The acetate, XIIe-OAc, boiled at a bath temperature of 180° (0.1 mm), n^{24}D 1.5370.

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.83; H, 7.87.

Kinetic Measurements. The kinetic procedure for the acetolysis studies was essentially the same as that employed previously.[3b] The glacial acetic acid contained 1 wt % of acetic anhydride.

Vapor Phase Chromatography. Vpc analyses were carried out on a Hitachi Perkin-Elmer Model F-6 equipped with a hydrogen flame ionization detector using either a 1 m × 3 mm stainless steel column packed with 10% diethylene glycol succinate polyester on 60–80 mesh Chromosorb W or a 45 m × 0.5 mm stainless steel capillary coated with SE-30. Helium was used as a carried gas at a pressure of approximately 1 kg/cm². In preparative vpc, each material separated on a 5 m × 14 mm stainless steel column packed with 5% diethylene glycol succinate polyester on 30–60 mesh Chromosorb

W was divided into two parts. The minor part was introduced to a flame detector and the main one was trapped in the tube cooled in Dry Ice–acetone. Helium was used as a carrier gas (200 cc/min).

Separation of Acetolysis Products. In a typical procedure, a sample of 5.78 g of Ia-OBs in 142 ml of glacial acetic acid containing 0.105 M sodium acetate and 1 wt % acetic anhydride was thermostated in a sealed tube at 86° for 18 hr. The solution was poured into ice–water and extracted three times with *n*-pentane. The combined extracts were washed with water and aqueous sodium bicarbonate and dried. After removal of the solvent, the residual oil was distilled (2 mm) to give 3.20 g of the products which were separated on a preparative vpc column at 200°.

Rearrangement of Esters in the Gas Phase. II. Substituent Effects on the Rate of Isomerization of Allylic Esters[1]

Edward S. Lewis, James T. Hill, and Edward R. Newman

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. Received August 21, 1967

Abstract: The earlier studies on rearrangement of crotyl esters are extended to the study of α- and γ-trifluoromethylallyl trifluoroacetates (IV and V), allyl-α-d_2 trifluoroacetate (I), allyl-^{18}O trifluoroacetate (III), α,β-dimethylallyl acetate (VII), and α,γ-dimethylallyl acetate (X). In some cases a minor but detectable rearrangement to *cis*- as well as *trans*-γ-substituted allyl derivatives is observed. The rate of rearrangement of allyl acetate is within experimental error the same whether followed by deuterium or [18]O labeling. The results are consistent with the transition state with carbonium carboxylate character proposed earlier.

The preceding paper of this series[2] showed that the rearrangement rates of crotyl esters increased in the order acetate < methyl carbonate < trifluoroacetate, and the less precisely determined rate for crotyl chloroformate was still faster.[3] A transition state was proposed (based upon the relation of the rates to the acid strengths) with substantial charge separation but with a structure resembling that of a Cope rearrangement, such as A. In this paper we explore the substituent effects

A
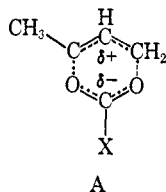
on the allyl moiety to establish further the charge distribution on the transition state.

Results and Discussion

Rates on α- and γ-trifluoromethylallyl trifluoroacetates (IV and V) and on α,β-dimethylallyl acetate (VII) were determined using the stirred flow reactor and gas chromatographic analysis described before.[2,3] The rearrangement of allyl-α-d_2 trifluoroacetate (I) to allyl-

γ-d_2 trifluoroacetate (II) was followed in the stirred flow system using an nmr analysis. The conversion of allyl-^{18}O trifluoroacetate (III) to allyl trifluoroacetate-carbonyl-^{18}O was followed by hydrolysis to the alcohol

Table I. Structures of Compounds Studied of General Formula

Compd	R_1	R_2	R_3	R_4	R_5	X
I	H	H	H	D	D	CF_3
II	D	D	H	H	H	CF_3
III[a]	H	H	H	H	H	CF_3
IV	H	H	H	H	CF_3	CF_3
V	CF_3	H	H	H	H	CF_3
VI	H	CF_3	H	H	H	CF_3
VII	H	H	CH_3	H	CH_3	CH_3
VIII[b]	CH_3	H	CH_3	H	H	CH_3
IX[b]	H	CH_3	CH_3	H	H	CH_3
X[c]	CH_3	H	H	H	CH_3	CH_3
XI	H	CH_3	H	H	CH_3	CH_3
XII[d]	H	H	H	H	CH_3	CF_3
XIII[d]	CH_3	H	H	H	H	CF_3
XIV[d]	H	H	H	H	CH_3	OCH_3
XV[d]	CH_3	H	H	H	H	OCH_3
XVI[d]	H	H	H	H	CH_3	CH_3
XVII[d]	CH_3	H	H	H	H	CH_3

[a] This compound was labeled with [18]O. [b] These two compounds are geometrical isomers, but the structural assignment is not rigorous. [c] This compound was used in optically active form. [d] From ref 2.

(1) From portions of the 1967 Ph.D. theses of J. T. Hill, National Defense Education Act Fellow, 1964–1967, and E. R. Newman, National Aeronautics and Space Administration Trainee, 1965–1967.

(2) E. S. Lewis and J. M. MacDonald, submitted for publication.

(3) E. S. Lewis and K. Witte, submitted for publication.

Table II. Rates of Isomerization of Allylic Esters

Process[a]	Temp, °C	$k \times 10^3$ sec^{-1} (av)[c]	Log A	E_a
I → II[b]	300.31	0.99		
	313.13	1.91		
	326.10	4.4[d]		
	338.67	6.4		
	350.83	15.7	10.9 ± 0.2	36.5 ± 0.4
	325.0 (calcd)	3.7		
III → III[e]	313.2	2.5		
	325.9	3.3[f]		
	338.7	8.5		
IV → V	323.0	2.55		
	337.0	4.34		
	353.5	9.0		
	363.0	12.8		
	376.0	23.6	9.2 ± 0.4	32.3 ± 1.0
	325.0 (calcd)	2.7		
V → IV	361.0	1.14		
	369.0	1.60		
	380.2	2.47		
	391.4	4.08		
	402.3	6.32	9.2 ± 0.2	35.3 ± 0.6
	325.0 (calcd)	0.21		
IV → VI	323.0	0.14		
	337.0	0.40		
	353.5	1.05		
	363.0	1.33		
	376.0	2.66	11.6 ± 1.0	42 ± 3
	325.0 (calcd)	0.18		
VI → IV	358.5	1.13		
	371.0	2.02		
	382.0	3.04	9.0 ± 0.7	35 ± 2
	325.0 (calcd)	0.25		
VII → VIII	300.8	0.169		
	311.8	0.377		
	323.6	0.776		
	334.3	1.54		
	346.6	3.24	13.53 ± 0.14	45.4 ± 0.4
	325.0 (calcd)	0.858		
VIII → VII	300.8	0.302		
	311.8	0.651		
	323.6	1.29		
	334.3	2.50		
	346.6	5.33	13.2 ± 0.1	44.0 ± 0.2
	325.0 (calcd)	1.5		
d-X → l-X	243.7	0.098		
	255.0	0.204		
	265.0	0.409		
	274.8	0.745		
	284.9	1.47		
	296.3	3.16		
	306.5	6.05		
	325.0 (calcd)	15.7	12.4 ± 0.2	38.8 ± 0.5
X → XI	Not determined, no more than 7% occurred with up to 70% racemization and up to 12% elimination			
XII → XIII	325 (calcd)	204	13.4	38.6
XIII → XII	325 (calcd)	204	13.2	38.1
XIV → XV	325 (calcd)	10.7	13.7	43
XV → XIV	325 (calcd)	12.4	11.8	38
XVI → XVII	325 (calcd)	0.59	11.3	40
XVII → XVI	325 (calcd)	0.67	10.3	37

[a] Compound identification in Table I. [b] The assumption was made that the rate for this process is the same as that of the unmeasured process II → I, i.e., equilibrium secondary isotope effects were neglected. There is a significant flow-rate dependence of the rates, which we attribute to analytical error. [c] Average rate constants are presented here and in Figure 1, but all the individual constants were used in the least-square fits to the Arrhenius equation. [d] This includes a run at markedly lower vaporizer temperature, which is essentially the same as the others at this temperature. [e] This reaction was followed by the equilibration of the ^{18}O label from the initial specific alkoxy position. The analytical precision limits the rate constant accuracy, so the Arrhenius constants are not reported. [f] Not an average; there was only one run at this temperature.

and the ^{18}O content of the alcohol was measured by mass spectrometry after conversion to carbon dioxide. The rearrangement of α,γ-dimethylallyl acetate (X) manifested itself as a conversion of one enantiomer to the other, resulting in racemization. Details of these methods are presented in the Experimental Section. The compounds studied are identified in Table I. The systematic names of these compounds appear in the Experimental Section; in the rest of the text they are named as substituted allyl esters. The rates of isomerization are in Table II, together with the Arrhenius constants and the calculated rate at 325°, and the rates of elimination (which are a by-product of this study and not determined with the same precision) are in Table III.

Table III. Rates of Elimination Processes

Process	Temp, °C	$k \times 10^3$ sec^{-1}(av)	Log A	E_a, kcal
VII →	300.8	0.212		
isoprene[a]	311.8	0.428		
	323.6	0.87		
	346.6	3.28	12.42 ± 0.11[a]	42.2 ± 0.3[a]
X →				
trans-piper-	255.0	0.073		
ylene[b]	265.0	0.113		
	274.8	0.183		
	284.9	0.27		
	296.3	0.47		
	306.5	0.73	(8)[c]	(29)[c]

[a] There were many points fitting the Arrhenius equation very satisfactorily, yet our general lack of precision in these eliminations yielding conjugated dienes leaves open the possibility that our error limits may be too small. The facile polymerization of dienes may cause this lack of precision. [b] The product was assigned the *trans* structure on the basis of its chromatographic retention time, identical with that of a commercial sample. [c] The rate constants show an unexplained flow-rate dependence and the fit to the Arrhenius equation is poor. The parentheses denote a lack of confidence in the significance of these numbers.

The question naturally arises as to the reliability of these rates and Arrhenius constants. We have therefore determined the rate of dissociation of dicyclopentadiene in the range from 156 to 209° in one apparatus and 179 to 209.8° in the other apparatus. There were some conspicuous sources of error in sampling, namely that at low sampling syringe temperatures, the starting materials condensed perceptibly on the syringe surfaces, as shown by a lubricating effect, and at high sampling temperatures, there was detectable reaction in the syringe. Nevertheless, this error was ignored and in the first apparatus this led to calculated rate constants which varied systematically with the flow rate, instead of being independent of flow rate. In the stirred flow system this is a rather sensitive indication of analytical error, or of failure of the assumptions leading to the steady-state equations. In the second apparatus the sample in the syringe had a smaller surface to volume ratio and there was no evidence of analytical error. Arrhenius constants are given in Table IV, together with those from other sources. It is clear that even with a known syste-

Table IV. Arrhenius Constants for the Cracking of Dicyclopentadiene

Dicyclopentadiene method	Ref	Log A	E_a, kcal
Stirred flow, I[a]	This work	13.5 ± 0.22[a]	34.7 ± 0.44[a]
Stirred flow, II	This work	12.67 ± 0.36	33.45 ± 0.77
Stirred flow	b	13.01 ± 0.27	33.97 ± 0.55
Static	c	13.0	33.7
Static (in solution)	d	13.0 ± 0.2	34.2 ± 0.4

[a] As described in the text there is a known systematic analytical error in this series. [b] W. C. Herndon, C. R. Grayson, and J. M. Manion, *J. Org. Chem.*, **32**, 526 (1967). We thank Professor Herndon for a copy of this paper sent before publication. [c] J. B. Harkness, G. B. Kistiakowsky, and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1937). [d] B. S. Khambata and A. Wasserman, *J. Chem. Soc.*, 375 (1939).

matic error present in the first entry, there is no gross effect on the Arrhenius constants, although the effect is easily perceptible, and the calculated standard errors are

not unrealistic. We therefore believe that our results on other compounds are equally reliable and believe that Arrhenius constants can reasonably well be expected to be correct and reproducible within a few standard deviations.

Let us return to a consideration of the results in Table II. For convenience, the rates of reaction at 325° are calculated and presented as the final entry under each compound in Table II. Since the rates are not the same in the forward and reverse directions, the substituent effects are to some extent distorted by equilibrium effects. The equilibrium data derived from the kinetic data of Table II are presented in Table V. The last column of

Table V. Thermodynamics of the Conversion of α-Substituted Allyl Carboxylates to the γ-Substituted Isomer

| Process	ΔH,[a] kcal	ΔS,[a] eu	K_{325}[b]
I ⇌ II	(0)[c]	(0)[c]	(1.00)[c]
IV ⇌ V	−3.1 ± 1	0 ± 2	12.7
IV ⇌ VI	7 ± 5	12 ± 7	0.72
VII ⇌ VIII	1.4 ± 0.5	1.4 ± 1	0.59
XII ⇌ XIII[d]	0.5 ± 1	0.9 ± 1.3	1.00
XIV ⇌ XV[d]	5 ± 3	9 ± 5	0.86
XVI ⇌ XVII[d]	3 ± 4	5 ± 5	0.88

[a] ΔH and ΔS are calculated from the Arrhenius constants of Table II and therefore contain the assumption that they are temperature independent. [b] The equilibrium constants are calculated from the rate constants at 325° in Table II. [c] Equilibrium isotope effects are neglected. [d] From ref 2.

Table V gives $K_{325} = (\gamma$-substituted ester)/(α-substituted ester). It is clear that we cannot yet get precise thermodynamic information, although the most recent results are the best, and hence there is a good possibility that useful thermodynamic data may ultimately be obtained this way. The distinct inversion of the position of the equilibrium with the trifluoromethyl substituent is clear, but notwithstanding the variation of equilibrium constant with substituent, these ground-state energy effects are not large enough to influence the following qualitative arguments based upon the rates. It is easily seen that the effects on the rates at 325° of substitution on the allyl fragment are opposite to those on the carboxyl; that is, for allyl substitution the rates are $CF_3 < H < CH_3 < \alpha,\gamma(CH_3)_2$, whereas for carboxyl substitution the rates are $CF_3 > OCH_3 > CH_3$. This supports the earlier conclusion that these are in the order of stabilities of the carbonium carboxylates, which was then based on carboxylate substitution only.[2] Further indication that the transition state resembles the allyl cation is found in the observations on the effect of the β-methyl group. The allyl cation has the positive charge localized in the α and γ but not the β position. In accord with the above picture of the transition state, the β-methyl substitution increases the rate at 325° by a factor of 1.8 (average for the two directions), whereas a second α- or γ-methyl group increases the rate by a factor of 25 (average), and with trifluoroacetate esters, one α- or γ-methyl group increases the rearrangement rate by a factor of 55. The retarding effect of the trifluoromethyl group is also very substantial: at 325° the α- or γ-trifluoromethyl group retards the rate compared to the unsubstituted allyl by a factor of 0.7 and 0.057, respectively. Indeed we studied the trifluoromethyl compound next after the crotyl esters, and were at first convinced

that there was no rearrangement; this first impression accounts for the rather poor experimental design on these compounds, described in the Experimental Section.

The correlation between rate and log A found before[2] persists, although having more points, it is not as well marked as before. Nevertheless, the most difficulty ionizable material, the trifluoromethylallyl ester, has log A = −9.2, while the most easily ionized acetate ester, the α,γ-dimethylallyl ester, has log A = 12.4, and the most easily ionized trifluoroacetate, the α-methylallyl ester, has log A = 13.4. We interpret these results as an indication that the transition state is qualitatively similar to that of the Cope rearrangement with a six-membered ring in the transition state A, when the ionic contributions are unfavorable. The new and old C–O bonds (indicated in A by dotted lines only) are reasonably strong, and the entropy of activation thus resembles those of Cope or Claisen rearrangements. When the ionic contributions are most favorable, the entropy of activation is almost zero and the binding in the transition state must be less constrained than structure A indicates. We are unwilling to call upon an intermediate ion pair, but this is certainly an important contributing structure to the transition state. A referee has kindly called our attention to a paper by O'Neal and Benson,[4] which appeared after the original submission of this article, in which the entropies of activation for a number of cyclic transition-state reactions are estimated. Our entropies of activation are larger than any of their estimates, and if these are rigorous upper limits for the loosely bound model that they use, our transition states must be even less constrained than the cyclic model of theirs, and must therefore be of rather ill-defined structure.

A remaining question pertains to the possibility of transition states of other ring size such as the rearrangement reaction with the transition state B or the normally undetectable reaction with the transition state C. These

B   C
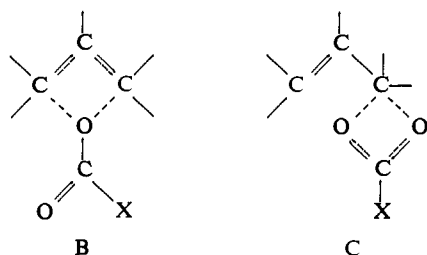
transition states are actually meant to imply only the products of the reactions, and no detailed structures. The existence of the rearrangement of the compounds with an alkyl or deuterium label shows that either A or B or some equivalent must occur. The rearrangement of the deuterium-labeled material goes at about the rate that one would expect from the rates of the methyl-labeled materials, so that the mechanism through A alone is entirely sufficient to explain the results. Figure 1 shows that within rather large uncertainties, the ^{18}O rates fall on the Arrhenius curve for the deuterium compound. Our results, which therefore show that the deuterium label and the oxygen label scramble, within experimental error, at the same rate do not exclude mechanisms through B or C. They do, however, sug-

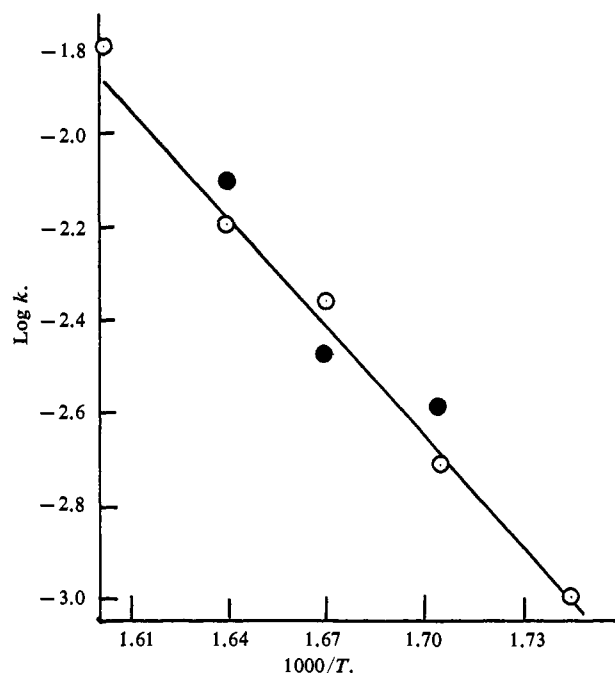(4) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967).

Figure 1. Arrhenius plot for the rearrangement of allyl-α-d_2 trifluoroacetate. The line is that from the Arrhenius constants of Table II; the open circles are the average of all rate constants at that temperature. Solid circles are points for the rearrangement of ^{18}O-labeled allyl trifluoroacetate.

gest that if either four-ring mechanism is important, then the other must be almost equally important. We believe that the six-membered ring mechanism (A) predominates, by analogy to the Cope and Claisen rearrangements[5] and by analogy with Goering's work in solution[6] (in which a six-ring intermediate was predominant but not exclusive), and by analogy with Braude and Turner's work[7] on another system in nonpolar solvents.

The stereochemical course of the reaction remains for consideration. In the three cases previously studied we found no evidence for the rearrangement of α-methylallyl esters to cis-crotyl esters, although no search was made for this isomer. In the present work we find that the α-trifluoromethylallyl trifluoroacetate (IV) does rearrange to the cis-γ-trifluoromethylallyl ester VI, but at a rate (at 325°) slower by a factor of 15 than the rearrangement of the *trans* ester V. In the rearrangement of α,β-dimethylallyl acetate (VII), one isomer is produced (presumably but not certainly that of the same configuration as *trans*-crotyl (VIII)) to an extent much greater than that of the other (presumably IX). The rate constant for formation of the minor isomer is not well established since it was not isolated in quantity sufficient for studying the reverse reaction, but since it was formed in no experiment to an extent as great as one-eighth of the major isomer and the extent of its formation is flow-rate dependent we can assume that it is not importantly equilibrium controlled. Thus we can approximate the rate as between one-eighth and one-twelfth

(5) These are discussed recently by S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.
(6) H. L. Goering and M. M. Pombo, *J. Amer. Chem. Soc.*, **82**, 2515 (1960).
(7) E. A. Braude and D. W. Turner, *Chem. Ind.* (London), 1223 (1955).

of that of the major reaction.[8] The rate of rearrangement of *trans*-α,γ-dimethylallyl acetate (X) to the *cis* isomer XI has likewise not been quantitatively established. Arguments similar to those above lead to the conclusion that this isomerization has a rate much less than half of that of the elimination, and hence less than one-sixth that of the rearrangement with optical inversion to the *trans* ester. While this evidence is not yet convincing, the suggestion is that even substituted *trans*-crotyl esters are the favored product. If we arrange the six-ring transition state I in a somewhat chairlike form, this can be understood, but there is too little evidence to determine the configuration with confidence.

The formation of *trans*-1,3-pentadiene from *trans*-α,γ-dimethylallyl acetate (X) does not bear relationship to the mechanism of this elimination, for the *trans* geometry remains intact throughout the reaction.

We find no reason to introduce further reactions, such as unimolecular *cis–trans* isomerization, unimolecular 1,4 eliminations, or any higher order reactions, with the following exceptions and considerations.

1. The rearrangements of trifluoromethylallyl trifluoroacetates (IV, V, and VI) were accompanied by the formation of several very short retention time unidentified substances. The amounts of these were reduced both by lowering the reaction temperature and by reducing the total concentration of ester in the reaction by reducing vaporizer temperature. They are therefore products of a higher order reaction with high activation energy.

2. In the same system a slightly better fit of the data could be obtained by introducing a direct interconversion path of *trans* and *cis* esters V and VI. However, the rate constants which came from the least-squares treatment for these processes were negative and showed little temperature dependence. We believe that this nonsensical result merely shows that a better fit can always be made by introducing more adjustable constants, which in this case have no physical significance. We reject therefore any important contribution of the reaction IV → VI.

3. In the elimination reaction from α,β-dimethylallyl acetate (VII), reproducible rate constants and agreement to the Arrhenius equation were obtained only with low vaporizer temperatures. Apparently the product isoprene dimerized or polymerized readily before analysis, and solids were found in the exit tube except when the vaporizer temperature was low.

Experimental Section

Apparatus. Two similar sets of apparatus were used for the work in this paper. One was essentially identical with the one described before;[2] this is the one described as II in Table IV. The other (I) was similar in construction except that a liquid bath (fused sodium nitrate–sodium nitrite for the higher temperature, silicone fluid for the lower temperatures) was used for heating the reactor instead of the aluminum block. Temperature was controlled by a commercial proportional controller with a resistance thermometer sensing element. The advantage of this design is that it is not limited to a single size of reaction vessel. Gas chromatographic analyses in a number of cases were facilitated by the use of a digital integrator,[9] but there was no indication that earlier relative area measurements were in error.

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(8) The data from which this conclusion is drawn can be found in the thesis of Newman.[1]

(9) We thank the Research Sponsors of Rice University for a grant which paid in part for this instrument.

Determination of Rate Constants from Experimental Data. Trifluoromethylallyl Trifluoroacetates. The system is represented in Scheme I. Because our first result was that there was no rearrange-

Scheme I

trans-CF₃CH=CHCH₂OCOCF₃ ⇌
V

CF₃CH(OCOCF₃)CH=CH₂ ⇌ *cis*-CF₃CH=CHCH₂OCOCF₃
IV   VI
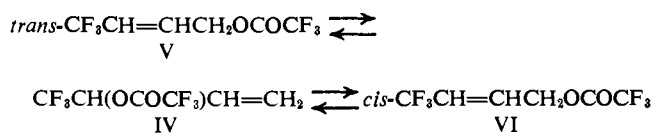
ment (since it was slower than any others), the data were obtained from imperfectly designed experiments. Specifically, data were not obtained starting with each compound at every temperature. Instead, we attempted to solve the simultaneous equations for the steady state by variation of the flow rate only, and to eliminate some of the uncertainties inherent in this method (as described in an earlier paper[3]) by using a great deal of data and getting a least-squares solution using a computer. This in fact gave only the rate constants for the direct reactions of the substance put into the reactor with satisfactory precision, and our various struggles to improve these results can be found in the thesis of Hill.[1] The results given in the table are essentially only these most precisely determined constants, although our effort to use the data from one temperature at another by the use of the Arrhenius equation did produce a slight improvement. The difficulty of preparation of the *cis* isomer VI accounts for the paucity of data and the low precision of the Arrhenius constants. The great data-handling capacity of the computer does not materially help get over the handicap of poor experimental design.

The Rearrangement of Allyl-α-*d₂* Trifluoroacetate (I). The chemistry of this example is simple; the only special feature is the analytical problem. The extent of rearrangement in a sample condensed from the effluent was determined by nmr analysis, since the α-protons are well resolved from the vinylic γ-protons. The accuracy of the analysis is however rather limited both by the inherent problems of nmr integration and probably also by the presence of small amounts of impurities. Errors from unresolved C¹³ satellites also limit the accuracy. Figure 1 shows an Arrhenius plot of these results, together with those of the ¹⁸O-labeled ester III, showing that the two reactions within a rather large experimental error have the same rate.

The Rearrangement of Optically Active α,γ-Dimethylallyl Acetate (X) was followed by racemization. We assume that each arrangement gives inversion, so we can write that

$$k_{rearr} = \left(\frac{[\alpha_0]}{[\alpha]} - 1 \right) U/2V$$

where $[\alpha_0]$ and $[\alpha]$ are the specific rotations measured before and after reaction. The ester was separated from optically inactive contaminants before measurement of rotation; thus the existence of side reactions has no effect on the rate constant for rearrangement. We did not isolate enough of the *cis* ester XI to see if it was optically active nor to establish rate constants for its formation or rearrangement.

α,β-Dimethylallyl Acetate (VII) and β,γ-Dimethylallyl Acetate (VIII). The methods followed closely those described for the crotyl esters.[10] Little error results from the existence of the minor isomer IX; only the reversion of this to the α,β isomer VII will influence the steady-state calculations, and this is not important. The data are more precise than those for the crotyl esters, in part because the gas chromatograph was coupled to a digital integrator for measuring peak areas and in part because the column used gave better resolution.

Materials. Allyl-α-*d₂* Trifluoroacetate (I). Allyl-α-*d₂* alcohol was kindly prepared by Mr. J. G. Welch by the reduction of acryloyl chloride with lithium aluminum deuteride. Esterification with trifluoroacetic anhydride gave the ester, bp 78–79° after distillation through a spinning-band column. The doublet at δ 4.8 (from tetramethylsilane) shown by the undeuterated sample was almost absent in this sample; integration of this almost absent peak compared to the complex multiplet between δ 5.1 and 6.3 showed that it was 96.5% deuterated.

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(10) See Table IV, footnote *b*.

Allyl Alcohol-[18]O. Acrolein dimethyl acetal (100 g, 1.0 mol), water (25 g, 1.4 mol) containing 5.2% excess ^{18}O, and 1 ml of concentrated sulfuric acid were stirred until gas chromatographic analysis showed the presence of large amounts of acrolein and methanol and little acetal. This solution (25 ml) was slowly added to sodium borohydride (40 g, 1.0 mol) in 300 ml of diethyl carbitol at ice-bath temperature. The mixture was stirred several hours and glacial acetic acid was added cautiously until hydrogen evolution ceased. The mixture was distilled and the fraction boiling above 80° (9.2 g) was collected. This procedure was carried out previously with normal water and it was found that the fraction boiling above 80° and below the diethyl carbitol (bp 188°) contained the allyl alcohol. Separation of the allyl alcohol from this fraction was difficult and for the labeled compound this separation was not attempted.

Allyl Trifluoroacetate-[18]O (III). The trifluoroacetate ester was prepared according to the standard procedure using the 9.2-g fraction mentioned in the section above. Preparative gas chromatography using a column of 30% diethylene glycol succinate on Chromosorb P yielded 4.4 g of material which was diluted with 4.4 g of normal allyl trifluoroacetate containing no excess [18]O. Mass spectral analysis of the carbon dioxide produced after hydrolysis and combustion of a sample of this material indicated 1.86% excess [18]O above the 0.204% natural abundance.

Hydrolysis of Allyl Trifluoroacetate. Normal allyl trifluoroacetate (0.5 g) was stirred with 5 ml of 1 N sodium hydroxide-[18]O (0.2 g of sodium hydroxide in 5 ml of water containing 5.2% excess ^{18}O) and the mixture was extracted with three portions of 10 ml each of ethyl ether. The ether was concentrated and allyl alcohol was obtained by preparative gas chromatography as before. This alcohol was converted to carbon dioxide and mass spectrometric analysis showed no incorporation of excess [18]O. Hence hydrolysis occurred by attack at the carbonyl carbon and would not interfere with the analysis. Neither alkyl oxygen cleavage nor S_N2' attack by hydroxide took place under the hydrolysis conditions. The same techniques were used to obtain allyl alcohol from the ^{18}O-labeled allyl trifluoroacetates.

Analysis of [18]O. The labeled compounds were converted to carbon dioxide following Doering and Dorfman.[11] The carbon dioxide samples were admitted to a mass spectrometer and the region m/e 44 to 46 was scanned several times, alternately with a standard carbon dioxide sample. In our hands the oxygen train showed some small memory effects, which we made negligible by disregarding the results on the first sample of each new substance burned in the train. We thank Mr. A. J. Mogenis for help with this analysis.

4,4,4-Trifluoro-1-buten-3-ol (α-Trifluoromethylallyl Alcohol). The procedure was essentially that of Pegolotti and Young,[12] except that the trifluoroacetaldehyde was prepared without isolation by the method of Brand[13] and added to the vinylmagnesium bromide solution as soon as it was ready. The alcohol was obtained only as the 60% component of the tetrahydrofuran azeotrope.

1-Trifluoromethyl-2-propenyl trifluoroacetate (α-trifluoromethylallyl trifluoroacetate, IV) was prepared by esterification of alcohol with trifluoroacetic anhydride. Distillation and preparative gas chromatography yielded material, bp 73°, characterized by its mass spectrum, ir spectrum, and proton magnetic resonance spectrum (details are found in the thesis of Hill[1]).

4,4,4-Trifluoro-2-butenoic Acid. Malonic acid (104 g, 1.0 mol) was dissolved in pyridine (90.2 g, 1.24 mol) by gentle heating and then trifluoroacetaldehyde hydrate (97 g, 0.84 mol) was slowly added to this cooled, stirred mixture. After brief stirring a small sample was removed and in addition to the malonic acid, the Knoevenagel adduct (2-carboxy-3-hydroxy-4,4,4-trifluorobutyric acid) was identified by its infrared spectrum. The original solution was boiled under reflux for 6 hr after which time the evolution of carbon dioxide ceased and the decarboxylated adduct (3-hydroxy-4,4,4-trifluorobutyric acid) could be isolated from a small sample. It melted at 70° (lit.[14] mp 78°). This last solution was cooled and stirred while concentrated sulfuric acid (100 ml, 1.78 mol) was slowly added. The mixture was boiled under reflux for 3 hr and then distilled. The fraction boiling at 153° was collected and recrystallized from ligroin to give 42 g (36% yield) of white crystals

melting at 50° (lit.[15] mp 51°) with a neutralization equivalent of 142.5 (calcd 140). The nmr spectrum showed a singlet at δ 11.9 ppm from tetramethylsilane and a complex multiplet from δ 6.3 to 7.3. The infrared spectrum was identical with that reported by Haszeldine.[15]

Ethyl 4,4,4-Trifluoro-2-butenoate. 4,4,4-Trifluoro-2-butenoic acid (30 g, 0.21 mol), ethanol (50 ml, 0.86 mol), and 3 ml of concentrated sulfuric acid were boiled under reflux for 3 hr and then cooled. To this mixture was added 50 ml of water and enough solid sodium carbonate to neutralize the acid. The mixture was extracted with ether and the ether washed with water to remove the excess ethanol. The ether was dried and distilled to give an azeotrope of undetermined composition boiling at 74°. The azeotrope was washed with several portions of water, extracted with ether, dried, and redistilled to give 20 g (56% yield) of material boiling at 112–113° (lit.[14] bp 112.5°).

4,4,4-Trifluoro-2-buten-1-ol. This alcohol could be prepared by reduction of ethyl 4,4,4-trifluorocrotonate with aluminum hydride (AlH_3) in ether.[16] Lithium aluminum hydride (9.6 g, 0.24 mol) was dissolved in 200 ml of ethyl ether, cooled to 0°, and stirred while aluminum chloride (13 g, 0.1 mol) in 100 ml of ether was slowly added. This mixture was allowed to warm to room temperature and lithium chloride precipitated but was not removed from the solution. The mixture was cooled to 0° again and ethyl 4,4,4-trifluorocrotonate (20 g, 0.12 mol) in 100 ml of ether was slowly added. The ice bath was removed and after 30 min of stirring, the excess active hydrogen was destroyed by cautious addition of water. After filtration, ether extraction, drying, and distillation of the ether, the residue was purified by preparative gas chromatography using a column of 20% Carbowax on Chromosorb P and yielded 8.85 g (69%) of material boiling at 128° (lit.[14] bp 128°).

trans-4,4,4-Trifluoro-2-butenyl Trifluoroacetate (trans-γ-Trifluoromethylallyl Trifluoroacetate, V). This ester was prepared according to the standard procedure using 4,4,4-trifluoro-2-buten-1-ol (8.85 g, 0.07 mol) and trifluoroacetic anhydride (44 g, 0.21 mol). Preparative gas chromatography using a column of 30% diethyleneglycol succinate on Chromosorb P afforded 11.2 g (72% yield) of material boiling at 122°.

cis-4,4,4-Trifluoro-2-butenyl trifluoroacetate (cis-γ-Trifluoromethylallyl Trifluoroacetate, VI). The effluent from all kinetic runs and from further passage of compounds IV and V through the reactor at low flow rates was passed through a cold trap, and the mixture of esters IV, V, and VI and minor by-products was separated by preparative gas chromatography. Compound VI, which came off after IV and before V, was characterized by its mass spectrum (which was very similar except for minor intensity differences to those of IV and V), its proton resonance spectrum, which was consistent with the assigned structure although no complete analysis was attempted because of its complexity, and the ir spectrum, similar to that of V, but showing absorption at (among others) 1378 and 712 cm⁻¹ compared to absorption at (among others) 1322, 1309, and 956 cm⁻¹ for V. While these are somewhat outside the regions normally considered characteristic of cis- and trans-disubstituted ethylenes,[17] the extreme effect of the trifluoromethyl group can reasonably distort these, and the general differences between cis and trans olefins are in this direction. The relative stability ($K = (V)/(VI) = 17.6$ from Table V) also indicates that V and VI are trans and cis, respectively.

1-Methyl-trans-2-butenyl Acetate (α,γ-Dimethylallyl Acetate, X). trans-α,γ-Dimethylallyl alcohol was prepared following the method of Kyriakides.[18] It was resolved via the brucine salt of the acid phthalate following the published procedure,[19] except that the crystalline resolved acid phthalate was converted to the alcohol by reduction with lithium aluminum hydride.[20] We confirm the rather peculiar polarimetric behavior of the free alcohol.[19] On esterification with acetic anhydride and pyridine and distillation, the ester (bp 136–137°, in agreement with the literature)[19] was obtained, which was further purified for the kinetics by chromatography. It had $[\alpha]_{5461} +67.5°$ (c 3.46, chloroform).

(11) W. von E. Doering and E. Dorfman, J. Amer. Chem. Soc., 75, 5597 (1953).
(12) J. A. Pegolotti and W. G. Young, ibid., 83, 3256 (1961).
(13) M. Brand, H. Iserson, and F. E. Lawlor, ibid., 76, 4027 (1954).
(14) E. T. McBee, O. R. Pierce, and D. D. Smith, ibid., 76, 3722 (1954).

(15) R. N. Haszeldine, J. Chem. Soc., 3495 (1952).
(16) M. J. Jorgenson, Tetrahedron Letters, 559 (1962).
(17) See, for example, J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 33.
(18) L. P. Kyriakides, J. Amer. Chem. Soc., 36, 657 (1914).
(19) H. W. Hill, J. Kenyon, and H. Phillips, J. Chem. Soc., 576 (1936).
(20) W. von E. Doering and H. H. Zeiss, J. Amer. Chem. Soc., 72, 147 (1950).

Rates were measured by observing the rotations of materials condensed from the exit stream and purified by gas chromatography. It was shown that the gas chromatographic procedure did not cause any change in rotation. Rotations were all measured in chloroform solution in a 1-cm cell using a Bendix polarimeter.[21]

1,2-Dimethyl-2-propenyl Acetate (VII). A solution of 44.0 g (0.512 mol) of 3-methyl-3-buten-2-ol (Columbia Organic Chemicals, bp 115–117°) in 147 g (1.86 mol) of pyridine was mixed with 162.5 g (1.59 mol) of acetic anhydride and heated on a steam bath for 90 min. The reaction mixture was worked up in the usual way to yield 53.3 g (81.3%) of α,β-dimethylallyl acetate, bp 130–131°. This product appeared pure on the analytical column used for the kinetic vpc analysis and was used for some of the kinetic measurements. By use of a different analytical column, this product was shown to contain a 10.8% inert impurity.

An 8.00-g (0.0931 mol) sample of 3-methyl-3-buten-2-ol which had been purified by preparative vpc was acetylated with 32.4 g (0.318 mol) of acetic anhydride and 29.4 g (0.372 mol) of pyridine as above. The yield was 9.51 g (79.8%) of 1,2-dimethylallyl acetate which was free of the impurity mentioned above, but the rates were insensitive to this impurity.

2-Methyl-*trans*-2-butenyl Acetate (VIII) and 2-Methyl-*cis*-2-butenyl Acetate (IX). These were from a sample trapped from the passage of VII through the reactor and fractionally distilled once to give a fraction, bp 135–150°, which was separated by preparative gas chromatography into the three pure isomers VII, VIII, and IX. Compounds VIII and IX had somewhat different nmr spectra, but no firm assignment could be made, and the assignment of the *trans* structure to VIII as the predominant rearrangement product of VII is based only on analogy with the other systems.

Reactions of Chloride Ion with 5-Methyl-2-cyclohexenyl Chloride. A Detailed Mechanism for Anion-Promoted Allylic Rearrangement

David G. Lesnini,[1] Paul D. Buckley,[2] and Richard M. Noyes

Contribution from the Departments of Chemistry of Columbia University, New York, New York 10017, and the University of Oregon, Eugene, Oregon 97403. Received July 25, 1967

Abstract: 5-Methyl-2-cyclohexenyl chloride in the presence of a chloride salt can undergo simultaneous *cis–trans* isomerization, isotopic exchange of chloride ion, and racemization. All of these reactions are first order in tetraethylammonium chloride in acetonitrile at 65° and constant ionic strength. The most important reaction in the system is S$_N$2 substitution on the same carbon initially containing chlorine. The rate of *cis–trans* isomerization is equal to that of isotopic exchange but less than that of mutarotation plus racemization; these observations rule out major contributions from S$_N$2′ mechanisms. The best explanation of the racemization reaction apparently involves a "sandwich" transition state in which a chloride ion on the opposite side of the ring promotes racemization of a *cis* allylic chloride molecule. The results do not contribute to the original objective of estimating lifetimes of intimate and solvent-separated ion pairs, and studies by other investigators suggest that such lifetimes may be very short in aprotic solvents.

I t has been shown that 5-methyl-2-cyclohexenyl chloride consists of *cis* and *trans* isomers (I and II) each of which can be converted to its enantiomorph by a stereospecific allylic isomerization.

I   II

Goering, Nevitt, and Silversmith[3] showed that both isomers racemized more rapidly than they were solvolyzed in either ethanol or acetic acid, but the isomers were not detectably interconverted prior to solvolysis. These observations were interpreted to involve the unimolecular formation of a racemic intimate ion pair that

either collapsed or continued on a path to solvolysis products.

We selected the same compounds for an attempt to determine the lifetimes of ion pairs in a nonsolvolyzing solvent. The racemization and *cis–trans* isomerization reactions indicate differences in the extent to which the components of an ion-pair intermediate became separated before they recombined. If the reaction mixture also contained isotopically labeled chloride ion, it was reasoned that it should exchange with these ion pairs by a diffusion-controlled process whose rate constant could be estimated with moderate reliability. Comparative rates of the various processes should then permit estimates of the lifetimes of ion pairs before the components recombined to isomeric products.

Such a kinetic analysis requires that unimolecular processes make major contributions to the racemization and *cis–trans* isomerization reactions in nonsolvolyzing solvents suitable for exchange studies. Although such an expectation is encouraged by the observations of Goering and Josephson[4] about the

(1) Based on the Ph.D. Dissertation of D. G. L. at Columbia University, May 1964.
(2) Based on the Ph.D. Dissertation of P. D. B. at the University of Oregon, Aug 1966.
(3) H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *J. Am. Chem. Soc.*, 77, 5026 (1955).