Stereochemistry of Solvolytic Displacement at Vinyl Carbon. Reactions of 1-Cyclopropyl-2-methylvinyl Cations Formed on Silver-Catalyzed Ionization of *cis*- and *trans*-1-Cyclopropyl-1-iodopropenes and 3,4-Hexadien-1-yl Iodide

Donald R. Kelsey[1b] and Robert G. Bergman*[1c]

Contribution No. 4111 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

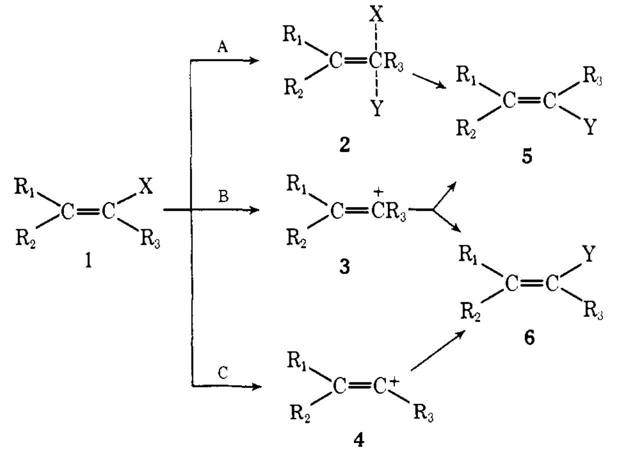
Received July 28, 1970

Abstract: On treatment with silver acetate in acetic acid, *cis*- and *trans*-1-cyclopropyl-1-iodopropene (**7C** and **7T**) give rise to product distributions which are identical within experimental error. The major products in this mixture are the *cis*- and *trans*-1-cyclopropyl-1-acetoxypropenes (**15C** and **15T**). However, acetates resulting from rearrangement and ring opening of the linear 1-cyclopropyl-2-methylvinyl cation (**25**), which is most likely the first-formed intermediate in both ionizations, have also been isolated. In addition, **7C** and **7T** interconvert to a small extent during the reaction. Subjection of 3,4-hexadien-1-yl iodide (**21**) to the same reaction conditions produces a product mixture which is almost identical with that formed from **7C** and **7T**, except for a small excess of direct displacement product. Iodide **21** also produces small amounts of vinyl iodides **7C** and **7T** during the reaction, which indicates that internal return can occur in silver-catalyzed ionizations. Such internal return probably also accounts for the observed interconversion of **7C** and **7T**. The nature of the carbonium ions formed in these reactions is discussed.

The observation of first-order kinetics in certain solvolysis reactions has given rise to a simple picture of the mechanisms of these reactions, involving rate-determining heterolysis of a C–X bond followed by rapid reaction of the generated carbonium ion with solvent.[2a] Later stereochemical investigations (as well as some more recent kinetic studies) have shown that in a great number of cases this picture is oversimplified—there now exists a large number of examples of strictly first-order reactions which proceed with varying degrees of inversion of configuration at carbon.[2b] Such investigations have led to an increased awareness of the role of solvent and ion pairing in solvolysis reactions.

Stereochemical studies parallel the use of other techniques which have been applied to the investigation of solvolytic displacement reactions in that they have almost always been conducted on aliphatic or tricoordinated carbonium ions. The increasing amount of evidence that dicoordinated carbonium ions (vinyl cations) can be generated with relative ease in many systems[3,4] makes a stereochemical investigation of S_N1 substitution at vinyl carbon an interesting and practicable possibility. As indicated in the preceding paper,[4] we feel that the perturbation of carbonium ion structure from aliphatic to vinyl can provide important information about the general displacement reaction, as well as about vinyl cations themselves.

Scheme I



The structure of a tetrahedral carbon compound requires that its absolute configuration be described in terms of its "left-handedness" or "right-handedness" (dissymmetry).[5] Because of this, one way to investigate the stereochemistry of an aliphatic displacement at tetrahedral carbon is to employ an optically active substrate, examine the optical activity of the products, and relate their absolute configurations in some way to that of the substrate.[2b] Because the ethylenic system in a vinyl halide is planar, however, the stereochemistry of displacement is no longer associated with a change in optical configuration, but with the stereochemical relationship between the leaving group and the remote substituents on the double bond. The situation is illustrated in Scheme I, which illustrates three extreme mechanisms for solvolytic displacement at a vinyl center. In path A, the nucleophile Y (which could either be solvent or some kinetically detectable species)

---

[1] (a) A preliminary account of this work has appeared: D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, 92, 228 (1970); (b) National Science Foundation Predoctoral Fellow, 1968–present; (c) Alfred P. Sloan Foundation Fellow, 1970–1972; Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1970–1975.

[2] (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 381; (b) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, pp 174–179.

[3] M. Hanack, *Accounts Chem. Res.*, 3, 209 (1970).

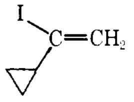
[4] S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, 93, 1925 (1971).

[5] K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, p 25.

interacts with the "backside" of the C–X bond in **1** and leads, *via* the "S$_N$2-like" transition state **2**, to the product of "inverted" configuration, **5**. A second possibility is illustrated in path B, where initial C–X ionization produces the linear vinyl cation **3**. This ion will show some "natural" ratio for solvent trapping to give both **5** and **6**, and a major feature of this mechanism is that both **1** and its stereoisomer (having R_2 and X in a cis rather than trans relationship) should give the same mixture of products. The final mechanism (path C) illustrates the generation of a configurationally "bent" vinyl cation **4** which should react with solvent giving the product of overall "retention" of configuration (**6**). It is of course true that the linear ion **3** cannot be distinguished by this experiment from a mixture of **4** and its stereoisomer which are interconverting at a rate much more rapid than that of reaction with solvent. However, if **4** loses its configuration at a rate *competitive* with that of solvent trapping, **1** and its stereoisomer should each give rise to both **5** and **6**, but in different ratios.

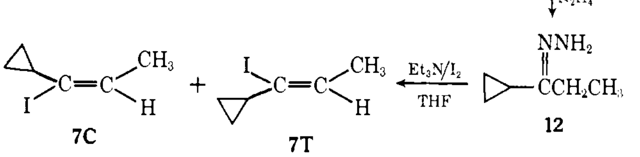
This is of course a rather skeletal analysis of the mechanistic possibilities. Other phenomena which have an effect on the stereochemistry of such reactions will have to be considered. Ion pair formation, for example, might tend to produce some inversion (excess **5** in path B of Scheme I) from the structurally linear cation **3**, and nonclassical ion formation might produce excess retention of configuration. Hopefully, however, these effects can be sought using other techniques, such as relative rate studies and salt and solvent effects, and the combination of information obtained used to develop a reasonably accurate picture of the reaction mechanism.

This paper, therefore, describes a study of the stereochemistry of solvolytic displacement at vinyl carbon. The compounds chosen for investigation are the *cis*- and *trans*-1-iodo-1-cyclopropylpropenes (**7C** and **7T**), since the structures of these compounds represent only a small perturbation (methyl substitution) on that of the parent 1-iodo-1-cyclopropylethylene (**8**), which we have shown undergoes solvolytic substitution under relatively mild conditions.[4]



8

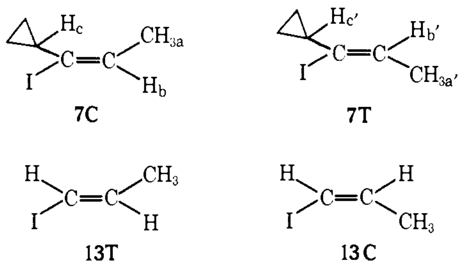
Synthesis. Preparation of the compounds selected for study, *cis*- and *trans*-1-cyclopropyl-1-iodopropenes (**7C** and **7T**), was effected by a method modeled on the synthesis of the parent compound **8**. Treatment of cyclopropanecarboxylic acid (**9**) with thionyl chloride gave the acid chloride **10** (80% yield),[6] which could be converted to cyclopropyl ethyl ketone[7] (**11**) in 74–78% yield by reaction with diethylcadmium. The hydrazone **12** was prepared in 72% yield by treatment of the ketone with an excess of hydrazine hydrate.



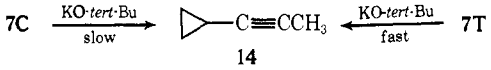
The yield of vinyl iodides produced in the reaction of **12** with triethylamine and iodine in THF[8] was at first erratic, but could be raised to 40–47% (after purification by preparative vapor chromatography (vpc)) by using an excess of iodine and carefully purified reagents (see Experimental Section).

That two vinyl iodides were formed in the I_2–Et_3N reaction was established by vpc; the cis–trans isomers were separated cleanly on a diethyleneglycolsuccinate (DEGS) column. Each isomer was obtained >99.4% pure by preparative vpc, and its gross structure was established by elemental analysis and infrared spectrum. The stereochemistry of the vinyl iodides was assigned on the basis of the following nmr and chemical observations. The chemical shift of H_b (Scheme II) is at δ 6.25 ppm, whereas $H_b{}'$ appears at 5.62 ppm. This strong deshielding by the *cis*-iodine atom in **7C** has been observed in similar compounds (**13C** and **13T**),[9] where the structures are firmly established[9] on the basis of the vinyl hydrogen coupling constants (J_{cis} for **13C** is 7.3 Hz and J_{trans} for **13T** is 14.3 Hz). Other data indicate that the effect of a cyclopropyl ring on the chemical shift of a cis- or trans-oriented hydrogen is small (*ca.* 0.03 ppm).[10] The chemical shifts of the methyl groups, though differing by a smaller amount than those of the vinyl hydrogens, are in accord with expectations based on model compounds,[9a,b,10] as are the long-range "homoallylic" coupling constants (J_{ac} = 0.7 Hz and $J_{a'c'}$ = 1.1 Hz).[11]

Scheme II



The assignments are confirmed by the relative rates of E2 elimination from **7C** and **7T**. Treatment of either isomer with potassium *tert*-butoxide in dimethyl sulfoxide at room temperature results in the formation of cyclopropylmethylacetylene (**14**), but **7T**, which can undergo trans elimination of HI, reacts seven to ten times faster than does **7C**. There is much precedent for this behavior.[12]



---

[6] L. I. Smith and E. R. Rogier, *J. Amer. Chem. Soc.*, 73, 4047 (1951).

[7] (a) M. Julia, S. Julia, and S.-Y. Tchen, *Bull. Soc. Chim. Fr.*, 1849 (1961); (b) V. A. Slabey and P. H. Wise, *J. Amer. Chem. Soc.*, **74**, 1473 (1952).

[8] D. H. R. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 470 (1962).

[9] (a) R. C. Neuman, Jr., and D. N. Roark, *J. Mol. Spectrosc.*, **19**, 421 (1966); (b) F. Hruska, D. W. McBride, and T. Schaefer, *Can. J. Chem.*, **45**, 1081 (1967); (c) see also R. C. Neuman, Jr., and G. D. Holmes, *J. Org. Chem.*, **33**, 4317 (1968).

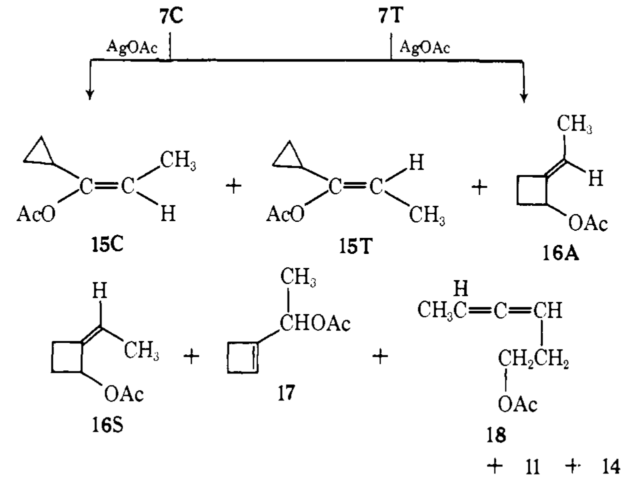
[10] M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, **90**, 3769 (1968).

[11] S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[12] (a) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **4**, 49 (1965); (b) S. J. Cristol and C. A. Whittemore, *J. Org. Chem.*, **34**, 705 (1969).

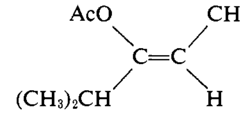
Preparative Ionization of the Vinyl Iodides 7C and 7T. Treatment of either 7C or 7T with excess silver acetate in acetic acid at room temperature gives rise to eight products in greater than 95% overall yield (Scheme III). In addition, 7C gives rise to a small amount of 7T (5.6%) and 7T to a small amount of 7C (5.9%) (*vide infra*). The products were separated and each compound obtained in pure form by preparative vpc on DEGS followed in some cases by chromatography on triscyanoethoxypropane (TCEP).

Scheme III

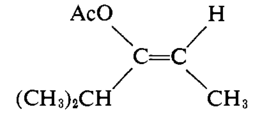


Homoallenyl acetate **18**, ketone **11**, and acetylene **14** were identified by comparison of their spectra with those of authentic samples, synthesized independently (see Experimental Section). The ir and nmr spectra of **15C** and **15T** indicate clearly that these materials are unsaturated acetates containing cyclopropane rings, and therefore are most reasonably assigned the gross structures indicated in Scheme III. The vinyl proton in **15T** appears at δ 5.02 and that in **15C** at 5.05 ppm. Although the shift is small, it is consistent with downfield shifts observed for vinyl hydrogens cis to acetoxy groups, *e.g.*, in **19T** (δ 4.97 ppm) and **19C** (δ 5.08 ppm).[13] The trend in vinyl methyl absorptions is reversed (1.42 for **15C** and 1.51 for **15T**),[13a] again in accord with previous observations on similar compounds.[14] The homoallylic coupling constants also agree with the structural assignments,[11] as do the carbon–carbon double bond absorptions in the ir (**15T**: 1693 cm^{-1}, **15C**: 1682 cm^{-1}; compare **19T**: 1692 cm^{-1}, **19C**: 1683 cm^{-1}). A number of other isomeric pairs of vinyl acetates also show differences of about 10 cm^{-1} in their ir double bond absorptions.[13a]

The gross structures of **16A**, **16S**, and **17** are consistent with the spectral evidence and expected solvolysis products. Compound **17** is differentiated from the other two by the chemical shift of its vinyl hydrogen, which is considerably further downfield than those of the **16** isomers. Its mass spectral fragmentation pattern is also much different from the rather similar spectra of **16A** and **16S**. Differentiation between the **16** isomers is less certain, and therefore must be considered tentative. The vinyl hydrogen as assigned shows a downfield shift of about 0.2 ppm when syn to the acetoxy group, and the vinyl methyl protons show an upfield shift of 0.04 ppm. These trends are similar to those discussed above for the cis–trans relationships.[13a,15]



19T



19C

Solvolysis of the Pure Vinyl Iodides. Each of the purified vinyl iodides 7C and 7T (>99% pure by analytical vpc) was treated with an excess of silver acetate in acetic acid at room temperature. It was immediately clear from inspection of the analytical vpc traces of each solvolysis mixture that the product distributions from both iodides were essentially identical. This impression was confirmed by careful integration of repeated solvolysis runs, and correction of the major product percentages for differing vpc detector response. The results are collected in Table I.

Control experiments showed that **14**, **11**, **15C**, **15T**, and **18** were stable to the reaction and work-up conditions. The starting vinyl iodides **7C** and **7T** show no detectable (<0.2%) reaction when stirred with silver iodide in acetic acid at room temperature and do not isomerize under the work-up conditions. In fact these compounds are remarkably stable to cis–trans interconversion, considering that they are vinyl halides—they undergo slow isomerization in the presence of silver iodide and acetic acid only at temperatures of 70° or higher.

The product distribution does not change within experimental error when the ionization is carried out under homogeneous conditions (Table I) in carefully cleaned reaction vials, indicating that deviations due to surface effects are negligible. Further evidence is the fact that the disappearance of iodide is a pseudo-first-order process, indicating that the concentration of reactive silver is constant, which it would be if "reactive" is synonomous with "dissolved." A rough kinetic plot of the disappearance of 7C gives $k_c = 2.0 \times 10^{-3}$ sec^{-1}; 7T gives $k_t = 2.2 \times 10^{-4}$ sec^{-1}. Aliquots taken during the reaction also show that with one exception, the ratio of products formed does not change with time. The exception is ketone **11** which, as with the parent compound,[4] forms quickly near the beginning of the reaction. Its formation is not affected by the presence of added water; this suggests that it is formed in an independent pathway involving catalysis by silver oxide or some other trace impurity.

The ionizations of 7C and 7T were also carried out in the presence of four molar equiv of sodium acetate. Essentially no change was observed in the product distribution (Table I).

The Possibility of Cis–Trans Iodide Isomerization. Because small amounts of iodide 7T are observed during the solvolysis of the cis isomer 7C (and *vice versa*), it is necessary to consider the possibility that a rapid preequilibrium between 7C and 7T precedes ionization,

---

(13) (a) H. O. House and V. Kramar, *J. Org. Chem.*, 28, 3362 (1963); (b) J.-J. Riehl, J.-M. Lehn, and F. Hemmert, *Bull. Soc. Chim. Fr.*, 224 (1963).

(14) (a) W. E. Parham and J. F. Dooley, *J. Org. Chem.*, 33, 1476 (1968); (b) A. P. Belov and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1, 139 (1966).

(15) (a) It should be pointed out that Jacobs and Macomber[15b,c] have assigned the reversed stereochemistry to **16A** and **16S**. However, due to contamination in their isolated samples of these materials, they were able to observe only the methyl resonances, and not the vinyl hydrogen chemical shifts, in the nmr. (b) T. L. Jacobs and R. S. Macomber, *J. Amer. Chem. Soc.*, 91, 4824 (1969); (c) R. S. Macomber, Ph.D. Thesis, University of California, Los Angeles, 1968.

Table I. Products Formed upon Ionization of *cis*- and *trans*-1-Cyclopropyl-1-iodopropenes (**7C** and **7T**) under Varying Reaction Conditions at 25°

Substrate	Conditions	Products, %[a–c]								
		7[g]	**11**	**14**	**15C**	**15T**[d]	**16A**	**16S**	**17**	**18**[e]
7T	Excess AgOAc–HOAc	(0.5)[h]	2.6 ± 1.5	16.2 ± 0.7	35.9 ± 0.3	30.3 ± 1.1	3.1 ± 0.1	8.0 ± 0.1	3.6 ± 0.2	(0.4)
7C	Excess AgOAc–HOAc	(2.0)[i]	0.9 ± 0.2	17.3 ± 1.0	33.5 ± 0.8	32.3 ± 0.5	2.8 ± 0.1	8.9 ± 0.2	3.8 ± 0.2	(0.7)[f]
7T	AgOAc–HOAc, homogeneous	(0.8)[j]	1.6 ± 1.0	19.8 ± 0.6	34.3 ± 0.5	30.2 ± 0.5	2.9 ± 0.1	7.4 ± 0.1	3.3 ± 0.2	(0.5)
7C	AgOAc–HOAc, homogeneous	(4.5)[k]	0.8 ± 0.4	17.6 ± 1.2	32.0 ± 0.7	33.8 ± 0.5	2.8 ± 0.2	8.6 ± 0.3	3.8 ± 0.1	(0.9)[f]
7T	Excess AgOAc–NaOAc–HOAc		1.2 ± 0.5	21.1 ± 2.3	32.2 ± 3.1	30.0 ± 0.3	3.4 ± 0.4	8.9 ± 0.4	2.7 ± 0.8	(0.5)
7C	Excess AgOAc-NaOAc–HOAc	(0.1)[l]	0.4	16.6	31.2	33.5	3.2	10.3	4.3	(0.4)

[a] Values shown are relative percentages from disk integration of vpc peaks on TCEP column T-1 (see Experimental Section), although experiments indicate >95% yield. [b] Percentages for **11, 14, 15T,** and **15C** are corrected for vpc flame detector response. The isomers **17, 16A, 16S,** and **18** were assumed to be close in response to **15T** and **15C**. [c] Errors shown are maximum deviations based on repetitive runs and repetitive vpc injections. Estimated accuracy that can be expected is about ±2% for **14**, **15T**, and **15C**, ±1% for **16S**, and ± 0.5% for the remaining products. [d] Percentage corrected for amount of **18** shown. [e] Percentages assumed on the basis of preliminary runs using Carbowax column C-2 (see Experimental Section), except as noted. [f] Percentages determined by reanalysis on Carbowax column C-3 (see Experimental Section). [g] Per cent (of total mixture) of isomeric vinyl iodide. [h] 20 min, 78.5% unreacted **7T**. [i] 4 min, 63.7% unreacted 7C. [j] 2 hr, 77.3% unreacted **7T**. [k] 2 hr, 56.7% unreacted 7C. [l] 2.5 hr.

and that this is responsible for the identical product distributions observed in the ionization reaction. This mechanistic possibility is diagrammed in Scheme IV.

Scheme IV

$$P_t \xleftarrow{k_3} 7T \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 7C \xrightarrow{k_2} P_c$$

We have already indicated that when exposed to silver iodide in acetic acid at room temperature, no interconversion of 7C and 7T is observed. However, this is necessarily only an approximation to the actual reaction situation, and so it is preferable to rule out the preequilibrium mechanism on a more rigorous kinetic basis.

This is easy to do starting from 7C. Since 7C reacts nearly ten times as fast as 7T, any isomerization would cause 7T to build up to a much greater extent than it is observed to do, and nearly all the acetate product would in any case arise from the more reactive 7C. A more difficult problem is the 7T reaction; any 7C formed in this process would react quickly, thus preventing buildup of its concentration. Knowledge of the 7C $\rightleftharpoons$ 7T equilibrium constant, however, would allow us to place a maximum limit on the amount of product which could have been formed from 7C when 7T was the starting substrate. This can be demonstrated in the following way. If the mechanism is that outlined in Scheme IV, the rate constant for the total disappearance of 7C is[16a] $k_c \cong k_2 + k_{-1}$, and that for 7T is[16b] $k_t \cong k_3 + k_1$. Since 7T reacts so much more slowly than 7C, from the percentage of 7T formed in the 7C ionization we know that $k_2/k_{-1} \cong 17$. The equilibrium constant for the 7C $\rightleftharpoons$ 7T isomerization can be determined at 80°; the experiment gives $K_{eq} \cong 9$. The energy difference for this equilibrium is small enough so that K_{eq} at room temperature will probably not be much different from this value. Defining $K_{eq} = k_{-1}/k_1$

$$\frac{k_c}{k_t} = \frac{k_2 + k_{-1}}{k_3 + k_1} \tag{1}$$

$$\frac{k_c}{k_t}(k_3 + k_1) = k_2 + k_{-1} \tag{2}$$

$$\frac{k_3}{k_1} = \frac{k_t}{k_c}\left(\frac{k_2}{k_1} + K_{eq}\right) - 1 \tag{3}$$

$$= \frac{K_{eq}(k_2/k_{-1})}{k_c/k_t} + \frac{K_{eq}}{k_c/k_t} - 1 \tag{4}$$

The value of k_3/k_1 calculated from eq 4 is the rate ratio needed to estimate the maximum amount of product which could have been formed from 7C when 7T is the starting substrate. Using the measured value of $K_{eq} \cong 9$, one finds that a maximum of 5.9% of total product could have come from the isomerization route. The percentages in Table I therefore represent, within experimental error, the product of kinetic control from iodides 7C and 7T.

Synthesis and Ionization of 3,4-Hexadien-1-yl Iodide. Because both the vinyl and cyclobutyl products from the ionization of 7T and 7C can exist in stereoisomeric forms, the product distribution of Scheme III can serve as a particularly sensitive probe for the identity of intermediates arising in cyclopropylvinyl and homoallenyl ionizations. Jacobs and Macomber[15b] have examined the products of solvolysis of 3,4-hexadien-1-yl tosylate (Table II), but as in the case of the parent compound,[4] the difference in reaction conditions between the tosylate solvolysis and the vinyl iodide reaction was large enough to make comparison difficult. The high percentage of direct displacement product (**18**) is also an annoyance in obtaining reliable percentages of cyclized material. For these reasons we decided to synthesize 3,4-hexadien-1-yl iodide (**21**) and examine the products of its ionization. In the parent 3,4-pentadien-1-yl system the use of silver-catalyzed ionization of a homoallenyl iodide enabled us to use reaction conditions comparable to those of the appropriate vinyl iodide reaction.[4] In addition, the silver-catalyzed reaction greatly reduced the percentage of direct displacement product arising from the homoallenyl substrate.[4]

---

(16) (a) This is a good approximation because $k_{-1} > k_1$. (b) This is a good approximation because $k_2 > k_{-1}$, preventing a significant amount of return from 7C to 7T.

Table II. Products Formed upon Ionization of 3,4-Hexadien-1-yl Iodide (**21**) under Varying Reaction Conditions at 25°

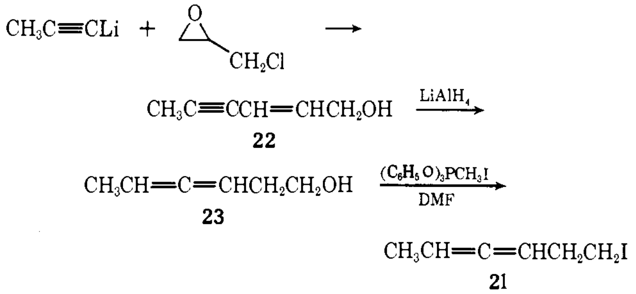
Conditions	Reaction time, min	Products, %[a] **18**[b]	**11**[c]	**14**	**15C**	**15T**[d]	**16A**[b]	**16S**	**17**	**7C**	**7T**
Excess AgOAc–HOAc	3	(3.3)		14.5	25.0	27.2	3.2	7.5	4.7	6.5	8.0
Excess AgOAc–HOAc	13	4.4		15.3	28.5	29.4	4.6	8.2	3.20	1.8	4.2
Excess AgOAc–HOAc	30	3.3		16.1	30.8	32.3	3.3	8.3	3.3	1.8	0.7
Excess AgOAc–HOAc	50	3.6		16.0	31.1	32.7	3.2	8.5	3.6	0.9	0.5
Excess AgOAc–HOAc	170	3.9	0.8	17.4	31.2	32.5	3.2	7.7	3.3		
Excess AgOAc–NaOAc–HOAc	180	6.1	1.0	14.1	30.2	32.3	3.1	10.3	3.1		
AgOAc-HOAc homogeneous	210	~5	0.3	13.3	27.0	27.4	3.3	8.9	3.9	3.9	7.0

[a] See footnotes for Table I. [b] Estimated by comparison of vpc on columns T-1 and C-3. [c] Value omitted because rapid formation at the beginning of the reaction obscures comparison of the remaining values. [d] Corrected for percentage of **18** which is coeluted with **15T** on column T-1.

Table III. Relative Amounts of Cyclopropyl and Cyclobutyl Products Formed in the Silver-Catalyzed Ionizations of *cis*- and *trans*-1-Cyclopropyl-1-iodopropenes (**7C** and **7T**) and 3,4-Hexadien-1-yl Iodide (**21**)

Substrate	Conditions	Products, % **11**	**14**	**15C**	**15T**	**16A**	**16S**	**17**
7T	Excess AgOAc–HOAc, 25°	2.6	16.2	36.0	30.4	3.1	8.0	3.6
7C	Excess AgOAc–HOAc, 25°	0.9	17.4	33.7	32.5	2.8	8.9	3.8
21	Excess AgOAc–HOAc, 25°	0.8	18.1	32.5	33.8	3.3	8.0	3.4

The synthesis of **21** was essentially an extension of that of Jacobs and Macomber.[15b] Propynyllithium was condensed with epichlorohydrin in DMSO to give a 21% yield of unsaturated alcohol **22**. Lithium aluminum hydride reduction followed by reaction of the product with triphenylphosphite methiodide[17] gave iodide **21** in 66% overall yield from **22**. The iodide could be purified by vpc on SE-30 and UCC-W982 columns, but tended to decompose under the preparative conditions unless care was taken (see Experimental Section).



Silver-catalyzed ionization of iodide **21** was carried out under conditions which matched those used in the ionizations of **7C** and **7T** as closely as possible. The results are recorded in Table II. Once again, negligible change in product distribution is observed in going from heterogeneous to homogeneous reaction conditions. Added sodium acetate also does not greatly affect the distribution; it is of some interest that even the amount of direct displacement product is not affected appreciably by the presence of added sodium acetate and therefore must arise from either attack by solvent or by the acetate ion associated with Ag^+ in a tight ion pair.

Iodide **21** was stable when stirred with AgI in acetic acid and to the work-up conditions. Rough kinetic studies gave a good pseudo-first-order rate constant of 1.03×10^{-3} sec^{-1} (corrected for the small extent of isomerization to **7C** and **7T**). Analysis of the isomerization rate data shows that a maximum of 16% of the products formed in the **21** ionization could have arisen from **7C** and **7T**.

In Table III are listed the product distributions from **7C**, **7T**, and **21**, normalized to exclude the isomeric iodides produced in each ionization and the direct displacement product **18** produced from **21**. The correspondence in product distributions is extremely close, making the conclusion essentially inescapable that the homoallenyl and vinyl ionization systems form products (except for a small amount of **18**) *via* identical sets of intermediates.

Internal Return. As mentioned above, **7C** and **7T** interconvert to a small extent under the ionization conditions. We first attributed this to conventional cis–trans isomerization which many vinyl halides undergo, but this explanation was rendered less likely by the difficulty of inducing cis–trans isomerization under simulated reaction conditions except at much higher temperatures than those used in the ionization. We therefore were forced to consider the possibility that the **7C** $\rightleftharpoons$ **7T** interconversion was occurring *via* "internal return" [18] from some sort of ion- or molecule-pair intermediate. The simplest variant of this mechanism is outlined in Scheme V.

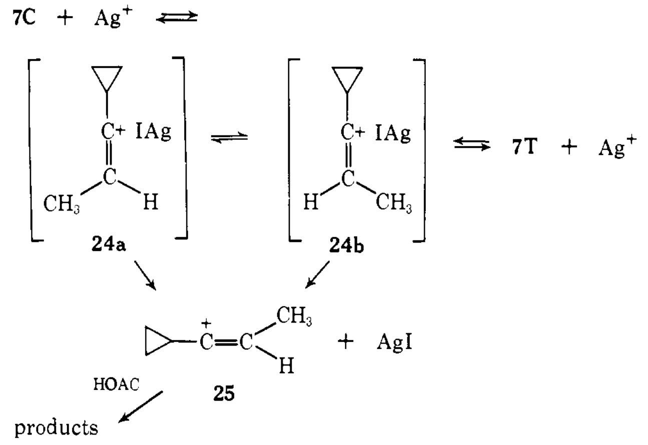
The phenomenological distinction between this mechanism and one which involves only rotation about the C–C double bond is the occurrence of C–I bond cleavage in the isomerization process. While it might

---

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

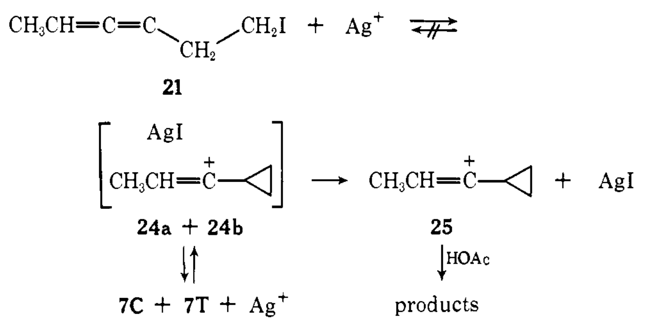
(18) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 86–91, 168–170.

Scheme V

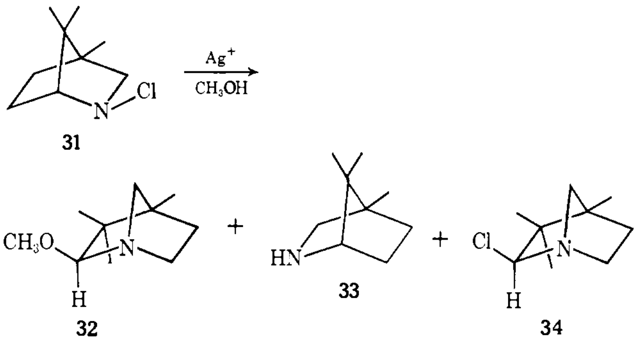


be possible to establish this bond cleavage using a labeled iodide, such an experiment might not be definitive if the isomerization were occurring through an intimate ion or molecule pair which did not exchange iodide with the medium. We felt that an isomerization process in which the structural change observed *required* C–I cleavage would be a more useful test of the mechanism, and we therefore looked carefully for the presence of **7C** and **7T** at early stages in the reaction of **21**. As can be seen from Table II, small but significant quantities of the vinyl iodides are in fact produced in this reaction. It therefore seems reasonable that all the processes which produce one iodide from another in these ionizations involve C–I bond cleavage and some variant of the internal return phenomenon; one possibility is the mechanism outlined in Scheme VI.

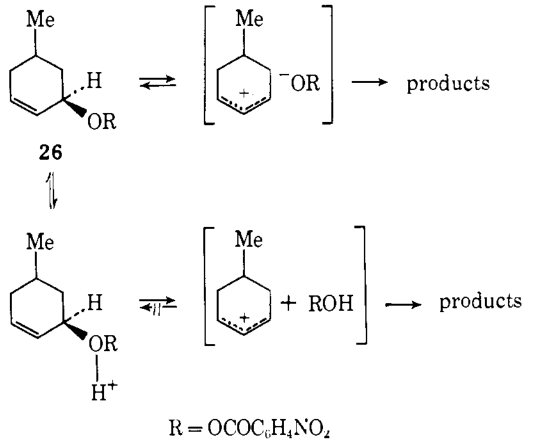
Scheme VI



Although this observation is surprising, there is at least one precedent for it in the literature, involving a much larger percentage of overall return than that which occurs in our system. Gassman and his coworkers have obtained convincing evidence that *N*-chloramines react with silver salts to produce nitrenium ions.[19] In the case of the bicyclic chloramine **31**, Gassman and Cryberg[20] found that reaction with silver perchlorate in methanol produces 8% rearranged methyl ether **32**, 4% amine **33**, and 78% rearranged chloride **34**. While Gassman and Cryberg invoke a concerted 1,2 shift assisted by Ag^+ to explain the formation of **34**, it seems just as likely that an intimate ion or molecule pair is involved, especially in view of the fact that a concerted transition state for the **7C** $\rightleftharpoons$ **7T** isomerization appears to be highly strained.



There are some serious problems involved in the details of the silver-catalyzed internal return picture. The most important one is that there is no apparent reason why a "molecule pair" such as **24a** or **24b** should have any significant lifetime at all in solution. One can also ask whether there should be any driving force for transfer of iodide ion in **24** back to the cation to regenerate silver ion. The C–I and Ag–I bond strengths are nearly identical,[21] so the thermodynamic difference between [**21** + Ag^+] and **24** would result mainly from solvation energies. While the solvation energy of **25** must be high, its solvation energy in the molecular pair **24** may be significantly reduced and is therefore difficult to estimate. In any case, there appears to be no obviously large driving force for internal return from such an intermediate. Experimental support for this inference comes from the studies of Goering and Silversmith, who found significant internal return during the solvolysis of *p*-nitrobenzenesulfonates such as **26** in buffered media, where the leaving group is *p*-nitrobenzoate anion, but no detectable return in the acid-catalyzed solvolysis, where the leaving group is the neutral *p*-nitrobenzoic acid.[22] As Goering and Silversmith point out, this suggests strongly that the major source of stabilization for an ion pair is the electrostatic interaction between the cation and leaving anion, and in cases where the leaving group is neutral no internal return should occur.



We therefore feel that the return mechanisms outlined in Schemes V and VI are incomplete. Our results can only be interpreted satisfactorily by as-

---

(19) P. G. Gassman, D. K. Dygos, and J. E. Trent, *J. Amer. Chem. Soc.*, **92**, 2084 (1970), and earlier papers; (b) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

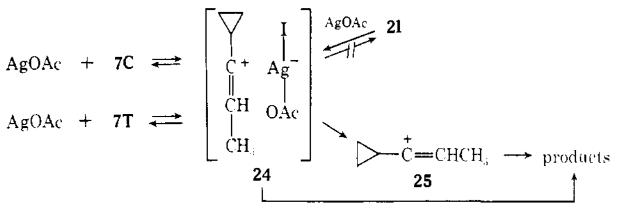
(20) P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 2047 (1969).

(21) (a) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed, Chapman and Hall, London, 1968, p 110; (b) L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, **90**, 7282 (1968).

(22) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 6249 (1955).

suming that silver acetate is essentially undissociated in acetic acid and the "active" reagent (at least that portion of the reagent resulting in internal return) is the silver acetate molecule, rather than free silver ion. Removal of I^- from one of the organic iodides would then result in a true ion pair which could either return I^- to the cation or donate OAc^-, producing acetate product. We have no reason to believe that donation of I^- to the cation will be faster than donation of acetate, and it is therefore interesting that even though a significant fraction of acetates may arise from the ion pair, the identity of product distributions from **7C** and **7T** suggests that any stereoisomeric ion pairs must be completely stereochemically equilibrated before acetate transfer occurs. The most satisfactory mechanistic hypothesis, as it applies to the ion pair situation, is outlined in Scheme VII.

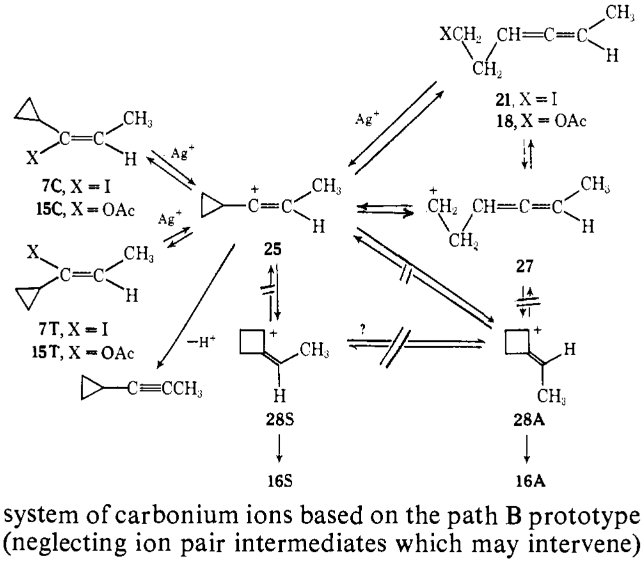
Scheme VII



It is equally difficult to specify the anion which is possibly associated with the nitrenium ion in Gassman and Cryberg's[20] ion pair. One possibility is perchlorate; another is that silver methoxide is the active reagent and $[CH_3OAgCl]^-$ is the counterion in the ion pair.

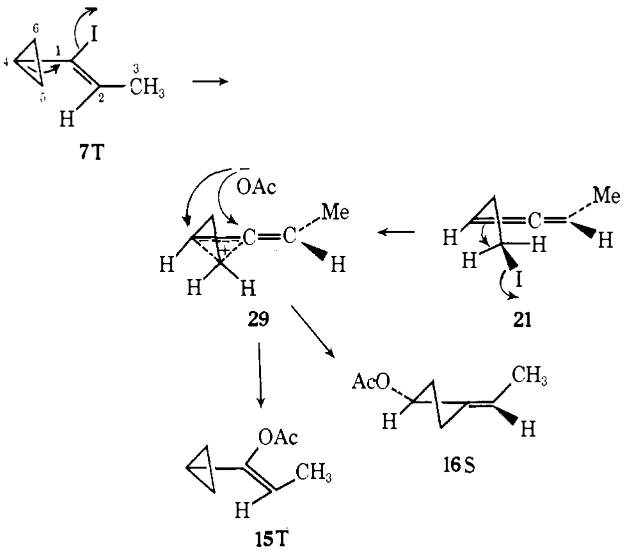
Nature of the Carbonium Ion System. In the beginning of this paper, three extreme possibilities were delineated for the mechanism of solvolytic substitution at vinyl carbon (Scheme I). The identity of product distributions from **7C** and **7T** immediately rules out the sole operation of any mechanism which requires a "nonrandom" stereochemical result. Therefore, neither the "S_N2-like" path A, which is an "inversion" process, nor path C, which is a "retention" process, can be operating in their simplest forms in these substitution reactions. A more detailed form of path B (leading to the linear vinyl cation) is clearly the most reasonable mechanistic choice, and in Scheme VIII we present a system of carbonium ions based on the path B prototype (neglecting ion pair intermediates which may intervene) which best accounts for the products observed in the ionization of **7C**, **7T**, and **21**.

Scheme VIII



The identity and nature of the product distributions require that independent paths leading from any of the substrates to any of the carbonium ions in the system must be negligible, and so it is likely that the first product-forming intermediate reached in all the solvolyses is **25**. This ion then undergoes solvent trapping and elimination, along with a small amount of ring opening (eventually leading to **18**) and rearrangement by two independent modes leading to **28A** and **28S**. Ion **27** is included for convenience, but we have no direct evidence that it intervenes, and **18** may be formed by direct trapping of (presumably delocalized) ion **25** at one of the cyclopropyl carbons with concurrent ring opening. We infer from results described in the previous paper[4] that return of ion **28** to **25** is unlikely, and direct formation of **28** from **21** by a path which avoids **25** is also ruled out because it would give rise to increased amounts of cyclobutyl product in the **21** ionization.

We have included a direct reaction pathway from **21** to **25** because of the large amount of evidence which has accumulated that uncatalyzed ionization of homoallenyl derivatives is accelerated by participation of the allenic π system.[15b,23] Consideration of possible transition states for this pathway and for those leading to **25** and **28** raises the possibility that the intermediate ions may retain some of the partial bonding which must develop in the activated complexes, *i.e.*, that they may be bridged. Let us consider the possibility that both **21** and **7T** ionize *via* the bridged intermediate **29**, **21** by interaction of the developing orbital at C-1 with the allenic π system and **7T** by "transantiparallel" 1,2 rearrangement of the C-4, C-5 cyclopropane ring bond concurrent with C–I bond cleavage. In the most extreme form of this mechanism, where **29** is the only intermediate, solvent trapping should occur stereospecifically to give only **15T** and **16S** from **7T**, and **15C**



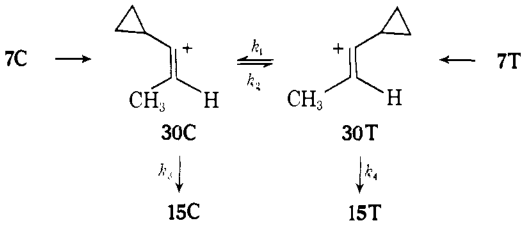
---

(23) (a) R. S. Bly, A. R. Ballentine, and S. V. Koock, *J. Amer. Chem. Soc.*, **89**, 6993 (1967); (b) R. S. Bly and S. V. Koock, *ibid.*, **91**, 3292, 3299 (1969); (c) R. Garry and S. Vessiere, *Bull. Soc. Chim. Fr.*, 1542 (1968); (d) M. Santelli and M. Bertrand, *Tetrahedron Lett.*, 2511, 2515, 3699 (1969); (e) C. Santelli-Rouvier, P. Archer, and M. Bertrand, *C. R. Acad. Sci., Ser. C*, **269**, 252 (1969); (f) M. Hanack and H. J. Schneider, *Angew. Chem.*, **79**, 709 (1967); (g) M. Hanack and J. Häffner, *Tetrahedron Lett.*, 2191 (1964); *Chem. Ber.*, **99**, 1077 (1966).

and **16A** from **7C**. This is therefore also a "nonrandom" pathway, and its sole occurrence cannot be supported by our observations.

A modified variation of path C must also be considered. This route involves the intermediacy of "bent" vinyl cations, which would undergo reaction with solvent with overall "retention." This assumption is valid, however, only if the two hypothetical bent cations undergo interconversion at a rate slower than that of reaction with solvent. An expanded version of path C is outlined in Scheme IX. Application of the steady-state approximation to cation **30C** formed from the **7T** reaction, and to **30T** formed from the **7C** reaction, provides two equations which can be solved for the rate constant ratios k_3/k_2 and k_4/k_1; the only parameters one needs for this solution are the ratios of acetates **15C** and **15T** formed in each reaction. If we let R_A = [**15C**]/[**15T**] formed from **7C**, and R_B = [**15T**]/[**15C**] formed from **7T**, we obtain

Scheme IX



$$R_A = \frac{k_3}{k_2}\left[\frac{k_1}{k_4} + 1\right] \tag{5}$$

and

$$R_B = \frac{k_4}{k_1}\left[\frac{k_2}{k_3} + 1\right] \tag{6}$$

These can be rearranged to give

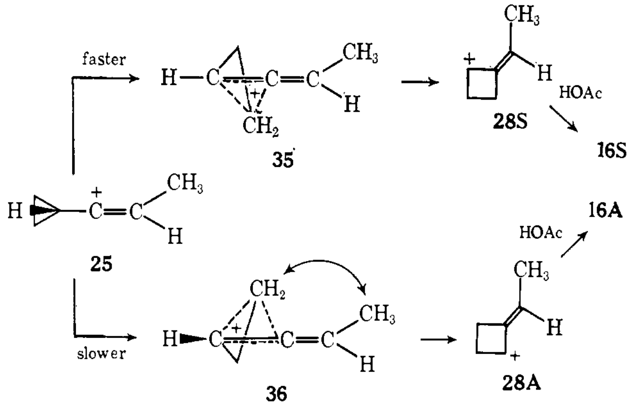
$$\frac{k_3}{k_2} = \frac{R_A R_B - 1}{1 + R_B} \tag{7}$$

$$\frac{k_4}{k_1} = \frac{R_A R_B - 1}{1 + R_A} \tag{8}$$

Vinyl anions isomerize very slowly, even at room temperature or above,[24] and vinyl radicals interconvert at a moderately rapid rate[25,26] at −78°. It is therefore reasonable that vinyl cations should be either linear or very rapidly equilibrating. The error limits in the acetate ratios R_A and R_B can be used to provide a lower limit to the relative rates of stereoequilibration and solvent capture of hypothetical ions **30C** (k_2/k_3) and **30T** (k_1/k_4). These error limits are difficult to estimate exactly, but even if they are as high as ±10%, eq 7 and 8 show that the stereoequilibration rate constants k_1 and k_2 must be an order of magnitude larger than the pseudounimolecular rate constants for solvent capture k_3 and k_4 in order to produce the level of stereochemical scrambling which we observe.

Little is known about the absolute rate constants for capture of reactive cations by acetic acid. However, if we employ Winstein's value[27] of 10^9 sec^{-1} for k_3 and k_4, a lower limit to k_1 or k_2 is 10^{10} sec^{-1}. If our error limits are closer to the more realistic ±5%, the lower limit for the stereoequilibration rate constant approaches 10^{11} sec^{-1}. As the equilibration rate constant approaches 10^{12}–10^{13}, the rate of a molecular vibration, the experimental distinction between equilibrating bent ions and vibration of a linear ion becomes less clear. While our data do not rigorously rule out the intervention of bent vinyl cations, therefore, such intermediates would have to undergo interconversion at a very rapid rate in order to become stereoequilibrated before solvent capture occurs. On the basis of theoretical calculations which we and others have carried out,[28] we therefore feel justified in retaining the linear cation as a working hypothesis until stronger evidence for the bent configuration presents itself.[29]

We do not yet know whether the rearrangement of vinyl ion **25** to **28** gives rise to a "memory effect" of the type observed in the parent system,[4] because the synthesis and direct ionization of the *syn*- and *anti*-2-ethylidenecyclobutyl bromides have not been carried out. However, the ratio of the corresponding stereoisomeric acetates **16S** and **16A** formed in the ionizations of **7** and **21** deserves comment. Assuming for the moment that our tentative stereochemical assignments are correct, we obtain more than twice the amount of (presumably) less stable syn isomer **16S** than we do the anti isomer **16A**. This can be understood if one considers the steric interactions which develop in the transition states for rearrangement of **25**. In transition state **35**, the migrating methylene group is remote from the vinyl methyl, but in **36**, both the migrating group



---

(24) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 130–135; (b) D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, **88**, 5765 (1966); (c) G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2788 (1967).

(25) (a) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968); (b) R. M. Kopchik and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **90**, 6733 (1968); (c) L. A. Singer and N. P. Kong, *ibid.*, **89**, 6805 (1967); (d) R. C. Newman, Jr., and G. D. Holmes, *J. Org. Chem.*, **33**, 4317 (1968).

(26) For a theoretical calculation of the barriers to inversion in vinyl radicals and anions, see M. J. S. Dewar and M. Shanshal, *J. Amer. Chem. Soc.*, **91**, 3654 (1969).

(27) S. Winstein, *ibid.*, **87**, 381 (1965).

(28) (a) P. E. Peterson and R. J. Kamat, *ibid.*, **91**, 4521 (1969); (b) R. Sustman, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *ibid.*, **91**, 5350 (1969); (c) private communication from Professor P. E. Peterson; (d) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4311 (1968); (e) D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1953 (1971).

(29) NOTE ADDED IN PROOF. Two communications have appeared recently[29a,b] which bear on the question of vinyl cation linearity. The first[29a] describes a stabilized system which, like our own, substitutes with stereochemical randomization. The second[29b] reports an observation of some excess retention in highly nonpolar solvents, where we feel long-lived intimate ion pairs must certainly be involved (although the authors invoke a double inversion mechanism and surface effects to explain their data). The stereochemistry of S$_N$1 substitution at an *unactivated* vinyl center under normal solvolytic conditions, therefore, is still unknown. (a) Z. Rappoport and Y. Apeloig, *ibid.*, **91**, 6734 (1969); (b) G. F. P. Kernaghan and H. M. R. Hoffmann, *ibid.*, **92**, 6988 (1970).

and methyl are on the same side of the molecule and their steric interaction must result in some destabilization of this transition state. State **35** is therefore the more stable, and it leads to syn isomer **16S**.

Experimental Section

General Methods. All boiling points are uncorrected. Infrared spectra were obtained in CCl_4 on a Perkin-Elmer IR-257 (grating) instrument unless otherwise indicated. Routine nuclear magnetic resonance spectra were taken on a Varian A-60A as a 10% solution in CCl_4 and tetramethylsilane (TMS) internal standard. Proton nmr spectra of some solvolysis products were obtained on a Varian HR 220 as a <1% solution in CCl_4 with TMS internal standard. Nmr spectra are reported as: chemical shift (in order of increasing δ); multiplicity, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; integration in units of H; splitting; assignment. Mass spectra were obtained on a CEC-21-103C instrument at 10 or 100 μA ionization current and 70 V ionization potential at 250° inlet temperature. Refractive indices were obtained on a Carl-Zeiss Abbe refractometer, No. 323165. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. 48106. Preparative and rough analytical glc was done on a Varian Aerograph A90-P3 instrument (thermoconductivity detector) with the injector at 200–210°, the detector at 200–210°, and the helium carrier flow at 60 ml/min, unless otherwise stated. Analytical glc was done on a Hewlett-Packard 5750 (flame ionization detector) equipped with a Disc integrator. Gas pressures used were He, 33; H_2, 8–9; air, 25 (lb/in.^{2}). The injector temperature was 200–210° and the detector temperature was 330–340°, unless otherwise noted (see Table IV).

Materials. The following lists the commercial source of the chemicals used: Aldrich Chemical Co., cyclopropanecarboxylic acid (Puriss); Alfa Inorganic, lithium aluminum hydride, potassium *tert*-butoxide; Allied Chemical, sodium acetate (anhydrous); J. T. Baker Chemical Co., iodine (resublimed), triphenyl phosphite, silver acetate ("purified"); Calbiochem, tetradecane; Foote Chemical Co., propynyllithium (97% min); Matheson Coleman and Bell, thionyl chloride, ethyl bromide, triethylamine, cadmium chloride (anhydrous), hydrazine hydrate (99–100%), methyl iodide, *o*-dichlorobenzene; Mallinkrodt, ethyl ether (anhydrous), benzene (reagent, "thiophene free"). These chemicals, and any of the "common" chemicals or solvents used but not listed, were used as received, except as indicated by the following purifications.

Triethylamine was dried over NaOH for 2 days and distilled through a 30-cm Vigreux column from a solution ~5% in phenyl isocyanate (~88°). Dimethyl sulfoxide (DMSO) was dried over Linde type 4A molecular sieves and distilled from CaO. It was collected at 67.5–68° (6–7 mm) and stored over molecular sieves. Acetic acid was refluxed with ~4% acetic anhydride and 3% CrO_3 and distilled through a 30-cm Vigreux column. About 1.0 g of acetic anhydride was added/500 ml of the distillate. Epichlorohydrin was heated on the steam bath with CaO for 1.5 hr. The liquid was decanted off and distilled at atmospheric pressure through a 25-cm Vigreux column. The fraction boiling at 113.8–114.8° was collected and stored in a covered flask. Cadmium chloride (anhydrous) was dried at 115° under aspirator vacuum for 24 hr and stored in a vacuum desiccator. Benzene (reagent) was dried over Linde type 4A molecular sieves for at least 2 days. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride prior to use. Silver acetate was stirred with glacial acetic acid and acetic anhydride for 2 days (protected from light). The mixture was filtered, and the AgOAc was washed with dried acetic acid. The acetic acid was removed at room temperature under ~0.5 mm pressure (6 hr). The dried AgOAc was stored over P_2O_5 under vacuum. Triphenyl phosphite was dissolved in ethyl ether. The solution was washed twice with a 5% NaOH solution, twice with water, twice with a saturated NaCl solution, and dried over Na_2SO_4 overnight. The ether was removed on the rotary evaporator and then by heating the solution at 100° at ~2 mm pressure for 1 hr.

Cyclopropanecarbonyl Chloride (10). Thionyl chloride (72.2 g, 0.6 mol) was placed in a 300-ml round-bottom flask (magnetic stir bar), and cyclopropanecarboxylic acid (43.1 g, 0.5 mol) was added from a dropping funnel (side arm) over a period of 1 hr. The reaction mixture was then heated in an oil bath under a reflux condenser at 60–70° for 1 hr. The flask was fitted with a 15-cm Vigreux column, a distillation head (5 cm of glass helices above the Vigreux column), and condenser, and the contents distilled at atmospheric pressure. The forerun was twice returned to the distillation flask and distillation resumed. The fraction boiling at 118–119.5° was collected. The total distillate was 41.9 g, bp 118–119.5°, 80% yield (lit.[7a] bp 114–119°); ir (0.1 mm) 3030 (cyclopropyl CH), 1780 cm^{-1} (acid chloride C=O); nmr δ 0.9–1.47 (complex m, 4 H, cyclopropyl CH_2), 1.85–2.27 (1 H, cyclopropyl CH).

Table IV. Gas Chromatography Columns[a]

Designation	Description	Size (ft × in.)
C-1	20% Carbowax 20M on Chromosorb P, Al or stainless steel	12 × 1/4
C-2	20% Carbowax 20M on Chromosorb P, small bore, stainless steel	12 × 1/8
C-3	15% Carbowax 20M on Chromosorb W-AWDMCS, stainless steel	12 × 1/8
D-1	20% DEGS on Chromosorb P, Al	10 × 1/4
D-2	20% DEGS on Chromosorb P, stainless steel	10 × 1/4
S-1	3% SE30 on Chromosorb P, stainless steel	5 × 1/4
S-2	5% SE30 on Chromosorb P, Al	8 × 3/8
S-3	20% SE30 on Chromosorb P, Al	10 × 1/4
S-4	20% SE30 on Chromosorb P, Al	15 × 3/8
T-1	15% TCEP on Chromosorb W-AWDMCS, stainless steel	12 × 1/8
T-2	20% TCEP on Chromosorb P, Al	10 × 1/4
U-1	10% UCC-W982 on Chromosorb W-AWDMCS, stainless steel	6 × 1/8
U-2	20% UCC-W982 on Chromosorb P, Al	15 × 3/8

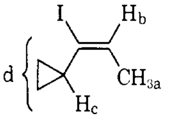
[a] 1/8-in. columns were used on the Hewlett-Packard flame ionization instrument; all others were used on the Varian Aerograph.

Cyclopropyl Ethyl Ketone (11). An oven-dried, 1000-ml three-necked flask was fitted with a mechanical stirrer (Teflon seal and blade), reflux condenser, and dropping funnel (side arm). The system was supplied with dry, high-purity nitrogen at the top of the condenser (Hg bubbler to control flow). Magnesium turnings (12.1 g, 0.5 mol) were placed in the flask, and the flask and turnings flamed and cooled under nitrogen (stopper on dropping funnel removed). The Mg was covered with 120 ml of anhydrous ethyl ether (fresh can), and a small piece of I_2 was added. A few milliliters of a solution of ethyl bromide (68.5 g, 0.63 mol) in 190 ml of ether was added, and the reaction began immediately. The remaining EtBr solution was added over a period of 50 min. The reaction mixture was then gently heated at reflux on the steam bath for 30 min. The Gilman test for Grignard reagent showed a strong blue-green positive test. The reaction mixture was cooled (ice bath) and $CdCl_2$ (50.0 g, 0.273 mol) was added. The mixture was stirred at room temperature for 15 min and then heated at reflux for 50 min. The Gilman test gave a yellow negative test. The dropping funnel was replaced with a distilling head, thermometer, and condenser, and the ether was distilled off and replaced with dry benzene. A solution of the cyclopropanecarbonyl chloride (**10**, 41.6 g, 0.41 mol) in 100 ml of dry benzene was added from a dropping funnel to the Et_2Cd mixture at a rate to produce reflux (about 25 min). The reaction mixture was heated at reflux on the steam bath for 90 min and cooled in an ice bath; 200 ml of ice water and then 200 ml of cold 20% H_2SO_4 were slowly added. The benzene and water layers were separated. The water layer was saturated with NaCl and extracted with ether. The extracts (ether and benzene) were combined and washed with water, saturated $NaHCO_3$ solution, water, and saturated NaCl solution, and dried over anhydrous Na_2SO_4.

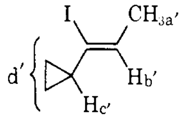
The ether and benzene were distilled off through a 30-cm Vigreux column. Vpc (column C-1, 150°) showed a slight amount of ketone in the benzene fraction. The Vigreux was washed down with a little of the collected benzene. The cyclopropyl ethyl ketone was distilled through a 15-cm Vigreux plus 5-cm glass helices: yield 78%, 30.5 g; bp 130–131° (1 atm) (lit.[7] bp 130°); $n^{23}\text{D}$ 1.4287 (lit. $n^{20}\text{D}$ 1.4292,[7a] $n^{20}\text{D}$ 1.4284[7b]); ir (0.1 mm) 3105, 3025 (cyclopropyl CH), 2990, 2955, 2920 (ethyl CH), 1700 cm^{-1} (C=O); nmr δ 0.6–1.25 (complex m, cyclopropyl CH_2), 1.03 (t, J = 7 Hz, methyl, total of 7 H for 0.6–1.25), 1.6–2.0 (complex m, 1 H, cyclopropyl CH), 1.49 (q of d, 2 H, J = 7 Hz, J = 1 Hz, methylene).

Hydrazone of Cyclopropyl Ethyl Ketone Hydrazone (12). Cyclopropyl ethyl ketone (**11**) (9.88 g, 0.10 mol) was placed in a 100-ml flask (drying tube and magnetic stir bar). Hydrazine hydrate (20 g, 0.40 mol) was added. Enough absolute ethanol (about 15 ml) was added to produce a homogeneous reaction mixture, and the solution was stirred overnight. The disappearance of ketone was followed by vpc (column D-1, 180°). The reaction mixture was then poured into brine and extracted with ether, the extract washed with saturated NaCl solution and dried over anhydrous $MgSO_4$, and the ether (and ethanol) removed by prolonged evaporation on the rotary evaporator at room temperature. Yield of crude hydrazone was 14.9 g, 90% pure by vpc (column D-1, 180°), 71% yield; ir (0.1 mm) 3400 (broad), 3300, 3220 (NH), 3090, 3010 (cyclopropyl CH), 2980, 2950, 2930 (ethyl CH), 1625 cm^{-1} (C=N).

***cis*- and *trans*-1-Iodo-1-cyclopropylpropene (7C and 7T).** The hydrazone of cyclopropyl ethyl ketone (2.04 g, ~90% pure, 16.4 mmol), 30 ml of THF, and 70 ml of Et_3N were placed in a 300-ml three-necked flask (drying tube, dropping funnel, magnetic stir bar) and cooled in an ice bath. I_2 (8.56 g, 33.7 mmol) was dissolved in 65 ml of THF, and the solution was added to the stirred hydrazone solution as rapidly as the orange color was bleached. Toward the end of the addition, the decolorization became slower, but the I_2 solution was added at the initial rate. After stirring the orange reaction mixture at room temperature for 1 hr, the excess I_2 was allowed to react with $Na_2S_2O_3$ solution. The reaction mixture was poured into ice water and extracted with ethyl ether. The extract was washed with cold water, $Na_2S_2O_3$ solution, water, 1 *M* HCl, water, saturated $NaHCO_3$ solution, water, and saturated NaCl solution, and dried over Na_2SO_4. The ether was removed on the rotary evaporator, and the dark residue vacuum distilled (bulb to bulb) at about 1 mm. The yellow distillate was purified by preparative vpc (column S-2, 90°) and collected over glass helices. The product was then vacuum transferred. Yield of isomeric vinyl iodides **7C** and **7T** was 1.62 g, 47%. Yields by this procedure (corrected for hydrazone purity) were generally 45–48%. Ratio of the isomers (**7T**/**7C**) ranged from 75/25 to 62/38. The isomers could be separated by preparative vpc in >99.4% purity on column D-1, 90–100°. *Anal.* Calcd for **7**: C, 34.64; H, 4.36; I, 61.00. Found (**7T**): C, 34.78; H, 4.23; I, 61.65. Found **7C**: C, 34.47; H, 4.26; I, 61.35. Ir (micro cavity) showed 3100, 3020 (cyclopropyl CH), 2935, 2875 (methyl CH), 1624 (C=C, **7C**), 1640, 1652 cm^{-1} (doublet, C=C, **7T**); nmr of **7C** δ 0.5–0.8 (complex m, 4 H, H_d), 1.2–1.75 (complex m, 1 H, H_c), 1.77 (d of d, 3 H, J_{ab} = 7.2 Hz, J_{ac} = 0.7 Hz, H_a), 6.25 (q of d, 1 H, J_{bc} = 1.2 Hz, H_b); nmr of **7T** δ 0.5–0.8 (complex m, 4 H, $H_{d'}$), 1.2–1.75 (complex m, 1 H, $H_{c'}$), 1.72 (d of d, 3 H, $J_{a'b'}$ = 6.5 Hz, $J_{a'c'}$ = 1.1 Hz, $H_{a'}$), 5.62 (q of d, 1 H, $J_{b'c'}$ = 1.2 Hz, $H_{b'}$).



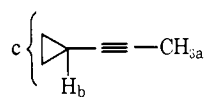
7C



7T

Competitive Elimination Reaction on Vinyl Iodides, 7C and 7T. The mixture of **7C** and **7T** (0.51 mmol, 61.7% **7T** by vpc, column C-2, 100–120°) was stirred with potassium *tert*-butoxide (0.34 mmol) in 1 ml of DMSO for about 5 min. The reaction mixture was poured into 3 ml of water and extracted with three 1-ml portions of pentane. Vpc analysis (as above) showed 21.1% **7T**, 36.1% **7C**, and 42.7% product. The ratio of the reaction rates k_t/k_c can be estimated to be between 7 and 11.5, probably nearer to 9–10. A preliminary experiment showed a similar dramatic change in the ratio of **7T**/**7C** from 3.00 to 0.10 under similar reaction conditions. There was no reaction and the ratio of the vinyl iodides remained the same when the iodides were stirred in DMSO without potassium *tert*-butoxide.

Cyclopropylmethylacetylene (14). The mixture of vinyl iodides, **7C** and **7T** (0.5 g, 2.4 mmol) and potassium *tert*-butoxide (0.44 g, 4.0 mmol) was stirred in 8 ml of dry DMSO for 3 hr at room temperature. The reaction mixture became yellow and the reaction was exothermic. The reaction solution was poured into 15 ml of water and extracted twice with 4 ml of pentane. The combined extracts were washed with water and saturated NaCl solution and dried over anhydrous Na_2SO_4. The acetylene was collected by preparative vpc (column C-1, 90°) over glass helices and then vacuum transferred. Yield of isolated pure acetylene was 0.15 g, 77%. *Anal.* Calcd for **14**: C, 89.94; H, 10.06. Found: C, 89.70; H, 10.11. Ir (micro cavity) showed 3107, 3025 (cyclopropyl CH), 2970, 2935, 2875 (methyl CH), 2250, 2275 cm^{-1} (doublet, C≡C, very weak); nmr δ 0.4–0.75 (complex m, 4 H, H_c), 0.75–1.35 (complex m, 1 H, H_b), 1.68 (d, 3 H, J_{ab} = 1.8 Hz, H_a).



14

Analytical Ionizations. The AgOAc and purified acetic acid (and, if used, the anhydrous NaOAc) were stirred in a vial (magnetic stir bar, serum cap) for at least 15 min. The *cis*- or *trans*-vinyl iodide (purified by vpc on column D-1, 90–100°, **7T**, generally >99.8% pure, **7C** >99.4% pure) was then added, and the vial was wrapped with aluminum foil. The reaction mixture or an aliquot (after stirring for an appropriate time) was poured into five times its volume of water and extracted with 4–6 ml of ether. The extract was washed with water, $NaHCO_3$ solution, saturated NaCl solution, and dried over Na_2SO_4 at −15°. For the homogeneous reactions, excess AgOAc was stirred in acetic acid for at least 1 hr. The solid AgOAc was filtered from the solution (oven-dried Hirsch funnels and filter flasks, three filtrations). Analysis of the solvolysis products was done by vpc (preliminary runs used column C-2, 100°, other runs used column T-1, 95–100°, and column C-3, 100–110°). The runs are listed in Table V. Preliminary runs (using untreated AgOAc and Carbowax analysis) are designated P, homogeneous runs by H, and runs where an excess of water was added, by W.

Table V

	Compd (mmol)[a]
1-P	**7T** (0.24), AgOAc (0.72), HOAc (2.5), 3 hr
2-P	**7C** (0.24), AgOAc (0.72), HOAc (2.5), 3 hr
3-P	**7T** (0.24), AgOAc (0.72), HOAc (2.0), 3 hr
4-P	**7C** (9.24), AgOAc (0.72), HAOc (2.0), 3 hr
5	**7T** (0.36), AgOAc (1.08), HOAc (3.0), aliquots at 10, 23, 40 min, 3 hr
6	**7T** (0.10), AgOAc (0.30), NaOAc (0.40), HOAc (1.0), 3 hr
7-H	**7T** (0.15), AgOAc–HOAc (3.0), 3 hr
8	**7C** (0.36), AgOAc (1.08), HOAc (3.0), aliquots at 10, 22, 40 min, 3 hr
9	**7C** (0.0975), AgOAc (0.0750), HOAc (1.0), 3 hr
10	**7C** (0.10), AgOAc (0.31), NaOAc (0.41), HOAc, (1.0), 3 hr
11	**7C** (0.10), AgOAc (0.32), HOAc (1.0), 2 hr
12-H	**7C** (0.082), AgOAc–HOAc (6.95), 2 hr
13	**7T** (0.106), AgOAc (0.32), HOAc (1.0), 3.5 hr
14-H	**7T** (0.117), AgOAc–HOAc (7.4), 3 hr
15	**7T** (0.24), AgOAc (0.72), HOAc (2.0), aliquots at 20, 61, 190 min
16	**7T** (0.112), AgOAc (0.335), NaOAc (0.45), HOAc (1.0), 3 hr
17	**7C** (0.24), AgOAc (0.72), HOAc (2.0), aliquots at 4, 16, 123 min
18	**7C** (0.11), AgOAc (0.32), NaOAc (0.48), HOAc (1.0), 2.5 hr
19	**7T** (0.12), AgOAc (0.34), NaOAc (0.46), HOAc (1.0), 3 hr
20-W	**7T** (0.11), AgOAc (0.36), NaOAc (0.44), H_2O (0.14), HOAc (1.0), 3 hr
21-H	**7T** (0.077), AgOAc–HOAc (3.5), 3 hr
22-HW	**7T** (0.07), H_2O (0.26), AgOAc–HOAc (3.3), 3 hr
23-H	**7T** (0.06), AgOAc–HOAc (6.0), 3 hr. Used carefully cleaned vials: CrO_3–H_2SO_4 solution overnight, rinsed with water, 30% KOH in MeOH overnight, rinsed, glacial HOAc overnight, rinsed with distilled water, then dried overnight at 110° under vacuum.

[a] HOAc (milliliters); AgOAc–HOAc solution (grams).

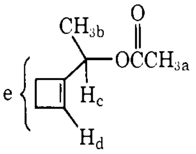
Preparative Ionizations. The preparative ionizations were done in a similar manner with excess AgOAc in acetic acid. After the work-up, the ether was carefully removed on the rotary evaporator at room temperature. The yield of the solvolysis products (corrected by vpc for small amounts of ether and evaporation of cyclopropylmethylacetylene) indicated >95% yield. The products were isolated by collecting six fractions by preparative vpc on DEGS (column D-1, 95–100°). The last two fractions were then repurified on TCEP (column T-2, 90–95°) to obtain four fractions (two fractions from each of the last two DEGS fractions). The small amount of product that was collected in some cases made it necessary to use the following procedure. The product was dissolved in CCl_4 for the ir spectrum (microcavity cell). This solution was then analyzed by vpc (column C-2) for purity and retention time. The solution (plus more CCl_4) was then used for the 220-MHz spectrum. The sample was reisolated by vpc (column D-1) for mass spectral analysis (and sometimes elemental analysis).

The products are given below. The values in parentheses after the fraction refer to the glc retention time (in minutes) for the *analytical* solvolysis mixtures on columns T-1 and C-2, respectively. The "first, second, etc. solvolysis peaks" refer to the product peaks in the analytical solvolyses in the order of their retention times on the Carbowax column.

Fraction 1 (5.4, 5.5). Cyclopropylmethylacetylene (14). The ir and nmr spectra and the vpc retention time (~90% pure) were identical with the prepared compound (from the vinyl iodides). In addition, the solvolysis mixture spiked with prepared cyclopropylmethyacetylene showed precise correspondence to the first solvolysis peak.

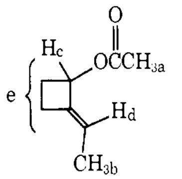
Fraction 2 (17.6, 13.4). Cyclopropyl Ethyl Ketone (11). The ir spectrum was identical with that of an authentic sample. The solvolysis mixture spiked with the prepared ketone showed precise correspondence with the second solvolysis peak. The small amount of the ketone produced in the solvolyses and its volatility prevented any further characterization.

Fraction 3 (23, 26.4). 1-Cyclobutenylethyl Acetate (17). The vpc (>99% pure) showed identical retention time with the third solvolysis peak (also by spiking the solvolysis mixture): ir 3055 (weak), 2990, 2960, 2935, 2850 (CH), 1735 cm^{-1} (C=O), spectrum weak, C=C not seen; nmr (220 MHz) δ 1.29 (d, 3 H, J_{bc} = 6.5 Hz, H$_b$), 2.00 (s, 3 H, H$_a$), 2.45 and 2.36 (two complex m, 2 H each, H$_e$), 5.21 (broad q, 1 H, H$_c$), 5.82 (s, broad at 250 Hz sweep width, 1 H, H$_d$); mass spectrum (given as *m/e* (per cent of main peak, assignment)) 140 (<0.5, P), 125 (<0.5, P − CH$_3$), 98 (4.5, P − CH$_2$=C=O), 80 (31.5, P − AcOH), 79 (22.4, P − AcOH − H ?), 43 (100, CH$_3$CO$^+$). *Anal.* Calcd for **17**: C, 68.55; H, 8.63. Found: C, 68.30; H, 8.75.



17

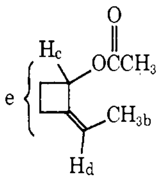
Fraction 4 (33.6, 37.2). ***anti*-2-Ethylidenecyclobutyl Acetate (16A).** Vpc (>99% pure) showed identical retention time to the fourth solvolysis peak: ir 2990, 2960, 2935, 2855 (CH), 1749 (C=O), 950 (C=C exocyclic cylobutanes), 900 (CH$_2$), 855 cm^{-1} (trisubstituted C=C); nmr δ 1.58 (d of d, 3 H, J_{bd} = 6.6 Hz, $J_{b?}$ = 1.5 Hz, H$_b$), 1.98 (s, 3 H, H$_a$), 2.18–2.68 (complex m, 4 H, H$_e$), 5.23 (complex m, 1 H, H$_c$), 5.57 (complex m, 1 H, H$_d$); mass spectrum *m/e* 140 (~1.5, P), 125 (2.3, P − CH$_3$), 106 (46.2, ?), 105 (21, 106 − H), 98 (20.1, P − CH$_2$CO), 91 (80.3, 106 − CH$_3$?), 43 (100, CH$_3$CO$^+$), 41 (20.6, C$_3$H$_5^+$?), 39 (34.6, C$_3$H$_3^+$?). *Anal.* Calcd for **16A**: C, 68.55; H, 8.63. Found: C, 68.38; H, 8.48.



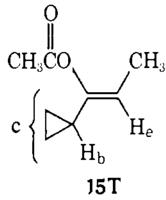
16A

Fraction 5a (40.3, 45.6). ***syn*-2-Ethylidenecyclobutyl Acetate (16S).** Vpc (>99% pure) showed the same retention time as the sixth solvolysis peak (also by spiking the solvolysis mixture): ir 3000 (C=CH ?), 2970, 2950, 2935, 2870 (CH), 1740 (C=O), weak 960 (CC exocyclic cyclobutanes), weak 900 (CH$_2$ exocyclic cyclobutanes), weak 855 cm^{-1} (trisubstituted C=C). Qualitatively, the ir spectra of fraction 4 and 5a are very similar: nmr δ 1.54 (d of d, 3 H, J_{bd} = 6.5 Hz (barely split again by 1 Hz), H$_b$), 1.97 (s, 3 H, H$_a$), 2.54 and 2.41 (two complex m, 4 H, H$_e$); 5.38 (broad m, 2 H, H$_c$ and H$_d$); mass spectrum *m/e* 140 (<0.5, P), 106 (58.6, ?), 105 (27.5, 106 − H ?), 91 (100, 106 − CH$_3$?), 43 (13.5, CH$_3$CO$^+$), 39 (20, C$_3$H$_3^+$). *Anal.* Calcd for **65**; C, 68.55; H, 8.63. Found: C, 68.55; H, 8.76.

Fraction 5b (47.1, 42.7). ***trans*-1-Cyclopropylpropenyl Acetate (15T).** Vpc (>99% pure) showed retention time identical with fifth solvolysis peak (also by spiking solvolysis mixture): ir 3100, 3060, 3025 (cyclopropyl CH and C=CH), 2955, 2935, 2880 (CH), 1755 (C=O), 1693 cm^{-1} (C=C); nmr δ 0.43–0.64 (complex m, 4 H, H$_c$), 1.42 (m, H$_b$), 1.42 (d, H$_b$ + H$_d$ = 4 H, J_{de} = 6.7 Hz, H$_d$), 2.07 (s, 3 H, H$_a$), 5.02 (q, 1 H, J_{db} = ~2 Hz, H$_e$); mass spectrum *m/e* 140 (6.4, P), 98 (62, P − CH$_2$CO), 83 (34, 98 − CH$_3$), 69 (62, 98 − Et), 56 (50.1, 98 − C$_3$H$_6$?), 43 (100, CH$_3$CO$^+$), 41 (38, C$_3$H$_5^+$?), 39 (36.1, C$_3$H$_3^+$?). *Anal.* Calcd for **15T**: C, 68.55; H, 8.63. Found: C, 68.27; H, 8.72.

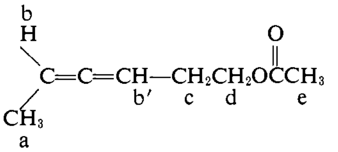


16S



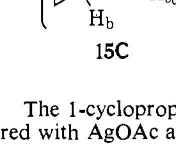
15T

Fraction 6a (47.1, 57). 3,4-Hexadien-1-yl Acetate (18). This product was obtained in too small an amount to risk vpc comparison of retention time and was assumed to correspond to the unaccounted for eighth solvolysis peak (~0.5%). Also, the qualitative comparison of this fraction's retention time under preparative conditions on TCEP to fraction 6b is in agreement with the relationship found for the homoallenic acetate formed in the solvolysis of the homoallenic iodide. A sample of authentic **18** added to the analytical solvolysis mixture showed precise enhancement of the eighth solvolysis peak. This acetate was identical spectroscopically with a sample prepared from the corresponding alcohol (*vide infra*): ir 3000 (C=CH ?), 2960, 2940, 2915, 2870 (CH), 1963 (C=C=C), 1740 cm^{-1} (C=O); nmr δ 1.67 (d of d, 3 H, J_{ab} = 7.0 Hz, $J_{ab'}$ = 3.2 Hz, H$_a$), 1.99 (s, 3 H, H$_e$), 2.27 (m with appearance of q of d, 2 H, $J_{cb'}$ = 7 Hz, J_{cd} = 7 Hz, J_{cb} = 3.2 Hz, H$_c$), 4.03 (t, 2 H, H$_d$), 5.00 (m (more than 11 peaks), 2 H, H$_b$ and H$_{b'}$); mass spectrum *m/e* 140 (~0.7, P), 106 (58.5, ?), 105 (26.0, 106 − H ?), 91 (100, 106 − CH$_3$?), 79 (22.5, ?), 43 (49.1, CH$_3$CO$^+$), 39 (27.0, C$_3$H$_3^+$?).



18

Fraction 6b (59.0, 50.7). ***cis*-1-Cyclopropylpropenyl Acetate (15C).** Vpc (>99% pure) showed identical retention time with the seventh solvolysis peak (also by spiking the solvolysis mixture): ir 3100, 3025 (cyclopropyl CH and C=CH), 2950, 2935, 2880 (CH), 1760 (C=O), 1682 cm^{-1} (C=C); nmr δ 0.42–0.72 (complex m, 4 H, H$_c$), 1.42 (complex m, 1 H, H$_b$), 1.51 (d, 3 H, J_{de} = 7.0 Hz, H$_d$), 2.00 (s, 3 H, H$_a$), 5.05 (q, 1 H, J_{de} = 7.2 Hz, finer splitting of J_{be} = 0.8 Hz, H$_e$); mass spectrum *m/e* 140 (3.6, P), 98 (37.2, P − CH$_2$CO), 83 (21.0, 98 − CH$_3$), 69 (38.6, 98 − Et), 56 (30.0, 98 − C$_3$H$_6$?), 43 (100, CH$_3$CO$^+$), 41 (24.5, C$_3$H$_5^+$), 39 (23.6, C$_3$H$_3^+$). *Anal.* Calcd for **15C**: C, 68.55; H, 8.63. Found: C, 68.62; H, 8.73.



15C

Control Experiments. The 1-cyclopropylpropenyl acetates, **15C** and **15T**, were each stirred with AgOAc and AgI in acetic acid for 3 hr and the mixture worked up as in the solvolyses. Analysis by vpc (column C-2, 100°) showed no trace of other components.

Likewise, cyclopropyl ethyl ketone (**11**) and cyclopropylemethylacetylene (**14**) were stable to the reaction conditions and work-up. (The latter compound showed a slight, <0.2%, conversion to cyclopropyl ethyl ketone.) The starting iodides were stable in acetic acid and AgI at room temperature for several hours and to the work-up.

(In addition to the estimate of solvolysis yield given previously, solvolysis run 9 indicates that the reaction is essentially quantitative. A deficiency of AgOAc was used and a quantitative reaction should produce a reaction mixture in which 23.1% is the starting iodide. In fact 21.2% was found, which is probably within the error of the vpc analysis. If the solvolysis went in, say, 90% yield, the per cent of iodide should be 25%.)

The fact that the solvolysis products were isolated by vpc at similar temperatures used in the analyses and found to be pure by vpc and nmr spectroscopy, shows that they were stable to the chromatography conditions. In addition, since the products were isolated on different columns than those used for analysis, it was shown (except for acetate **18**) by comparison of retention times and/or spiking that the isolated products corresponded to the peaks observed in the analytical solvolysis mixtures.

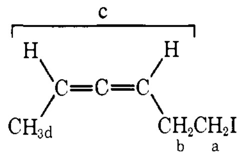
Cis–Trans Isomerization of the Vinyl Iodides. Several attempts at obtaining cis–trans isomerization of the vinyl iodides, **7C** and **7T**, failed. These include using KI, I_2, and AgI (also generated in solution from $AgNO_3$ and KI or from a trace of AgOAc) in DMSO or acetic acid at room temperature or above. The following cases appeared successful. (1) A mixture of **7C** and **7T** was stirred with AgI in HOAc at 70° with tetradecane internal standard. The work-up was that used in the analytical solvolyses. Aliquots were taken at times 0, 2.75, 6.5, 14.75, and 24.25 hr. The ratio K_{eq} = **7T**/**7C** was 2.58, 4.18, 5.21, 7.20, and 8.71 at these times, which extrapolates to about 9. Decomposition after 24 hr amounted to about 30%. (2) The mixture of **7C** and **7T** was stirred with AgI in acetic acid at 80° with *o*-dichlorobenzene internal standard. Aliquots were taken at times 0, 7, and 22.25 hr. The corresponding **7T**/**7C** ratios were 2.61, 4.21, and 5.7, which extrapolates to about 7.3. Decomposition after 22.25 hr was about 20%. (3) The trans isomer was stirred with AgI in acetic acid at 80°. Aliquots were taken at times 0, 19, and 62.5, and 237 hr. The corresponding ratios **7T**/**7C** were 162.7, 29.8, 19.2, and 16.5, which extrapolates to <15. (4) The cis isomer was stirred with AgI in acetic acid at 80°. Aliquots were taken at times 0, 22.5, 64.25, and 206 hr. The corresponding ratios **7T**/**7C** were 0.0026, 0.355, 0.684, and 3.67, which extrapolates to >9.

It appears that the iodides are definitely isomerizing, as can be seen from the dramatic change in **7T**/**7C** in run 4 and the appearance of the cis isomer from nearly pure trans in run 3. These changes are too great to be attributed to selective decomposition, since similar aliquot volumes, extraction volumes, and vpc injection volumes gave peaks of relatively constant height in all cases. It appears that $4 < K_{eq} < 15$, and more likely that K_{eq} lies between 7 and 10, according to the two best runs, 1 and 2. Note this indicates a relative composition, **7T**/**7C**, of from 87.5/12.5 to 91/9.

2-Hexen-4-yn-1-ol (22). Propynyllithium (48 g, 1.01 mol, handled under N_2) was dissolved in 330 ml of dry DMSO in a 1000-ml three-necked flask. The flask was fitted with an N_2 inlet, thermometer, magnetic stir bar, and a dropping funnel (side arm), the top of which was connected to a bubbler. Epichlorohydrin (43.5 g, 0.47 mol) was added slowly so as to maintain a moderate evolution of gas at a temperature of 42–48° (exothermic). After complete addition, the reaction mixture was heated at 50–55° for 1 hr and then at 55–60° for 30 min. The mixture was cooled to 15°, poured into ice water, and extracted six times with ether. The extract was washed with water and saturated NaCl solution and dried over Na_2SO_4. The ether was removed on the rotary evaporator, leaving 13.2 g of crude product, which was distilled (short path) at ~5 mm (77–87°) to give 11.36 g of the alcohol (82% pure by vpc on column S-1, 150°), yield 21% (corrected for purity). The spectral data were in accord with those reported.[16a,b]

3,4-Hexadien-1-ol (23) was prepared in 84% yield from **22** by the literature method.[15b,c] Its properties were in accord with those reported.

1-Iodo-3,4-hexadiene (21). Freshly purified triphenyl phosphite (10 g, 32 mmol) and methyl iodide (10 g, 70 mmol) were heated at 115° (magnetic stir bar, N_2 inlet at top of condenser, oil bath) for 23 hr. The mixture was cooled to room temperature giving a viscous red-orange liquid.[17] Dimethylformamide (30 ml) was added to dissolve the reagent. A solution of 3,4-hexadienol (**23**, 2.04 g, 90% pure, 30.7 mmol) in 30 ml of DMF was added. Vpc (S-1, 100°) showed the reaction complete in 1 min. After 0.5 hr, the mixture was poured into water and extracted twice with ether. The combined extracts were washed with water, 5% NaOH solution, water, 1 *N* HCl, water, saturated $NaHCO_3$ solution, and saturated NaCl solution and dried over Na_2SO_4. The solvent was removed on the rotary evaporator, and the residue was bulb-to-bulb distilled at ~2 mm to give 3.47 g of distillate (89% pure, column S-3, 100°), 78% yield. The iodide could be purified by careful vpc on column S-4 (150°, 90 ml of He/min) and column U-2 (160°, 90 ml of He/min). It was necessary to pretreat the columns periodically with ammonia in order to prevent decomposition of the iodide. Vpc analysis (T-1, 95°) of the neat purified iodide showed ~96% purity. Spectra were obtained on the purified sample: ir (microcavity) (no OH) 2980, 2960, 2920, 2900, 2850 (CH), 1960 cm^{-1} (strong C=C=C); nmr δ 1.55–1.7 (perturbed m, 3 H, H_d), 2.3–2.75 (complex m, 2 H, H_b), 3.14 (perturbed t of d, 2 H, J_{ab} = 6 Hz, plus further splitting, H_a), 4.7–5.3 (complex m, 2 H, H_c).



Solvolyses of 1-Iodo-3,4-hexadiene (21). The solvolyses in acetic acid with silver acetate, and with added sodium acetate or under homogeneous conditions were all done in the same manner as for the vinyl iodides, **7C** and **7T**. Each aliquot or run was analyzed twice, once on TCEP (T-1, 95°) and once on Carbowax (C-3, 110°). The repurified iodide was used in the solvolyses. The identity of the products rests on exact correspondence to the retention times of the products from solvolysis of the vinyl iodide, **7C**, and to the retention times of a mixture of **7C** and **7T**. In addition, iodides **7C** and **7T** were isolated from the acetolysis of homoallenic iodide **21** (0.5 g of **21**, excess AgOAc, 10-min reaction time) by vpc (column S-4, 160°, 90 ml of He/min). Further separation (column D-2, 100°) afforded pure samples whose ir spectra were identical with those of the authentic vinyl iodides, **7C** and **7T**.

3,4-Hexadienyl Acetate (18). The authentic homoallenic acetate was prepared in 96% yield by treating the alcohol **23** with acetic anhydride in pyridine.[15b,c] Preparative vpc (column D-2, 150°, 75 ml of He/min) gave material that was 99.8% pure. Its properties were in accord with those reported.[15b,c]

Acknowledgments. The authors are grateful for financial support of this work from the National Institutes of Health.