The Acid-Catalyzed Isomerization of the Butenyl Acetates[1]

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Abstract: The rates of the acid-catalyzed isomerization of cis- and trans-crotyl and α-methylallyl acetates and their equilibrium ratios have been determined in acetic acid at several temperatures. In addition, the acid-catalyzed rate of loss of optical activity of α-methylallyl acetate in acetic acid was studied at two perchloric acid concentrations. The results are interpreted in terms of a carbonium ion mechanism which involves cis- and trans-crotyl carbonium ions which retain their geometrical configuration and interconvert only through the intermediary of the secondary butenyl acetate. The data obtained are also used to calculate equilibrium constants as well as thermodynamic and activation parameters for the isomerization.

The present investigation is a reexamination of the acid-catalyzed isomerization of the butenyl acetates, cis-crotyl (cis-I-OAc), trans-crotyl (trans-I-OAc), and α-methylallyl acetate (II-OAc), in acetic acid. This system was investigated previously by Young and Webb,[2] who determined the relative equilibrium concentrations of the primary and secondary acetates by distillation methods. Since cis- and trans-crotyl acetate are not separable by distillation, their efforts were limited to providing the gross primary:secondary equilibrium ratio (65:35 at 60°).

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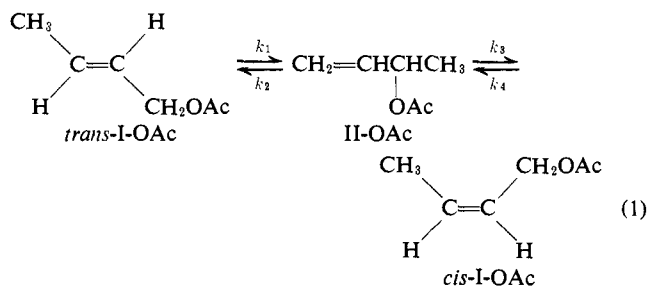
It seemed instructive to quantitatively evaluate the equilibrium mixture of the isomeric allylic acetate mixture as well as the rates of allylic rearrangement using the now available gas chromatography techniques. Here we wish to report the results of such an investigation designed to provide insight on the question of conformational integrity of allylic carbonium ions[3] which, along with the allylic radical[4] and carbanion[5] counterpart, has received considerable recent attention.

Results

Butenyl Acetates. α-Methylallyl alcohol and trans-crotyl alcohol were prepared by lithium aluminum hydride reduction of methyl vinyl ketone and trans-crotonaldehyde, respectively.[3d] cis-Crotyl alcohol was

produced by the partial hydrogenation of 1-butynol.[3d] Purification of the butenyl alcohols was accomplished by preparative gas chromatography. The butenyl acetates were prepared by acetylation of the respective carbinols with acetic anhydride and purified by preparative gas chromatography. Identification and stereochemistry of the butenyl acetates were established by their method of preparation and their ir and nmr spectra.

Isomerization Equilibrium. The butenyl acetates (ca. 0.1 M) were equilibrated in acetic acid containing 0.0084 M perchloric acid at 50.0 and 75.0°. A sample run is listed in Table I starting with α-methylallyl acetate at 75.0° where the reaction mixture was analyzed between ca. 15 and 120 reaction half-lives.

All of the experimental equilibrium points exhibited some loss of allylic material and this loss was found to increase with reaction time. Accompanying the loss of butenyl acetate was a concurrent darkening of the reaction solutions. While it is not clear which allylic acetate(s) is undergoing decomposition, the rate of decomposition is ca. 100 times slower than the rate of equilibration; thus the measured proportions of the isomeric acetates were always the equilibrium amounts. Inspection of the experimental data used in the compilation of Table I revealed no trend in the equilibrium concentrations of the butenyl acetates. This is true even when there is as much as 56.6% loss of material as in the run with cis-I-OAc.

The equilibrium amounts of II-OAc, cis-I-OAc, and trans-I-OAc found at 50.0° are 38.22 ± 0.30, 9.24 ± 0.05, and 52.54 ± 0.30%, respectively, while at 75.0° the values are 38.19 ± 0.22, 10.41 ± 0.08, and 51.41 ± 0.17%, respectively. As seen in Table II the same equilibrium mixture is attained starting from the three isomeric acetates. Also listed in the table are the equilibrium ratios I-OAc/II-OAc for the equilibria

$$\text{II-OAc} \rightleftharpoons \textit{cis}\text{-I-OAc} \quad \Biggr\} \quad K_{(1/11)} \qquad (2)$$
$$\text{II-OAc} \rightleftharpoons \textit{trans}\text{-I-OAc} \qquad (3)$$

where $K_{(I/II)}$ is the equilibrium constant.

Isomerization Rates. The kinetic experiments performed were of two varieties. One measurement provided the rates of rearrangement of the butenyl acetates, while the other measured the rate of loss of optical activity of (−)-α-methylallyl acetate. The rates of allylic rearrangement (k_r) were determined by gc analysis using the same experimental procedures

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(1) This research was supported in part by the National Science Foundation.
(2) W. G. Young and I. D. Webb, J. Amer. Chem. Soc., 73, 780 (1951).
(3) (a) W. G. Young, S. H. Sharman, and S. Winstein, ibid., 82, 1376 (1960); (b) P. D. Sleezer, S. Winstein, and W. G. Young, ibid., 85, 1890 (1963); (c) J. H. Brewster and H. O. Bayer, J. Org. Chem., 29, 105 (1964); (d) W. G. Young and J. S. Franklin, J. Amer. Chem. Soc., 88, 785 (1966).
(4) C. Walling and W. Thaler, ibid., 83, 3877 (1961).
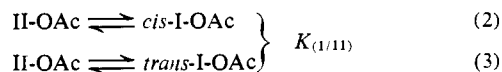(5) (a) D. H. Hunter and D. J. Cram, ibid., 86, 5478 (1964); (b) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., ibid., 87, 3244 (1965).

Table I. Equilibrium Distribution of Butenyl Acetates Formed from α-Methylallyl Acetate[a] in Acetic Acid Containing 0.008345 M HClO₄

Temp, °C	Time, hr	Weight % ROAc[b] trans-I-OAc	cis-I-OAc	II-OAc	Recovd acetates
50.0	72	52.50	9.267	38.23	83.3
	120	52.11	9.279	38.62	80.4
	144	52.89	9.332	37.78	76.3
	168	52.79	9.108	38.10	76.3
	Av:	52.57 ± 0.27	9.247 ± 0.069	38.18 ± 0.24	
75.0	3.0	51.78	10.27	37.95	84.2
	5.8	51.30	10.38	38.33	78.2
	9.6	51.43	10.51	38.06	72.8
	12.0	51.30	10.42	38.28	70.3
	Av:	51.45 ± 0.16	10.40 ± 0.07	38.16 ± 0.15	

[a] 0.10 M ROAc. [b] Values normalized to 100%.

Table II. Equilibrium Distribution of the Butenyl Acetates in Acetic Acid Containing 0.008435 M Perchloric Acid

Starting ROAc[a]	Temp, °C	Weight % ROAc cis-I-OAc	trans-I-OAc	II-OAc	$K_{(I/II)}$ trans-I-OAc/ II-OAc	cis-I-OAc/ II-OAc
cis-I-OAc	50.0	9.220 ± 0.068	52.48 ± 0.03	38.30 ± 0.04		
trans-I-OAc	50.0	9.251 ± 0.050	52.54 ± 0.46	38.41 ± 0.24		
II-OAc	50.0	9.247 ± 0.069	52.57 ± 0.27	38.18 ± 0.24		
	Av:	9.239 ± 0.013	52.53 ± 0.03	38.30 ± 0.08	1.372	0.2412
cis-I-OAc	75.0	10.38 ± 0.06	51.42 ± 0.14	38.20 ± 0.19		
trans-I-OAc	75.0	10.43 ± 0.11	51.34 ± 0.24	38.23 ± 0.35		
II-OAc	75.0	10.41 ± 0.07	51.45 ± 0.14	38.15 ± 0.12		
	Av:	10.41 ± 0.03	51.40 ± 0.04	38.19 ± 0.03	1.346	0.2726

[a] 0.1 M ROAc.

Table III. Rate Constants and Activation Parameters for the Acid-Catalyzed Isomerization of the Butenyl Acetates in Acetic Acid Containing 0.008435 M HClO₄

ROAc[a]	$10^6 k$, sec⁻¹ [b] 25.0°	50.0°	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
trans-I-OAc	3.35 ± 0.06	68.9 ± 1.4	23.1	22.5	−8.21
cis-I-OAc	0.594 ± 0.012	14.2 ± 0.6	24.2	23.6	−7.79
II-OAc	4.78 ± 0.003	100.0 ± 2.0	22.6	22.6	−7.06

[a] 0.1 M ROAc. [b] Average of first-order k's measured during the first 10% reaction.

employed in the equilibrium study. Good pseudo-first-order rate constants for the disappearance of the starting acetate were obtained during the first 10% of reaction at 25.0 and 50.0°. The instantaneous rate constants, k_r, were computed from the experimental data with the expression

$$k_r = \frac{2.303 \log C_0/C_t}{t}$$

where C_0 is the weight percentage of starting allylic acetate at (experimental) zero time and C_t is the weight percentage of that acetate at time t. Table III contains average values for these rate constants and activation parameters.

An independent check on the accuracy of the rate measurements is provided by comparing equilibrium constants calculated from the rate data with experimentally determined values. For example, using eq 1 and the data in Tables II and III, it can be shown that the equilibrium constant for the interconversion of trans-crotyl acetate and α-methylallyl acetate at 50.0° calculated from the rate constants is 1.404 which agrees within 2% of the experimental value of 1.372. Thus from the equilibrium ratio (0.2419) for cis-I-OAc and II-OAc ($K_{I/II} = k_3/k_4$) and the rate constant for the disappearance of cis-I-OAc (k_4) the value 3.44 × 10⁻⁶

sec⁻¹ is calculated for k_3. Since the measured k_r for isomerization of II-OAc equals $k_2 + k_3$ the value for k_2 is 96.6 × 10⁻⁶ sec⁻¹. Therefore, using the rate constant for the disappearance of trans-I-OAc (k_1) and the calculated value for k_2, the equilibrium constant for eq 3 is calculated to be 1.404.

Implicit in this calculation is the assumption that direct interconversion of the cis- and trans-acetates is unimportant. Therefore the excellent agreement between the experimental and calculated equilibrium constants would seem to provide substantial support for the validity of this assumption.

To the extent that the reaction under study occurs by a process which can be represented by eq 1, where there is no direct cis–trans isomerism, there should be a close correspondence between the experimentally determined concentrations of one of the isomeric crotyl acetates developing from the other and values for these concentrations calculated on the basis of eq 1. Equations which may be used to perform such calculations have been derived.[6] This derivation includes the assumption that the starting material is completely pure at zero time. In the present investigation this requirement was fulfilled best in the case of the isomerization of trans-

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 175–176.

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crotyl acetate at 25.0°. Here, the starting acetate was 99.10% pure at (experimental) zero time, where the percentage of cis-acetate present can be determined with an accuracy of 0.04% (absolute).

In view of the greater analytical accuracy and higher initial purity obtained in the trans-crotyl acetate experiment at 25.0°, comparison of the empirical and calculated concentrations was carried out for this situation. The method of calculation is detailed in the Experimental Section and the results of the calculations, along with the experimental values, are tabulated in Table IV. The close correspondence of the observed

Table IV. Comparison of the Observed and Calculated Development of cis-Crotyl and α-Methylallyl Acetate from trans-Crotyl Acetate at 25.0° [a]

Time, hr	Weight % of cis Obsd	Weight % of cis Calcd	Weight % of sec Obsd	Weight % of sec Calcd
0.0[b]	0.475		0.430	
1.783	0.476	0.494	2.587	2.571
2.533	0.493	0.495	3.352	3.384
3.383	0.496	0.496	4.282	4.266
4.267	0.499	0.504	5.277	5.257
6.167	0.515	0.514	7.560	7.549
12.233	0.574	0.543	11.39	11.80
27.683	0.754	0.709	23.08	23.42

[a] The butenyl acetate concentration was 0.1028 M; the perchloric acid concentration was 0.008435 M. [b] Experimental zero point. The starting material contained 0.43% cis-acetate and <0.01% secondary acetate.

and calculated concentrations provides strong support for the assumption that there is no direct cis–trans isomerization.

The rate of acid-catalyzed loss of optical activity (k_α) of (−)-α-methylallyl acetate was measured in acetic acid containing 0.008272 and 0.01654 M HClO$_4$ at 50.0°. Good first-order kinetics were observed between 20 and 90% reaction, where the experimental infinity readings at ten reaction half-lives exhibited no residual optical rotation within experimental error (±2%). The k_α values are summarized in Table V

Table V. Polarimetric Rate Constants and H_0 Values for (−)-α-Methylallyl Acetate in Acetic Acid at 50.0°

[ROAc]	10^3[HClO$_4$]	$10^6 k_\alpha$, sec^{-1}	log k_α	$-H_0$[a]
0.1520	8.272	359 ± 6	−3.45	1.84
0.1535	16.54	717 ± 10	−3.14	2.16

[a] Values calculated from ref 7.

along with the H_0 values calculated using literature data.[7,8] The dependence of log k_α on $-H_0$ is with a slope of 1, which is in good agreement with the value of 1.1 obtained by Pocker[9] for the acid-catalyzed rearrangement of 1-phenylallyl acetate in acetic acid.

Discussion

Equilibrium. It is clear from the results presented that a state of equilibrium was achieved by the butenyl acetates in acetic acid under the reaction conditions employed in the present investigation. The same

(7) L. P. Hammett and A. J. Deyrup, J. Amer. Chem. Soc., **54**, 2721 (1932).
(8) F. J. Ludwig and K. H. Adams, ibid., **76**, 3853 (1954).
(9) Y. Pocker, Proc. Chem. Soc., 226 (1959).

mixture of butenyl acetates was obtained starting from each of the isomers. This mixture, once attained, did not change with time, although substantial quantities of allylic material were consumed.

The observed 62:38 crotyl to α-methylallyl equilibrium ratio (at 50.0 and 75.0°) is in good agreement with the 65:35 ratio (60°) found by Young and Webb[2] using distillation techniques.

Predominance of a primary over a secondary or tertiary allylic isomer at equilibrium is the usual result in allylic systems.[10] The greater thermodynamic stability generally observed for a primary isomer is ascribed to stabilization of the internal double bond by hyperconjugation,[11] resonance (with aromatic substituents), or hybridization.[12]

The position of the double bond is not the only factor that determines the relative stability of allylic isomers. Equally important is the nature of the functional group. Thus, the trans-I-X/II-X ratio varies from 0.37 for the allyl alcohols (X = OH),[3d] to 1.4 for the allyl acetates (X = OAc), to 12.4 for the butenes (X = H).[13]

Steric effects also exert an influence on the composition of the equilibrium mixture. The 3.1:1 trans- to cis-2-butene ratio at equilibrium[11] is probably due almost entirely to greater steric congestion (nonbonded repulsions) in the cis isomer. Apparently, this steric congestion is aggravated by the presence of an acetate group, since the trans:cis ratio for the crotyl acetates is increased to 4.9:1.

Mechanism. The butenyl acetates are subject to uncatalyzed and to acid-catalyzed isomerization in acetic acid. However, since the isomerization rate is increased by ca. 10^5 with 0.008435 M HClO$_4$ the uncatalyzed reaction does not make a significant contribution to the acid-catalyzed isomerizations studied here. Accordingly, we will concern ourselves solely with the mechanism of the acid-catalyzed reaction.

DeWolfe and Young[10] have reviewed the literature pertinent to the question of the mechanism of acid-catalyzed allylic ester isomerization and, in summary, it appears that these reactions proceed by an A-1 mechanism involving a rate-determining alkyl-oxygen cleavage of the protonated ester to produce the allyl cation. The degree of association of the carbonium ion and the leaving group is governed by the nature of the substrate and the reaction conditions. The allylic carbonium ion may combine with a carboxylic acid molecule to regenerate the ester with rearranged or retained allylic structure, or it may unite with other available nucleophiles. It is also possible for the carbonium ion to succumb to various degradation and polymerization processes.

In addition to the simple carbonium ion (A-1) mechanism, SNi' and SN2' mechanistic paths are, in principle, available to the protonated ester molecule. Although little evidence has been found for the operation of the SNi' or SN2' mechanisms in similar reactions[8,14] an effort was made to estimate their importance in the isomerization of the butenyl acetates.

(10) R. H. DeWolfe and W. G. Young, "The Chemistry of the Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, Chapter 10.
(11) J. W. Baker, "Hyperconjugation," Oxford University Press, Amen House, London, 1952.
(12) M. J. Dewar, Tetrahedron, **5**, 166 (1959).
(13) K. W. Egger, D. M. Golden, and S. W. Benson, J. Amer. Chem. Soc., **86**, 5420 (1964).
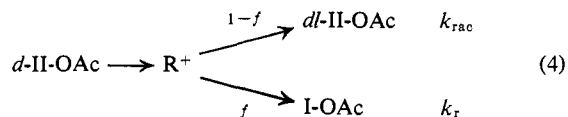(14) H. L. Goering and E. F. Silversmith, ibid., **77**, 6249 (1955).

A comparison of the polarimetric (k_α) and gc (k_r) rates of α-methylallyl acetate in 0.008 M perchloric acid (Tables III and V, respectively) reveals that this ester lost optical activity 3.6 times as fast as it rearranged to its allylic isomers ($k_\alpha/k_r = 3.6$). Thus, the best measure of ionization is provided by the polarimetric rate, k_α, which is equal to the sum of the rate of rearrangement, k_r, and the rate of racemization, k_{rac} (loss of optical activity without rearrangement) ($k_\alpha = k_r + k_{rac}$).

$$d\text{-II-OAc} \longrightarrow R^+ \begin{array}{c} \xrightarrow{1-f} dl\text{-II-OAc} \quad k_{rac} \\ \\ \xrightarrow{f} \text{I-OAc} \quad k_r \end{array} \qquad (4)$$

The results can be explained by an ionization process generating an allylic cation which can collapse with HOAc at the primary carbon to produce I-OAc or at the secondary carbon to produce II-OAc. The fraction collapse at the primary (f) and secondary ($1 - f$) carbons is provided by the k_{rac}/k_r ratio. Thus, the k_{rac}/k_r of 2.6 indicates that chemical capture of the allylic cation occurs 28% at the primary carbon and 72% at the secondary carbon.

$$f = \frac{k_r}{k_r + k_{rac}}$$

$$1 - f = \frac{k_{rac}}{k_r + k_{rac}}$$

In the $HClO_4$-catalyzed demercuration of trans-crotylmercuric acetate in acetic acid the kinetic products are 29% I-OAc and 71% II-OAc.[3b] The product ratio produced in the demercuration reaction is in good agreement with the relative rates of chemical capture of the primary and secondary carbon atoms of the allylic cation, as calculated from the rate studies with II-OAc. This result is in line with having the same series of allylic cation intermediates present in both of these reactions.

The slight discrepancy observed may be due to the fact that the trans-crotylmercuric acetate used in the demercuration[2b] produced only trans-crotyl cations rather than the mixture of cis and trans ions (vide infra) expected when α-methylallyl acetate ionizes. That the discrepancy is not greater is probably a consequence of the relatively small number of cis-carbonium ions produced by the secondary acetate, as evidenced by the 40:1 trans- to cis-crotyl acetate ratio in the initial stages of the isomerization of α-methylallyl acetate.

The existence of racemization in excess of rearrangement and the similar product story in the allylic acetate and allylic mercuric acetate reactions are inconsistent with rearrangement occurring exclusively via either the $SN2'$ or SNi' process. In both of these processes the rate of loss of optical activity and the rate of rearrangement are expected to be equal.

Cis-Trans Isomerization. In the Results of this paper strong evidence was presented to support the validity of the assumption that interconversion of the cis- and trans-crotyl acetates occurs mainly through the intermediacy of α-methylallyl acetate. It was found that good agreement was obtained between experimental values for equilibrium constants and developing acetate

concentrations, and those calculated on the basis of this assumption.

In terms of carbonium ion intermediates the simplest interpretation of the absence of direct cis–trans interconversion is that cis- and trans-crotyl acetate generate only their respective allylic cations. These ions retain sufficient double bond character as to make rotation about the $C \cdots C$ bonds highly unfavorable. Thus, interconversion between the two isomeric cations must occur most readily by collapse with AcOH at the secondary carbon followed by rotation about the generated single bond and reionization. This process is diagrammed in eq 5.

$$ \text{(5)} $$
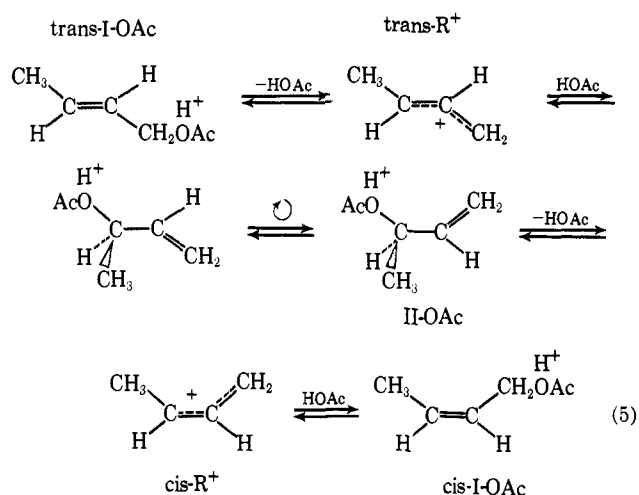
With the information at hand it is possible to calculate the free-energy relationships in the interconversion of trans-crotyl, α-methylallyl, and cis-crotyl acetate. The difference in the ground-state free energies between trans-I-OAc, II-OAc, and cis-I-OAc is 0.21 and 0.91 kcal/mol, respectively (Table VI). The best mea-

Table VI. Equilibrium Constants and Thermodynamic Parameters for the Butenyl Acetates in Acetic Acid[a]

Acetate ratio	K 50.0°	K 75.0°	ΔF (50.0°), cal/mol	ΔH, cal/mol	ΔS (50.0°), eu
trans-I-OAc/II-OAc	1.375	1.346	−205	−187	0.055
cis-I-OAc/II-OAc	0.2419	0.2726	912	1069	0.486

[a] ROAc concentration was ca. 0.1 M. Perchloric acid concentration was 0.008435 N.

sure of the ionization rate constant is provided by correcting the measured k_r for rearrangement by the fraction of the intermediate that gives rise to rearranged ester. Thus, the ionization rate constant for trans-I-OAc is 9.57×10^{-5} sec^{-1}, where the measured k_1 is 6.89×10^{-5} sec^{-1} and the fraction of the intermediate (trans-R$^+$) that produces II-OAc ($1 - f$) is 0.72. The corresponding free energy of activation is 24.90 kcal/mol. A similar correction provides the value 34.5×10^{-5} sec^{-1} for the ionization k for II-OAc going to trans-I-OAc ($\Delta F^{\ddagger} = 24.10$ kcal/mol). The difference between 34.5×10^{-5} sec^{-1} and k_α for II-OAc, 35.9×10^{-5} sec^{-1}, is the ionization k for II-OAc going to cis-I-OAc (1.5×10^{-5} sec^{-1}, $\Delta F^{\ddagger} = 25.88$). Since the ionization k is 4.37 times greater than k_3 (0.344 $\times$ 10^{-5} sec^{-1}) for II-OAc $\rightarrow$ cis-I-OAc, the fraction of the
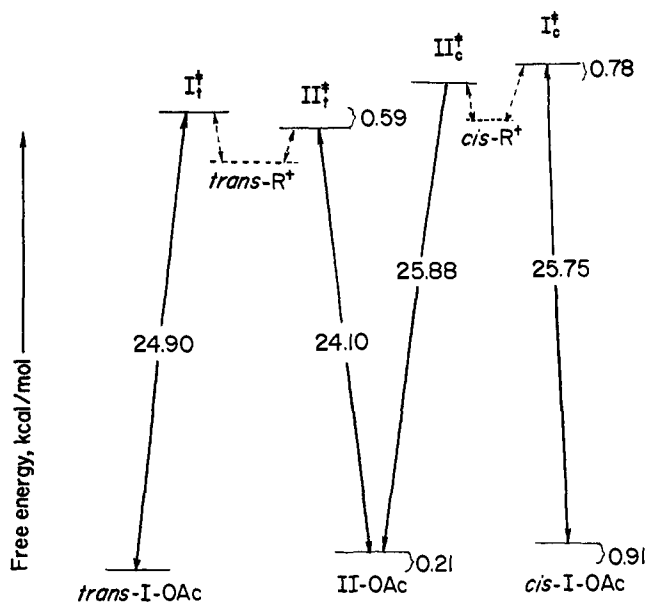
Figure 1. Free-energy relationships for the acid-catalyzed isomerization of the butenyl acetates.

cis-allylic cation (cis-R+) that collapses to produce cis-I-OAc is 0.23. Finally, correcting k_r for cis-I-OAc → II-OAc (1.42×10^{-5} sec^{-1}) for the fraction of cis-R+ which gives II-OAc (0.77) provides the value 1.85×10^{-5} sec^{-1} ($\Delta F^{\ddagger} = 25.75$ kcal/mol) for the ionization k for cis-I-OAc.

The calculated ionization k's are listed in Table VII along with the corresponding values for free energy of activation. The result of these calculations brings out

Table VII. Summary of Reaction Rate Constants for the Isomeric Allylic Acetates

Ionization process	$10^{6}k$, sec^{-1} k_r	k_{ion}	$\Delta F^{\ddagger}$ for k_{ion}, kcal/mol
trans-I-OAc → II-OAc (k_1)	6.89	9.57	24.90
cis-I-OAc → II-OAc (k_4)	1.42	1.85	25.75
II-OAc → trans-I-OAc (k_2)	9.66	3.45	24.10
II-OAc → cis-I-OAc (k_3)	0.344	1.5	25.88

two interesting points. First, collapse of the allyl cation with HOAc occurs preferentially at the secondary carbon atom with only a small variation in the collapse ratio due to the isomeric structure of the allylic cation. Secondly, the ground-state energies of the isomeric butenyl acetates do not seem to influence the relative stabilities of the rate-determining transition states. This is best seen in the energy diagram in Figure 1.

The extent to which the allylic cation can distinguish the originally attached HOAc from the rest of the solvent was not measured. However, based on other studies, it is suspected that rearrangement proceeds with complete exchange of the leaving HOAc with solvent. Thus, in the isomerization of acetate-labeled 1-phenylallyl acetate in acetic acid, isomerization proceeds with complete exchange.[9] Similarly, acetate-labeled p-chlorobenzhydryl acetate in acetic acid racemizes in acetic acid with complete exchange.[15]

(15) A. F. Diaz and S. Winstein, J. Amer. Chem. Soc., 86, 4484 (1964).

Experimental Section

Materials. Unless otherwise specified the chemicals employed in this investigation were reagent grade and were used without further purification. All boiling points are uncorrected.

Butenyl Acetates. The butenyl alcohols were prepared and purified as described by Young and Franklin.[3d] The acetates were prepared by heating each of these alcohols (0.125 mol) and purified acetic anhydride (0.25 mol) on a steam bath for 9.5 hr. The acetate product was recovered by extraction with ether and purified by distillation. The secondary acetate was further purified by preparative gc on a 15 ft × ³/₈ in., 15% tricresyl phosphate (TCP) on 60–80 mesh Chromosorb W column.

The trans-γ-methylallyl acetate was 99.57% pure (see Table VIII) and had bp 137.5–138°; n^{25}D 1.4150 [lit.[2] bp 132–133°; n^{20}D 1.4183].

Table VIII. Purity of Butenyl Acetates

ROAc	Purity of ROAc, % trans-I-OAc	cis-I-OAc	II-OAc
trans-I-OAc	99.57	0.43	<0.01
cis-I-OAc	1.30	98.70	<0.01
II-OAc	<0.02	<0.02	>99.96

The cis-γ-methylallyl acetate was 98.70% pure (see Table VIII) and had bp 134°; n^{25}D 1.4193.

The α-methylallyl acetate was >99.96% pure (see Table VIII) and had bp 112.5°; n^{25}D 1.4015 [lit.[2] bp 112.5°; n^{20}D 1.4048].

(−)-α-Methylallyl Acetate. Optically active (+)-α-methylallyl alcohol (prepared by K. L. Oliver) was converted to the acetate ester with acetic anhydride containing a small amount of pyridine. The ester was recovered by extraction in the usual manner and the last traces of solvent were removed at room temperature and ca. 1.5 mm. The ROAc was 98% pure by glc analysis: $[\alpha]^{25}$D −19.83° (c 0.0174, acetic acid).

Acetic Anhydride. Acetic anhydride distilled through a 42-stage Oldershaw column had bp 138.5–139.0°; n^{25}D 1.3870 [lit.[16] bp 139.55°, n^{26}D 1.39006].

n-Pentane. Pure pentane was prepared by washing approximately 5.5 l. of technical grade pentane with 100-ml portions of concentrated sulfuric acid repeatedly until the acid no longer turned yellow. The pentane was then washed with 200 ml of water, dried over calcium chloride, and distilled from phosphorus pentoxide through a 42-stage Oldershaw column.

n-Butyl Acetate. n-Butyl acetate was purified by preparative gc on the 15-ft TCP column and then distilled through a simple apparatus: bp 122.5°; n^{25}D 1.3917 [lit.[16] bp 126.5°; n^{26}D 1.3941].

Dry Acetic Acid. Glacial acetic acid containing ca. 1% added acetic anhydride was refluxed overnight prior to distillation through a 42-stage Oldershaw distillation column. Acetic acid, with bp 117.5°, was collected directly in a 4-l. dispensing flask.

Acetic anhydride (1.800 g) was added to the acetic acid in the dispenser to ensure dryness. Tests for water (Karl Fischer) and acetic anhydride (anthranilic acid method[17]) content showed that the acetic acid contained less than 0.0518 mg/ml of water and was 0.0021 N in acetic anhydride.

Perchloric Acid–Acetic Acid Solution. To an oven-dried 500-ml volumetric flask, partially filled with acetic acid, were added 7.4646 g of 67.2% perchloric acid and 13.7727 g of acetic anhydride, which was made up to volume with acetic acid. (It is important that the perchloric acid be diluted before the acetic anhydride is added, since concentrated solutions of these reagents may explode!) A Karl Fischer titration of this solution showed it to contain 0.000248 mmol of water/ml. Acetic anhydride (0.5095 g) was added to the solution to react with the water and to provide a 0.01 M concentration of the anhydride. The perchloric acid concentration (0.1071 N) was determined by standardization with standard sodium acetate in acetic acid to a brom phenol blue end point.

Gas Chromatography. A 20 ft × ¹/₈ in. o.d., 4.8% TCP on 80–100 Chromosorb W column was used for the analysis of all

(16) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969–1970.

(17) E. Grunwald, Ph.D. Dissertation, University of California at Los Angeles, 1947.

kinetic and equilibrium samples. Standard operating conditions for the analyses were: column, 70°; detector, 80°; injector, 145°; nitrogen, 30 cm³/min; hydrogen, 20 cm³/min; air, 330 cm³/min. Under these standard conditions the butenyl acetates were eluted in the order: II-OAc (6.2 min after the solvent peak); cis (14.9 min); trans (15.8 min); the internal standard, n-butyl acetate, was eluted after 10.9 min.

Gc Rates and Equilibria. All of the reaction solutions were prepared in the same manner, with the exception of those for the polarimetric rates. To a weighed sample (ca. 0.285 g) of butenyl acetate in a dry 25-ml volumetric flask, was added 15–20 ml of dry acetic acid, a 1.969-ml aliquot of 0.1071N perchloric acid in acetic acid, and dry acetic acid to volume. Portions of the reaction solution (3.5 ml) were sealed in ampoules and immersed in a constant temperature bath. The ampoules were removed from the bath at appropriate times and quenched in Dry Ice–acetone. The frozen reaction solution was brought to room temperature and a 1.969-ml aliquot of this solution was transferred into a flask containing a Dry Ice–cold pentane solution of the internal standard, n-butyl acetate. This mixture was allowed to warm until the acetic acid was just melted, at which time the contents of the flask were extracted with 38 ml of ice-cold saturated potassium carbonate. The emulsion that formed was broken by centrifugation. The organic layer was isolated, concentrated to 2 ml, and analyzed by glc.

Control experiments showed that there was essentially no loss or factionation of the butenyl acetates during the work-up procedure.

To test the uncatalyzed rate of butenyl acetate rearrangement in acetic acid, a 0.1 M solution of butenyl acetate in anhydrous acetic acid was heated for 72 hr at 75.0° and analyzed as above. The greatest amount of isomerization occurred in the case of the secondary acetate, 0.68%.

Polarimetric Rates. The reaction solutions were prepared by carefully weighing a ca. 0.175-g sample of (−)-α-methylallyl acetate into a 10-ml volumetric flask and then diluting the acetate to the capacity mark with 0.008435 or 0.01687 M perchloric acid in acetic acid. The concentration of perchloric acid in the reaction solution was calculated by assuming additive volumes (the density of α-methylallyl acetate is 0.90235[18]). The reaction rates were

(18) J. Brandreghein, *Bull. Soc. Chim. Belg.*, **31**, 160 (1922).

measured in a sealed 0.2-dm all-glass cell placed in a holder thermostated at 50.0° using a modified Bendix Ericsson automatic polarimeter.

Estimation of Cis–Trans Isomerization *via* α-**Methylallyl Acetate.** The calculated concentrations of cis-crotyl acetate and α-methylallyl acetate listed in Table IV were obtained with the aid of eq 6 and 7, where C_t^c = percentage of cis-acetate at time t; C_t^s = percentage

$$C_t^c = A_0\left(\frac{k_1 k_3}{\lambda_2 \lambda_3} + \frac{k_1 k_3}{\lambda_2(\lambda_2 - \lambda_3)}e^{-\lambda_2 t} - \frac{k_1 k_3}{\lambda_2(\lambda_2 - \lambda_3)}e^{-\lambda_3 t}\right) + C_0^c \quad (6)$$

$$C_t^s = A_0\left(\frac{k_1 k_4}{\lambda_2 \lambda_3} + \frac{k_1(k_4 - \lambda_2)}{\lambda_2(\lambda_2 - \lambda_3)}e^{-\lambda_2 t} + \frac{k_1(\lambda_3 - k_4)}{\lambda_3(\lambda_2 - \lambda_3)}e^{-\lambda_3 t}\right) + C_0^s \quad (7)$$

of secondary acetate at time t; C_0^c = percentage of cis-acetate at zero time; C_0^s = percentage of secondary acetate at zero time; A_0 = percentage of trans-acetate at zero time; $\lambda_2 = \frac{1}{2}(p + q)$; $\lambda_3 = \frac{1}{2}(p - q)$; $p = (k_1 + k_2 + k_3 + k_4)$; $q = [p^2 - 4(k_1 k_3 + k_2 k_4 + k_1 k_4)]^{1/2}$. These expressions were adapted from equations derived for two consecutive first-order reactions.[6] A term (C_0) was added to the original equations to compensate for the presence of isomeric impurities at (experimental) zero time. The rate constants are labeled in accordance with eq 1, and at 25° are: $k_1 = 3.35 \times 10^{-6}$, $k_2 = 4.62 \times 10^{-6}$, $k_3 = 1.64 \times 10^{-7}$, $k_4 = 5.94 \times 10^{-7}$ sec⁻¹. The values used for k_1 and k_4 are the experimentally determined pseudo-first-order rate constants for the disappearance of trans- and cis-crotyl acetate, respectively (Table III). The values for k_2 and k_3 were obtained from the corresponding rate constants at 50° with the aid of the activation energy for the acid-catalyzed isomerization of the secondary acetate (Table III). The sum of these calculated values for k_2 and k_3 should be (and is) equivalent to the experimental pseudo-first-order rate constant for the disappearance of α-methylallyl acetate at 25° (4.78 × 10⁻⁶ sec⁻¹, Table III).