Table I. Products Formed in the Trifluoroethanolysis of (*Z*)- and (*E*)-3-Methyl-2-heptenyl 2-Trifluoromethanesulfonates ((*Z*)-**1** and (*E*)-**1**) at 60°

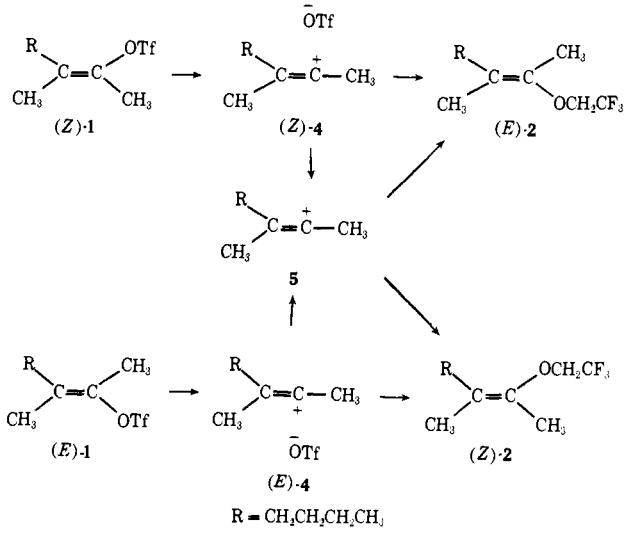
Substrate[d] (concn, *M*)	Buffer[a] concn, *M*	Products,[b] % (*Z*)-**2**	(*E*)-**2**	**3**	Ratio,[c] (*E*)-**2**/(*Z*)-**2**
(*Z*)-**1** (0.09)	0.18	15.2	70.6	14.2	4.6
(*Z*)-**1** (0.09)	0.36	15.6	69.1	15.3	4.4
(*Z*)-**1** (0.023)	0.045	15.8	71.2	12.9	4.5
(*E*)-**1** (0.09)[e]	0.18	23.9	58.6	17.5	2.4

[a] 2,6-Lutidine. [b] All products shown to be stable to the solvolysis conditions. Absolute yields were determined by vpc using an internal standard to be >95%. [c] Some irreproducibility in the percentage of **3** increases the error in the product percentages to about ±4%; however, the trifluoroethyl ether ratio is accurate to ±0.1. [d] No interconversion of (*Z*)-**1** and (*E*)-**1** is observed, indicating that ion-pair equilibration and internal return do not occur under these reaction conditions. [e] Product distribution listed for (*E*)-**1** is an average of two runs.

reported in Table I.[5] The data show unequivocally that, unlike systems in which the vinyl center is activated by cyclopropyl[1a,b] or aromatic[1c,d] substituents, triflates (*Z*)-**1** and (*E*)-**1** give rise to *different* ratios of products. Although the (*E*)/(*Z*) trifluoroethyl ether ratio is greater than 1 in both solvolyses, considerably more (*Z*)-(**2**) is produced from (*E*)-**1** than from (*Z*)-**1**. The mechanism of this reaction can therefore *exclusively* involve neither free vinyl cations nor direct, backside SN2 displacement. Presently, we feel that the data are most economically rationalized by the intervention of ion pairs (*Z*)-**4** and (*E*)-**4**, where the side of the molecule from which the triflate group is departing (Scheme I) is shielded to some extent from attack by solvent. However, our data do not distinguish between this mechanism and an alternative scheme involving ionization directly to **5** and concurrent backside attack by solvent on (*Z*)-**1** and (*E*)-**1**.[6]

These results have prompted us to further investigate the stereochemistry of cyclopropyl-stabilized systems, in order to carefully determine whether some small in-

Scheme I



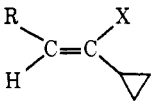
(6) For a discussion of attempts to settle this (still unsolved) problem in the solvolysis of aliphatic substrates, see (a) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 6031 (1969); (b) J. L. Kurz and J. C. Harris, *ibid.*, **92**, 4117 (1970); (c) D. J. Raber, J. M. Harris, R. E. Hall, and P. von R. Schleyer, *ibid.*, **93**, 4821 (1971).

Table II. Ratios of (*E*)- and (*Z*)-Vinyl Acetate Products Formed on Ionization of Alkyl-Substituted Cyclopropylvinyl Iodides in AgOAc–HOAc at 25°

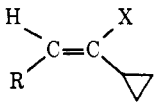
Substrate	Ratio,[a,b] *E*/*Z*
(*Z*)-**6**	1.21 ± 0.04
(*E*)-**6**	1.03 ± 0.02
(*Z*)-**8**	1.49 ± 0.02
(*E*)-**8**	1.38 ± 0.03

[a] Analyses performed on a 0.03 in. i.d. × 300 ft open tubular column coated with TCEP used in a Hewlett-Packard 5750 gas chromatograph equipped with an HP 3370 digital integrator. [b] Errors given as average deviation.

version component occurs in those cases as well. The use of electronic digital vpc integration and open tubular columns for very precise measurement of product distributions has revealed a previously undetectable[1a,b] stereoselectivity in the silver-catalyzed ionization of iodides (*Z*)-**6** and (*E*)-**6** in acetic acid (Table II). Even



(*Z*)-**6**, X = I; R = CH_3
(*Z*)-**7**, X = OAc; R = CH_3
(*Z*)-**8**, X = I; R = cyclopropyl
(*Z*)-**9**, X = OAc; R = cyclopropyl



(*E*)-**6**, X = I; R = CH_3
(*E*)-**7**, X = OAc; R = CH_3
(*E*)-**8**, X = I; R = cyclopropyl
(*E*)-**9**, X = OAc; R = cyclopropyl

in the case of dicyclopropyl-substituted iodides (*Z*)-**8** and (*E*)-**8**, repeated digital integration of a number of ionization runs reveals a small but identifiable inversion selectivity.

In summary, inversion is a prominent part of the stereochemistry of SN1 substitution of simple vinyl substrates, and even persists to some extent in cyclopropyl-activated systems. Our results suggest that careful investigation of other activated systems may also reveal small inversion components in those reactions. Finally, it seems clear that the overall net *retention* observed in the silver-catalyzed ionization of solvolytically *un*reactive vinyl halides in nonpolar, aprotic solvents[2] means that such ionizations are not in fact SN1 reactions, as has been claimed,[2] but must be proceeding by more complex mechanisms, perhaps involving catalysis and nucleophilic trapping by aggregated silver salts.

Acknowledgments. We are grateful for support of this work by the National Institutes of Health.

(7) (a) National Science Foundation Predoctoral Fellow, 1969–present; (b) National Science Foundation Predoctoral Fellow, 1968–1971. (c) Alfred P. Sloan Foundation Fellow, 1970–1972; Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1970–1975.

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Observation of Olefinic Cyclization at a Vinyl Cation Center. An Inversion Preference for Intramolecular Nucleophilic Substitution by a Double Bond

Sir:

We wish to report the first observation of olefinic cyclization[1] at a vinyl cation center. We have also in-

Scheme I

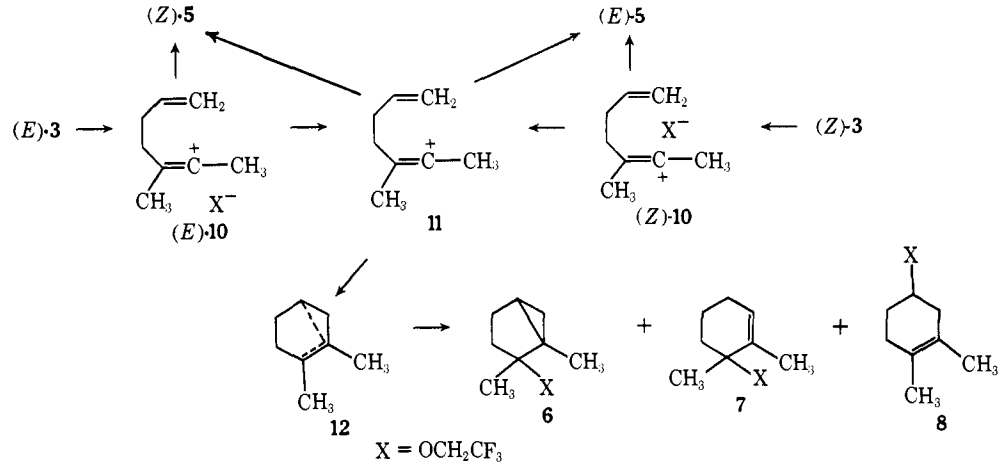
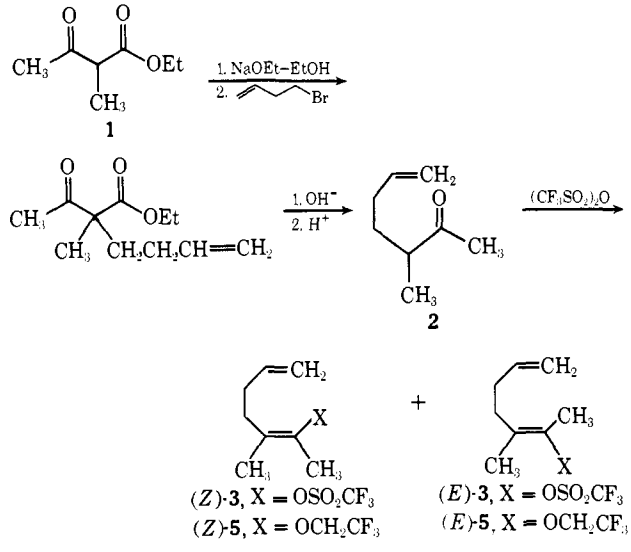


Table I. Products Formed on Trifluoroethanolysis[a] of (*Z*)- and (*E*)-2,6-Heptadienyl 2-Trifluoromethanesulfonates ((*Z*)-**3** and (*E*)-**3**) at 60°

Substrate	Reaction time, hr	Products,[b] %						Ratios	
		4	(*Z*)-**5**	(*E*)-**5**	**6**[d]	**7**	**8**	(*E*)-**5**/(*Z*)-**5**	(C/U)[c]
(*Z*)-**3**	36.5	12.9	15.2	52.0	6.3	8.3	5.4	3.42	0.250
(*Z*)-**3**	48	14.3	14.2	51.2	5.9	8.0	6.5	3.65	0.256
(*Z*)-**3**	71	14.8	14.4	49.3	5.8	9.2	6.7	3.44	0.276
(*E*)-**3**	37.5	12.0	22.6	33.3	9.4	12.4	10.3	1.47	0.473
(*E*)-**3**	49	9.9	22.9	33.5	9.9	13.1	10.7	1.46	0.508
(*E*)-**3**	72	8.5	22.9	33.9	8.8	13.9	12.1	1.48	0.535

[a] Solvolyses buffered with 2 equiv of 2,6-lutidine. Substrate concentration normally *ca.* 0.095 *M*. [b] Product percentages determined by integration (Hewlett-Packard Model 5750 gas chromatograph equipped with HP 5370 digital integrator) of solvolysis gc traces. Absolute yields were determined by vpc using internal standard to be >95%. [c] Ratio of total cyclized to total uncyclized products. [d] Stereochemistry undetermined.



vestigated the stereochemistry of this reaction and found a preference for inversion of configuration[2] at the cyclization origin.

Alkylation of commercially available[3] ethyl 2-methylacetoacetate (**1**) with 4-bromo-1-butene followed by saponification and decarboxylation gave[4] 3-methyl-6-hepten-2-one (**2**) in an overall yield of 24% based on **1**. Ketone **2** was converted to vinyl trifluoromethanesulfonates (triflates) (*Z*)-**3** and (*E*)-**3** (plus some terminal vinyl sulfonate) by treatment[5] with trifluoromethanesulfonic anhydride and 2,6-lutidine in methylene chloride at −20°. The triflates could be purified by careful gas chromatography (10 ft × 1/4 in. 10% DEGS on 60–80 Chromosorb P, 120°).

Solvolysis of (*Z*)-**3** and (*E*)-**3** in aqueous ethanol buffered with 2,6-lutidine led only to ketone **2** and 3-methyl-1,2-6-heptatriene (**4**). Solvolysis in buffered trifluoroethanol,[6] however, produced a more complex mixture containing, besides some allene **4**, solvolytic displacement products (*Z*)-**5** and (*E*)-**5** and cyclized trifluoroethyl ethers[4,7] **6**, **7**, and **8**. The product distributions are presented in Table I.

It is clear from inspection of Table I that the stereoisomeric triflates (*Z*)-**3** and (*E*)-**3** give rise to different ratios of vinyl trifluoroethyl ethers as well as to different proportions of cyclized products. As with their

(1) See, for example: (a) R. G. Lawton, *J. Amer. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *ibid.*, **87**, 1308 (1965); (c) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *ibid.*, **87**, 1314 (1965); (d) W. S. Trahanovsky and M. P. Doyle, *ibid.*, **89**, 4867 (1967); (e) W. D. Closson and D. Gray, *J. Org. Chem.*, **35**, 3737 (1970); (f) H. Felkin and C. Lion, *Tetrahedron*, **27**, 1375, 1387 (1971); (g) R. B. Clayton, *Quart. Rev., Chem. Soc.*, **19**, 168 (1965), and references cited therein; (h) E. E. van Tamelen, J. D. Willett, R. B. Clayton, and K. E. Lord, *J. Amer. Chem. Soc.*, **88**, 4752 (1966); (i) E. J. Corey, W. E. Russey, and P. R. Ortiz de Montellano, *ibid.*, **88**, 4750 (1966); (j) W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

(2) T. C. Clarke, D. R. Kelsey, and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 3626 (1972).

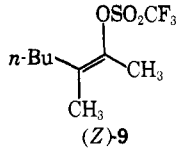
(3) Aldrich Company.

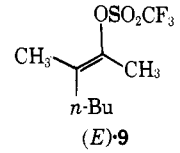
(4) All new compounds exhibited analytical data consistent with their assigned structures. Details will be reported in a full paper. Stereochemistries of vinyl triflates and ethers were assigned by the method used in the preceding paper (*cf.* footnote 4 of ref 2).

(5) A similar procedure has been reported: T. E. Dueber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. A. Imhoff, P. von R. Schleyer, K. Hummel, S. Bocher, C. E. Harding, and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **9**, 521 (1970).

(6) See ref 2, footnote 5.

(7) The products of cyclization were prepared independently by trifluoroethanolysis of 3,4-dimethylcyclohex-3-enyl *p*-toluenesulfonate (**8**, X = OTs). The sulfonate was prepared by Birch reduction of 3,4-dimethylanisole followed by acid hydrolysis, hydride reduction, and reaction of the unsaturated alcohol thus formed with *p*-toluenesulfonyl chloride. A detailed comparison of the trifluoroethanolysis of (*Z*)-**3**, (*E*)-**3**, and **8** (X = OTs) will be made in a full paper.


(Z)-9


(E)-9

6,7-dihydro analogs (*Z*)-**9** and (*E*)-**9**,[2] which cannot cyclize, there appears to be a significant inversion component in the solvolytic displacement reaction. Interestingly, the cyclization reaction also displays an inversion preference—more cyclization is observed in the isomer (*E*)-**3** in which the leaving group and remote double bond are trans to one another. While one might expect a similar (and perhaps even stronger) inversion preference in saturated cation cyclization systems,[1b-e] an experiment designed to determine this preference has not been reported. Once formed, the cyclized cation (whatever its structure[8]) appears to react independently of the stereochemistry of its acyclic precursor; the relative ratios of **6**, **7**, and **8** produced from (*Z*)-**3** and (*E*)-**3** are quite similar.

Because (1) both the inter- and intramolecular displacement processes are stereoselective rather than stereospecific, (2) (*Z*)-**3**, (*E*)-**3**, and their 6,7-dihydro analogs[2] react at qualitatively similar rates,[9] and (3) the cis/trans vinyl trifluoroethyl ratios are very similar to those observed[2] for (*Z*)-**9** and (*E*)-**9**, we feel that intervention of ion pairs is the most reasonable way of accounting for the results reported here.[1a,b] A mechanism is outlined in Scheme I; we assume that ion pairs (*Z*)-**10** and (*E*)-**10** undergo solvent trapping with inversion of configuration and competitive escape to the "free" ion **11**. The counterion in (*Z*)-**10** is properly oriented to prevent attack at C_2 by the remote double bond; in (*E*)-**10** this attack can occur without hindrance. This accounts for the excess cyclization observed from (*E*)-**3**. Vinyl cation **11** also gives rise to (*Z*)-**5**, (*E*)-**5**, and **12**, but its selectivity is presumably not influenced by the stereochemistry of either precursor.

Acknowledgments. We are grateful to the National Institutes of Health for financial support of this work.

(8) For convenience, a nonclassical "homoallylic" structure for cyclized cation **12** is employed in Scheme I.

(9) Half-lives for disappearance of each of the four vinyl triflates discussed have been estimated by monitoring each solvolysis by vpc. Relative rates calculated from these data are: (*Z*)-**3**, 1.0; (*E*)-**3**, 1.84; (*Z*)-**9**, 1.13; (*E*)-**9**, 2.12. The lack of evidence for concerted cyclization is consistent with the mechanism outlined in Scheme I.

(10) National Science Foundation Predoctoral Fellow, 1969–present.

(11) (a) Alfred P. Sloan Foundation Fellow, 1970–1972; (b) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1970–1975.

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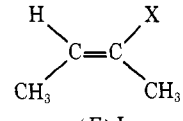
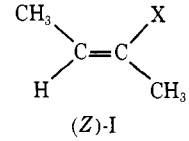
The Stereochemistry of Solvolysis of Simple Vinyl Trifluoromethanesulfonates (Triflates)

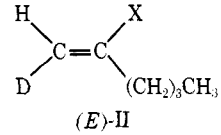
Sir:

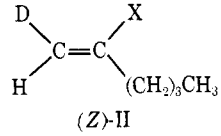
The solvolysis behavior of simple alkyl-substituted aliphatic and vinylic substrates provides an interesting contrast. Despite their lower stability relative to comparable aliphatic carbonium ions,[1] vinyl cations appear to be involved in typical solvolyses of substrates bearing only alkyl substituents.[1,2] Simple primary and secondary aliphatic substrates, on the other hand, prefer to react by SN2 or ion-pair SN2 pathways with considerable solvent assistance[3] and complete inversion.[3,4] The available evidence for a predominate SN1 rather than SN2 mechanism for alkyl vinyl solvolyses is somewhat indirect, *e.g.*, the observation of rearrangements[5a,b] and the lack of rate depressions of cycloheptenyl and cyclooctenyl triflates (relative to acyclic models), despite the impossibility of rear-side attack.[5c] Recent theoretical calculations emphasize the relative difficulty of SN2 displacements in vinyl systems.[6]

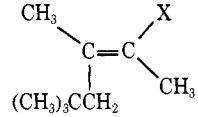
We have now studied the stereochemistry of buffered acetolysis of the (*Z*) and (*E*) isomers[7] of three simple vinyl triflate systems, I-OTf–III-OTf.[2] Although net inversion predominated in most, but not all of the cases studied, the results confirm the essential SN1 character of vinyl solvolyses.[2,5]

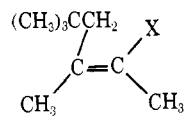

(E)-I


(Z)-I


(E)-II


(Z)-II


(E)-III


(Z)-III

The preparation of (*E*)-I-OTf and (*Z*)-I-OTf by addition of trifluoromethanesulfonic acid to 2-butyne (glc separation) has already been reported.[5d] The prepara-

(1) For recent reviews, see: M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970); H. G. Richey and J. M. Richey in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1970, p 899; Z. Rappoport, T. Bässler, and M. Hanack, *J. Amer. Chem. Soc.*, **92**, 4985 (1970); G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, **9**, 185 (1971).

(2) The case for vinyl cation intermediates from substrates bearing stabilizing aryl, vinyl, or cyclopropyl substituents is even stronger.[1] Stereochemical studies on such substrates have indicated that complete racemization occurs in the solvolysis of these compounds. See: (a) Z. Rappoport and Y. Apeloig, *Proc. Israel J. Chem.*, **7**, 34 (1969); (b) Z. Rappoport and Y. Apeloig, *J. Amer. Chem., Soc.*, **91**, 6734 (1969); (c) D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970); (d) D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1941 (1971); (e) however, *cf.* G. F. P. Kernaghan and H. M. R. Hoffman, *ibid.*, **92**, 6988 (1970); (f) during the course of this work we became aware of a similar study by T. C. Clarke, D. R. Kelsey, and R. G. Bergman, *ibid.*, **94**, 3626 (1972). Triflates similar to (*E*)-III and (*Z*)-III were solvolyzed in trifluoroethanol and results analogous to those we found were obtained.

(3) See a recent review: D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972).

(4) (a) A. Streitwieser, Jr., and T. D. Walsh, *J. Amer. Chem. Soc.*, **87**, 3686 (1965); (b) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *ibid.*, **87**, 3682 (1965); (c) H. Weiner and R. A. Sneen, *ibid.*, **87**, 287 (1965).

(5) (a) A. G. Martinez, M. Hanack, R. H. Summerville, P. v. R. Schleyer, and P. J. Stang, *Angew. Chem., Int. Ed. Engl.*, **9**, 302 (1970); (b) 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); (c) W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *ibid.*, **93**, 1513 (1971); (d) P. J. Stang and R. H. Summerville, *ibid.*, **91**, 4600 (1969).

(6) P. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1953 (1971).

(7) J. E. Blackwood, C. L. Gladys, K. I. Loening, A. E. Petrarca, and J. E. Rush, *ibid.*, **90**, 509 (1968).