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(19) NOTE ADDED IN PROOF. T. Sasaki, S. Eguchi, T. Kiriyama, and Y. Sakito, *J. Chem. Soc., Chem. Commun.*, 725 (1974), have recently reported the PES of three bridgehead diphenyl analogs of **5**, R,R = H,H; R,R = O; and R,R = H,OH. Their assignment and the n_-,n_+ splitting of 1.06 eV for diphenyl **5**, R,R = H,H, agree well with ours for for **5**, R,R = $(CH_2)_5$. For our work on the first two compounds, see the Ph.D. Thesis of J.M.B.

Stereochemistry of Olefinic Cyclization and Solvolytic Displacement at Vinyl Carbon

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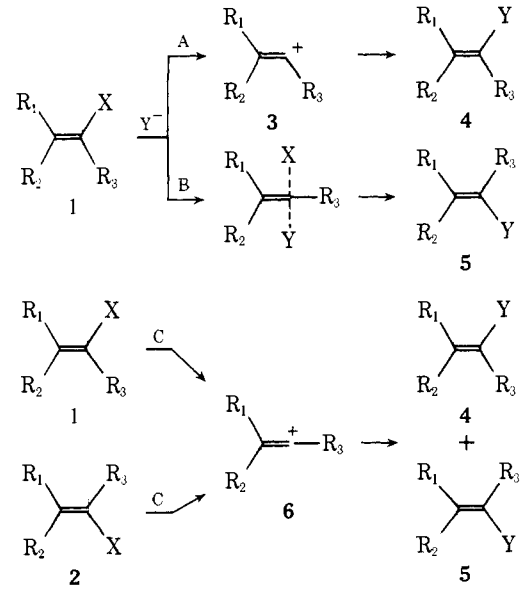
Abstract: In order to determine the stereochemistry of solvolytic displacement and intramolecular nucleophilic substitution by a remote double bond at a vinyl center, the synthesis and solvolysis in trifluoroethanol of (*Z*)- and (*E*)-3-methyl-2,6-heptadien-2-yl trifluoromethanesulfonates (**9Z** and **9E**) and (*Z*)- and (*E*)-3-methyl-2-hepten-2-yl trifluoromethanesulfonates (**30Z** and **30E**) were undertaken. In the case of **9Z** and **9E**, in addition to 3-methyl-1,2,6-heptatriene and the products of solvolytic displacement, four cyclized trifluoroethyl ether products were formed. These four products were also generated in the trifluoroethanolysis of 1,2-dimethyl-1-cyclohexen-4-yl tosylate. Net inversion of stereochemistry was observed in both the solvolytic displacement and cyclization processes in the vinyl triflates. Solvolysis of **30Z** and **30E** also resulted in net single inversion of the vinyl trifluoroethyl ether products. These results are explained in terms of competitive attack on the initially formed ion pairs and on free vinyl cation intermediates.

The stereochemistry of solvolytic displacement at a saturated (sp^3) carbon center has been the subject of extensive research over the past 4 decades. One of the more important tools in the demonstration of the importance of the SN1 mechanism[3a] in many of these displacements has been the use of optically active substrates whose absolute configuration could be correlated with the configurations of the solvolytic products. In the solvolyses of optically active substrates which would be expected to lead to highly stabilized carbonium ions on ionization, the observation of racemic products provided striking confirmation of the predictions of the simple SN1 mechanism.[3] However, the reactions of substrates leading to less stable carbonium ions have played an even more important role in the evolution of a more detailed understanding of the ionization process. The observation of significant amounts of inversion at the carbon center in the solvolyses of these substrates prompted the elaboration of the SN1 mechanism to include such features as solvent participation and ion pair formation.[3b,c]

The expectation that comparable experiments might provide valuable insight into the nature of solvolytic displacement at a vinyl (sp^2) center has only recently begun to be realized. Undoubtedly, this delay in the investigation of vinyl systems was due in large part to the presumed inaccessibility of dicoordinated carbonium ions (vinyl cations) under reasonable solvolytic conditions. However, beginning with the demonstration of Grob and Cseh in 1964 that certain α-bromostyrenes solvolyze *via* vinyl cations in 80% aqueous ethanol at 100°,[4] a convincing body of evidence has been presented to show that vinyl cations can be generated under relatively mild conditions from a variety of precursors.[5] The SN1 nature of these processes has been established quite conclusively.[5,6]

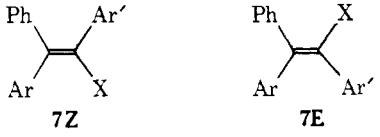
The planar nature of the ethylenic system of course rules out the use of chirality as a tool in the investigation of the displacement stereochemistry at a vinyl center. Instead, the relationships of the leaving group and the displacing nucleophile to the remote substituents on the double bond must be employed. Scheme I depicts the three extreme possibilities for the stereochemical outcome of displacement at a vinyl center. Retention of configuration, shown as path A, could presumably arise by the formation and trapping of a configurationally stable bent vinyl cation **3** (or, alternatively, by participation of a migrating R_2, leading to a bridged ion). Direct backside participation by the nucleophile or backside attack on an ion pair formed by the initial ionization of **1** would lead to the inverted product **5** (path B). The stereochemical randomization shown in path C would result from the intermediacy of either a linear vinyl cation (**6**) or a rapidly equilibrating pair of bent vinyl cations. The observation of the same ratio of products **4** and **5** from either starting isomer becomes the vinyl equivalent of the racemization process observed at tetrahedral centers.

Scheme I



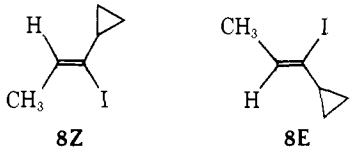
The results in saturated systems suggest, of course, that the above scheme is an oversimplification.[3] Combinations of the various possibilities would lead to varying amounts of retention and inversion from each starting isomer. In particular, formation of a bent cation which loses its configuration at a rate competitive with trapping would produce net retention of configuration, that is, an excess of product **4** from **1** and an excess of **5** from **2**. Net inversion could result from competitive solvent trapping of both the initial ion pair and a free linear cation.

At the time we began the work reported here, the results of such stereochemical studies at vinyl centers had been reported only for substrates leading to highly stabilized vinyl cations. Rappoport and Apeloig have shown that both **7Z** and **7E** give rise to identical product distributions under a



X = Cl, Br

variety of solvolytic conditions.[6b] Initial results suggested that the cyclopropyl stabilized systems **8Z** and **8E** also lead



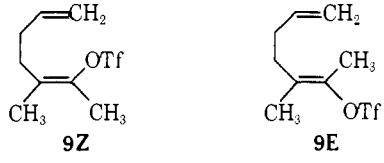
to the same product distribution on ionization.[6c,d] Thus, in direct analogy with the results in saturated systems, highly activated vinyl substrates are found to undergo extensive or complete "racemization" on solvolysis. Extension of this comparison with saturated systems, however, suggests that the above results cannot be generalized to less activated vinyl systems and that the examination of substrates leading to less stable vinyl cations should, in fact, provide additional insight into the detailed nature of the SN1 process at an sp^2 center.[7]

The examination of reactions where a remote double bond within the substrate acts as a nucleophile, either in concert with the initial ionization or in a subsequent step, has also led to an increased understanding of the fundamental processes involved in the SN1 reaction at saturated carbon centers.[8] Moreover, these cyclizations have proved to have great synthetic value, as evidenced by the now familiar biogenetically patterned cyclizations of polyolefinic substrates to give multicyclic products.[9] Stereochemically one would expect a high degree of inversion at the ionizing center in those cases where participation of the double bond has been shown to be important in the ionization step; surprisingly, experimental verification of this prediction has so far been reported in only one case.[8i] Similar experiments in vinyl systems have again been hampered until recently by the lack of suitable vinyl cation precursors.

In this work we present an investigation of the stereochemistry of displacement at a simple alkyl substituted center both by solvent and, potentially more useful synthetically, by a remote double bond.

Results

Synthesis and Solvolysis of (*Z*)- and (*E*)-3-Methyl-2,6-heptadien-2-yl Trifluoromethanesulfonate (9Z and 9E). Use of the very reactive[10] trifluoromethanesulfonate (triflate) leaving group has been shown to be the method of choice for the generation of alkyl substituted vinyl cations under solvolytic conditions.[5b,11] Thus, in order to study both the stereochemistry of solvolytic displacement and the preferences for cyclization at a vinyl center, vinyl triflates **9Z** and **9E** were chosen for our initial studies. The inclusion of the



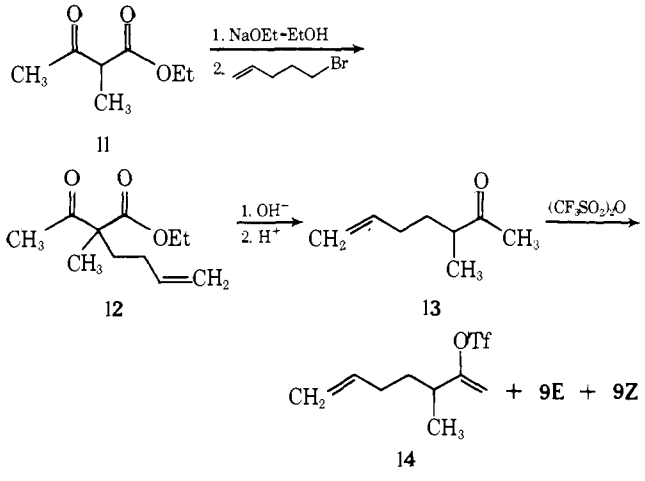
Tf = SO_2CF_3

methyl group at C3 was prompted by the observation of Stang and Summerville that although **10E** solvolyzes *via* a vinyl cation mechanism in 80% aqueous ethanol at 76°, **10Z**

undergoes a concerted trans elimination to give dimethylacetylene as the only product. Since the acetylene product obviously provides no stereochemical information, the methyl group was used to block the elimination process in **9Z**.

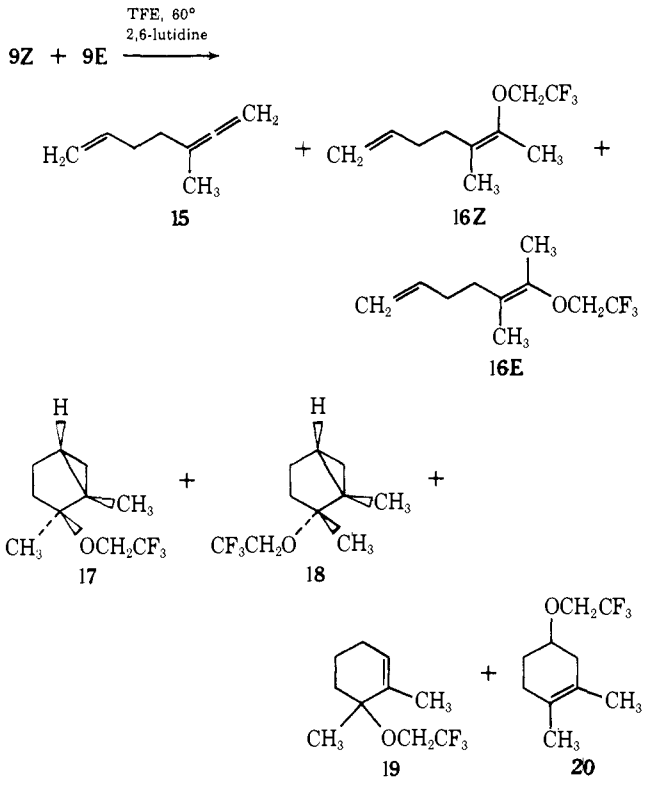
The synthesis of **9Z** and **9E** is shown[12] in Scheme II. (See Experimental Section for details.)

Scheme II



The stereochemical assignments of **9Z** and **9E** were based primarily on β-methyl group chemical shifts[2,11] and homoallylic coupling constants[13] (see Experimental Section) in the nmr spectra of these materials. A preliminary solvolysis of a mixture of **9Z** and **9E** in 80% aqueous ethanol at 70° produced only ketone **13** and a product identified as 3-methyl-1,2,6-heptatriene (**15**) on the basis of its characteristic allene infrared absorption at 1958 cm^{-1}. Since these results provided no stereochemical information, the reaction was next attempted in 2,2,2-trifluoroethanol, a solvent of high ionizing power but low nucleophilicity which has been shown in the past to provide enhanced cyclization in other systems.[8e,f,14] Solvolysis of a mixture of **9Z** and **9E** in absolute trifluoroethanol buffered with 2,6-lutidine provided a mixture of products including allene **15**, the solvolytic displacement products **16Z** and **16E**, and the cyclized trifluoroethyl ethers **17, 18, 19,** and **20** (Scheme III). These products were all identified on the basis of their infrared and proton nmr spectra.

Scheme III



The stereochemistries of the isomeric vinyl trifluoroethyl ethers **16Z** and **16E** were again assigned on the basis of β-methyl chemical shifts and homoallylic coupling constants,[13] as well as by the trifluoroethoxy group deshielding of the β-methyl[15] observed for **16E**. The identification of the isomeric bicyclo[3.1.0]hexane derivatives **17** and **18** was also accomplished by nmr.[16] (See Experimental Section.) Products **16Z** and **18** eluted as a single peak under the analytical conditions chosen and the sum of these compounds is shown as a single entry in Table I. Vpc isolation and nmr examination of this peak after completion of the solvolyses allowed the complete product distribution analysis shown in Table II; the ratio of the two vinyl ether products and the percentage of cyclized products from each starting isomer are also shown.[17]

No interconversion of the vinyl triflates could be detected, although the contamination of each starting material with approximately 4% of the other isomer might have masked a small degree of interconversion. In particular, no accumulation of the slower reacting isomer **9Z** was observed during the solvolysis of **9E**. The apparent interconversion of the cyclized products was confirmed in the solvolysis of 1,2-dimethyl-1-cyclohexen-4-yl tosylate (**26**) described below.

Scheme IV

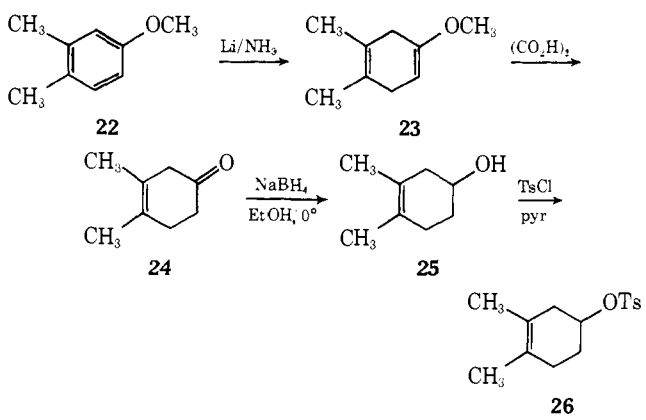


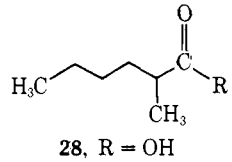
Table I. Products Formed in Trifluoroethanolysis[a] of (*Z*)- and (*E*)-3-Methyl-2,6-heptadien-2-yl Trifluoromethanesulfonates (**9Z** and **9E**) at 60°

Substrate	Reaction time, hr	Products, %[b] 15	16E	(16Z + 18)[c]	17	19	20
9Z	36.5	12.7	51.3	15.0	7.4	8.2	5.4
9Z	48	14.1	50.5	14.0	7.0	7.9	6.4
9Z	71	14.6	48.6	14.2	6.8	9.1	6.6
9E	24	12.9	33.8	23.4	11.3	10.6	8.0
9E	37.5	11.8	32.7	22.2	11.0	12.2	10.2
9E	49	9.8	33.2	22.8	10.9	13.0	10.6
9E	72	8.4	33.4	22.6	10.2	13.7	12.0

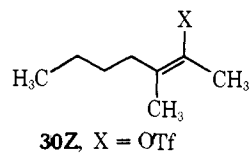
[a] Solvolyses buffered with 2 equiv of 2,6-lutidine. Substrate concentration normally *ca.* 0.095 *M*. [b] Product percentages determined by direct integration of solvolysis vpc traces (Hewlett-Packard Model 5750 gas chromatograph equipped with HP 3370A digital integrator). Absolute yields determined by vpc using internal standard to be >95%. [c] Eluted as single peak; see Table II for relative amounts of **16Z** and **18** after 72 hr as estimated by nmr.

Synthesis and Solvolysis of 1,2-Dimethyl-1-cyclohexen-4-yl Tosylate (26). The independent preparation of the cyclized products obtained in the trifluoroethanolyses of **9Z** and **9E** was accomplished by the solvolysis of tosylate **26**, whose synthesis is shown in Scheme IV. Tosylate **26** was then solvolyzed in buffered trifluoroethanol at 60°. In addition to traces of unidentified olefinic products the same cyclic trifluoroethyl ethers were obtained as in the solvolysis of **9Z** and **9E**. Although reaction of the tosylate was over well within the first hour, the reaction was allowed to stir for an additional 65 hr at 60° to provide information on the product stabilities under the reaction conditions. The change of the product distribution with time is shown in Table III. The mass balance suggests that these changes are due to interconversion of the product isomers rather than selective destruction of products **17** and **18**. Thus **17** and to a lesser extent **18** are gradually converted to **19** and **20** during the course of the reaction.

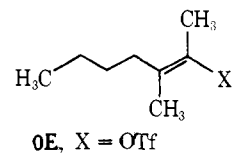
Synthesis and Solvolysis of (*Z*)- and (*E*)-3-Methyl-2-hepten-2-yl Trifluoromethanesulfonate (30Z and 30E). In order to determine whether the different product ratios observed in the reactions of **9Z** and **9E** were generally characteristic of the solvolyses of isomeric alkyl substituted vinyl triflates, or whether the differences were in fact due to some selective interaction with the remote double bond, the solvolyses of triflates **30Z** and **30E** were also undertaken. Since commercial samples of 3-methyl-2-heptanone (**29**) proved to be



28, R = OH
29, R = CH_3



30Z, X = OTf
32Z, X = $OCOCH_3$
33Z, X = $OSi(CH_3)_3$
37Z, X = OCH_2CF_3



0E, X = OTf
2E, X = $OCOCH_3$
33E, X = $OSi(CH_3)_3$
37E, X = OCH_2CF_3

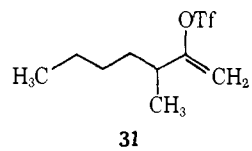


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Table II. Product Distribution on Trifluoroethanolysis[a] of (*Z*)- and (*E*)-3-Methyl-2,6-heptadien-2-yl Trifluoromethanesulfonate (**9Z** and **9E**) after 72 hr at 60°

Substrate	Products, %[b]							16E/16Z	% cyclized products[c]
	15	**16E**	**16Z**	**17**	**18**	**19**	**20**		
9Z	14.6	48.6	9.9	6.8	4.3	9.1	6.6	4.9	0.27
9E	8.4	33.4	16.2	10.2	6.4	13.7	12.0	2.1	0.42

[a] Solvolyses buffered with 2 equiv of 2,6-lutidine. Substrate concentration normally *ca.* 0.095 *M*. [b] See footnotes *b* and *c*, Table I. [c] Sum of **17**, **18**, **19**, and **20**.

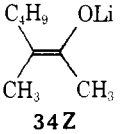
Table III. Product Distribution in the Trifluoroethanolysis[a] of 1,2-Dimethyl-1-cyclohexen-4-yl Tosylate (**26**) at 60°

Time, hr	Product, %[b]			
	17	**18**	**19**	**20**
3	37.6	13.7	19.5	29.2
66	14.6	11.4	32.4	41.6

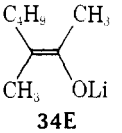
[a] Solvolyses buffered with 2 equiv of 2,6-lutidine. Substrate concentration 0.1 *M*. [b] Product percentages determined by direct integration of solvolyses vpc traces.

highly contaminated with isomeric ketones,[19] the reaction of methyllithium with 2-methylhexanoic acid (**28**) was instead employed for the generation of **29**. A mixture of vinyl triflates **30Z**, **30E**, and **31** was then obtained by reaction of **29** with trifluoromethanesulfonic anhydride; **30Z** and **30E** were isolated in >96% purity by preparative vpc. The stereochemistries of **30Z** and **30E** were assigned in the same manner as those of **9Z** and **9E** (*vide supra*).

Attempts to provide corroborative information on the stereochemistries of the vinyl triflates by use of the europium shift reagent Eu(fod)$_3$[20,21] failed, apparently because of a lack of complexation between the shift reagent and the vinyl triflates. However, an alternate approach did provide additional evidence for the stereochemical assignments of **30Z** and **30E**. Vinyl acetates **32Z** and **32E** were prepared from ketone **29** by the procedure of House, *et al.*[22] The stereochemical assignments of the vinyl acetates were again made by nmr[23] and confirmed by the use of Eu(fod)$_3$ according to the method of Kelsey.[24] The trimethylsilyl enol ethers **33Z** and **33E** were then prepared from ketone **29** by another of House's procedures.[25] The initial stereochemical assignments of **33Z** and **33E** based on nmr were confirmed by conversion of **33Z** to vinyl acetate **32Z** and of **33E** to vinyl acetate **32E**. In each case the stereospecific transformation was accomplished by quenching in acetic anhydride enolates **34Z** and **34E** formed respectively by the cleavage



34Z

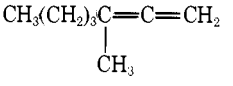


34E

of silyl ethers **33Z** and **33E** with methyllithium. (The trimethylsilyl enol ethers also failed to show any interaction with the Eu(fod)$_3$ shift reagent.)

The enolates were treated with trifluoromethanesulfonic imidazolide[26] (**35**) in an attempt to generate the vinyl triflates **30Z** and **30E**. Unfortunately, this procedure was not as stereospecific as the acetate formation. **34Z** gave a 70:30 mixture of **30Z** and **30E**, respectively, and **34E** led to a 31:69 mixture of **30Z** and **30E**; the source of the stereochemical crossover is not clear. Although the lack of complete stereospecificity makes these results less definitive than might have been hoped, the observed stereoselectivity in the formation of **30Z** and **30E** does support the assigned stereochemistries.

Vinyl triflates **30Z** and **30E** were then subjected individually to solvolysis at 60° in trifluoroethanol buffered with 2,6-lutidine. Only three products were formed in these reactions: allene **36** and the two solvolytic displacement products **37Z** and **37E**. The products were identified on the basis of their infrared and nmr spectra. Product **36** exhibited a characteristic allene ir absorption at 1960 cm^{-1} and an nmr spectrum consistent with the structure shown. Once again,



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vinyl trifluoroethyl ethers **37Z** and **37E** fail to form complexes with Eu(fod)$_3$.

Table IV. Product Distributions in the Trifluoroethanolysis[a] of (*Z*)- and (*E*)-3-Methyl-2-hepten-2-yl Trifluoromethanesulfonate (**30Z** and **30E**) at 60° as a Function of Time

Substrate	Reaction time, hr	Product, %[b]			Ratio (37E/37Z)[c]
		36	**37Z**	**37E**	
30Z	12.5	14.9	14.8	70.4	4.8
30Z	85	13.3	15.4	71.4	4.6
30Z[d]	72	15.0	15.3	69.6	4.5
30E	12.5	18.9	23.5	57.6	2.4
30E	85	14.4	24.9	60.8	2.4
30E[d]	72	15.1	24.6	60.4	2.5

[a] Solvolyses buffered with 2 equiv of 2,6-lutidine. Substrate concentration normally *ca.* 0.09 *M*. [b] Product percentages determined by direct integration of solvolysis vpc traces (Hewlett-Packard Model 5750 gas chromatograph equipped with HP 5370A digital integrator). [c] Some irreproducibility in the percentages of **30** increases the error in the product percentages to ±3%; however, the trifluoroethyl ether ratio is accurate to ±0.1. [d] Duplicate runs; absolute yields determined by vpc using an internal standard to be >95%.

Table V. Product Distributions in the Trifluoroethanolysis[a] of (*Z*)-3-Methyl-2-hepten-2-yl Trifluoromethanesulfonate (**30Z**) at 60° at Varying Concentrations

30Z concn (*M*)	Buffer[b] concn (*M*)	Product, %			(37E/37Z)
		36	**37Z**	**37E**	
0.09	0.18	13.3	15.4	71.4	4.6
0.023	0.046	12.5	15.9	71.6	4.5
0.09	0.36	12.1	16.2	71.7	4.4

[a] See footnotes *b–d*, Table IV. [b] 2,6-Lutidine.

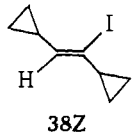
The product distributions in the solvolysis of **30Z** and **30E** are shown in Table IV as a function of time. Aside from some irreproducibility in the percentages of allene **36**, it can be seen that the product distributions do not change significantly with time; in particular, the constancy of the ratios of **37E** to **37Z** suggests that no interconversion of the trifluoroethyl ether products occurs. The ratio of **37E** to **37Z** has also been shown to be insensitive to variations in the concentrations of substrate and buffer (Table V). Again no interconversion of vinyl triflate isomers **30Z** and **30E** could be detected.

Discussion

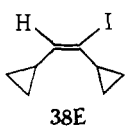
As mentioned earlier, previous studies in more activated vinyl systems showed stereochemical randomization on sol-

volysis of either of the geometrically isomeric starting materials.[5b,6c,d] These results are best explained by the assumption that both reactions proceed through a common vinyl cation intermediate. Examination of the data presented above, however, suggests that the case is more complex for solvolyses proceeding through simple alkyl substituted vinyl cations.[27] In particular, systems **9** and **30** both show significant amounts of inversion at the vinyl center in the solvolytic displacement process. Although the (*E*)/(*Z*)-trifluoroethyl ether ratio is always greater than unity in both systems, considerably more (*Z*)-trifluoroethyl ether is produced from the *E* vinyl triflate than from the *Z* triflate.

In light of the above observations Kelsey has reexamined the stereochemistry of the silver acetate catalyzed ionization of the *Z* and *E* isomers of 1-cyclopropyl-1-iodopropene (**8Z** and **8E**) using more sophisticated analytical techniques than were previously available.[2a] Earlier results had suggested that both isomers gave rise to the same distribution of solvolytic products.[6c,d] The more precise measurements, however, revealed the presence of an inversion component in these systems as well. Moreover, investigation of the dicyclopropyliodoethylenes **38Z** and **38E** demonstrated that these compounds also show a small but detectable preference for inversion.[2a] Thus, even in these systems leading to highly stabilized vinyl cations net inversion of stereochemistry may be observed on solvolysis. These results suggest that careful investigation of other activated systems[5b] may reveal a similar stereochemical preference.



38Z

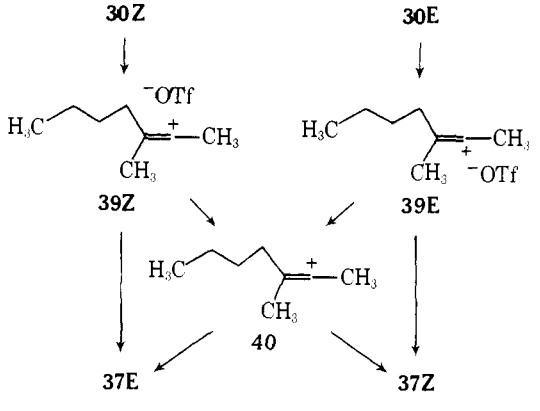


38E

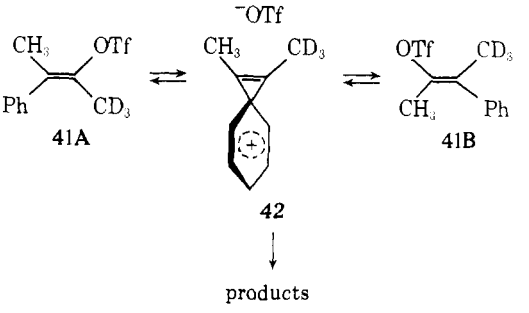
The observation of partial but not complete inversion of stereochemistry obviously rules out the exclusive involvement of either free vinyl cations or direct SN2 displacement by solvent in these systems. Although we have obtained no direct evidence for their involvement.[27c] we presently feel that these results are best rationalized by the intervention of ion pairs as shown for vinyl triflates **30Z** and **30E** in Scheme V. In analogy to the results in displacements at saturated carbon centers,[3] the presence of the triflate counterion in ion pairs **39Z** and **39E** would be expected to shield the side of the molecule from which the triflate departed. Competition between solvent trapping of ion pairs **39Z** and **39E** and the free vinyl cation **40** would lead to the net inversion of configuration observed.

There is no reason to suspect that ion pairing should play a less important role in these ionizations than in comparable reactions at saturated centers. Other authors have also invoked ion pairs to explain results observed in vinyl systems.[27] In a recent paper, Stang and Dueber suggested that internal return from the intimate ion pair **42** is responsible for the presence of some of the rearranged isomer **41B** in reisolated samples of partially solvolyzed **41A** (Scheme VI).[15]

Scheme V



Scheme VI

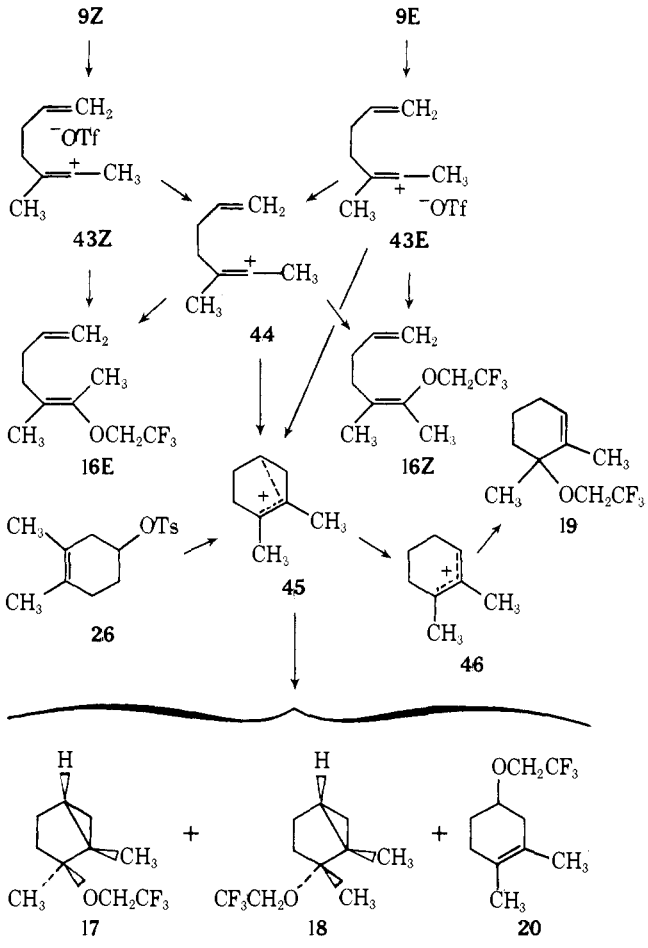


An alternate mechanistic possibility which would also result in net inversion involves direct ionization to the free vinyl cation **40** and competitive SN2 attack by solvent on the vinyl triflates. Although considerable evidence has been presented elsewhere for the SN1 nature of the reaction of vinyl substrates under the solvolytic conditions employed here,[5,11] the distinction between solvent trapping of an ion pair and direct backside attack by solvent on the starting material is not easily determined experimentally. Indeed, this problem has still not been fully resolved in saturated systems.[29] However, there are some considerations which militate against the SN2 reaction at a vinyl center. In recent theoretical calculations, Kelsey and Bergman have demonstrated the unfavorableness of SN2 attack at a vinyl carbon relative to a saturated carbon.[30] The observation of extensively rearranged products in certain vinyl triflate solvolyses has been taken as evidence for the ionic nature of the reaction.[31] Also, cycloheptenyl and cyclooctenyl triflates do not show any substantial rate depression over *cis*-2-buten-2-yl triflate at 100° in 50% aqueous ethanol.[32] In both of these systems backside attack would be expected to be severely hindered. Although none of these results strictly precludes the possibility of SN2 attack by solvent in the present system, they do make it seem less plausible than the ion pair explanation.

It is interesting to note that not only the solvolytic displacement process but also the cyclization reactions of vinyl triflates **9Z** and **9E** show a preference for inversion. More cyclized product is obtained from **9E** where the remote double bond is trans to the triflate function than from **9Z** where they are cis (Table II). This can again be explained by the intervention of ion pairs as shown in Scheme VII. In ion pair **43Z** the vinyl cation is shielded by the triflate counterion from nucleophilic attack by the remote double bond; thus the cyclized products from **9Z** must arise from the free vinyl cation **44**. In the reaction of **9E**, however, both ion pair **43E** and the free ion **44** may undergo cyclization.

The observation of more cyclization from **9E** than **9Z** raises the question of direct double bond participation in the ionization process, a phenomenon which has been shown to be important in cyclization reactions at saturated centers.[8] One criterion for such participation in the present case would be the observation of a kinetic acceleration in **9E** relative to its 6,7-dihydro analog **30E**. Qualitative estimates of the relative reaction rates show, however, that all four vinyl triflates react at very similar rates and that **30E** in fact reacts somewhat faster than **9E**; the estimated relative rates for **9Z, 9E, 30Z,** and **30E** are 1.0, 1.8, 1.8, and 3.0, respectively. This lack of evidence for concerted cyclization is consistent with the mechanism outlined in Scheme VII.

Scheme VII



The cyclized products may all be explained in a relatively straightforward manner. Cyclization of vinyl cation **44** (or **43E**) would lead to cation **45**, which for the sake of convenience is represented here as having a "homoallylic" structure. Solvent trapping of **45** would lead directly to products **17**, **18**, and **20**, while hydride shift to give allylic cation **46** followed by trapping at the tertiary center gives product **19**. The observation of the same products on solvolysis of tosylate **26**, which would be expected to lead to ion **45** directly, provides additional evidence for the proposed pathway.

Although it would be interesting to compare the ratios of cyclic products arising from the vinyl triflate cyclizations and from tosylate **26**, the gradual conversion of **17** and **18** to **19** and **20** during the course of the reaction make a quantitative comparison of product distributions somewhat difficult. Also since under the analytical conditions used, product **17** appears in the end of the solvent tail while product **18** is coeluted with **16Z** (*vide supra*), complete analysis of product distributions at low conversion was not possible. However, it is clear that throughout the reaction the product distribution from tosylate **26** contains relatively more of product **20** than does the distribution from the triflate cyclizations. This excess of direct displacement product might be attributable to a small amount of backside participation by the weakly nucleophilic[8e,f] trifluoroethanol solvent in the ionization of **26**. It may be noted that to the extent that cation **45** does have homoallylic character arising from direct participation of the double bond in the initial ionization step, product **20** would be expected to be formed with retention of configuration at the displacement center in analogy with the results obtained by Shoppee in the solvolyses of Δ^5-cholestene derivatives.[33] No suitable stereochemical test of this possibility has yet been made, although direct participation by the double bond has been implicated in the parent system (4-tosyloxycyclohexene) by the moderate acceleration of its solvolysis rate relative to a saturated analog.[34]

The synthetic possibilities of cyclization to a vinyl cation center have already been exploited by Johnson, *et al.*[35c] Several examples of acetylene participation in polyolefinic cyclizations have also been presented.[35]

Finally, it is of interest to compare the results of the present study with those obtained by Kernaghan and Hoffmann for the silver trifluoroacetate catalyzed ionization of the *Z* and *E* isomers of 1-bromo-1-phenylpropene in isopentane at 25°.[36] Under these heterogeneous conditions, the trifluoroacetate substitution products are formed with *net retention* of configuration. It was suggested by the authors that interactions with the surface of the silver salt might be responsible for these results. In any event it is clear that these reactions are fundamentally different from the true solvolyses of vinyl triflates such as those carried out here in trifluoroethanol; thus it is not particularly surprising that different stereochemical outcomes are observed.

The reaction of (*E*)-1-bromo-1-phenylpropene with silver trifluoroacetate under *homogeneous* conditions (diethyl ether at 25°) was also reported to proceed with net retention of configuration.[36] Kernaghan and Hoffmann chose to explain this observation by a double inversion mechanism involving nucleophilic participation by solvent to form an intermediate oxonium ion. However, this mechanism does not easily explain the lack of reactivity under these conditions of the *Z* isomer, which would be expected to show less steric hindrance to backside attack by solvent. The alternate possibility of nucleophilic trapping of ion pairs by aggregated silver salts has been suggested previously to account for the small degree of ion pair return product in the homogeneous silver acetate catalyzed solvolyses of cyclopropyl substituted vinyl iodides **8Z** and **8E** in acetic acid.[7] The lack of reactivity of (*Z*)-1-bromo-1-phenylpropene is still puzzling, however.

Experimental Section

General Procedure. Infrared spectra were obtained as CCl_4 solutions on a Perkin-Elmer 257 grating infrared spectrophotometer. Nmr spectra were obtained on either an A-60-A or a T-60 Varian Associates analytical nmr spectrometer as carbon tetrachloride or deuteriochloroform solutions with tetramethylsilane (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; splitting; integration in units of H; and assignment. Qualitative and preparative vapor phase chromatography (vpc) was performed on a Varian Aerograph 90-P3 instrument equipped with a thermal conductivity detector and helium carrier gas. Except when chromatographing sensitive materials, injector and detector temperatures were maintained at 200–210°. Analytical vpc was carried out on a Hewlett-Packard 5750 instrument with a flame ionization detector and Hewlett Packard 3370A integrator. The injector temperature was maintained at approximately 200° and the detector at 340°; the following gas pressures were used (lb/in.^{2}): He, 40; H_2, 14; air, 30. The following vpc columns were used: column A, 10 ft × ¼ in. 10% DEGS on 60/80 Chromosorb P-NAW, stainless steel; column B, 5 ft × ¼ in. 5% DEGS on 60/80 Chromosorb P-NAW, stainless steel; column C, 5 ft 3% SE30 on 100/120 Varaport 30, stainless steel; column D, 15 ft × ⅛ in. 10% DEGS on 100/120 Chromosorb P-NAW, stainless steel; column E, 10 ft × ¼ in. UCC-W98 on 60/80 Chromosorb W-AWDMCS, glass; column F, 10 ft × ¼ in. 20% DEGS on Chromosorb P-NAW, stainless steel; column G, 10 ft × ¼ in. 20% Carbowax on Chromosorb P-NAW, stainless steel; column H, 7 ft × ¼ in. 8% FFAP on Chromosorb P-NAW, stainless steel; column I, 10 ft × ¼ in. 20% SE30 on Chromosorb W-AWDMCS, glass. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. All boiling points are uncorrected.

Trifluoromethanesulfonic Acid Anhydride (53). **53** (bp 83–84°) was prepared in 77.6% yield by treatment of trifluoromethanesulfonic acid (3M Co.) with fresh phosphorus pentoxide according to the procedure of Gramstad and Haszeldine.[37] The anhydride was found to be stable indefinitely when opened only under an inert atmosphere and stored in the refrigerator in a glass bottle with a Teflon lined cap.

3-Carboethoxy-3-methyl-6-hepten-2-one (12). Into a dry 500 ml three-necked flask fitted with a mechanical stirrer, an addition funnel, and a reflux condenser protected with a calcium sulfate drying tube were placed 85 ml absolute ethanol and 3.95 g (172 mmol) of freshly cut sodium. The mixture was stirred for 3 hr to allow complete reaction of the sodium. To this solution was added dropwise with vigorous stirring 22.2 g (154 mmol) of ethyl 2-methylacetoacetate (Aldrich Chemical Co.) to give a viscous reaction mixture. This mixture was heated to reflux and 25 g (185 mmol) of 4-bromo-1-butene (J. T. Baker Chemical Co.) was added dropwise. The solution was stirred at reflux for 7 hr. After cooling, the reaction mixture was decanted off of the sodium bromide salt, which was rinsed with a small portion of ethanol. Most of the ethanol was distilled off through a 40-cm Vigreaux column at atmospheric pressure.

In the most successful procedure the remaining solution was subjected directly to saponification and decarboxylation to give 3-methyl-6-hepten-2-one (**13**, *vide infra*). However, in one instance **12** was isolated by the following procedure. The concentrated reaction mixture was dissolved in 150 ml of ether and washed with 50 ml of water and 2.50 ml of saturated aqueous sodium chloride solution. After drying over calcium sulfate the ether solution was subjected to fractional distillation to give 7.2 g of **12** (23.6% yield): ir 3070, 2970, 2920, 2860, 1735, 1710, 1640, 1450 (br), 1375, 1350, 1255, 1190, 1145, 1100, 1020, 990, 915, 860 cm^{-1}; nmr δ 1.26 (s, 3 H, CH_3, and t, 3 H, $-CH_3$ of ethyl group), 1.9 (m, 4 H, $-CH_2CH_2-$), 2.07 (s, 3 H, $-COCH_3$); 4.16 (q, 2 H, $-CH_2$ of ethyl group), 4.75–5.15 (m, 2 H, vinyl CH_2), and 5.3–5.9 (m, 1 H, vinyl CH).

3-Methyl-6-hepten-2-one (13). In the most efficient procedure the concentrated reaction mixture described above was stirred for 22 hr at 50° with 246 g of a 5% sodium hydroxide solution (308 mmol of NaOH). This mixture was washed with ether to remove the small amount of **13** already formed. The aqueous solution was then acidified to pH <2 with concentrated hydrochloric acid causing the vigorous evolution of carbon dioxide. After stirring for 0.5 hr, the solution was extracted with ether; the aqueous portion was stirred overnight at room temperature and again extracted with ether. The combined ether solutions were washed with saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride solutions and dried over magnesium sulfate. The ether was then removed by distillation through a 20-cm Vigreaux column and the residue was subjected to fractional distillation to give 4.7 g of **13**: bp 54° at 15 mm (24% yield based on ethyl 2-methylacetoacetate); ir 3070, 2960, 2915, 1710, 1640, 1460, 1355, 1170, 995, 915 cm^{-1}; nmr δ 1.05 (d, 3 H, $-CH_3$), 2.03 (s, 3 H, $-COCH_3$), 2.45 (m, 1 H, -CH-), 1.2–2.2 (m, 4 H, $-CH_2CH_2-$), 5.0 (m, 2 H, vinyl CH_2), 5.7 (m, 1 H, vinyl CH). *Anal.* Calcd for **13**: C, 76.14; H, 11.18. Found: C, 75.87; H, 11.45.

(*Z*)- and (*E*)-3-Methyl-2,6-heptadien-2-yl Trifluoromethanesulfonate (9Z and 9E). Into an oven-dried 50-ml round-bottomed flask equipped with a magnetic stirring bar was placed 20 ml of methylene chloride (dried over magnesium sulfate) and 1.71 g (16 mmol) of 2,6-lutidine (dried over molecular sieves). The reaction flask was flushed with argon, sealed with a rubber serum cap, and cooled to −78°. In a glove bag under a nitrogen atmosphere 4.23 g (15 mmol) of trifluoromethanesulfonic acid anhydride was taken up into a syringe; the syringe needle was quickly inserted through the reaction flask septum, and the anhydride was slowly added to the reaction mixture over 10 min. During this time the solution turned a light yellow color and a small denser second layer was formed. The mixture was stirred for 15 min after which 0.631 g (5.0 mmol) of 3-methyl-6-hepten-2-one (**13**) was added dropwise. The reaction was stirred for 15 min at −78° and was then allowed to warm to −30°, during which time the two-phase solution became cloudy (−55°) and cleared again as a single layer (−35°). Aliquots were taken at regular intervals, quenched in a mixture of pentane and saturated aqueous sodium bicarbonate solution, and examined by vpc (column B, 100°, 100 ml/min). After stirring at −30 to −20° for 15 hr the reaction was found to be complete.

The reaction was warmed to 0° and 10 ml of saturated aqueous sodium bicarbonate was added dropwise. This mixture was extracted with 30 ml of ether. The organic solution was washed rapidly three times with cold 0.5 *N* hydrochloric acid followed by saturated aqueous sodium chloride solution. After drying over sodium sulfate most of the ether was distilled at atmospheric pressure. The remaining solution was then vacuum transferred off of the polymeric residue typical of this reaction. Vpc analysis showed formation of **9Z** and **9E** in a roughly 1:1 ratio in addition to a smaller amount of the isomeric terminal double bond triflate (**14**). In small scale reactions, estimates based on vpc comparison with an internal standard suggest a combined yield of 12–13% for **9Z** and **9E**.

9Z and **9E** were then separated by preparative vpc (column A, 115°, 100 ml/min); each product was contaminated with approximately 2–4% of the other isomer: ir of **9Z** 3080, 2990, 3050, 2970, 1691, 1642, 1415, 1380, 1255, 1235, 1215, 1150, 1095, 1023, 995, 920 cm^{-1}; nmr of **9Z** δ 1.83 (q, J = 1.1 Hz, 3 H, β-CH_3), 2.06 (m, 3 H, α-CH_3), 2.14–2.35 (m, 4 H, $-CH_2CH_2-$), 4.82–5.32 (m, 2 H, vinyl CH_2), 5.45–6.2 (m, 1 H, vinyl CH); ir of **9E** 3080, 2990, 3050, 2970, 1691, 1642, 1415, 1380, 1255, 1235, 1215, 1150, 1095, 995, 920; nmr of **9E** δ 1.98 (q, J = 1.5 Hz, 3 H, β-CH_3), 2.05 (m, 3 H, -2-CH_3), 2.2 (m, 4 H, $-CH_2CH_2-$), 4.82–5.23 (m, 2 H, vinyl CH_2), 5.45–6.2 (m, 1 H, vinyl CH).

Anal. Calcd for mixture of **9Z** and **9E**: C, 41.86; H, 5.04; S, 12.40. Found: C, 41.97; H, 5.37; S, 12.44.

3-Methyl-2-heptanone (29). Reaction of 2-methylhexanoic acid (**22**, Eastman Organic Chemicals) with methyllithium was accomplished by a modification[38] of the procedure of Bare and House.[39] A 300-ml three-necked flask, equipped with a reflux condenser, a nitrogen inlet, a pressure equalizing addition funnel, and a mechanical stirrer, was charged with 430 mg (54.1 mmol) of lithium hydride in 90 ml of ether (distilled from LAH). A solution of 5.81 g (44.6 mmol) of 2-methylhexanoic acid in 20 ml of ether was added dropwise over a period of 30 min with rapid precipitation of a white salt. The viscous reaction mixture was heated to reflux and stirred overnight, after which it was cooled to 10° and 22.7 ml of methyllithium (2.2 *M*, 49.9 mmol) was added dropwise over 25 min with vigorous stirring, causing all the solid to dissolve. After stirring an additional 4 hr at room temperature, the reaction mixture was siphoned under a positive pressure of nitrogen into a vigorously stirred 0° solution of 6.83 ml of concentrated hydrochloric acid in 100 ml of water. The aqueous layer was extracted with ether, and the combined organic solutions were washed with saturated aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride. After drying over magnesium sulfate, the ether was distilled off through a 20-cm Vigreaux column at atmospheric pressure and the residue subjected to fractional distillation at reduced pressure to give 4.75 g of **29**: yield 83%; bp 63–64° at 25 mm (lit.[40] bp 162° at 760 mm); ir 2952, 2922, 2867, 2852, 1706, 1462, 1455, 1374, 1349, 1169, 1132, 947 cm^{-1}; nmr δ 0.8–1.55 (m, 12 H, including doublet, J = 6.5 Hz, $-CH_3$), 2.02 (s, 3 H, $-COCH_3$), 2.4 (m, 1 H, -CH-). *Anal.* Calcd for **29**: C, 74.94; H, 12.58. Found: C, 75.13; H, 12.80.

(*Z*)- and (*E*)-3-Methyl-2-hepten-2-yl Trifluoromethanesulfonate (30Z and 30E). The procedure described above for the production of **9Z** and **9E** was followed using 3-methyl-2-heptanone, except that the reaction was instead run at −10° for 16 hr. After work-up, preparative vapor phase chromatography (column A, 100°, 100 ml/min) provided **30Z** and **30E**, each contaminated with approximately 2–4% of the other isomer: nmr of **30Z** δ 0.92 (t, J = 6.5 Hz, 3 H, $-CH_3$), 1.1–1.55 (m, 4 H, $-CH_2CH_2-$), 1.72 (q, J = 0.9 Hz, 3 H, β-CH_3), 2.02 (m, 3 H, α-CH_3), 2.15 (m, 2 H, allylic CH_2); nmr of **30E** δ 0.93 (t, 3 H, $-CH_3$), 1.1–1.6 (m, 4 H, $-CH_2CH_2-$), 1.78 (q, J = 1.3 Hz, 3 H, β-CH_3), 2.02 (m, 5 H, α-CH_3 and allylic CH_2).

Anal. Calcd for **30Z**: C, 41.54; H, 5.77; S, 12.31. Found: C, 41.32; H, 5.85; S, 12.31. *Anal.* Calcd for **30E**: C, 41.54; H, 5.77; S, 12.31. Found: C, 41.62; H, 5.80; S, 12.28.

(*Z*)- and (*E*)-3-Methyl-2-hepten-2-yl Acetate (32Z and 32E). The vinyl acetates were prepared according to the procedure of House, *et al.*[22] A 10-ml round-bottomed flask with a magnetic stirring bar was charged with 0.4 g (3.13 mmol) of 3-methyl-2-heptanone (**29**), 1.44 g of acetic anhydride, and 3.76 ml of carbon

tetrachloride. A catalytic amount of 70% aqueous perchloric acid (~2 μl) was added causing the solution to turn yellow immediately. The reaction was stirred at room temperature and followed by vpc (column A, 110°, 100 ml/min); aliquots were shaken with a pentane–saturated aqueous sodium bicarbonate solution before vpc injection. After 3.5 hr the reaction was complete. The reaction mixture was then poured into a cold (0–5°) mixture of 15 ml of pentane and 15 ml of saturated aqueous sodium bicarbonate solution. Solid sodium bicarbonate was added until the solution had been neutralized. The aqueous layer was extracted with pentane, and the combined pentane solutions were washed with saturated aqueous sodium chloride solution and dried over sodium sulfate. The pentane was distilled off at atmospheric pressure through a 20-cm Vigreaux column; the residue was subjected to fractionation at reduced pressure to give 3.7 g (70% yield) of a 1:1 mixture of **32Z** and **32E**. Several vpc columns were used in an effort to obtain clean separation of the two isomers; columns F and G provided very little separation, but column A (100°, 100 ml/min) provided adequate separation when small injections were used. Enough **32Z** and **32E** were isolated to obtain their spectra and to conduct the shift reagent studies (see text): ir of **32Z** 2970, 2930, 2870, 1750, 1697, 1470, 1460, 1450, 1390, 1370, 1265, 1225, 1200, 1140, 1050, 1020, 940, 865 cm^{-1}; nmr of **32Z** δ 0.9 (t, 3 H, CH_3), 1.1–1.55 (m, 4 H, $-CH_2CH_2-$), 1.65 (q, J = 0.9 Hz, 3 H, CH_3 trans to OAc), 1.81 (m, 3 H, CH_3 gem to OAc), 1.91 (m, 2 H, allylic CH_2), 2.04 (s, 3 H, $-COCH_3$); ir of **32E** 2970, 2930, 2870, 1750, 1699, 1470, 1460, 1445, 1370, 1260, 1200, 1140, 1050, 1020, 940, 930, 865 cm^{-1}; nmr of **32E** 0.93 (t, 3 H, CH_3), 1.1–1.55 (m, 4 H, $-CH_2CH_2-$), 1.48 (q, J = 1.4 Hz, 3 H, CH_3 cis to OAc), 1.81 (m, 3 H, CH_3 gem to OAc), 2.0 (m, 2 H, allylic CH_2), 2.05 (s, 3 H, $-COCH_3$).

Anal. Calcd for mixture of **32Z** and **32E**: C, 70.55; H, 10.66. Found: C, 70.62; H, 10.77.

Shift reagent studies were carried out with $Eu(fod)_3$ (Norell Chemical Co.) as a 0.2–0.5 M solution in carbon tetrachloride according to the procedure of Kelsey.[24]

(*Z*)- and (*E*)-2-Trimethylsilyloxy-3-methyl-2-heptene (33Z and 33E). The procedure of House, *et al.*,[25] was used to prepare the trimethylsilyl enol ethers of 3-methyl-2-heptanone (**29**). To a solution of 1.81 g (16.7 mmol) of chlorotrimethylsilane (distilled immediately prior to use) and 3.38 g (33.3 mmol) of triethylamine (dried over molecular sieves) in 6.3 ml of dimethylformamide (dried over molecular sieves) was added 2.0 g (15.8 mmol) of **29**. The solution turned a brown-orange color almost immediately with formation of a light yellow salt (triethylamine hydrochloride). The reaction was refluxed for 72 hr, then cooled to room temperature, diluted with 15 ml of pentane, and washed rapidly with three 20-ml portions of cold saturated aqueous sodium bicarbonate solution. The aqueous solution was extracted with pentane, and the combined pentane solutions were washed rapidly in succession with cold 1 N hydrochloric acid, cold saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride. After drying over magnesium sulfate, the solution was concentrated by distillation of the pentane through a 20-cm Vigreaux column. Vpc analysis (column I, 120°, 100 ml/min) showed large amounts of terminal double bond silyl enol ether and smaller amounts the 2,3 double bond isomers. Pure **33Z** and **33E** were isolated by preparative vpc (column 1, 110°, 100 ml/min): ir of **33Z** 2967, 2927, 2867, 1677, 1468, 1456, 1446, 1387, 1265, 1251, 1217, 1182, 1012, 948, 852 (br) cm^{-1}; nmr of **33Z** δ 0.15 (s, 9 H, $-SiMe_3$), 0.92 (m, 3 H, $-CH_3$), 1.1–1.55 (m, 4 H, $-CH_2CH_2-$), 1.55 (q, J = 1.0 Hz, 3 H, CH_3 trans to silyloxy group), 1.75 (m, 3 H, CH_3 gem to silyloxy group), 1.75–2.2 (m, 2 H, allylic CH_2); ir of **33E** 2950, 2870, 1679, 1470, 1385, 1372, 1263, 1252, 1188, 1050, 1009, 956, 855 cm^{-1}; nmr of **33E** δ 0.13 (s, 9 N, $-SiMe_3$), 0.92 (m, 3 H, CH_3), 1.1–1.15 (m, 4 H, $-CH_2CH_2-$), 1.51 (q, J = 1.5 Hz, 3 H, CH_3 cis to silyloxy group), 1.74 (m, 3 H, CH_3 gem to silyloxy group), 1.94 (m, 2 H, allylic CH_2).

Conversion of (*Z*)- and (*E*)-2-Trimethylsilyloxy-3-methyl-2-heptene (33Z and 33E) to Vinyl Acetates 32Z and 32E. Using the procedure of House, *et al.*,[25] 103 mg (0.515 mmol) of silyl ether **33Z** in 0.5 ml of dimethoxyethane (distilled from LAH) was treated under nitrogen with 0.26 ml (0.507 mmol) of 1.95 M methyllithium in diethyl ether. The reaction was allowed to stir at room temperature for 1 hr and then the mixture was diluted with 3 ml of dry dimethoxyethane. Next, 1.8 ml of this reaction mixture was transferred into 2 ml of rapidly stirring acetic anhydride. (The remainder of the enolate solution was used in the vinyl triflate synthesis described below.) After stirring for 15 min the acetic anhydride solution was added to a 0° mixture of pentane, saturated aqueous sodium bicarbonate, and excess sodium bicarbonate. After complete hydrolysis of the acetic anhydride, the aqueous layer was extracted with pentane, and the combined pentane layers were washed with water and saturated aqueous sodium chloride before being dried over sodium sulfate. Vpc analysis (column A, 105°, 100 ml/min) and comparison of retention times showed formation of vinyl acetate **32Z** as the only major product. In addition a few per cent of 3-methyl-2-heptanone (**29**) was observed.

Using the same procedure silyl ether **33E** was treated with methyllithium and quenched with acetic anhydride. In this case vinyl acetate **32E** and a few per cent of ketone **29** were the only significant products.

Conversion of (*Z*)- and (*E*)-2-Trimethylsilyloxy-3-methyl-2-heptane (33Z and 33E) to Vinyl Triflates 30Z and 30E. To the remaining 1.7 ml of the enolate solution produced from **33Z** as described above was added 150 mg (0.75 mmol) of trifluoromethanesulfonic imidazolide.[26] The reaction was stirred for 1 hr at room temperature before being diluted with 5 ml of pentane and quenched with 2 ml of water. The aqueous layer was extracted with pentane, and the combined pentane layers were washed with saturated aqueous sodium chloride and dried over sodium sulfate. Vpc analysis (column A, 105°, 100 ml/min) showed that the reaction was only 10–20% complete at this point resulting in the formation of large amounts of ketone **29**. However, the only additional products were vinyl triflates **30Z** and **30E**, which were formed in a 70:30 ratio, respectively.

In a similar procedure the enolate derived from silyl ether **33E** gave, in addition to large amounts of ketone **29**, a 29:71 mixture of **30Z** and **30E**, respectively. The vinyl triflate products were identified by comparison of retention times with authentic samples of **30Z** and **30E** (column A, 120°, 100 ml/min).

1,2-Dimethyl-3-methoxy-1,4-cyclohexediene (23). Birch reduction of 3,4-dimethylanisole (**22**, Aldrich Chemical Co.) was carried out by the method of Wilds and Nelson.[41] A 250-ml three-necked flask equipped with a glass-covered magnetic stirring bar, gas inlet, pressure equalizing addition funnel, and a Dry Ice condenser with a soda lime drying tube was charged with 6.25 g (46 mmol) of **22** in 25 ml of ether (distilled from LAH); 100 ml of ammonia was condensed into the flask and 1.61 g (230 mmol) of lithium wire was added in small pieces over 5 min. The deep blue solution was stirred for 10 min after which 12.4 g (270 mmol) of absolute ethanol was added dropwise over 20 min. The reaction was stirred for an additional 0.5 hr during which time the blue color disappeared. The ammonia was allowed to evaporate slowly through a Vigreaux column, and a mixture of 50 ml of ether and 80 ml of water was added to the remaining solution. The aqueous layer was extracted with three 25-ml portions of ether, and the combined ether layers were washed with saturated aqueous sodium chloride and dried over potassium carbonate.

Vpc analysis of the reaction work-up proved to be difficult due to the decomposition of the vinyl ether; however, treatment of column B (100°, 100 ml/min) with ammonia before each injection made successful analysis possible; reaction of starting material was complete and **23** proved to be the only significant product. Vinyl ether **23** was kept in the freezer as a dilute ether solution until immediately prior to use, at which point the solvent was removed on a rotary evaporator and the crude **23** used without further purification.

1,2-Dimethyl-1-cyclohexen-4-one (24). The 1,2-dimethyl-3-methoxy-1,4-cyclohexadiene (**23**) produced above (theoretical, 46 mmol) was added slowly to a solution of 7.57 g (60 mmol) of oxalic acid dihydrate in 100 ml of methanol and 5 ml of water. The reaction was stirred at room temperature and followed by vpc (column B, 100°, 100 ml/min); after 1.5 hr, the reaction was complete. The solution was diluted with 15 ml of water and neutralized with 6.34 g of sodium bicarbonate. After stirring for 15 min this solution was added to a mixture of 75 ml of pentane and 150 ml of water. The aqueous layer was extracted with pentane, and the combined pentane solutions were washed with water and saturated aqueous sodium chloride and dried over sodium sulfate. The pentane was dis-

tilled off at atmospheric pressure and the resulting crude product subjected directly to sodium borohydride reduction. Vpc analysis of the crude product showed in addition to solvent residue an 87:13 mixture of **24** and the rearrangement product 3,4-dimethyl-2-cyclohexen-1-one (**27**). Small amounts of these two compounds were isolated *via* preparative vpc (column B, 100°, 100 ml/min) for spectral purposes: ir of **24** 2975, 2915, 2865, 2855, 1718, 1445, 1425, 1404, 1385, 1355, 1296, 1255, 1225, 1195, 1138, 1117, 1022, 921 cm^{-1}; nmr of **24** δ 1.68 (broad singlet, 6 H, $-CH_3$), 2.36 (m, 4 H, $=CCH_2CH_2CO-$), 2.68 (m, 2 H, $=CCH_2CO-$); ir of **27** 3030, 2970, 2935, 2880, 1670, 1625, 1460, 1450, 1440, 1425, 1375, 1340, 1325, 1305, 1290, 1245, 1200, 1175, 1140, 1040, 1005, 950, 925, 860, 690 cm^{-1}; nmr of **27** δ 1.19 (d, 3 H, CH_3), 1.91 (m, 3 H, allylic CH_3), 1.5–2.5 (m, 5 H, $-CHCH_2CH_2-$), 5.65 (m, 1 H, vinyl CH).

1,2-Dimethyl-1-cyclohexen-4-ol (25). The method of Heathcock, *et al.*,[18] for reduction of a β,γ-unsaturated ketone in the presence of an α,β-unsaturated ketone was used. A solution of the crude mixture of **24** and **27** described above in 61.8 absolute ethanol was placed in a dry 250-ml flask equipped with a magnetic stirring bar, a pressure equalizing addition funnel, and a Drierite drying tube. The flask was cooled to 0° and a solution of 4.76 g (12.6 mmol) of sodium borohydride in 103 ml of absolute ethanol was added dropwise over 35 min. The light yellow reaction mixture was stirred at 0° for an additional 30 min before being quenched with 1.15 ml of glacial acetic acid. The resulting solution was added to a mixture of 100 ml of pentane and 200 ml of water. The aqueous layer was extracted with several small portions of pentane, and the combined pentane solutions were washed with water and saturated aqueous sodium chloride and dried over sodium sulfate.

The pentane was distilled off through a 40-cm Vigreaux column and the residue subjected to fractional distillation at reduced pressure to give 1.45 g of an 85:15 mixture (bp ~76° at 6 mm) of 1,2-dimethyl-1-cyclohexen-4-ol (**25**) and unreacted α,β-unsaturated ketone **27**. The overall yield of **25** based on 3,4-dimethylanisole (**32**) was 21.6%. A sample of **25** isolated *via* preparative vpc (column B, 120°, 100 ml/min) gave the following analytical data: ir of **25** 3610, 3355, 2990, 2920, 2870, 2855, 1445, 1440, 1385, 1365, 1130, 1045, 950 cm^{-1}; nmr of **25** 1.57 (broad singlet, 6 H, $-CH_3$), 1.4–1.8 (m, 2 H), 1.8–2.2 (m, 4 H), 2.8 (shift dependent on concentration, s, 1 H, -OH), 3.76 (m, 1 H, carbinol CH). *Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.85; H, 11.41.

1,2-Dimethyl-1-cyclohexen-4-yl Tosylate (26). Into a 10-ml pear-shaped flask was placed 1.0 g (6.74 mmol of **25**) of the 85:15 mixture of **25** and **27** described above in 4.15 ml of pyridine (dried over molecular sieves). A solution of 1.33 g (6.98 mmol) of recrystallized *p*-toluenesulfonyl chloride in 2.8 ml of pyridine was added with stirring. The reaction mixture was placed in a refrigerator for 3 days, during which time white needles of pyridine hydrochloride formed in the pale yellow solution. The mixture was added to 30 ml of cold water and the aqueous solution was extracted with ether, which was in turn washed in succession with cold 0.5 *N* hydrochloric acid, water, and saturated aqueous sodium chloride solution before being dried over sodium sulfate.

After removal of the ether on a rotary evaporator, the residual oil was crystallized twice from pentane at −80° to give the white crystalline tosylate **26**. Vpc analysis (column C, 120°, 100 ml/min) of the pentane solution (column C, 120°, 60 ml/min) showed **27** and a small amount of unreacted **25**, but vpc analysis of an ether solution of tosylate **26** (which did not survive the vpc conditions) showed no contamination with **27** or **25**: ir of **26** 2965, 2925, 2875, 1600, 1445, 1395, 1192, 1181, 1100, 1014, 946, 925, 855 cm^{-1}; nmr of **26** δ 1.55 (broadened singlet, 6 H, $-CH_3$), 1.65–2.3 (m, 6, H, $-CH_2$), 2.43 (s, 3 H, *p*-Me), 4.65 (five-line pattern, J = 6.5 Hz, 1 H, -CHPTs), 7.5 (AB quartet, 4 H, aromatic protons).

Solvolysis of (*Z*)- and (*E*)-3-Methyl-2,6-heptadien-2-yl Trifluoromethanesulfonate (9Z and 9E) in 80% Aqueous Ethanol. Into 11.4 ml of aqueous ethanol was placed 58.8 mg (0.227 mmol) of a roughly 1:1 mixture of **9Z** and **9E** purified by preparative vpc (column E, 120°, 100 ml/min). To this solution was added 33.2 mg (0.30 mmol) of 2,6-lutidine (distilled before use). The reaction was stirred at 70–75° for 22 hr, at which time reaction of the triflates was essentially complete. The reaction mixture was diluted with 70 ml of pentane and washed with cold 0.5 *N* HCl, water, and saturated aqueous sodium chloride solution. Most of the pentane was distilled off through a 20-cm Vigreaux column at atmospheric pressure. Vpc analysis of the remaining solution (column B, 100°, 75°, 100 ml/min; column C, 80°, 100 ml/min) showed only two products in a 3:4 ratio in order of increasing retention time. The first product was isolated by preparative vpc (column B, 80°, 100 ml/min) and identified as 3-methyl-1,2,6-heptatriene (**15**) on the basis of its ir spectrum: 3090, 2990, 2920, 2860, 1958 (allene), 1642 (CH_2=CH-), 1448, 1432, 1373, 1292, 1202, 1173, 1154, 1000, 968, 853 cm^{-1}. (See trifluoroethanol solvolysis below for the nmr of **15**.) The second product was identified as 3-methyl-6-hepten-2-one (**13**) by comparison with an authentic sample of **13** (*vide supra*).

Solvolysis of (*Z*)- and (*E*)-3-Methyl-2,6-heptadiene-2-yl Trifluoromethanesulfonate (9Z and 9E) in Trifluoroethanol. I. Preparative Solvolyses. Trifluoroethanol (Aldrich "Gold Label" 99+%) was dried over molecular sieves and distilled through a molecular sieve packed column before use. 2,6-Lutidine was dried over molecular sieves before use. Failure to follow these procedures led to formation of significant amounts of 3-methyl-2-hepten-6-one (**13**) in the solvolyses of **9Z** and **9E**.

Into an oven-dried 10-ml pear-shaped flask with a magnetic stirring bar was placed 126.2 mg (0.49 mmol) of a roughly 1:1 mixture of **9Z** and **9E** (purified by preparative vpc—column B, 90°, 100 ml/min) and 105 mg (0.98 mmol) of 2,6-lutidine in 4.9 ml of trifluoroethanol. The reaction was stoppered and stirred at 70° for 31 hr, after which it was added to a mixture of 15 ml of water and 10 ml of pentane. The aqueous layer was extracted with pentane, and the combined pentane solutions were washed with cold saturated aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride before being dried over potassium carbonate. The pentane was distilled off at atmospheric pressure through a 20-cm Vigreaux column, and the reaction products were then isolated *via* preparative vpc (column A, 120°, 100 ml/min).

The following spectral data were obtained for the product compounds (in order of increasing retention time): ir of 3-methyl-1,2,6-heptatriene (**15**) 3090, 2990, 2920, 2860, 1958, 1642, 1448, 1432, 1373, 1292, 1202, 1173, 1154, 1000, 968, 853 cm^{-1}; nmr of **15** δ 1.67 (t, J = 3, 3 H, $-CH_3$), 2.06 (m, 4 H, $-CH_2CH_2-$), 4.55 (sextet, J = 3, 2 H, allene CH_2), 4.75–5.17 (m, 2 H, vinyl CH_2), 5.33–6.17 (m, 1 H, vinyl CH); ir of 1,2-dimethyl-2-*anti*-(2′,2′,2′-trifluoroethoxy)bicyclo[3.1.0]hexane (**17**) 3070, 3035, 2945, 2885, 1460, 1420, 1377, 1342, 1285 (br), 1165 (br), 1130, 1050, 1025, 1005, 977, 908, 888, 848, 690, 655 cm^{-1}; nmr of **17**: δ 0–0.4 (m, 2 H, cyclopropyl CH_2), ~0.9–1.43 (m, 1 H, cyclopropyl CH), 1.13 (s, 3 H, CH_3 gem to OCH_2CF_3), 1.23 (s, 3 H, cyclopropyl CH_3), 1.43–2.0 (m, 4 H, $-CH_2CH_2-$), 3.66 (q, J = 8.5 Hz, $-CH_2CF_3$); ir of 1,2-dimethyl-2-*syn*-(2′,2′,2′-trifluoroethoxy)bicyclo[3.1.0]hexane (**18**) 3070, 3035, 2945, 2885, 1479, 1456, 1417, 1389, 1377, 1282, 1163 (br), 1128 (br), 1048, 1020, 1011, 975, 910, 879, 848, 689 cm^{-1}; nmr of **18** δ 0.34 (d of d, 1 H, C6 cyclopropyl H), 0.84 (d of d, 1 H, cyclopropyl H), ~0.8–1.1 (m, 1 H, C5 cyclopropyl H), 1.15 (s, 3 H, CH_3 gem to $-OCH_2CF_3$), 1.31 (s, 3 H, cyclopropyl CH_3), 1.62 (m, 4 H, $-CH_2CH_2$), 3.77 (q, J = 8.5 Hz, CH_2CF_3); ir of (*Z*)-3-methyl-2-(2′,2′,2′-trifluoroethoxy)-2,6-heptadiene (**16Z**) 3080, 2955, 2875, 1683, 1640, 1463, 1415, 1388, 1375, 1283, 1160 (br), 1120, 1088, 998, 970, 913, 850, 665 cm^{-1}; nmr of **16Z** δ 1.56 (q, J = 0.9 Hz, 3 H, CH_3 trans to OCH_2CF_3), 1.79 (m, 3 H, CH_3 gem to OCH_2CF_3), 2.10 (m, 2 H, CH_2), 2.14 (~s, 2 H, CH_2), 3.90 (q, J = 8.5 Hz, 2 H, CH_2CF_3), 4.14–5.15 (m, 2 H, vinyl CH_2), 5.25–6.0 (m, 1 H, vinyl CH); ir of (*E*)-3-methyl-2-(2′,2′,2′-trifluoroethoxy)-2,6-heptadiene (**16E**) 3080, 2990, 2930, 2870, 1683, 1641, 1444, 1419, 1388, 1377, 1312, 1287, 1160 (br), 1088, 971, 919, 852, 661 cm^{-1}; nmr of **16E** δ 1.64 (q, J = 1.3 Hz, 3 H, CH_3 cis to OCH_2CF_3), 1.79 (m, 3 H, CH_3 gem to OCH_2CF_3), 2.03 (~s, 2 H, CH_2), 2.08 (m, 2 H, CH_2), 3.90 (q, J = 8.5 Hz, 2 H, $-CH_2CF_3$), 4.74–5.17 (m, 2 H, vinyl CH_2), 5.31–6.2 (m, 1 H, vinyl CH); ir of 2,3-dimethyl-3-(2′,2′,2′-trifluoroethoxy)-1-cyclohexene (**19**) 2980, 2930, 2855, 1449, 1440, 1379, 1357, 1276, 1160, 1122, 978, 880, 849, 679, 659 cm^{-1}; nmr of **19** δ 1.18 (s, 3 H, CH_3 gem to OCH_2CF_3), 1.65 (m, 5 H, allylic CH_3 and CH_2), 2.00 (m, 4 H, allylic CH_2 and CH_2 α to OCH_2CF_3), 3.69 (q, J = 8.5 Hz, 2 H, CH_2CF_3), 5.33 (m, 1 H, vinyl CH); ir of 1,2-dimethyl-4-(2′,2′,2′-trifluoroethoxy)-1-cyclohexene (**20**) 2925, 2875, 2850, 1447, 1373, 1280, 1160, 1133, 1000, 972, 868, 672 cm^{-1}; nmr of **20** δ 1.58 (s, 6 H, CH_3), 1.58–

2.2 (m, 6 H, CH_2), 3.77 (q, J = 8.5 Hz, 2 H, CH_2CF_3). Compounds **18** and **16Z** were collected as a single peak containing roughly 70% **16Z** and 30% **18**. Pure **18** was isolated as a product of the solvolysis of 1,2-dimethyl-1-cyclohexen-4-yl tosylate (**37**) (*vide infra*). The nmr of **17** also showed traces of what may have been *o*-xylene (δ 2.24 and 7.0 in a ratio of 3:2); an authentic sample of *o*-xylene had the same retention time as the impurity in **17**. No *o*-xylene was present in any of the starting materials.

II. **Analytical Solvolyses.** In a typical procedure 24.5 mg (0.95 mmol) of **9Z**, 20.4 mg (0.190 mmol) of dry 2,6-lutidine, and 1.0 ml of trifluoroethanol were placed with a magnetic stirring bar in an oven-dried 2-ml vial, which was then sealed with a rubber serum cap. The solution was stirred in an oil bath at 60 ± 2° for 72 hr. Next, 1-2-μl aliquots were withdrawn at regular intervals and injected directly onto column D (130°) for analysis and direct digital integration using the Hewlett-Packard 3370A integrator. Products were identified by comparison of retention time with the samples obtained in the preparative scale reaction described above. Compounds **18** and **16Z** eluted as a single peak; the relative amounts of **18** and **16Z** at the end of the solvolysis run were determined in a somewhat larger scale comparable reaction by preparative vpc isolation of this peak (column A, 120°, 100 ml/min) and nmr analysis of this mixture. Solvolyses of **9E** were performed in a similar manner. In each case estimation of overall yield was made by comparison with an internal standard; after correction for relative response factors (all trifluoroethyl ethers were assumed to have the same relative response as **37E**) the overall yield was found to be >95%. No interconversion of **9Z** and **9E** could be detected during the course of the reaction.

Solvolysis of (*Z*)- and (*E*)-3-Methyl-2-hepten-2-yl Trifluoromethanesulfonate (30Z and 30E) in Trifluoroethanol. Analytical solvolyses were performed in the same manner as the **9Z** and **9E** above, except that the vpc analyses were carried out at 110° on column D. In addition to the experiments carried out using 0.09 *M* **30E** or **30E** and 0.18 *M* 2,6-lutidine concentrations, runs were made using 0.9 *M* **30Z** with 0.36 *M* 2,6-lutidine and 0.23 *M* **30Z** with 0.46 *M* 2,6-lutidine. No significant change in the vinyl ether product ratio was observed under any of these conditions (see text). Again overall product yield was >95% and no interconversion of **30Z** and **30E** was detected.

For identification of products, the final reaction mixtures of six of the analytical solvolyses were combined and added to a mixture of 10 ml of pentane and 15 ml of water. The aqueous layer was extracted with pentane, and the combined pentane solutions were washed with cold 0.5 *N* hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride before being dried over magnesium sulfate. Most of the pentane was removed by distillation through a 20-cm Vigreaux column at atmospheric pressure. The three reaction products were then isolated *via* preparative vpc (column A, 110°, 100 ml/min): ir of 3-methyl-1,2-heptadiene (**36**) 3050, 2930 (br), 2880, 2865, 1960, 1470, 1460, 1448, 1430, 1380, 1371, 1290, 1250, 1205, 1180, 1102, 968, 850 cm^{-1}; nmr of **36** δ 0.92 (m, 3 H, CH_3), 1.15-1.7 (m, 4 H, $-CH_2CH_2-$), 1.66 (t, J = 3 Hz, 3 H, allenic CH_3), 1.92 (m, 2 H, allylic methylene), 4.53 (sextet ?, J = 3 Hz, 2 H, allenic CH_2); ir of (*Z*)-3-methyl-2-(2′,2′,2-trifluoroethoxy)-2-heptene (**37Z**) 2960, 2930, 2870, 1685, 1470, 1460, 1450, 1422, 1390, 1285 (br), 1165, 1088, 970, 850, 660 cm^{-1}; nmr of **37Z** δ 0.92 (m, 3 H, CH_3), 1.1-1.55 (m, 4 H, $-CH_2CH_2-$), 1.58 (q, J = 0.8 Hz, 3 H, CH_3 trans to OCH_2CF_3), 1.80 (m, 3 H, CH_3 gem to OCH_2CF_3), 2.08 (~broadened triplet, 2 H, allylic methylene), 3.90 (q, J = 8.5 Hz, 2 H, CH_2CF_3); ir of (*E*)-3-methyl-2-(2′,2′,2-trifluoroethoxy)-2-heptene (**37E**) 2960, 2930, 2870, 1686, 1470, 1460, 1420, 1376, 1310, 1285 (br), 1165 (br), 1085, 970, 907, 850, 660 cm^{-1}; nmr of **37E** δ 0.92 (m, 3 H, CH_3), 1.1-1.55 (m, 4 H, $-CH_2CH_2-$), 1.62 (q, J = 1.3 Hz, 3 H, CH_3 cis to OCH_2CF_3), 1.80 (m, 3 H, CH_3 gem to OCH_2CF_3), 1.93 (broadened triplet, 2 H, allylic CH_2), 3.90 (q, J = 8.5, 2 H, $-CH_2CF_3$).

Estimates of the half-lives for reaction of **9Z, 9F, 30Z,** and **30E** at 60° were made by monitoring the disappearance of starting material in each solvolysis. Because the vinyl triflates are known to give somewhat irreproducible results from injection to injection (variances of up to 10-15%) and because the oil bath temperature was subject to ±2° fluctuations, these numbers are at best very rough estimates. The approximate half-lives of 21, 11.4, 11.6, and 7 hr for **9Z, 9E, 30Z,** and **30E,** respectively, lead to relative rate estimates of 1:1.8:1.8:3 for these compounds.

Solvolysis of 1,2-Dimethyl-1-cyclohexen-4-yl Tosylate (26) in Trifluoroethanol. I. Preparative Solvolysis. Into a 10-ml pear-shaped flask with magnetic stirring bar and rubber serum cap was placed 150 mg (0.54 mmol) of **26** and 112 mg (1.07 mmol) of 2,6-lutidine (dried over molecular sieves) in 5.4 ml of trifluoroethanol (dried over molecular sieves and distilled through a molecular sieve packed column). The reaction mixture was stirred in an oil bath at 60 ± 2° for 3 hr and then added to a mixture of 10 ml of pentane and 15 ml of water. The aqueous layer was extracted with pentane, and the combined pentane solutions were washed with cold 0.5 *N* hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated aqueous sodium chloride. After drying over magnesium sulfate the pentane was distilled off at atmospheric pressure. The reaction products were then isolated by preparative vpc (column A, 100°, 100 ml/min). Products **17, 19,** and **20** gave spectra identical with those of the samples of these compounds obtained above in the preparative scale solvolysis of **9Z** and **9E**. In addition, **18** was obtained in pure form and shown to have the same spectra as the minor product isolated with **16Z** in that experiment (*vide supra*). Three very minor products showing olefinic ir and nmr absorptions were collected together but were not further characterized due to lack of material.

II. **Analytical Solvolyses.** Into a 2-ml vial with magnetic stirring bar and a rubber serum cap were placed 28.3 mg (0.1 mmol) of tosylate (**26**) and 21 mg (0.2 mmol) of 2,6-lutidine in 1.0 ml of trifluoroethanol. The reaction mixture was stirred at 60 ± 2°, and aliquots were analyzed directly as in the above solvolyses. Although the reaction was complete within the first hour, it was then allowed to stir for an additional 65 hr at 60° to determine the stabilities of the cyclic trifluoroethyl ethers to the reaction conditions (see text for discussion). Although no formal studies of overall product yield were performed, the total integrated areas of the products for the same size injection at 3 and 66 hr did not differ significantly, suggesting that the changes in product ratios with time were indeed due to interconversion of the products and not to selective decomposition of **17** and **18**.

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Reaction of 1-Bromo-1-alkynes with Alkoxide Ion. Generation of Vinylidene Carbenes[1]

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Abstract: Sodium alkoxides react with 1-bromo-1-alkynes in refluxing benzene, toluene, or xylene solutions by proton abstraction at C-3 generating an intermediate zwitterion-carbene, which in the presence of equimolar quantities of alcohol (or alkoxide) gives four products. Mechanisms involving nucleophilic attack by alcohol (alkoxide) on the ambident vinylidene carbene, prototropic rearrangement, and carbene insertion into the carbon–hydrogen bond α to the oxygen of the alcohol or alkoxide are proposed.

Substitution of bromine in 1-bromo-1-alkynes proceeds in good yield with a variety of nucleophiles[2a] (eq 1). Several mechanisms have been suggested

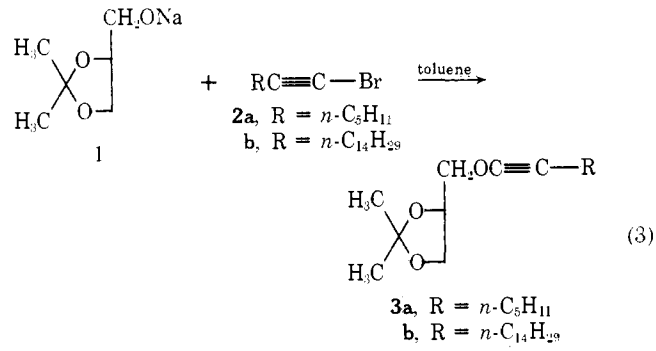
$$RC{\equiv}C{-}Br + X^- \longrightarrow RC{\equiv}C{-}X + Br^- \quad (1)$$
$$X = R'S^-,\ R'_2N^-,\ P(OR')_3$$

including α addition and β elimination[2b]; β addition, α elimination, and rearrangement;[2c] and attack on bromine followed by direct substitution[2d] (eq 2). Efforts to extend

$$RC{\equiv}CBr + X^- \longrightarrow RC{\equiv}C^- + XBr \quad (2)$$

the scope of this method to the preparation of acetylenic ethers ($X = R'O^-$) have been largely unsuccessful.[2d,3] Instead of substitution, 1-bromo-1-acetylenes react with alkali metal hydroxides or alkoxides to give the free acetylenes and recovery of starting materials.[3] Arens[2d] has attributed this to nucleophilic attack on bromine, which in protic solvents results in reversal of a useful preparative method based on hyprobromite–acetylene equilibria.

A notable exception to this generalization was reported by Preobrazhenskii and coworkers[4a] in which the preparation of **3a** was claimed as shown in eq 3. Unfortunately, lit-



(3)