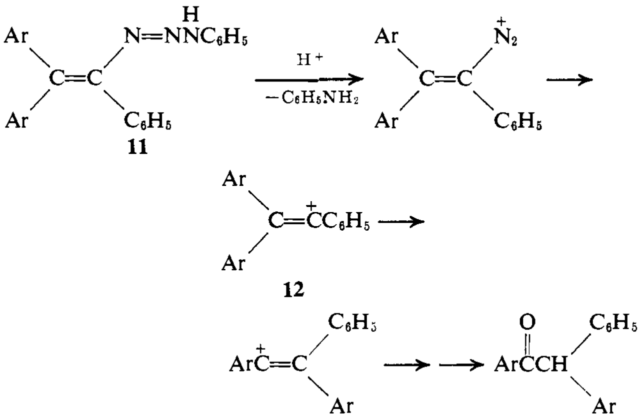
tion of acetylenic ethers (3). More recently, Noyce and his coworkers have obtained a large amount of evidence that vinyl cations intervene generally in acetylene hydration,[5] and Fahey's group has made similar observations along with directing attention to the rather complex involvement of ion pairs in additions of acids to acetylenes.[6] Evidence had also been obtained that electrophiles could participate in intramolecular reactions with acetylene and allene functions to generate vinyl cations; Hanack and his coworkers showed,[7] for example, that both "homoallenyl" and "homopropargyl" derivatives (**5** and **7**) underwent solvolysis to give products which could be understood to have arisen from vinyl cations **6** and **8**.



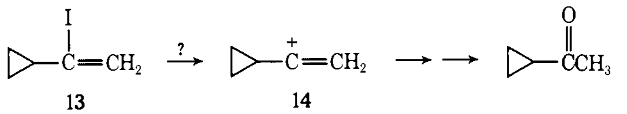
Of the few instances in which ionization of an ethylene derivative could be presumed to have taken place during the substitution process, two sets of experiments were especially intriguing. The first was the work of Grob and Cseh, who showed that para-substituted α-bromostyrenes (**9**) underwent solvolytic conversion to the corresponding acetophenones in a reaction that had all the characteristics expected of an SN1 reaction, including first-order kinetics essentially unaffected by varying amounts of triethylamine buffer in the solution.[8] The second paper described work of Jones and Miller, who observed[9] a 1,2 phenyl shift in vinyl cation **12** generated by deamination of triazene **11**. These papers indicated that vinyl ionization could be activated by conventional electron-donating groups, and that rerrangements of the sort normally observed in aliphatic ion chemistry could also take place to vinyl cation termini.[10]



With these considerations in mind, we decided that a thorough study of solvolytic ionization at a vinyl center would require a substrate which ideally incorporated the following characteristics: (1) a group attached to the ionizing center which could accelerate the ionization rate, thus allowing us to use less reactive leaving groups than N_2 at reasonable temperatures in order that we might carry out kinetic studies; (2) a leaving group that we could examine under conditions which involved little or no ion-pair return; (3) reactants and products that were easily and quantitatively analyzed, preferably by vapor phase chromatography (vpc); (4) a substrate that would form a cation which potentially could undergo rearrangements (hopefully interesting ones) as well as reaction with solvent.



The system that seemed to satisfy best these requirements was 1-cyclopropyl-1-iodoethylene (**13**). It was hoped that the three-membered ring would accelerate C-1 heterolysis; in addition, vinyl cation **14** is formally of the "cyclopropylcarbinyl" type.[11] We felt this study might therefore also shed some additional light on the mechanism by which cyclopropane rings interact with and stabilize positively charged centers, and on the extent to which such species have "bicyclobutonium ion" character.[11]



Since the inception of our study, the vinyl cation field has undergone a rapid maturation. Other techniques now exist for the solvolytic generation of vinyl cations from ethylene derivatives, and studies in several laboratories,[7,10,12–19] in addition to our own,[1a,20]

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(5) (a) D. S. Noyce, M. A. Matesich, O. P., M. D. Schiavelli, and P. E. Peterson, *J. Amer. Chem. Soc.*, **87**, 2295 (1965); (b) D. S. Noyce, Sr., M. A. Matesich, and P. E. Peterson, *ibid.*, **89**, 6225 (1967); (c) D. S. Noyce and K. E. DeBruin, *ibid.*, **90**, 372 (1968); (d) D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020 (1968).

(6) (a) R. C. Fahey and D.-J. Lee, *ibid.*, **88**, 5555 (1966); (b) R. C. Fahey and D.-J. Lee, *ibid.*, **90**, 2124 (1968).

(7) (a) M. Hanack and J. Häffner, *Tetrahedron Lett.*, 2191 (1964); (b) M. Hanack, J. Häffner, and I. Herterich, *ibid.*, 875 (1965); (c) M. Hanack, I. Herterich, and V. Vött, *ibid.*, 3871 (1967); (d) M. Hanack and J. Häffner, *Chem. Ber.*, **99**, 1077 (1966).

(8) (a) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964); (b) see also, C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, **47**, 1590 (1964).

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

(10) For some recent examples of rearrangements to vinyl cationic centers, see (a) G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968); G. Capozzi, G. Melloni, G. Modena, and U. Tonellato, *Chem. Commun.*, 1520 (1969); G. Modena and U. Tonellato, *ibid.*, 1363, 1676 (1968); (b) K. Griesbaum and Z. Rehman, *J. Amer. Chem. Soc.*, **92**, 1416 (1970); (c) M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *ibid.*, **92**, 3802 (1970).

(11) For some recent references discussing this problem in the aliphatic series, see (a) ref 3a, Chapter 7; (b) M. Vogel and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2262 (1966); (c) G. W. Van Dine and P. von R. Schleyer, *ibid.*, **88**, 2321 (1966); (d) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969); (e) P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969), and references cited there.

(12) (a) M. Hanack and I. Herterich, *Tetrahedron Lett.*, 3847 (1966); (b) M. Hanack, S. Bocher, K. Hummel, and V. Vött, *ibid.*, 4613 (1968); (c) M. Hanack, V. Vött, and H. Ehrhardt, *ibid.*, 4617 (1968).

(13) (a) P. E. Peterson and J. E. Duddey, *J. Amer. Chem. Soc.*, **88**, 4490 (1966); (b) P. E. Peterson and J. M. Indelicato, *ibid.*, **90**, 6515 (1968); (c) P. E. Peterson and J. M. Indelicato, *ibid.*, **91**, 6194 (1969); (d) P. E. Peterson and R. J. Kamat, *ibid.*, **88**, 3152 (1966); (e) P. E. Peterson and R. J. Kamat, *ibid.*, **91**, 4521 (1969).

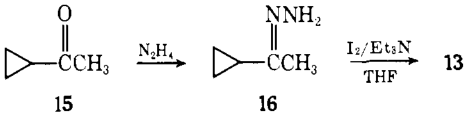
(14) (a) R. S. Bly, A. R. Ballentine, and S. U. Koock, *ibid.*, **89**, 6993 (1967); (b) R. S. Bly and S. U. Koock, *ibid.*, **91**, 3292 (1969); (c) R. S. Bly and S. U. Koock, *ibid.*, **91**, 3299 (1969).

(15) (a) M. Bertrand and M. Santelli, *C. R. Acad. Sci. Paris*, **259**, 2251 (1964); (b) M. Bertrand and M. Santelli, *ibid.*, **266**, 231 (1968); (c) M. Bertrand and M. Santelli, *Chem. Commun.*, 718 (1968).

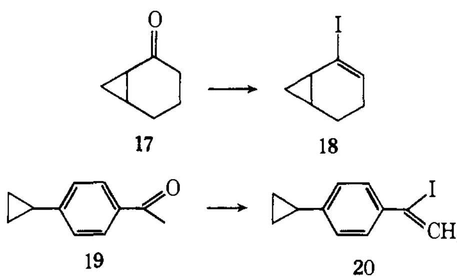
have greatly improved the general understanding of reactions in which vinyl cations intervene. A number of these more recent studies will be discussed in the body of this paper and the one following.[20b]

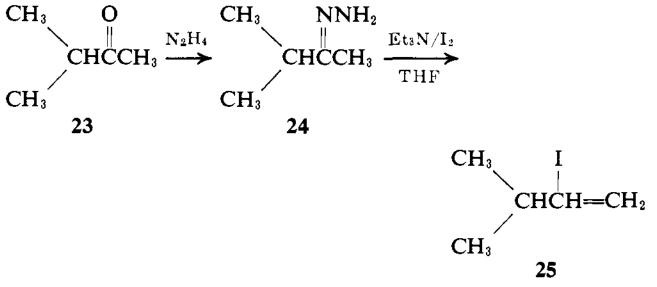
Results and Discussion

Ionization of 1-Cyclopropyl-1-iodoethylene (13). The synthesis of **13** was achieved in moderate yield by extension of a reaction discovered[21] by Barton, O'Brien, and Sternhell in 1962. These workers found that methyl ketones could be transformed into vinyl iodides by treatment of their hydrazones with iodine and triethylamine in tetrahydrofuran (THF). When the hydrazone (**16**) of cyclopropyl methyl ketone (**15**) was subjected to these reaction conditions, one relatively volatile product appeared in the vpc, accompanied by higher boiling materials. The volatile product could be isolated by distillation, and was obtained in 20% yield after purification by preparative vpc. In the nmr it showed resonances at δ 0.75–1.1 ppm (4 H, mult), 1.5–2.0 ppm (1 H, mult), 5.9 ppm (1 H, singl), and 6.3 ppm (1 H, broadened singl). Principal infrared (ir) bands were observed at 3090, 3015, 1620, and 1605 cm^{-1}, and in the mass spectrum the parent ion appeared at *m/e* 194 and the base peak at *m/e* 67. On the basis of these data, the elemental analysis, and the method of synthesis, this material was assigned the structure of 1-cyclopropyl-1-iodoethylene (**13**). The reaction appears to be reasonably general for various cyclopropyl-substituted ketone hydrazones; for example, both **17** and **19** have been converted to vinyl iodides **18** and **20** in moderate yield using the same method.[22a]

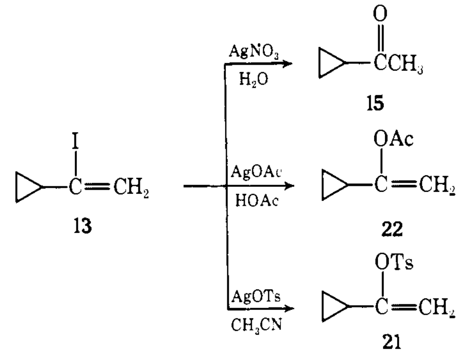


The vinyl iodide **13** was first treated with aqueous silver nitrate solution; we were gratified to observe that an immediate and copious precipitate was formed. The solid was identified by conventional means as silver iodide, and work-up of the aqueous solution gave cyclopropyl methyl ketone (**15**) as the predominant (>90%) organic product.[22b] This indicated that the cyclopropyl ring was responsible for considerable rate acceleration in the silver-catalyzed ionization process, since the normal unreactivity of vinyl halides with aqueous silver nitrate has long been a part of the lore of classical organic structure determination.[23] We confirmed the impression that the ionization reaction of **13** was unusually rapid by converting isopropyl methyl ketone (**23**) to 1-isopropyl-1-iodoethylene (**25**), and observing that it gave no reaction with silver nitrate in water or aqueous ethanol at room temperature. Compound **25**, in fact, was extremely unreactive, undergoing slow conversion back to the ketone only at temperatures near 140° in the presence of silver ion.





Other media were also sufficient to induce ionization of **13**. Silver acetate in acetic acid produced a good yield of 1-cyclopropylvinyl acetate (**22**) in addition to several other acetates (*vide infra*) when exposed to the iodide **13** at room temperature. Surprisingly, even an anion as unreactive as *p*-toluenesulfonate (tosylate) was nucleophilic enough apparently to trap ion **14**; when treated with silver tosylate in acetonitrile at room temperature, a crystalline but thermally unstable product was formed which was isolated in 17% yield after two low-temperature recrystallizations. This material quickly resinified on standing at room temperature, but was stable enough to yield analytical and spectroscopic data consistent with its assignment as 1-cyclopropylvinyl tosylate (**21**). The only other product isolated from this reaction was cyclopropylacetylene (**38**).



Kinetics. The facile silver-catalyzed ionization of **13** suggested that it might be feasible to induce ionization of **13** without catalysis at higher temperatures. This proved to be correct. Upon exposure to 77.5% aque-

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(16) (a) G. Modena, U. Tonellato, and F. Naso, *Chem. Commun.*, 1363 (1968); (b) G. Modena and U. Tonellato, *ibid.*, 1676 (1968); (c) G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968).

(17) (a) P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, 91, 4600 (1969); (b) A. G. Martinez, M. Hanack, R. H. Summerville, P. v. R. Schleyer, and P. J. Stang, *Angew. Chem.*, **82**, 323 (1970); (c) 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, 3802 (1970).

(18) (a) Z. Rappoport and A. Gal, *ibid.*, **91**, 5246 (1969); (b) Z. Rappoport and Y. Apeloig, *ibid.*, 91, 6734 (1969).

(19) (a) D. Kaufman and L. L. Miller, *J. Org. Chem.*, **34**, 1495 (1969); (b) L. L. Miller and D. Kaufman, *J. Amer. Chem. Soc.*, 90, 7282 (1968).

(20) (a) D. Kelsey and R. G. Bergman, *ibid.*, 92, 228 (1970); (b) D. Kelsey and R. G. Bergman, *ibid.*, **93**, 1941 (1971).

(21) (a) D. H. R. Barton, R. E. O'Brien and S. Sternhell, *J. Chem. Soc.*, 470 (1962); (b) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1969).

(22) (a) V. J. Rajadhyaksha and R. G. Bergman, unpublished results; (b) similar results have been obtained with the corresponding chloride by M. Hanack and T. Bässler, *J. Amer. Chem. Soc.*, 91, 2117 (1969).

(23) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1956, p 141.

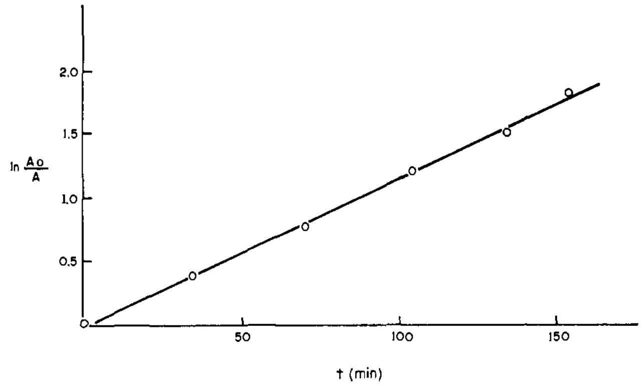


Figure 1. First-order plot for the solvolysis of 1-cyclopropyl-1-iodoethylene (**13**) in 77.5% aqueous methanol at 150 ± 0.1°. Slope of the line gives $k = 1.94 \pm 0.04 \times 10^{-4}$ sec^{-1}.

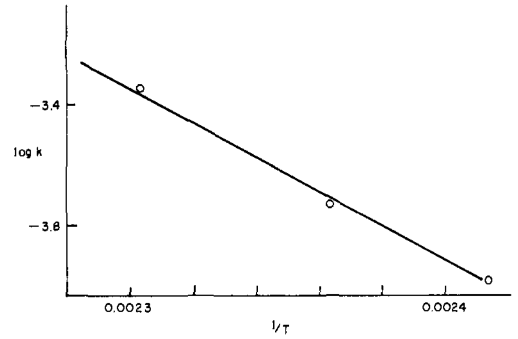


Figure 2. Arrhenius plot (log k *vs.* $1/T$) for the solvolysis of 1-cyclopropyl-1-iodoethylene (**13**) in 77.5% aqueous methanol. Slope of the line gives $E_a = 24.6 \pm 0.7$ kcal/mol, and intercept gives $\Delta S^{\ddagger} = 20.0 \pm 1.7$ eu.

ous methanol containing slightly more than 1 equiv of triethylamine buffer in the neighborhood of 140°, **13** underwent solvolytic conversion to **15** at a convenient rate. The rate was cleanly first order (Figure 1), and showed only a slight depression, consistent with a medium effect, when the concentration of buffer was tripled.[24] Rate measurements at three temperatures gave an Arrhenius plot (Figure 2) from which the following activation parameters were calculated: E_a = 24.6 kcal/mol, $\Delta S^{\ddagger} = -20.0$ eu.

The need for a special explanation (the vinyl cation mechanism) for these hydrolysis data is emphasized by the results of a study of uncatalyzed hydrolysis of the structurally similar 1-isopropyl-1-iodoethylene (**25**). This material proved to be extremely unreactive in triethylamine-buffered aqueous methanol, undergoing reaction at a convenient rate only in the neighborhood of 230°. Furthermore, the reaction does not obey a simple first-order rate law, and the rate was considerably accelerated by an increase in the concentration of triethylamine (Figure 3).

These observations are consistent with a bimolecular reaction between **25** and the buffer, and are strong evidence that the cyclopropyl ring serves to accelerate greatly the S_N1 process in vinyl iodide **13**. A lower limit of 1.2×10^3 can be placed on the S$_N$1 rate constant ratios for **13** and **25**, but the level of assistance may be much higher.

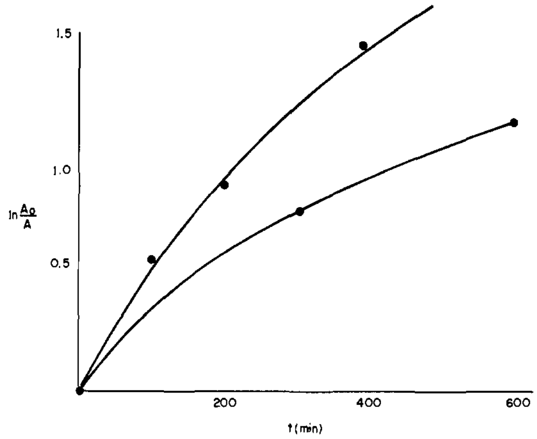
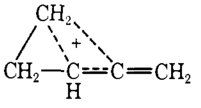


Figure 3. Solvolysis of 1-isopropyl-1-iodoethylene in 77.5% aqueous methanol at 233.5 ± 0.1°. Initial concentrations of triethylamine buffer were 0.094 *M* (upper curve) and 0.036 *M*.

Detailed Studies in Acetic Acid. An interesting and somewhat unexpected aspect of the initial product studies described above is that the major products in all cases are nonrearranged cyclopropane derivatives. Intuitively, one might expect that relief of some of the instability of the vinyl cationic center in **14** might be obtained by rearrangement of the molecule, producing either the allylic, cyclobutyl ion **27**, or the primary homoallenyl ion **28**, especially in view of the high rearrangement propensity of aliphatic cyclopropyl carbinyl cations.[11] Furthermore, the possible intervention of nonclassical ions in the aliphatic series[11] raised the possibility that delocalized species such as **26**, **29**, or **30** might be intervening in the vinyl iodide solvolysis. Because the extent of rearrangement in our solvolysis bears directly on these questions, it was important to establish the exact extent to which such rearrangement processes were occurring.



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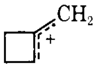

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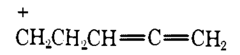
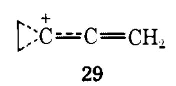


$\overset{+}{C}H_2CH_2CH{=}C{=}CH_2$

28



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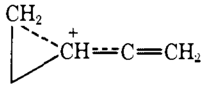

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A careful vpc analysis of the product mixture revealed that six components were produced on treatment of **13** with an excess of silver acetate in acetic acid at 25°. These materials were isolated and purified by preparative vpc and identified on the basis of their spectral and analytical properties and, where possible, by comparison with authentic samples. The structures assigned are indicated in Scheme I, along with a tentative mechanism designed to account for their formation. The percentages of these products formed in the ionization reaction are listed in Table I.

All of the products are accounted for in a straightforward way by the mechanism presented in Scheme I; the rearrangements illustrated are, formally at least, of the same type that occur in cyclopropylcarbinyl ioniza-

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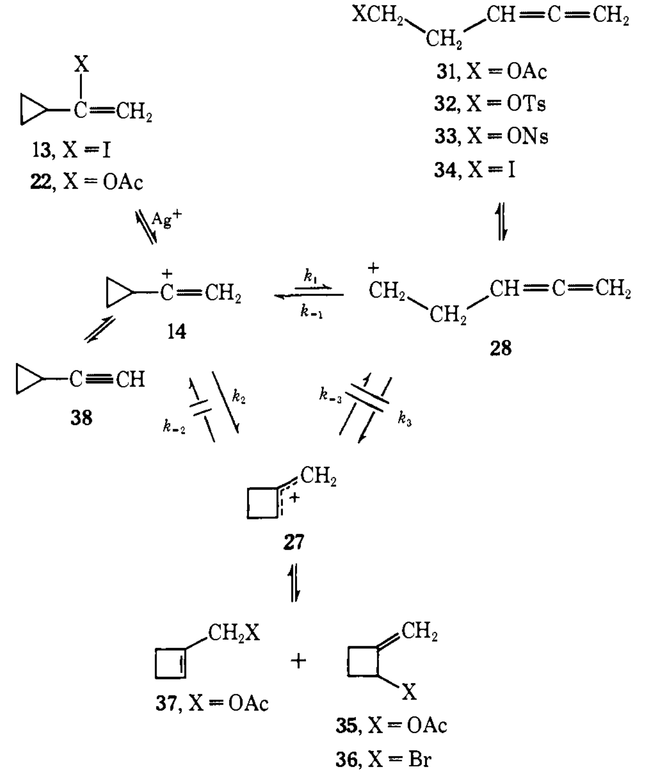
(24) This behavior rules out both nucleophilic triethylamine addition–elimination and proton addition–HI elimination mechanisms; *vide infra* and (b) W. M. Schubert and G. W. Barfknecht, *J. Amer. Chem. Soc.*, 92, 207 (1970).

Scheme I



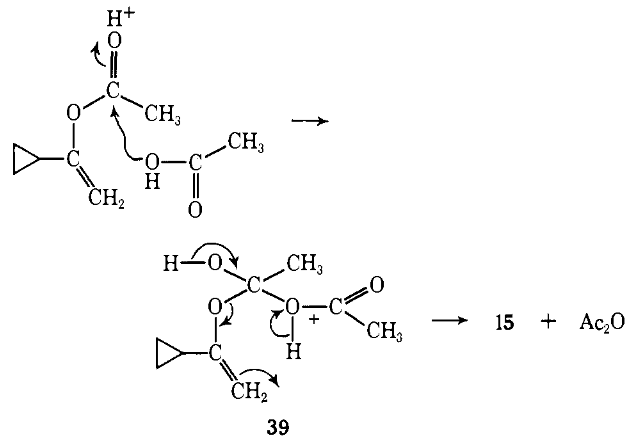
tion reactions. For convenience, the cations are represented by charge-localized structures. It should be understood that this is an oversimplification; σ delocalization undoubtedly plays a role in the transition states for formation of these intermediates, and probably is involved in the ground-state structures of the ions as well.

Table I. Products (Other than Acetylenic) Formed in the Reaction of 1-Cyclopropyl-1-iodoethylene (**13**) with Silver Acetate in Acetic Acid at Varying Temperatures

Temp, °C	Products, mol % 15	22	31	35	37
25.0[a]	17.3	79.7	1.33	1.58	0.18
25.0[b]	34.5	62.8	1.11	1.38	0.20
34.9[c]	13.0	83.8	1.37	1.76	0.19
44.6[c]	15.9	80.7	1.40	1.87	0.21
55.0[c]	17.1	78.7	1.66	2.28	0.25
64.8[c]	28.1	67.7	1.80	2.34	0.26

[a] Reaction time: 250 min. [b] Reaction time: 1320 min. [c] Reaction time adjusted to give about 20% **15**.

Before this mechanism is discussed, some comment on the amount of cyclopropyl methyl ketone (**15**) in the product mixture is warranted. Our initial studies[1a] indicated that significant amounts of **15** were formed in the ionization reaction even when special precautions were taken to dry the acetic acid and silver acetate before use and to run the reaction in a dry atmosphere. It was established by subjecting the vinyl acetate **22** to the reaction conditions that it slowly was converted to ketone even in the absence of water. This reaction is unusually facile, and its mechanism is unknown, but one possibility is attack of acetic acid at the carbonyl carbon of **22** to give **39**, followed by C–O bond cleavage and proton transfer. The products of this transformation would be **15** and acetic anhydride. In order to

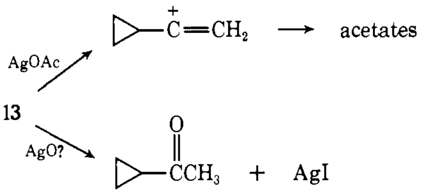


39

determine whether any **15** was formed as a kinetic product of the reaction, aliquots were removed from the reaction medium at varying per cent conversion of iodide **13**. The results are presented in Figure 4, and show that the per cent of ketone product (but not its *absolute* yield) goes through an initial minimum. The only reasonable way to interpret these data is to assume that some **15** (about 8%) is formed at a rate greater than that at which silver acetate catalyzed solvolysis products are formed, and that this reaction is over at low per cent conversion of **13**. A subsequent slow rise in the per cent of **15** is due to decomposition of acetate **22**.

The fact that **15** is formed in a rapid burst at the beginning of the reaction rules out the possibility that it arises from the same rate-determining step that leads to acetates in this system. It therefore must be formed in a parallel path, and furthermore must be formed without intervention of water. At present, we are inclined to believe that silver oxide or some other contaminant in the silver acetate is responsible for the small amount of **15** produced as kinetic product (Scheme II).

Scheme II



An additional disclaimer must be voiced with regard to the percentage of acetylene reported in the silver-catalyzed ionizations. When the ionizations of **13** are run to completion, the buildup of a white precipitate occurs which we assume is the silver salt of cyclopropylacetylene (**38**). Even at relatively low conversion of iodide **13** to products, a noticeable amount of the precipitate has formed. The mass balance (see Experimental Section) can be calculated to be around 73% in the complete reaction, indicating that the maximum amount of acetylene formed is 27%. This is in reasonable agreement with the amount of acetylene product (incapable of forming a silver salt) formed in the methyl-substituted system, as reported in the following paper.[20b]

Mechanism of the Reaction. As has been noted a number of times before, substitution at a vinyl center can in principle occur by any one of a number of mechanisms.[25] Although an SN1 mechanism appears to be

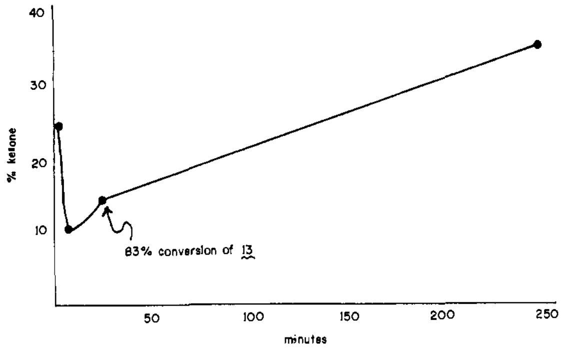
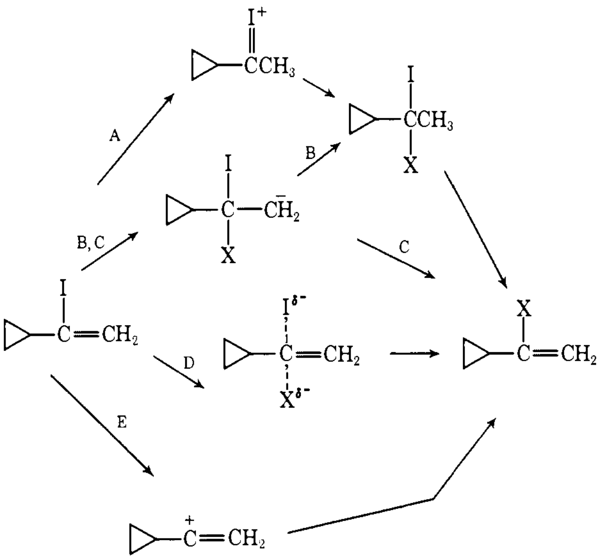


Figure 4. Cyclopropyl methyl ketone (**15**) as percentage of the products (other than **38**) formed from silver-catalyzed ionization of 1-cyclopropyl-1-iodoethylene (**13**) in acetic acid at 45° as a function of time.

the most likely pathway for the transformations under study here, the large number of examples of vinyl substitutions proceeding *via* other routes recorded in the literature requires that we discuss the reasons behind this choice.

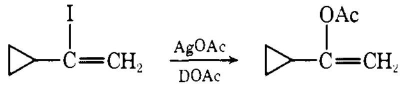
The most likely vinyl substitution pathways are illustrated in Scheme III. Paths A and B are addition–elimination routes, which differ only in the chronology of attack of proton and nucleophile. Path C is a nucleophile addition mechanism proceeding through a carbanion intermediate which eliminates I^- faster than it is protonated, path D is the vinyl analog of the well-known SN2 reaction, and path E is the ionization mechanism.

Scheme III



The fact that **13** undergoes uncatalyzed hydrolysis with clean first-order kinetics, with rates that show no increase with increasing buffer concentration, rules out path A and paths B, C, and D *when X is a nucleophile other than solvent.* The situation where X = solvent is more complicated, since its concentration does not change appreciably during the reaction and thus its kinetic role normally goes undetected. Therefore, in order to rule out paths A and B in the catalyzed ionization at least, iodide **13** was exposed to silver acetate in *o*-deuterioacetic acid. The vinyl acetate produced was isolated in pure form by preparative vpc, and shown to have incorporated no ($<1\%$) deuterium by nmr, ir, and mass spectrometric analysis. This makes a mechanism involving protonation and deprotonation very unlikely.

We are therefore left with paths C, D, and E. Paths C and D, where X = HOAc, have not been ruled out on a kinetic basis. Path D is rendered unlikely by the experiments described in the following paper.[20b] Mechanism C is therefore the most difficult noncationic pathway to rule out rigorously; however, the following pieces of circumstantial evidence make this mechanism also seem unlikely: (1) HOAc is a relatively weak nucleophile, and if triethylamine and acetate ion do not induce an addition–elimination process, it is difficult to see why acetic acid should; (2) if expulsion of I^- is to be faster than proton transfer, the addition step must constitute the rate-determining part of the mechanism, and it then becomes difficult to understand the source of the observed powerful silver catalysis and rate acceleration by the cyclopropyl group; (3) rearrangement processes are difficult to account for by this mechanism.



We therefore feel justified in assuming that this reaction takes place by initial rate-determining silver-catalyzed ionization of iodide **13**, followed by rearrangement and solvent trapping of the intermediate vinyl cation (path E).

Nature of the Ionic Intermediates. Ionization of 3,4-Pentadien-1-yl Iodide. In 1964, Hanack and Häffner examined the solvolysis of a number of 3,4-pentadienyl-1-yl ("homoallenyl") derivatives,[7a,d] and found that in all cases large amounts of cyclopropyl alkyl ketones were produced (*cf.* Table II). This suggests that cyclopropylvinyl cation **14** is an intermediate in such solvolyses, and it was of interest to determine just how closely the product distribution (and hence by inference, the intermediates involved) corresponded to that observed on ionization of **13**. If evidence could be obtained that the cations formed in both reactions were substantially the same, a comparison study of this type might also provide an opportunity to investigate subtle environmental effects such as ion pairing upon the extremely rapid reactions which determine the fates of the ions involved in product formation.

Unfortunately, however, most of these studies were carried out in media which differed substantially from our own, or employing leaving groups which also differed or required higher temperatures to induce ionization.[7a,b] In addition, we had no indication as to whether the large amounts of **15** formed in these solvolyses represented the product formed from kinetic control, or were derived from enol ester precursor. Also, in a number of the studies several minor products were left unidentified. Finally, a large amount of direct substitution (SN2?) product (*e.g.*, **31**) is formed in most of the solvolyses studied (Table II). These considerations rendered a careful comparison with our own results difficult or impossible.

While our work was in progress, Jacobs and Macomber reported[26] a more detailed investigation of the

(25) See, for example, (a) M. Hanack, *Accounts Chem. Res.*, 3, 209 (1970); (b) Z. Rappoport, *Advan. Phys. Org. Chem.*, 7, 1 (1969).

(26) (a) T. L. Jacobs and R. Macomber, *Tetrahedron Lett.*, 4877

Table II. Product Distributions from Substrates Leading to the Cyclopropylvinyl Cation System under Various Solvolytic Conditions

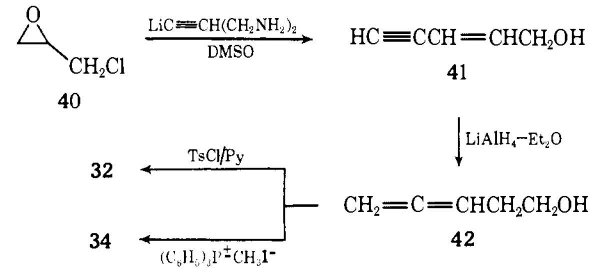
Substrate	Conditions	Products, %							Ref
		15	38	22	31	35	37	Unident	
3,4-Pentadien-1-yl β-naphthalenesulfonate (33)	H_2O, DMK, $CaCO_3$, 60°	37						11	7d
	HOAc–NaOAc, 60°	20			61			7, 12	7d
	HCOOH–NaOOCH, 60°	80			5[a]			15	7d
	CH_3OH, $CaCO_3$, 60°				92[b]			8	7d
3,4-Pentadien-1-yl tosylate (32)	HOAc–NaOAc, 100°	11		3	76	6			26b
	HOAc–NaOAc, 100°	55.9	0.92	0	37.8	4.67	0.38	0.17	This work
3,4-Pentadien-1-yl bromide	H_2O, Ag_2O room temp	32			44[c]				7d
3,4-Pentadien-1-yl iodide (34)	AgOAc, HOAc 25°	4.8	23	61.5	9.4	1.21	0.14	0	This work
1-Cyclopropyl-1-iodoethylene (13)	AgOAc, HOAc 25°	12.6	27	58.2	0.97	1.15	0.13	0	This work

[a] Formate. [b] Methyl ether. [c] Alcohol.

solvolysis of 3,4-pentadien-1-yl tosylate (**32**). They found not only vinyl ester, but also cyclobutyl products; however, even discounting the large amount of direct substitution product formed, the product proportions reported (Table II) differed substantially from those we obtained in the ionization of **13**. Once again, a precise comparison was difficult, due mainly to the ambiguity in the source of ketone and to the fact that the solvolysis was run at 100°.

It was for these reasons that we decided to synthesize and carry out the silver-catalyzed ionization of 3,4-pentadien-1-yl iodide (**34**), and to repeat the solvolysis of tosylate **32**. The alcohol precursor to these derivatives (**42**) was prepared by a modification of the method of Hanack and Häffner[7d] (Scheme IV). Treatment of

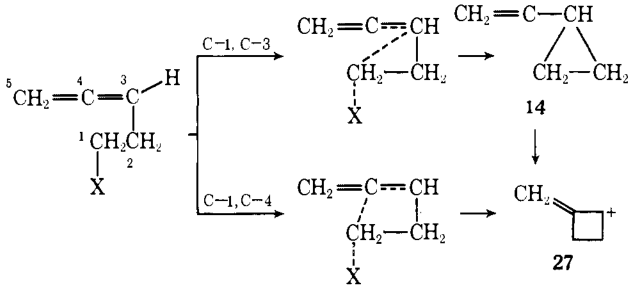
Scheme IV



epichlorohydrin with lithium acetylide–ethylenediamine in DMSO (in place of sodium acetylide in liquid ammonia) gives an improved yield (49%) of 2-penten-4-yn-1-ol (**41**). Alcohol **42** is then obtained in 85% yield by reaction of **41** with lithium aluminum hydride. Conversion of **42** to tosylate **32** was effected using *p*-toluenesulfonyl chloride in pyridine, and the iodide **34** is the product of the reaction of **42** with triphenyl phosphite methiodide[27] (25% yield).

Evidence has been presented which suggests that ionization of tosylate **32** is anchimerically assisted.[7d,26b] The level of acceleration is low enough, however, that solvolysis occurs at a convenient rate only in the neighborhood of 100°. We therefore repeated the solvolysis at this temperature, and confirmed that a major product of the reaction was the direct-substitution acetate **31**, as is indicated in Table II. There is serious discrepancy between our results and those of Jacobs and Macomber[26] with respect to the amount of both **31** and the other products formed in this reaction, however. The large amount of ketone **15** we obtained is due to a correction for material poorly extracted from water in the work-up, which the earlier workers may well have missed. As we indicated earlier, most and probably all this material is formed by decomposition of vinyl acetate **22**, which control experiments show is extremely rapid at this temperature. We observed no residual **22** in the mixture. Finally, about the same amount of cyclobutyl product **35** was isolated by both groups, and in addition we found a small amount of cyclobutenyl product **37** and a trace of acetylene **38**.

We can account for the major differences in percentages reported in Table II on the basis of our improved analysis for ketone **15**. A more important comparison is that of the tosylate solvolysis with the vinyl iodide ionization, since that is the mechanistically important one. It is obvious from Table II that there are important differences in product distribution, the main one being the large amount of homoallenyl acetate **31** formed in the tosylate solvolysis. This is most easily accounted for by assuming it is formed by a parallel solvent participation pathway independent of the cyclization route. A more realistic comparison then is the profile of *cyclized* products formed in both entries to the cation pool; specifically it is important to examine the relative amounts of products having cyclopropyl and cyclobutyl structures. The larger proportion of cyclobutyl product arising from tosylate **32** indicates that an additional independent pathway might be required in this system. The double bond in **32** can interact with the developing electrophilic center at C-1



(1967); (b) T. L. Jacobs and R. S. Macomber, *J. Amer. Chem. Soc.*, **91**, 4824 (1969).

(27) S. Landauer and N. H. Rydon, *J. Chem. Soc.*, 2224 (1953).

in two ways, the C-1, C-3 pathway giving cyclopropyl product, and the C-1, C-4 pathway leading directly to cyclobutyl product. If the amount of cyclobutyl product arising from **13** and **32** are the same, it is probably reasonable to infer that little of this material arises by direct 1,4 cyclization; rather it is formed by 1,3 cyclization followed by subsequent 1,2 rearrangement in cation **14**.[28]

The difficulty with associating the larger amount of **35** and **37** with an independent mechanistic pathway in the solvolysis is due to the high temperature at which the reaction was run, and the differing leaving groups in this ionization and that of **13**. In addition, a control experiment showed that acetylene **38** was unstable at 100° in acetic acid, being converted to a mixture of other products (>60% yield) which contained a disproportionately large amount of cyclopropyl product. For these reasons, we also examined the ionization of the corresponding iodide **34** under conditions as closely comparable to those of the **13** ionization as possible. An interesting aspect of this experiment (Table II) is that the percentage of direct substitution occurring is much lower than in the tosylate solvolysis, allowing a more accurate comparison of cyclized product ratios. This comparison is made in Table III, and an examination of the data indicates that the relative amounts of cyclobutyl product formed in each ionization are nearly the same. Because the accuracy of these ratios is limited by the accuracy with which we could determine the denominators (which represent only about 1% of the product mixtures), the values obtained are probably equal within experimental error. However, since we have observed that cation **27** gives only cyclobutyl products (*vide infra*), the cyclized product ratios provide such a sensitive test for the C-1, C-4 pathway that a strong conclusion may still be drawn from the data. For example, if in the solvolysis of **34** only 0.5% of the cyclized products resulted from the C-1, C-4 pathway and the remainder from the C-1, C-3 pathway, the expected value for the product ratio would be only 36.4, which is far smaller than the observed value. We can therefore say with some confidence that less than 0.5% of the C-1, C-4 pathway is required to explain the solvolytic behavior of the homoallenyl system.[28]

Table III. Profile of Cyclized Acetate Products Formed in Cyclopropylvinyl and Homoallenyl Systems

		Products, %		
Substrate	Conditions	**22** + **15**	**35** + **37**	[**22** + **15**/**35** + **37**]
3,4-Pentadien-1-yl tosylate (**32**)	HOAc–NaOAc, 100°	55.9	5.05	11
3,4-Pentadien-1-yl iodide (**34**)	HOAc–AgOAc, 25°	64.0[a]	1.35	47.4
1-Cyclopropyl-1-iodoethylene (**13**)	HOAc–AgOAc, 25°	65.8[b]	1.28	51.4

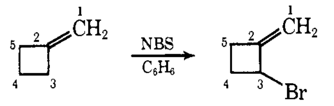
[a] From the reaction time allowed and the observed rate of **22** to **15** conversion at 25°, it may be estimated that at least 2.5 of the 4.8% **15** observed came from **22** under the reaction conditions. Only this amount is included in calculating the ratio. [b] Corrected for the amount of **15** which is apparently not derived from **22**.

With the precise mode of formation of cyclobutyl product established, the question now arises as to why the propensity for rearrangement of cation **14** is so low. In the cyclopropylcarbinyl series, the product of kinetic control includes a significant amount of cyclobutyl material;[11] one might naively expect that transforming the cyclopropylcarbinyl carbon into a vinyl, rather than an alkyl, cationic center might make it less comfortable carrying positive charge, and thereby induce a faster rate of rearrangement. Furthermore, the initial product of rearrangement is cation **27** (Scheme I), which is not only characterized by the relatively stable cyclobutyl structure, but also must derive extra stabilization from its allylic character. One therefore might expect the **14** → **27** rearrangement to be very exoergic, perhaps providing a great driving force for rearrangement.

Before examining the reasons for the low rearrangement propensity of **14**, then, we first felt it necessary to establish experimentally the exoergicity of the **14** → **27** rearrangement. That is, one possible (though unlikely) reason for the small amount of **35** and **37** in the product mixture might be that cation **14** is much more stable than we had expected, due perhaps to a larger than normal effect of the cyclopropyl ring. This is essentially a thermodynamic argument, and restated in analytical terms it relates to the relative values of k_2 and k_{-2} (Scheme I). We do not have a way of measuring this equilibrium constant directly, but if k_{-2} is the larger of the pair, generation of **27** by an independent route should produce product derived mainly from **14**. We therefore decided to prepare bromide **36** by repeating Buchman's *N*-bromosuccinimide bromination of methylenecyclobutane.[29a]

This bromination was carried out as the earlier workers had described, but once isolated the proton nmr spectrum was not a definitive indication of structure, due to overlap of the α-bromo and vinyl hydrogen signals. We therefore examined its ^{13}C nmr spectrum,[29b,c] which when completely proton decoupled showed resonances outlined in Table IV along with those of methylenecyclobutane (**43**). This spectrum rules out by symmetry a structure such as **44** for the bromide, and primary bromide **45** can be ruled out on the basis of the distinctive chemical shift of the vinyl methylene carbon.

Table IV. ^{13}C Magnetic Resonance Spectra of Methylenecyclobutane (**43**) and 2-Bromo-1-methylenecyclobutane (**36**)



43 **36**

Carbon	Chemical shift (in ppm upfield from CS_2) **43**	**36**
1	87.9	83.7
2	42.7	41.7
3	160.7	147.3
4	176.0	163.9
5	160.7	162.2

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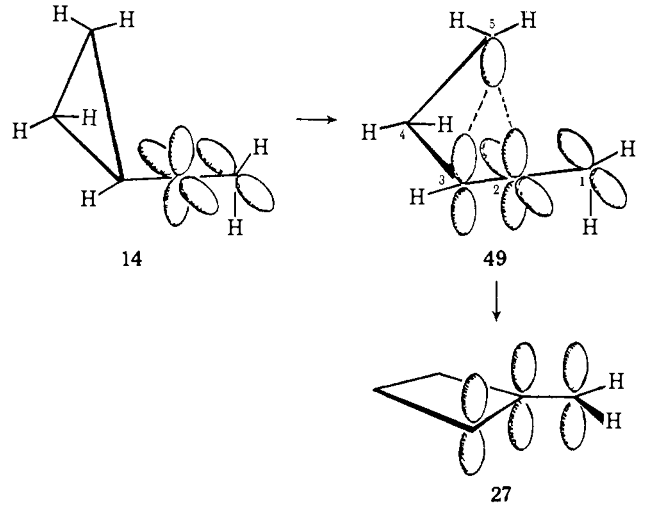
[28] For evidence that direct 1,4 cyclization occurs in more favorable systems, see M. Santelli and M. Bertrand, *Tetrahedron Lett.*, 2515 (1969).

[29] (a) E. N. Buchman and D. R. Howton, *J. Amer. Chem. Soc.*, 70, 2517 (1948); (b) F. J. Weigert and J. D. Roberts, *ibid.*, 89, 2967 (1967); 90, 3543 (1968). We are grateful to Dr. John B. Grutzner of Professor J. D. Roberts' research group for obtaining these spectra.

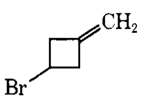
Exposure of bromide **36** to silver acetate in acetic acid at room temperature produced only two acetates, **35** and **37**, in a 2.61:1 ratio. Neither cyclopropyl methyl ketone (**15**) nor vinyl acetate **22** could be detected in the reaction mixture (limits of detectability were 0.3%). It is therefore established that when formed in this medium, cation **27** undergoes no detectable conversion to **14**, and assuming rates of solvent trapping are comparable, k_2 is significantly larger than k_{-2}.

We therefore need some kinetic basis on which to rationalize the rather low magnitude of k_2 compared to the rate of reaction of **14** with solvent. An examination of models indicates that in the most likely transition state for rearrangement, the migrating cyclopropyl carbon is beginning to bond to the empty orbital carrying the initial positive charge at the vinyl carbon. This transition state is pictured in Scheme V, and it is evident from the drawing that the developing p orbital at C-3 is nearly orthogonal to the π system of the double bond while the rearrangement is taking place. It therefore seems likely that very little of the allylic stabilization of the final ion **27** is felt in the **14** → **27** transition state.

Scheme V



Although this accounts for the lack of rearrangement driving force due to allylic stabilization, we still must account for the fact that the vinyl character of the ion **14** alone is not sufficient to promote fast rearrangement. Some insight into this problem might be obtained by the inspection of hydride affinity values in the gas phase (Table V).[30] The hydride affinity of a carbonium ion is the enthalpy change for its reaction with a hydride ion (H^-) and therefore hydride affinities should parallel gas-phase carbonium ion stabilities. It is of some interest that the "ultimate" vinyl cation $C_2H_3^+$ has a hydride affinity in between those of methyl and ethyl cations (CH_3^+ and $C_2H_5^+$). While large differences in solvation energies will make hydride affinities difficult to extrapolate quantitatively to solution stabilities, it is at least conceivable that a vinyl cation is not too greatly different in stability from a primary alkyl cation. This raises the possibility that cation **47** is a better model for **14** than is cation **46**. It is significant therefore that no rearrangement in **47** is detected when it is generated in solution.[11b]



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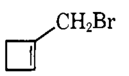

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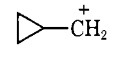
Table V. Hydride Affinities ($-\Delta H$ for the Reaction $R^+ + H^- \rightarrow RH$ in the Gas Phase) for Simple Cations

Cation	$-\Delta H$, kcal/mol
CH_3^+	312
$C_2H_3^+$	290
$C_2H_5^+$	272
$C_6H_5^+$	298
$C_6H_5CH_2^+$	237



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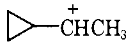
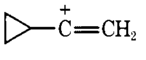


47



14

A Possible Memory Effect in the Vinyl Cation Ring Expansion. The selectivity of the second step in a double carbonium ion rearrangement is often influenced by the stereochemistry of the initial migration. Berson and his coworkers have thoroughly studied a number of systems in which such "memory effects" operate, and have considered a number of possible structural explanations for the effect, including intervention of "twisted" intermediates, the generation of a transitory environment in the neighborhood of the cation, and the possible intervention of nonclassical ions.[31]

An examination of the cyclobutyl product distributions formed from vinyl iodide **13** and 2-methylenecyclobutyl bromide **36** (*cf.* Table VI) reveals an interesting fact: the ratio of primary and secondary allylic acetates **35** and **37** is different when formed from the different precursors. In the direct ionization of **36**, secondary bromide is formed with a selectivity of only 2.6:1, but in the ionization of **13**, the ratio of these two products has increased significantly to about 9:1. It is possible that ion pairs are responsible for this variation in selectivity. However, careful integration of the cyclobutyl product peaks in the ionization mixtures from **13** and **34** (Table VI) showed that the ratios of these compounds were identical within experimental error, even though the two iodides should produce intermediate ion pairs having counterions (or countermolecules) in quite different locations. Bromides **36** and **45** give somewhat different **35**:**37**

Table VI. Secondary:Primary Acetate Product Ratio Formed in the Reaction of a Number of Halides with Silver Acetate in Acetic Acid at 25°

Substrate	Ratio, **35**/**37**
13	8.85 ± 0.8
34	8.65 ± 0.8
36	2.61 ± 0.09
45	0.96 ± 0.03
55 + **56**	2.12 ± 0.08

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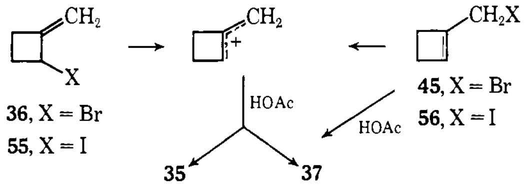
(30) (a) G. R. Freeman, *Radiat. Res. Rev.*, **1**, 1 (1968); (b) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Bur. Stand. (U. S.) Monogr.*, No. **26**, 36, 55, 66, 260, 261, 262 (1969); (c) F. P. Lossing and G. P. Semelnk, *Can. J. Chem.*, **48**, 955 (1970).

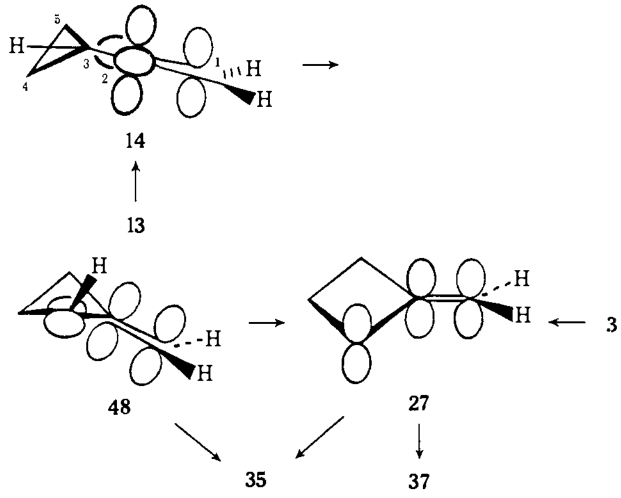
(31) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Amer. Chem. Soc.*, **91**, 5601 (1969), and earlier papers.

ratios (2.61 and 0.96), but the difference here is well rationalized[32] by the intervention of some direct displacement at the primary carbon atom in **45**. Further evidence against a mechanism somehow associated with the nature of the leaving group is provided by silver-catalyzed solvolysis of an 83:17 mixture[33] of iodides **55** and **56**. The **35**:**37** ratio in this case is 2.12,



very close to that predicted assuming behavior identical with that of **36** and **45**. It therefore seems inescapable that the dramatic alteration in acetate product distribution observed in these experiments depends on whether **35** and **37** arise in a rearrangement reaction, and not on the structure of a hypothetical ion pair.

Inspection of Scheme V suggests an alternative way of rationalizing this discrepancy. As indicated before, the transition state for rearrangement of **14** is highly distorted with respect to the eventual stable structure of the allylic cation **27**. Scheme V suggests that the completion of the rearrangement process and structural relaxation to **27** occur in a smooth process, but this may not necessarily be the case. If for some reason structural relaxation is an independent process, and occurs at a rate competitive with that of rearrangement, it is possible that the initial cation formed from **14** is the "twisted" species **48**. This ion is essentially a "buckled" methylenecyclobutyl cation in which very little positive charge has yet been delocalized into the double bond, because the π system is nearly orthogonal to the newly generated p orbital at C-3. It is reasonable that this twisted ion undergo reaction with solvent mainly at C-3, where most of the positive charge still resides. Relaxation of the ion to the planar **27** would then compete with solvent trapping. If **48** is trapped completely at C-3, and the "natural" ratio for secondary–primary reaction is that formed from reaction of **36** (2.6), one can estimate that 63% of the cyclobutyl product from **14** arises by trapping the twisted ion **48**, and 37% arises from the relaxed isomer **27**.



Because relaxation of a simple "twisted" ion such as **48** should occur at a much more rapid rate than that associated with solvent capture, we feel that some additional force must be acting to preserve its distorted structure. The most reasonable suggestion[31] is that **48** is in fact a σ-delocalized species having structure **49**; *i.e.*, that **49** is an intermediate rather than simply a transition state (Scheme V) for the **14** → **27** rearrangement. In any case, whatever the structural basis of this "memory effect"[31] may be, it is clear that the cation precursors to cyclobutyl products must differ in some way when they are generated from different starting materials.

Examination of the structure of ions such as **48** and **49** suggests an interesting experimental means of verifying the occurrence of a memory effect in this system. Unlike **13**, compound **50** is nonsuperimposable on its mirror image, and therefore is capable of supporting optical activity. Two cations (**51** and **52**) can now be produced on ring expansion, and these are also dissymmetric. They should therefore lead to optically active product, whereas the "relaxed" planar cation will produce racemic product. This experiment will not distinguish between nonclassical and twisted structures for the initially formed ions, but it at least will demonstrate that a dissymmetric intermediate is required in the ring-expansion system.

Temperature Dependence of the Cyclopropyl–Cyclobutyl Product Ratio. Estimation of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ for Carbonium Ion Reactions. Although carbonium ions have been studied for many years, little is known about the absolute rates and energetics of the fast reactions (solvent trapping and rearrangement) these species undergo in solution. It has been suggested[34] that the pseudo-first-order collapse of the norbornyl cation occurs at room temperature with a rate constant of about 10^9 sec^{-1}. In acetic acid this would correspond to a second-order rate constant of roughly an order of magnitude less, and so appears to be somewhat slower than that predicted on the basis of simple diffusion or electrostatic control. Berson has calculated[35] from the tritium-labeling data of Lee and Lam[36] that a minimum activation energy for reaction of the norbornyl cation with solvent is 4.65 kcal/mol. It is obviously of interest to know whether rearrangement of carbonium ions is also an activated process.

In order to examine this problem, we have studied the temperature dependence of the ratio of cyclopropyl methyl ketone (**15**) and vinyl acetate **22** to cyclobutyl compounds **35** and **37** produced in the ionization of **13**. This ratio was selected for two reasons. First, our experiments with the ionization of **36** suggested that cation **27** does not return to **14**, thereby allowing us to interpret the product ratio as simply equivalent to the partitioning ratio k_2/k_s for cation **14**. Second, the product ratio is large, and if the selectivity is due mainly

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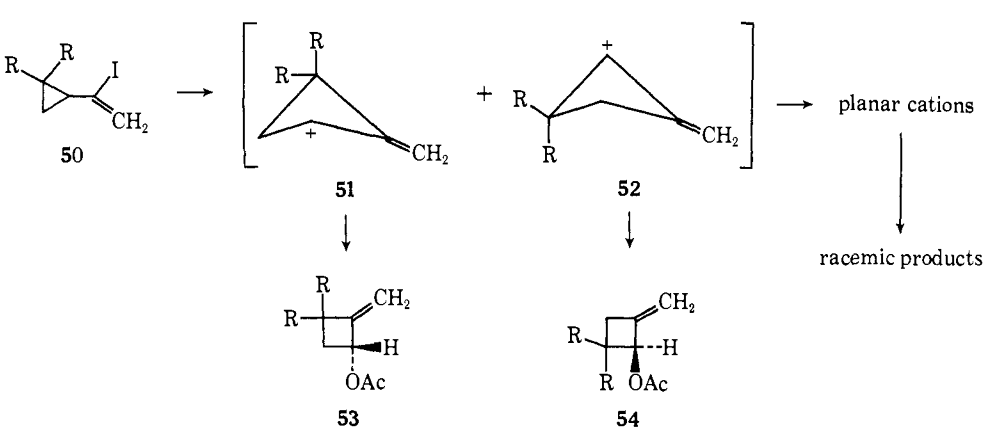
[32] A number of variously substituted allylic halides have been shown to undergo essentially uncomplicated S$_N$1 ionization in AgOAc–HOAc. Primary:secondary (and even tertiary:secondary) ratios are almost always near 1 and allylic isomers give closely similar distributions: *cf.* R. H. DeWolfe and W. G. Young in S. Patai, Ed., "Chemistry of Alkenes," Interscience, London, 1964, pp 701–703.

[33] It was necessary to subject a mixture of **55** and **56** to acetolysis because rapid interconversion of these compounds occurs (even in the neat liquid) at room temperature. See ref 32, pp 720–723.

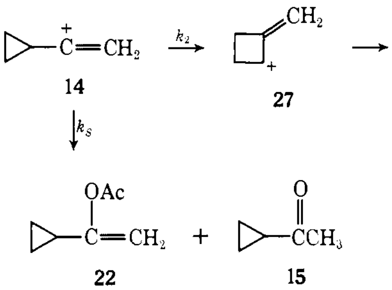
[34] S. Winstein, *J. Amer. Chem. Soc.*, **87**, 381 (1965).

[35] J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **89**, 2581 (1967).

[36] (a) C. C. Lee and L. K. Lam, *ibid.*, **88**, 2831 (1966); (b) *ibid.*, **88**, 5355 (1966).



to a difference in enthalpy, our chances of seeing a significant temperature dependence would be reasonably great.



A number of precautions had to be taken in order to obtain reliable data, however. The product percentages were determined by disk integration of vapor phase chromatograms. In order to determine $\Delta\Delta S^{\ddagger}$ one must determine molar ratios. Therefore the crude chromatographic integrals had to be corrected for extraction and response. The fact that the minor products were only a few per cent of the major products made desirable the use of different attenuations in the course of each analysis. Thus, the response factors had to account for the difference in attenuation and the errors associated with very dissimilar absolute sample sizes, such as result from column holdup. Particularly large and important was the extraction factor for **15**, which was relatively water soluble and only partially recovered in the work-up. This in turn demanded that the rather involved work-up be duplicated as accurately as possible from run to run. Since the rate of **22** to **15** conversion increased as the temperature was raised, progressively shorter reaction times were allowed at the higher temperatures in order to keep the relative amounts of **22** and **15** approximately constant. This avoided the need to calibrate the response factors for **22** and **15** over wide ranges of concentration. It was also necessary to correct the observed amount of **15** for that portion which did not come from **22**.

The corrected data were obtained from the reaction of **13** with silver acetate in acetic acid at five temperatures from 25.0 to 64.8°. The log of the product ratio was plotted *vs.* the reciprocal of temperature, and as is shown in Figure 5, is not only significantly temperature dependent, but the dependence is reasonably linear. It is possible to calculate from this line an approximate value of $\Delta\Delta H^{\ddagger}$ for k_2 and k_s of 2.2 kcal/mol. It therefore appears that rearrangement is an activated process, and must have an activation energy equal to or greater than this value.

The calculation of $\Delta\Delta S^{\ddagger}$ is complicated by the problem of standard states. The difficulty is avoided if the solvent-trapping step (k_s) is treated as a pseudounimolecular process; in that case the rate ratio is really $k_s'[\mathrm{HOAc}]/k_2$, which, since k_s is a second-order rate constant, makes the ratio a unitless quantity. With this treatment, $\Delta\Delta S^{\ddagger} = +0.5$ eu. If the concentration of HOAc is extracted from the rate ratio, however, it now has units of inverse molarity and requires specification of a standard state in order to calculate the difference in activation entropies. Specifying the usual standard state of 1 mol/cc,[37] $\Delta\Delta S^{\ddagger}$ now becomes $+8.55$ eu rather than $+0.5$ eu as calculated for the pseudounimolecular reaction. This number suggests that the rearrangement transition state has a somewhat lower $\Delta S^{\ddagger}$ than "normal," and/or the solvent capture transition state a somewhat larger $\Delta S^{\ddagger}$ than normal. Both of these inferences are consistent with considerations based on structural and electrostriction factors.

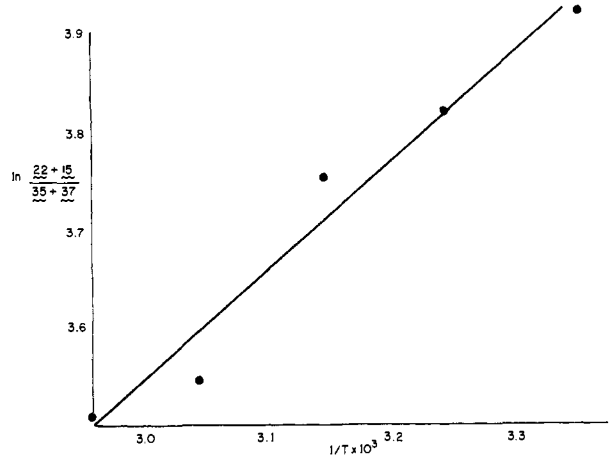


Figure 5. Logarithm of cyclopropyl to cyclobutyl product ratio *vs.* the reciprocal of temperature.

Conclusions

In summary, we feel that the evidence is very strong that cyclopropyl vinyl iodide undergoes both silver-catalyzed and uncatalyzed hydrolysis in protic solvents through the initial intermediacy of vinyl cation **14**. This ion appears to be somewhat more stable than one

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(37) K. J. Laidler, "Chemical Kinetics," 2nd ed, McGraw-Hill, New York, N. Y., 1965, p 90.

might intuitively expect; rearrangement and probably solvent trapping are most likely activated processes, and the propensity for rearrangement is low. Furthermore, the set of ions in Scheme I appears to be adequate to account for the processes which are observed to occur in the hydrolysis of **13**, and also make up essentially the same set of intermediates generated in the ionization of homoallenyl iodide **34**. A number of statements can now be made with regard to the rate constants which interconvert intermediates in Scheme I. We know from studies on the ionization of **36** that k_2 is probably much greater than k_{-2}. Since a small amount of primary acetate **31** is formed from **13**, k_1 is at least competitive with k_2. The rate constant k_{-1} appears to be large, but this is definitely an oversimplification—**34** may well be converted to **14** as the C–X bond is broken, and probably bypasses the free primary cation **28** completely. For simplicity, however, the fast conversion of **34** to **14** is represented by a large rate constant k_{-1}. Finally, since the amounts of cyclobutyl product arising from **13** and **34** appear to be the same, both k_3 and k_{-3} are small enough to be undetectable under solvolytic conditions.

A number of important questions still remain to be answered about this system and about the generation, structure, and fate of vinyl cations in general. One is the question of whether a memory effect can explain the cyclobutyl products formed from **13**. A second set of questions involves the true structure of **14**—is the cation linear or bent, by what mechanism does the cyclopropane ring stabilize the positive charge, and is there a favored conformation for the ion—and the detailed mechanism by which acetate replaces iodide at the vinyl carbon. A number of these questions are dealt with in the following paper.

Experimental Section

Materials. Acetic acid (du Pont reagent) was purified by refluxing 500 ml with 10 ml of acetic anhydride and 25 g of chromic oxide for 2 hr and then fractionally distilling under nitrogen. Silver acetate (J. T. Baker, purified) was purified by stirring 5 g in 75 ml of 20% acetic anhydride in acetic acid for 12 hr at 110°. The liquid was decanted and after drying for 4 hr at 85° and 0.05 mm the solid was transferred to an oven dried bottle in a nitrogen drybag. All boiling points are uncorrected. Infrared (ir) spectra were determined on a Perkin-Elmer IR 257 instrument, as an approximately 10% solution in carbon tetrachloride unless otherwise indicated. Proton nuclear magnetic resonance (nmr) spectra were obtained on a Varian A60-A spectrometer; carbon tetrachloride was the solvent and chemical shifts are reported in parts per million downfield from tetramethylsilane. Carbon-13 nmr spectra were recorded on a Varian DSF-60 spectrometer; dioxane was the solvent and chemical shifts are reported in parts per million upfield from carbon disulfide. Mass spectra were obtained on a CEC-21-103C instrument at 10 μA ionizing current and 70 V ionizing potential; the inlet temperature was 250°. Elemental analyses were performed by Spang Microanalytical Lab., Ann Arbor, Mich., unless otherwise noted. Qualitative and preparative vapor phase chromatography (vpc) was carried out on Varian Aerograph 90-P3 instruments. Quantitative analytical vpc was carried out on a Hewlett-Packard 5750 (flame ionization detector) equipped with a Disc integrator. The following columns were used: column A, 8 ft × $^3/_8$ in. 5% SE-30 on 60–80 Chromosorb P; column B, 21 ft × 0.25 in. 15% Carbowax 20M on 60–80 Chromosorb P; column C, 12 ft × 0.25 in. 20% Carbowax 20M on 60–80 Chromosorb P; column D, 12 ft × 0.25 in. 8% SE-30 on 60–80 Chromosorb P; column E, 5 ft × 0.25 in. 3% SE-30 on 100–120 Varaport 30; column F, 12 ft × $^1/_8$ in. 15% Carbowax 20M on 100–120 Chromosorb WAWDMCS; column G, 12 ft × $^1/_8$ in. 15% TCEP on 100–120 Chromosorb WAWDMCS; column H, 6 ft × $^1/_8$ in. 10% UCC-W98 on Chromosorb WAWDMCS; column I, 20 ft × $^3/_8$ in. 30% Carbowax 20M on 60–80 Chromosorb P; column J, 10 ft × 0.25 in. 20% SE-30 on 60–80 Chromosorb P.

1-Cyclopropyl-1-iodoethylene (13). Cyclopropyl methyl ketone (**15**) (Aldrich) was treated with hydrazine hydrate to obtain the hydrazone (**16**),[38] which was converted to the desired iodide by the general procedure of Barton, *et al.*,[21] as follows. In a 1-l. round-bottomed flask, 14 g of hydrazone (**16**) and 140 ml of triethylamine were dissolved in 350 ml of tetrahydrofuran (THF). While stirring this solution magnetically and cooling it in an ice bath, a solution of 70 g of iodine in 280 ml of THF was added dropwise from an unstoppered, pressure-equalizing addition funnel until a red color persisted. Sodium thiosulfate (0.5 g in 100 ml of water) was added and then the reaction mixture was poured into 2000 ml of ice water, followed by extraction with one 150-ml portion and two 75-ml portions of pentane. The combined pentane solution was washed with 1000 ml of ice water, two 175-ml portions of 1 N HCl, 500 ml of ice water, 250 ml of saturated aqueous sodium bicarbonate, and 500 ml of water. After drying over sodium sulfate, most of the pentane was removed by distillation through a Vigreux column under nitrogen at atmospheric pressure. The crude product was distilled under pump vacuum into a Dry Ice cooled receiver and was obtained in pure form by preparative vapor phase chromatography (vpc) on column A at 90° in a yield of 5.7 g (about 20% when roughly corrected for impurities in the hydrazone). The colorless iodide slowly became red even when stored at $-10°$ so samples were freshly purified by vpc on column C at 140° for critical applications such as kinetics and quantitative product determinations. *Anal.* Calcd for C_5H_7I: C, 30.95; H, 3.64; I, 65.41. Found: C, 30.96; H, 3.66; I, 65.28.

1-Isopropyl-1-iodoethylene (25). The conversion of isopropyl methyl ketone (**23**) (Matheson Coleman and Bell) to the hydrazone **24** has been reported.[39] A 250-ml round-bottomed flask was charged with 100 ml of triethylamine and 3.64 g of crude **24** (contaminated with 36% ethanol according to nmr). The solution was stirred magnetically and cooled in ice while 12.5 g of iodine in 50 ml of THF (distilled from LAH) was added over a period of about 5 min from an unstoppered, pressure-equalizing addition funnel. After stirring 1 hr at room temperature, the mixture was poured into 400 ml of ice and water and extracted with 100 ml of pentane. The pentane solution was washed with four 100-ml portions of cold 1 N HCl; during the fourth wash the color of the solution turned from yellow to orange. The pentane was then washed with 100 ml of saturated sodium bicarbonate, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator. The concentrate was distilled for 1 hr under pump vacuum at room temperature into a Dry Ice cooled receiver. The pot residue was a red viscous liquid the nmr of which indicated only a trace of olefin.

The distillate was analyzed on column I at 190°. Four major components were observed: first component, 4.5%; second component, 10.1% (retention time of **23**); third component, 62%; fourth component, 23.5%. The third and fourth components were isolated by preparative vpc on the same column. The third component was identified as **25**. Its infrared spectrum exhibited bands at 2965, 2930, 2880, 1615, and 898 cm^{-1}. The mass spectrum gave a parent peak at m/e 196. The nmr spectrum indicated a vinyl proton as an apparent triplet at δ 6.05 ppm, a vinyl proton doublet at 5.62 ppm ($J = 1.5$ Hz), a methine proton septet (1 H, $J = 6.5$ Hz) from 1.77 to 2.55 ppm, and a methyl doublet centered at about 1.04 ppm (6 H, $J = 6.5$ Hz). Also observed in the spectrum was a small singlet (0.34 H) at 3.58 ppm which could be attributed to column bleed (the nmr spectrum of Carbowax 20M is a singlet at δ 3.58 ppm). Analytical samples could be obtained by preparative vpc on column D at 140°. *Anal.* Calcd for C_5H_9I: C, 30.64; H, 4.63; I, 64.74. Found: C, 30.59; H, 4.63; I, 64.66. The fourth component was apparently 3-methyl-2-iodo-2-butene. Its infrared spectrum exhibited bands at 2190, 2850, 1645, 1440, 1375, 1210, 1057, and 880 cm^{-1}. The nmr spectrum displayed a very poorly resolved methyl quartet at 2.47 ppm (3 H) and a total of six protons as a multiplet at about 1.90 ppm partly overlapping a broad singlet at 1.80 ppm. The total yield of the vinyl iodides after vpc isolation was 15.3%.

2-Penten-4-yn-1-ol (41). The procedure of Hanack and Häffner was modified by the use of lithium acetylide–ethylenediamine in place of sodium acetylide. A 500-ml three-necked flask was equipped with a pressure-equalizing addition funnel, an adapter with a thermometer and gas inlet tube, a drying tube, and a mag-

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(38) N. A. Rosanow, *Chem. Zentrabl.*, 1490 (1923).

(39) G. J. Karabatsos and C. E. Osborne, *Tetrahedron*, 24, 3361 (1968).

netic spin bar. After purging the flask with nitrogen it was charged with 200 ml of dimethyl sulfoxide (distilled from calcium hydride) and 70.3 g (0.74 mol) of lithium acetylide–ethylenediamine (Foote Mineral Co.). While stirring and cooling externally as needed to keep the reaction temperature from 30 to 35°, 34.2 g (0.37 mol) of freshly distilled epichlorohydrin was added dropwise over a period of 2 hr. The reaction mixture was then heated for 0.5 hr at 40° and poured into 1 l. of ice and water. After extraction with three 400-ml portions of ether, the combined ether solution was washed with two 200-ml portions of saturated sodium chloride solution, dried over sodium sulfate, and concentrated on a rotary evaporator. Distillation through a short Vigreux column (58° (5 mm); lit.[7d] 65–66° (12 mm)) gave 14.8 g of a clear liquid the infrared and nmr spectra of which were appropriate for a mixture of the cis and trans isomers of **41**, but the presence of an impurity was suggested. Vpc analysis on column F showed that the desired cis and trans isomers comprised 89% of the sample and that there was an 11% impurity. The yield corrected for the impurity was 49%.

3,4-Pentadien-1-ol (42). A 500-ml three-necked flask equipped with a pressure-equalizing addition funnel, a cold water condenser with a drying tube, and a magnetic spin bar was charged with 5.8 g of lithium aluminum hydride (LAH) and 100 ml of dry ether (distilled from LAH). A solution of 12.6 g of **41** (89% pure, *vide supra*) in 125 ml of dry ether was added dropwise to the stirred reaction mixture over a period of 1 hr. The mixture was then heated under reflux for 18 hr. The excess LAH was decomposed by dropwise addition of saturated aqueous sodium sulfate and the ether layer was separated, dried over sodium sulfate, and concentrated on a rotary evaporator. Distillation of the concentrate through a short Vigreux column (57° (10 mm); lit.[26b] 52–53° (10.5 mm)) gave 10.9 g of a colorless liquid which was 90% pure by vpc analysis on column F. The infrared and nmr spectra of this sample agreed with those reported except for apparent impurity (a weak infrared band at 3310 cm^{-1} suggested some acetylene). Pure samples of **42** and of the major impurity were isolated by preparative vpc on column C. The impurity showed adsorption at 3640 and 3310 cm^{-1} in its infrared spectrum; it is probably 4-pentyl-1-ol. A second impurity of considerably longer retention time was not further examined. The yield corrected for impurities was about 85%.

3,4-Pentadien-1-yl Tosylate (32). The tosylate **32** was obtained by conventional means through the reaction of the alcohol **42** with tosyl chloride in pyridine (dried over molecular sieves) at −10°. When the tosylate was prepared from 90% pure **42** (*vide supra*) the infrared and nmr spectra were in general accord with those reported[26b] but impurity was apparent even after two recrystallizations from pentane. This impure tosylate was used only for preparative solvolyses. For quantitative product studies pure tosylate was prepared from vpc purified **42**.

3,4-Pentadien-1-yl Iodide (34). Triphenylphosphite (J. T. Baker) was purified by dissolving it in ether, washing with 2 *M* sodium hydroxide and saturated aqueous sodium chloride, and drying for 2 hr over magnesium sulfate with stirring. The ether was then removed on a rotary evaporator at about 50° for 2 hr. A 250-ml three-necked flask equipped with a magnetic stir bar, a gas inlet tube, a pressure-equalizing addition funnel, and a reflux condenser with a drying tube was charged with 16 g of purified triphenylphosphite and 16 g of methyl iodide and was heated with stirring under a nitrogen atmosphere in an oil bath. The bath temperature was kept at 70° for 10 hr, brought to 120° over a period of 5 hr, and kept at 120° for 3 hr. The mixture was cooled in ice, and 50 ml of dimethyl sulfoxide (DMSO), dried over molecular sieves and distilled from calcium oxide, was added; a bright red color resulted. A solution of 3 g of **42** (90% pure) in 20 ml of DMSO was added dropwise to the reaction mixture while stirring and cooling in ice. After stirring at room temperature for 12 hr, the reaction mixture was partitioned between 500 ml of water and 100 ml of pentane, and the separated pentane solution was washed with three 150-ml portions of 2 *M* sodium hydroxide, three 150-ml portions of water, and one 150-ml portion of saturated sodium chloride and was dried over magnesium sulfate. The pentane was removed at a rotary evaporator and the product was flash distilled at 0.1 mm with a heat gun into a Dry Ice-cooled receiver; 1.35 g of a colorless liquid was obtained which was 96% pure by vpc analysis on column H at 100°. Attempted analysis on column F at 160° resulted in almost total decomposition of the sample. The yield corrected for impurities was about 25%; a better yield might have been obtained if dimethylformamide had been used instead of DMSO.[20b] Pure samples of the iodide **34** were obtained as needed by preparative vpc on column E at 75°. The nmr spectrum of the pure iodide showed vinyl multiplets at δ 4.82–5.35 ppm (1 H) and 4.50–4.82 ppm (2 H), a perturbed triplet ($J = 7$ Hz) at about 3.15 ppm (2 H) due to the iodomethylene protons, and an allylic methylene multiplet at 2.15–2.92 ppm (2 H). The infrared spectrum showed absorptions at 3060, 3000–2800, 1954, 1425, 1245, 1235, 1170, and 850 cm^{-1}. The mass spectrum gave a parent peak at *m/e* 194. *Anal.* Calcd for C_5H_7I: C, 30.95; H, 3.64. Found: C, 30.79; H, 3.49.

2-Methylenecyclobutyl Bromide (36) and 1-Cyclobutenylcarbinyl Bromide (45). Following the method of Buchman and Howton,[29a] bromides **36** and **45** were prepared by the benzoyl peroxide catalyzed reaction of methylenecyclobutane with *N*-bromosuccinimide in benzene. Distillation of the product through a 12-cm vacuum-jacketed Vigreux column gave a colorless liquid which was 83% **36** by analysis on column H; the major impurity was benzene. The 60-MHz nmr spectrum of this sample showed a complex multiplet from 2.0 to 2.9 ppm (4 H), a multiplet from 4.6 to 5.1 ppm (3 H) roughly consisting of a two-proton multiplet centered at about 4.83 ppm and a one-proton multiplet centered at about 5.0 ppm, and a singlet at 7.18 ppm due to benzene. A pure sample of **36** was obtained by preparative vpc on column D; its 220-MHz nmr spectrum exhibited a multiplet (1 H) centered at about 2.31 ppm, a multiplet (3 H) from 2.5 to 2.84 ppm consisting of a perturbed doublet (about 2 H, $J = 2$ Hz) at 2.7 ppm overlapping a complex multiplet (about 1 H), and a doublet (1 H, $J = 2$ Hz) with further poorly resolved coupling at about 5.06 ppm. The infrared spectrum of pure **36** displayed bands at 3090, 1678, 1180, and 900 cm^{-1}, and its mass spectrum gave a parent peak at *m/e* 146 with the p + 2 peak at *m/e* 148 being 97.7% as large. The base peak was *m/e* 67. The above evidence is in accord with the structure **36** but does not definitively exclude the isomeric 3-methylenecyclobutyl bromide as a possibility. An argument based on chemical shifts could be invoked but more conclusive is the ^{13}C nmr spectrum (in dioxane, proton decoupled) which shows distinct chemical shifts for each of the five carbon atoms: 41.7, 83.7, 147.3, 162.2, and 163.9 ppm, eliminating the symmetrical structure from consideration. The assignments for this spectrum and its appropriate analogy to that of methylenecyclobutane are presented in Table IV of the text. For subsequent studies pure samples of **36** were obtained as needed by preparative vpc on column D.

Preparative vpc of the above-mentioned distillate on column J at 90° revealed two poorly resolved minor components with somewhat longer retention times than that of **36**. These were collected together and could be separated by rechromatography on column C at 90°. The component of longer retention time was found to be **45**. Its infrared spectrum displayed bands at 3050, 2960, 2930, 2840, 1430, 1260, 1198, 916, 862, and 676 cm^{-1}. Its nmr showed a vinyl proton triplet ($J = 1$ Hz, 1 H) at 5.95 ppm, a broad doublet ($J = 1$ Hz, 2 H) at 3.80 ppm due to the methylene protons α to bromine, and a multiplet from 2 to 2.95 ppm (4 H) due to the methylene protons on the ring. Vpc analysis of a neat sample of **45** after standing for 24 hr at room temperature revealed about 15% conversion to **36**.

Ethynylcyclopropane (38). A mixture of 149 mg of **13** and 94 mg of triethylamine in 2 ml of 2,2,2-trifluoroethanol was sealed in 0.25 in. heavy wall Pyrex tubing and heated at 150° for 21.5 hr. Analysis on column C revealed two volatile products (2.25 and 82.5%), one other major product (15.25%), and some minor products. This solution was partitioned between 8 ml of water and 0.75 ml of decane. After separation, the aqueous solution was extracted with 0.25 ml of decane and the combined decane solution washed with 2 ml of 10% aqueous sodium bisulfate, dried over magnesium sulfate, and subjected to preparative vpc on column E with temperature programming from 100 to 160°. The two volatile products were collected together. The infrared spectrum of this fraction displayed bands at 3320, 3100, 3025, 2140, 1430, 1355, 1195, 1060, 1040, and 945 cm^{-1}, in reasonable agreement with the Raman spectrum reported for ethynylcyclopropane.[40] The nmr spectrum showed the acetylenic proton as a doublet ($J = 2$ Hz) centered at 1.53 ppm, the cyclopropyl methine proton as a complex multiplet from 0.95 to 1.45 ppm, and the cyclopropyl methylene protons as two multiplets from 0.55 to 0.88 ppm (4 H).

Reaction of 1-Cyclopropyl-1-iodoethylene (13) with Aqueous Silver Nitrate. In a preliminary assessment of the reactivity of **13** toward silver catalysis, 0.1 g of **13** and 3 ml of 0.3 *M* aqueous

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(40) Y. M. Slobodin and I. N. Shokhor, *J. Gen. Chem. USSR*, 22, 243 (1952).

silver nitrate were stirred magnetically while heating in a stoppered flask at 55° for 2 hr. The yellow precipitate, which had begun to form immediately upon mixing of the reactants, was filtered off and the solution was extracted with ether. The ether solution was dried over sodium sulfate and concentrated. Analysis of the concentrate on column C showed that no starting material remained and that two products were evident. These were isolated by preparative vpc on the same column and the major product was identified as cyclopropyl methyl ketone (**15**) by means of its infrared spectrum. The infrared spectrum of the minor product indicated that it was an alcohol. No further work was done with this reaction.

Reaction of 1-Cyclopropyl-1-iodoethylene (13) with Silver Tosylate. A 100-ml three-necked flask, equipped with a gas inlet and a drying tube and charged with 0.725 g (2.6 mmol) of silver tosylate and 5 ml of acetonitrile, was purged with nitrogen and cooled in an ice bath. After adding 0.5 g (2.58 mmol) of **13**, the flask was swirled and allowed to stand in ice for 6 hr. While continuing to cool the flask in ice, the acetonitrile was distilled under pump vacuum into a Dry Ice cooled receiver. The solid residue was washed vigorously with two 75-ml portions of cold ligroin (30–60° fraction) which was then filtered into a flask blanketed with nitrogen. Upon cooling this solution slowly in Dry Ice–acetone with scratching, white crystals separated and the ligroin was decanted. Following a recrystallization from 40 ml of ligroin, the crystals were dried at 0° under pump vacuum. All evidence suggests that the 104 mg (17% yield) of nearly pure white solid was 1-cyclopropylvinyl tosylate (**21**). The compound could be stored for days at −78°, but a sample kept at room temperature was observed to become a black tar in a few hours. The nmr spectrum (in $CDCl_3$) exhibited an aromatic AA′BB′ pattern (4 H) from 7.28 to 8.0 ppm, vinyl protons (2 H) from 4.6 to 4.82 ppm as an approximate AB quartet (J = about 2.2 Hz) with finer unresolved coupling, a methyl singlet (3 H) at 2.49 ppm, a cyclopropyl methine multiplet (1 H) from 1.17 to 1.72 ppm, and a cyclopropyl methylene multiplet (4 H) from 0.50 to 0.63 ppm. The infrared spectrum had bands at 1700, 1600, 1370, 1190, and 1180 cm^{-1}. By delivering a freshly recrystallized sample stored in Dry Ice to the nearby Elek Microanalytical Lab., Torrance, Calif., it was possible to obtain reasonable analytical data. *Anal.* Calcd for $C_{12}H_{14}O_3S$: C, 60.50; H, 5.92. Found: C, 59.74; H, 5.95. Preparative vpc of the acetonitrile distillate on column B at 200° allowed the collection of a volatile component which was shown to be mainly ethynylcyclopropane by ir.

Reaction of 1-Cyclopropyl-1-iodoethylene (13) with Silver Acetate in Acetic Acid. I. Analytical Solvolyses and Temperature Dependence of Product Ratios. A 5-ml flask containing a magnetic spin bar, 0.75 ml of dry acetic acid, and about 45 mg of silver acetate was sealed with a rubber septum cap, placed in a constant-temperature bath (consisting of an insulated vessel through which water from a Lauda Ultrathermostat, type K-2, was circulated; temperature control was observed to be better than ±0.1°), and stirred magnetically. After 15 min, about 20 mg of **13** was introduced with a hypodermic syringe. After several half-lives, the flask was removed and 0.5 ml of the contents was squirted into a centrifuge tube containing 2 ml of water and 1 ml of ether (during this and the following extractions the tubes were kept in an ice bath at all times except when transferring or centrifuging). After vigorously agitating with a pipet, the tube was centrifuged and the ether layer transferred to a second tube. The aqueous solution was extracted with 0.5 ml of ether and the combined ether solution was washed with two 0.5-ml portions of saturated sodium bicarbonate solution and 1 ml of saturated sodium chloride solution and was dried over anhydrous potassium carbonate. Analysis on column E resolved all of the products except **22** and **37**, which exhibited identical retention times. These components could be separated on column G, however, so that through analysis of the samples on both columns the relative amounts of all components could be ascertained. The retention times in minutes of the products on column F at 120° and a flow rate of 12 ml/min were: **38**, 2.45; **15**, 6.2; **13**, 10.7; **35**, 12.2; **22**, 14.7; **37**, 14.7; **31**, 19.0. The retention times in minutes of the products on column G at 100° and a flow rate of 12 ml/min were: **38**, 2.2; **13**, 9.0; **15**, 9.8; **35**, 15.2; **37**, 18.0; **22**, 23.0; **31**, 24.6. Correction factors for relative extraction and response were determined for all components except **38**, and where necessary, on both analytical columns. Also, corrections factors for deviations from linearity of response *vs.* absolute sample size were determined where necessary. Owing to a secondary reaction of cyclopropyl acetylene (**38**) with silver acetate to form the silver salt (*vide infra*), the relative amount of **38** observed in the vpc analysis varied from run to run and it was not possible to determine precisely the mole percentage of this component. In one run at 25° which employed pentyl acetate as an internal standard, only 6.4% **38** was observed but the products other than **38** accounted for only 73% of the starting material; thus **38** is a maximum of 27 mol % of the total products (in one run at about 100° in which the reaction was worked up after only 2 min, 24.2% **38** was observed). The product distribution for 25° given in Table II of the text incorporates the estimate of 27% **38**.

The solvolysis, as described above, was carried out at five different temperatures from 25.0 ± 0.1 to 64.8 ± 0.1°. No effort to estimate the percentage of **38** formed at temperatures other than 25° was made. The molar ratios of **35**/**37** at 25 and 64.8° determined on column G were 9.97 and 8.58, respectively. Considering the difficulties involved in measuring the amount of **37**, which was less than 0.3% of the total products, it is felt that these values are within experimental error of one another. Therefore, for the product distributions at the intermediate temperatures the average value of 9.22 was used in calculating the amount of **37** (hidden under the **22** peak) from the amount of **35** observed on column H. The product mixture obtained at 64.8° was analyzed three times in order to obtain an estimate of the reproducibility in the determination of the minor components. The values and standard deviations were 28.1 ± 0.7% **15**, 2.34 ± 0.14% **35**, and 1.80 ± 0.06% **31**. The mole percentages of products other than **38** are summarized in Table I of the text.

It was found that about 8 mol % of the reaction products at completion was **15** from a source other than the decomposition of **22**, and that this percentage was rather independent of temperature (*vide infra*). Therefore the amount of **15** coming from **22** was estimated as the mole per cent of 15 produced minus 8 mol %.

II. Preparative Solvolysis. In a 5-ml flask containing a magnetic stir bar were placed 1.1 ml of dry acetic acid, 239 mg of **13**, and 206 mg of silver acetate (1 equiv); the flask was stoppered and stirred for 23 hr after which the contents were rinsed into a centrifuge tube with 1 ml of acetic acid. After centrifuging, the clear acetic acid solution was transferred to a clean tube and 5 ml of water was added. A rather copious white precipitate resulted. The solution was extracted with 2 ml and three 1-ml portions of ether and the combined ether solution was washed with four 1-ml portions of saturated sodium bicarbonate and 2 ml of saturated sodium chloride and was dried over sodium sulfate as sample A. To the aqueous solution containing the white precipitate were added 1 ml of 20% sodium iodide solution and 1 ml of ether. A dense yellow precipitate formed. After agitating for a few minutes the ether layer was removed and worked up as above to provide sample B. Analysis of sample A on column F revealed a product distribution analogous to that observed in the analytical run at 25° except for 26.5% of remaining starting material. Analysis of sample B on the same column revealed a considerable amount of a component with the same retention time as the volatile product in sample A and as **38** obtained from base-catalyzed dehydrohalogenation of **13** as described above. A sample of this product was isolated by preparative vpc on column B and its infrared spectrum was found to be identical with that of **38**.

No effort was made to collect the small amount of **38** in sample A. The other five products and the remaining starting material in sample A were collected in four fractions by preparative vpc on column C at 140°; they are discussed in order of increasing retention time. The first fraction was identified as cyclopropyl methyl ketone by comparison of its infrared spectrum and vpc retention time with those of an authentic sample (Aldrich). The second fraction consisted of a mixture of **13** and 2-methylenecyclobutyl acetate (**35**), which were not resolved on this column. The identity of the components in the mixture was established by comparing its infrared spectrum with that of pure **13** and that of **35** isolated and fully characterized from the acetolysis of **36**. On column F the components were resolved and the acetate product was observed to have the same retention time as known **35**.

The third fraction, which was the major product, was identified as 1-cyclopropylvinyl acetate (**22**). Its infrared spectrum exhibited bands at 3090, 3010, 1755, 1655, and 1200 cm^{-1} and was identical with that of a sample independently synthesized by treating the lithium enolate of cyclopropyl methyl ketone (prepared through the reaction of the ketone with triphenylmethyllithium in dimethoxyethane) with acetic anhydride. Its nmr spectrum consisted of a broad vinyl singlet (2 H) at 4.62 ppm, a methyl singlet (3 H) at 2.08 ppm, a cyclopropyl methine multiplet (1 H) from 1.2 to 1.7 ppm, and a cyclopropyl methylene multiplet (4 H) from 0.5 to 0.8 ppm. The mass spectrum gave a parent ion at m/e 126. Careful efforts to obtain good analytical data were frustrated. *Anal.* Calcd for

$C_7H_{10}O$: C, 66.65; H, 7.99. Found: C, 67.11; H, 8.29; C, 65.70; H, 7.89. The third fraction also presumably contains about 0.2% 1-cyclobutenylcarbinyl acetate (**37**), since **22** and **37** have identical retention times on column C. No attempt to isolate this minor component was made; its presence was concluded from the observation of a vpc peak on column G with a retention time identical with that of **37** which was isolated and fully characterized from the acetolysis of **36**.

The fourth fraction was identified as 3,4-pentadien-1-yl acetate by comparison of its infrared spectrum and retention time with those of an authentic sample prepared from the alcohol and acetic anhydride.

III. Solvolysis in *O*-Deuterioacetic Acid. To a 5-ml flask containing a magnetic stir bar were added 250.4 mg of **13**, 618 mg of silver acetate, and 2 ml of *O*-deuterioacetic acid (International Chemical and Nuclear). The stoppered flask was stirred for 2.5 hr at room temperature and then the contents were worked up in the same manner as was the preparative solvolysis. Preparative vpc on column C was used to isolate **22** from the product mixture. The infrared spectrum of a 20% solution of this sample in carbon tetrachloride showed negligible absorption in the region appropriate for a vinyl carbon–deuterium bond stretching mode. In the nmr spectrum the integral ratio of the acetate methyl protons to the vinyl protons was compared to that observed in **22** obtained from undeuterated medium and within the error limits of the nmr integration no incorporation was detected. Comparison of the corresponding mass spectra suggested -0.45% incorporation.

Silver Acetate Catalyzed Acetolysis of 2-Methylenecyclobutyl Bromide (36). Analytical solvolyses were carried out and analyzed in the same way as those with **22**, except **36** was notably less reactive and a reaction time of 72 hr at 25° was allowed in order to assure completion and because of silver bromide formation the reaction was protected from light. The product mixtures were analyzed on column F. The averages of two runs and the observed deviations were 71.9 ± 0.8 mol % of **35**, 27.5 ± 0.6 mol % of **37**, and about 0.4% of an unidentified product. Analysis of the mixture on column G revealed no other products and demonstrated that neither **15** nor **22** was present. Analysis of a solution of **35** and **15** in known concentrations indicated that 0.3 mol % of **15** (corrected for extraction and response) could have been detected. Studies of the stability of **22** under the reaction conditions (*vide infra*) showed that over half of any **22** formed in the above reaction would have been converted to **15**. The more favorable extraction factor of **22** would put the limit of its detectability at about 0.1 mol %. Thus less than 0.4 mol % of cyclopropyl products was formed in this reaction.

Preparative Solvolysis. A 50-ml flask equipped with a magnetic spin bar was charged with 0.485 g of **36**, 1.0 g of silver acetate, and 25 ml of dry acetic acid, and the mixture was stirred at room temperature with protection from light for 72 hr. The acetic acid solution was decanted, diluted with 100 ml of water, and extracted twice with ether. The combined ether solution was washed twice with saturated sodium bicarbonate, once with saturated sodium chloride, and dried over anhydrous potassium carbonate. Concentration on a rotary evaporator was followed by preparative vpc on column C at 145°. Impurities known to be in the **36** used were ignored, while the two major products observed in the analytical solvolysis were isolated in pure form. The first fraction was identified as 2-methylenecyclobutyl acetate (**35**). Its infrared spectrum exhibited bands at 3055, 1740, 1680, 1370, 1235, 1078, and 895 cm^{-1}. The nmr showed the cyclobutyl proton α to the acetate function as a multiplet (1 H) from 5.07 to 5.65 ppm, vinyl multiplets centered at about 4.92 ppm (1 H) and 4.76 ppm (1 H), and a complex pattern from 1.6 to 2.7 ppm (7 H) in which a singlet (about 3 H) at 1.94 ppm was evident. The mass spectrum gave a parent ion at *m/e* 126. *Anal.* Calcd for $C_7H_{10}O$: C, 66.65; H, 7.99. Found: C, 66.72; H, 8.16. A sample of this product was treated with excess lithium aluminum hydride (LAH) in dry ether for 1 hr. Following a typical aqueous work-up, the ether solution was subjected to preparative vpc on column C. The infrared spectrum of the isolated product was identical with that of 2-methylenecyclobutanol.[41]

The second fraction was identified as 1-cyclobutenylcarbinyl acetate (**37**). Its infrared spectrum exhibited bands at 3040, 1740, 1437, 1372, 1230, and 1030 cm^{-1}. The nmr spectrum showed a broad vinyl singlet (1 H) at 5.9 ppm, a broad singlet due to the methylene protons α to the acetate function (2 H) at 4.42 ppm, a broad cyclobutyl methylene singlet (4 H) at 2.46 ppm, and a sharp methyl singlet (3 H) at 2.02 ppm. The mass spectrum gave a parent ion at *m/e* 126. *Anal.* Calcd for $C_7H_{10}O$: C, 66.65; H, 7.99. Found: C, 66.44; H, 8.24. A sample of this product was reduced with LAH as above, and the isolated alcohol gave an infrared spectrum identical with the published spectrum of 1-cyclobutenylcarbinol.[42]

Silver Acetate Catalyzed Acetolysis of 3,4-Pentadien-1-yl Iodide (34). Analytical solvolyses were carried out as with **13**, and the same problems were encountered in efforts to quantitate **38**. Again, pentyl acetate was used in one run as an internal standard and the mass balance based on products other than **38** was determined to be 77%. Thus a maximum of 23% **38** was formed in the reaction. The product distribution given in Table II for this reaction at 25° is the result of an accurate determination of the relative molar amounts of all products other than **38** adjusted in accord with an estimated 23% yield of **38**.

Preparative Solvolysis. A 10-ml flask was charged with 250 mg of **34**, 430 mg of silver acetate, 3 ml of dry acetic acid, and a magnetic stir bar. After stirring the mixture for 12 hr at room temperature a work-up analogous to that used in the preparative solvolysis of **13** was employed. Again, a white precipitate was formed on addition of water to the decanted acetic acid solution. Treatment of this precipitate with sodium iodide solution liberated **38**, which was isolated as before and identified by means of its infrared spectrum. Preparative vpc of the main product mixture allowed the isolation of **15**, **35**, **22**, and **31**, which were identified by comparison of their infrared spectra and vpc retention times with those of known samples. Also isolated in about 2.3% yield was 4-pentyn-1-yl acetate, which presumably comes from a small amount of 4-pentyn-1-yl iodide present in the impure **34** used for the preparative solvolysis. This product was not found when pure **34** was solvolyzed as in the analytical runs. The minor product **37** was not isolated. Evidence for its presence in the product mixture consists of the observation of a peak with the correct retention time on column G.

Acetolysis of 3,4-Pentadien-1-yl Tosylate (32). Analytical Solvolysis. A mixture of 16.1 mg of 32 and 0.37 ml of 0.201 *M* sodium acetate in acetic acid (1.1 equiv of acetate) was sealed under aspirator pressure in 0.25-in., heavy-walled Pyrex tubing, and this sample was heated at 100° for 54.5 hr. Then the contents of the tube were diluted with 0.7 ml of water and extracted with a total of 0.7 ml of ether in three portions. The combined ether solution was washed with three 0.7-ml portions of saturated sodium bicarbonate and 0.7 ml of saturated sodium chloride and was dried over sodium sulfate. The sample was analyzed by vpc on column F. The extraction factor for **15** relative to pentyl acetate under the conditions of the above work-up was determined to be only 0.46. It was assumed that the extraction factors of the other products, being five-carbon acetates (except for **38**), were about equal to that of pentyl acetate. The product distribution corrected only for the extraction factor of **14** was: **38**, 0.92%; **15**, 55.9%; **35**, 4.67%; unidentified, 0.17%; **37**, 0.38%; **31**, 37.8%.

Preparative Solvolysis. In a 50-ml flask, 1.0 g of **32** and 1.1 equiv of sodium acetate were dissolved in 23 ml of dry acetic acid, and the solution was heated at $100 \pm 5°$ for 49 hr. After cooling in ice water, the contents were diluted with 50 ml of water and extracted with a total of 50 ml of ether in three portions. The combined ether solution was extracted with three 50-ml portions of saturated sodium bicarbonate and 50 ml of saturated sodium chloride and was dried over sodium sulfate. The presence of **38** and **15** in the product mixture was indicated by observation of the correct retention times (compared with known samples) on column F (**15** has been isolated from the acetolysis of **32** and well characterized[26]). Four other components of the reaction mixture were isolated by preparative vpc on column C. The first was identified as **35** by comparison of its retention time and its infrared and nmr spectra with those of a known sample. The second and third components were identified as **37** and **31**, respectively, by comparison of their infrared spectra and retention times with those of known samples. The infrared spectrum of the fourth component indicated that it was 4-pentyn-1-yl acetate, which presumably came from the corresponding tosylate as an impurity in **32**; this product was not observed in the analytical solvolyses which employed pure **32**.

Stability of Products under the Reaction Conditions. When the silver acetate catalyzed acetolysis of **13** at 25 or 45° was followed

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[41] We are grateful to Professor D. E. Applequist for supplying nmr and ir spectra of this compound.

[42] K. Heyn, K. Molge, and W. Walter, *Chem. Ber.*, **94**, 1015 (1961).

by taking aliquots at various intervals, it was obvious after long reaction times that **22** was being converted to **15**, and extrapolation showed that most but not all of the **15** observed had this origin. The observation that **15** as a percentage of the observed products exhibited a minimum at about 80% conversion of **13** (Figure 4) also requires another source for part of the observed **15**. In an effort to discover this source it was demonstrated that under the conditions of the work-up and analysis, **13** was stable while **22** gave less than 0.5% **15**. The amount of **15** apparently arising from the unknown source was about the same at the two temperatures, being an average of about 8 mol % of the products other than **38**. This amount persisted even when freshly dried silver acetate and acetic acid and freshly chromatographed **13** were used with all transfers being made under nitrogen. The rate of conversion of **22** to **15** at 45° was about five times as fast as that at 25°. When a sample of **22** with pentyl acetate as an internal standard was heated in acetic acid 0.201 *M* in sodium acetate at 100° for 17 hr, quantitative conversion to **15** was observed. Therefore, **15** is stable to the reaction conditions.

Evidence for the stability of **31**, **35**, and **37** under the silver-catalyzed acetolysis conditions may be seen in Table I, where the product distributions from the solvolysis of **13** for 250 and 1320 min at 25.0° show almost identical amounts of these components. The similar percentages obtained in the acetolysis of **32** at 100° suggest that these components are at least reasonably stable even under those more stringent conditions.

A sample of **38** with pentyl acetate as an internal standard was stirred with silver acetate and silver iodide in acetic acid at 25° for 280 min. In the course of the work-up, a copious white precipitate (apparently the silver salt of ethynylcyclopropane) was observed; vpc analysis of the ether solution obtained in the work-up showed negligible conversion of **38** to any of the other products. However, when **38** and pentyl acetate were heated in acetic acid 0.201 *M* in sodium acetate at 100° for 49 hr (the solvolysis conditions for **32**), analysis revealed conversion to a mixture of the other products in the following yields: **15**, 57.8%; **31**, 1.1%; **35**, 1.1%; **37**, 0.07%.

Reaction of 1-Cyclobutenylcarbinyl Bromide (45) with Silver Acetate in Acetic Acid. A freshly chromatographed sample (about 0.5 mg) of **45**, 8.2 mg of silver acetate, and 150 μl of acetic acid were sealed in a 2-in. length of 0.25-in. Pyrex tubing. The sealed tube was placed in a magnetically stirred 100-ml round-bottomed flask full of water in a constant-temperature bath at 25° with protection from light. After 72 hr, 100 μl of the solution was subjected to the usual work-up (appropriately scaled down). Analysis of the resulting sample on column F revealed four components: 46.3 mol % of **35**, 4.13% of an unknown (this component has a retention time which is different from those of all the products studied in this work; it is probably the result of a minor contaminant), 48.2 mol % of **37**, and 1.4% of the unknown observed in the solvolysis of **36**.

Preparation of a Mixture of 2-Methylenecyclobutyl Iodide (55) and 1-Cyclobutenylcarbinyl Iodide (56). Reaction with Silver Acetate in Acetic Acid. An impure sample of **36** (containing about 70 mg of **36**) and about 3 ml of a 25% solution of lithium iodide in dry acetone were sealed in stainless steel tubes and heated at 70° for 15 hr. The combined solution was diluted with 10 ml of water and extracted with six 1-ml portions of pentane. The combined pentane solution was dried over magnesium sulfate and concentrated to a volume of about 1 ml on a rotary evaporator. Analysis on column J at 120° revealed a small amount of remaining **36** followed by a major and a minor component which could almost be resolved. However, after collection of each new product, reinjection showed that each of the two fractions had the same composition as the starting mixture. The nmr spectrum of the "isolated" major component showed that it was a mixture of 83% **55** and 17% **56**. The following assignments could be readily made by comparison with the spectra of **36** and **45**: a broad singlet at 6.0 ppm (0.176 H) due to the olefinic proton in **56**, a multiplet from 4.7 to 5.4 ppm (2.54 H) due to the terminal methylene protons and the proton α to iodine in **55**, a broad singlet at 3.75 ppm (0.353 H) due to the protons α to iodine in **56**, and a multiplet from 2.0 to 3.04 ppm (4.33 H) due to the ring-methylene protons in **56** and **55**. The infrared spectrum of this sample displayed bands at 3080, 2985, 2950, 2925, 2830, 1672, 1425, 1140, 890, and 650 cm^{-1}. The infrared spectrum of the "isolated" minor component was essentially identical.

The silver-catalyzed reaction of the 83:17 mixture of **55** and **56** with acetic acid was carried out as with the other substrates. The usual light-stable yellow precipitate of silver iodide was noted. Reaction times of 5.5 and 72 hr were allowed at 25°. The following product percentages are the averages of the two runs given with the observed deviation: 67.8 ± 0.6 mol % **35**, 31.9 ± 0.8 mol % **37**, and 0.4 ± 0.1% of an unknown.

The reaction of **55** and **56** with acetic acid in the absence of silver acetate was found to be very slow. When 5 mg of the mixture of 55 and 56 was stirred in 0.8 ml of acetic acid 0.4 *M* in sodium acetate for 2.2 hr at 25°, vpc analysis showed only a very small conversion to **35** and **37**. Silver iodide (12 mg) was added and, after stirring an additional 2.7 hr, analysis showed little or no increase in conversion.

Kinetics of the Solvolysis of 1-Cyclopropyl-1-iodoethylene (13). For each kinetic run about 0.05 ml of a 0.2 *M* solution of **13** in 77.5 aqueous methanol was prepared, and the appropriate amounts of triethylamine as a buffer and *o*-dichlorobenzene as an internal standard were added. The solution was divided into six equal portions, which were then sealed in sections of 0.25-in., heavy-walled Pyrex tubing under aspirator pressure while frozen in liquid nitrogen. The tubes were placed simultaneously in a kinetic bath (Gebrüder Haake Ultra-Thermostat, Model NBB) equilibrated to ±0.1°. Beginning after about 10 min, tubes were pulled at appropriate intervals and quenched in ice water. Each tube was opened, 60 μl of pentane was introduced and agitated, and the pentane layer was analyzed on column H at 100°. The concentration of **13** found in the first tube was taken as the initial value. One run was conducted with 1.1 equiv of triethylamine at 150.0°, and three runs were conducted with 3.0–3.2 equiv of triethylamine at 140.9, 150.0, and 161.1°. The thermal stability of **13** in the absence of an ionizing solvent was demonstrated by heating a mixture of **13** and *o*-dichlorobenzene in a tube sealed at aspirator pressure for 12 hr at 150°. Vpc analysis before and after heating revealed no change in composition.

Kinetics of the Solvolysis of 1-Isopropyl-1-iodoethylene (25). For each kinetic run, about 18.5 mg of **25**, the appropriate amount of triethylamine, and 4 mg of *n*-nonane as an internal standard were dissolved in 77.5% (by weight) aqueous methanol to make 3 ml. The amounts of triethylamine used were 28.4 mg (3.0 equiv) and 11.0 mg (1.13 equiv), giving initial concentrations of 0.0937 and 0.0363 *M*, respectively. Having sealed 0.5-ml portions of this solution in stainless steel tubes (these tubes have a volume of 1.5 ml, a wall thickness of 4 mm, and are sealed by threaded caps which employ Teflon gaskets), the samples were heated at 233.5 ± 0.1° in the kinetic bath described above. Beginning after 15 min, tubes were removed at intervals and quenched in ice water. The contents of each tube were agitated with 2 ml of 10% sodium bisulfate and 0.1 ml of pentane, and the pentane layer was analyzed on column H at 90°.

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