The Allylic Rearrangement of Linalyl Acetate in the Medium of Acetic Acid, Propionic Acid, or Acetic Acid Containing Dioxane or Sulfuric Acid

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The mechanism of the allylic rearrangement of linalyl acetate in the medium of acetic acid, propionic acid, or acetic acid containing dioxane or sulfuric acid has been investigated. The nature of the carbonium-ion pairs generated from linalyl acetate in low-dielectric-constant solvents or in strong acids, and the behavior of the active intermediate in the transition state were postulated from the kinetic data as well as from the physicochemical properties and distributions of the products.

It has been well known that linalyl acetate (designated as LA), an ester of tertiary monoterpene alcohols, is isomerized through allylic rearrangement. Young and Webb[1] isomerized LA to geranyl acetate in acetic acid (designated as HOAc) containing phosphoric acid (0.1 mol H_3PO_4), and Crabalona[2] to geranyl- and terpinyl acetate, geraniol, terpineol, and terpene hydrocarbons in HOAc containing 5 volume percent of water.

The foregoing studies gave qualitative results, but no quantitative data relating to the mechanism of the rearrangement or to the product distribution are available. In order to clarify the reactivity of LA in non-aqueous solvents containing HOAc, we have investigated rearrangements in the medium of HOAc, propionic acid, and HOAc containing dioxane or sulfuric acid.

The present paper discloses how the rearrangement of LA in the medium of HOAc or HOAc–dioxane has been found to be an S_N1-type solvolytic reaction[3] accompanied by both allylic rearrangement[4] and the common ion effect of the acetate anion.[5] In the case of propionic acid, the rearrangement followed a pseudo-first-order condition. An internal return[6] was postulated from the formation of racemized linalyl propionate via an intimate ion pair[7] which had formed among a carbonium ion, an acetate anion, and a propionic acid molecule. A typical acid-catalyzed A1 reaction[8-10] was found in the medium of HOAc containing sulfuric acid.

Experimental

Materials.   LA prepared by the acetylation of linalool with ketene[11,12] was supplied by T. Hasegawa Co., Ltd; its purity was analyzed by gas-liquid chromatography (designated as glc and found to be 100%: n_D^{30} 1.4501, d_{30}^{30} 0.9050, bp 88—89 °C/4 mmHg, $[\alpha]_D^{25}$ −7.6° (optical purity 96%). Commercially-available reagents of a chemical pure grade were used in this study. HOAc free from moisture was obtained by the Noyce method[13] (bp 119 °C). Dioxane, which had been refluxed with metallic sodium for 8 hr beforehand, was rectified (bp 101 °C). Sodium acetate was dehydrated by the usual method. o-Nitroaniline was recrystallized from ethanol (mp 71 °C).

Measurement of the Acidity Function H_0.   The acdity function, H_0, was estimated by spectrophotometry for each medium–LA–HOAc, HOAc–dioxane, and HOAc–sulfuric acid; we then calculated according to the following equation:

$$H_0 = \log (C_B/C_{BH^+}) + pk_a$$

where C_B and C_{BH^+} are the concentrations of the indicator used, o-nitroaniline ($pk_a = -0.17$, $\varepsilon = 5000$), and the conjugated acid respectively, both of which values were obtained at 412 mμ.[14] The measurements were carried out at 30 °C, and the density of HOAc was found to be d_{30}^{30} 1.0380.

Estimation of the Reaction Rate.   1) Rearrangement in HOAc: A mixture (20 ml) of LA and HOAc in a given ratio (10 : 90, 20 : 80 or 30 : 70 vol%) was ampouled in cleaned glass tubes (30 ml) and then dipped at once into an oil bath kept at a desired temperature (80, 100, or 120 °C). At prescribed intervals an ampoule was taken off from the bath and cooled to room temperature with water. The reaction product was poured into 200 ml of ice water, neutralized with a 10% aqueous solution of sodium carbonate, saturated with sodium carbonate, saturated with sodium chloride, and then extracted several times with 100-ml portions of ether. The extracts were then put together and dried over sodium sulfate. An oily matter obtained after the removal of the ether was weighed, and the composition was analyzed by glc using an internal standard method using methyl caprylate. In order to determine the amount of polymeric material present, oily products simultaneously collected from several amouples were distilled in vacuo by means of a micro Claisen flask.

The rate constant (k) of the rearrangement was calculated according to the following equation:

$$k = 2.303 \log (a/(a-x))/t$$

where a is the initial concentration of LA and where $a-x$ is the concentration at time t.

2) Rearrangement in the Medium of HOAc Containing Dioxane: A mixture (50 ml) of HOAc and dioxane in a given ratio (90 : 10, 80 : 20, or 70 : 30 vol%) containing 1 ml of LA (0.0046 mol) was ampouled in a glass tube (60 ml) and then placed in a thermostated oil bath at a desired temperature (80, 90, or 100±0.1 °C).

3) Rearrangement in Propionic Acid: LA and propionic acid were ampouled in glass tubes (60 ml) in a given ratio 10 : 90 vol%). The ampoules were kept in a thermostat (100±0.1 °C) for a precribed time.

4) Rearrangement in the Medium of HOAc Containing Sulfuric Acid: A mixture (50 ml) of 90% HOAc and sulfuric acid, the acidity function of which is known,[14] containing 1 ml of LA was put into a 100-ml Erlenmeyer flask. The flask was then closed with a stopper, placed in a thermostat regulated at 0±0.01 °C, and reacted while being stirred with a magnetic stirrer.

Identification of Products.   The reaction products, such as LA, d-α-terpinyl,[15] neryl- and geranyl acetates, racemized linalool, and linalyl propionates, were separated by distillation with a spinning-band-type column (dia. 6 mm; length 1.5 m) and by preparative gas liquid chromatography

TABLE 1. REARRANGEMENT OF LA IN HOAc

Reaction time (min)	T.H. Total	T.H. Comp.		Composition of product (%) LA (a)	TA	NA	GA	Dist. residue	Total yield (%) (b)	LA theor. (a)×(b)	Remarks
20	11.0	M	8.7	74.0	4.0	4.0	5.6	1.4	92.1	69.1	Reaction temp.; 80 °C.
		L	1.3								HOAc; 90 vol% (15.57 mol).
		O	0.7								LA; 10 vol% (0.5 mol).
		T	0.3								log C (HOAc) = 1.19
40	12.7	M	9.7	58.4	4.2	4.3	16.2	4.2	90.2	52.6	$H_0 = +1.02$.
		L	1.8								Optical purity $[\alpha]_D^{25}$
		O	0.9								LA (−6.8°); TA (+17°)
		T	0.3								k_1 (mean) = 0.000282 1/s.
60	15.7	M	10.2	42.4	8.5	10.9	18.2	5.0	87.9	37.3	
		L	3.9								
		O	1.0								
		T	0.6								
90	18.1	M	10.3	25.2	10.6	10.9	30.1	5.1	88.2	22.2	
		L	5.6								
		O	1.0								
		T	1.2								
90	7.0	M	5.0	78.0	4.2	4.2	6.2	0.4	90.2	70.2	Reaction temp.; 80 °C
		L	1.3								HOAc: 70 vol% (12.11 mol).
		O	0.6								LA; 30 vol% (1.5 mol).
		T	0.1								log C (HOAc) = 1.08.
180	10.6	M	7.2	68.0	4.2	4.3	11.3	1.6	90.0	61.3	$H_0 = +1.09$.
		L	2.4								Optical purity $[\alpha]_D^{25}$
		O	0.8								LA (−7.0°).
		T	0.2								k_1 (mean) = 0.0000481 1/s.
285	11.6	M	7.9	55.4	4.6	6.4	18.2	3.6	89.1	49.3	
		L	2.5								
		O	1.0								
		T	0.4								
360	12.9	M	8.6	47.5	5.8	7.6	21.2	5.0	88.3	41;9	
		L	2.7								
		O	1.2								
		T	0.4								
5	11.2	M	5.6	48.8	3.6	7.8	25.1	3.1	89.2	43.4	Reaction temp.; 120 °C.
		L	4.6								HOAc; 90 vol% (15.57 mol).
		O	0.8								LA; 10 vol% (0.5 mol).
		T	0.2								log C (HOAc) = 1.19
10	14.6	M	6.8	22.0	10.4	12.8	33.2	7.0	86.8	19.1	$H_0 = +1.02$.
		L	6.6								Optical purity $[\alpha]_D^{25}$
		O	0.9								LA (−6.4°).
		T	0.8								k_1 (mean) = 0.00257 1/s.
20	15.5	M	7.0	8.4	11.8	14.7	40.8	8.8	86.3	7.3	
		L	7.1								
		O	1.0								
		T	0.4								
20	12.0	M	7.8	53.5	5.1	9.5	16.5	3.4	87.8	49.1	Reaction temp.; 120 °C.
		L	3.8								HOAc; 70 vol% (12.11 mol).
		O	0.4								LA; 30 vol% (1.5 mol).
		T	0								log C (HOAc) = 1.08.
40	13.6	M	8.2	28.3	7.3	13.2	30.7	7.0	86.2	24.3	$H_0 = +1.09$.
		L	4.4								Optical purity $[\alpha]_D^{25}$
		O	0.8								LA (−6.9°).
		T	0.2								k_1 (mean) = 0.000589 1/s.
60	15.1	M	8.6	14.1	8.1	15.9	38.6	8.2	86.0	12.1	
		L	5.4								
		O	0.8								
		T	0.3								

Inscriptions for terpene hydrocarbons (TH): Myrcene-M, limonene-L, ocimene-O, terpinolene-T; for acetate: Linalyly acetate-LA, terpinyl acetate-TA, neryl acetate-NA, geranyl acetate-GA. Product distributions at 100 °C and in 80 vol% of HOAc are abbreviated owing to the same tendency as the others.

according to demand; they were identified by comparing the NMR, IR, and mass spectra with those of an authentic sample.[11,12] Terpene hydrocarbons, such as myrcene, limonene, β-trans-ocimene,[16] and terpinolene, were identified by comparing the mass spectra and the retention times on gas chromatography with those of the authentic samples described in the previous paper.[11,12]

Analyses of Composition. The composition of the rearrangement products of LA obtained in the prescribed medium were analyzed by glc by the internal standard method using methyl caprylate. The calibration curves of components were obtained in the usual way. Thus, LA, for instance, was analyzed within the relative experimental error of $\pm 0.5\%$, and the other components, within $\pm 1.0\%$. A 2-m stainless steel column (dia. 3 mm) packed with Rac-2R-446 (10 wt%) on Celite 545 sk of 60—80 mesh was used. The operating conditions of the gas chromatograph (Kotaki GU-21): column temperature, 150 °C; flash evaporator, 220 °C; carrier gas, (helium); flow rate, 22 ml/min. In the case of the medium of propionic acid or HOAc containing sulfuric acid, only LA was analyzed by the internal standard method, using methyl caprylate and other components and the area ratio method.

Calculation of the Total Energy of Carbonium Ions. The total energy was calculated for a few typical carbonium ions by Hoffmann's Extended Hückel Molecular Orbital Method.[17] In determining the geometry, the following assumptions were used:

1) *Bond Length*: C–C (1.541 Å), C–C, adjacent to double bond (1.53 Å), C=C (1.337 Å), C–H, monosubstituted (1.101 Å), C–H, disubstituted (1.073 Å), C–H, trisubstituted (1.070 Å), C–H, olefinic (1.071 Å).

2) *Bond Angle*: The bond angle between C=C and C–C is 120 °C; the one between two C–C, 109.5 °C; the one of a charged C atom in the plane sp² hybrid structure, 120 °C.

A method of charge iteration was incorporated in the Kikuchi-Konakahara-Ishihara EHMO (Extended Hückel Molecular Orbital) program.[18] For the calculation, a HITAC 5020 computer at the Tokyo University Computer Center was used.

Results and Discussion

Previously we reported that LA prepared by acetylation with acetic anhydride, using sodium acetate or phosphoric acid as a catalyst, is rearranged with ease, and that the rearrangement proceeds from HOAc originating in the acetylation and is accompanied by various by-products as well.[11] The latter fact led us to study the preparation of LA as pure as possible. Thus, it has been found that a method of acetylating linalool with ketene in the presence of phosphoric acid

TABLE 2. RATE CONSTANTS k_1 (1/s) OF REARRANGEMENT
OF LA IN HOAc

HOAc	80 °C	100 °C	120 °C
90 vol%	2.82×10^{-4}	9.58×10^{-4}	2.57×10^{-3}
80 vol%	1.26×10^{-4}	4.37×10^{-4}	1.45×10^{-3}
70 vol%	4.81×10^{-5}	1.50×10^{-4}	5.89×10^{-4}

Remarks: HOAc 90 vol% (15.57 mol)–LA
                                        10 vol% (0.5 mol)
            HOAc 80 vol% (13.84 mol)–LA
                                        20 vol% (1.0 mol)
            HOAc 70 vol% (12.11 mol)–LA
                                        30 vol% (1.5 mol)

gives neither HOAc nor by-products.[11] In order to reveal the mechanism of rearrangement in LA, the following Reactions (1)—(4) were examined.

(1)   Rearrangement of LA in HOAc. The results obtained under controlled conditions were as follows. The rates of rearrangement in HOAc were found to be of the first order in any of the concentrations examined on LA (Table 1). The rate contant increased with an increase in both the concentration of HOAc and the reaction temperature (Table 2). Ratios of logarithm of the rate constant against that of the molar concentration of HOAc yield straight lines, with the slope varying from 5.0 to 7.0 (order of solvent participation).[3] This fact proves that the rearrangement of LA in HOAc is an S_N1-type solvolytic reaction. The ionization of LA to carbonium-ion pairs is assumed to result from a solvation due to the formation of hydrogen bonds among a carbonium ion, and an acetate anion and some HOAc molecules. The Arrhenius plots of log k_1 versus $1/T$ gave straight lines. The estimated activation energy ranged from 15.00 to 17.20 kcal/mol, and the entropy of activation, from -34.8 to -31.5 e.u. As the concentration of HOAc increases, both the activation energy and the entropy decrease as follows:

HOAc vol%	LA vol%	ΔE kcal/mol	ΔS^* (e.u.)		
			120 °C	100 °C	80 °C
70	30	17.20	-34.7	-32.4	-31.9
80	20	16.65	-31.9	-31.7	-31.5
90	10	15.00	-34.8	-34.6	-34.6

The results indicate that the carbonium-ion pairs are easily formed in the transition state, and that the formation of a solvent shell due to the surrounding acetic acid molecules diminishes the degree of freedom to react.

The above discussion is based on the apparent kinetical data; however, the product distribution in the rearrangement should be considered as well. The compositions of the rearrangement products were analyzed by glc by the internal standard method using methyl caprylate. The calibration curves of the components,
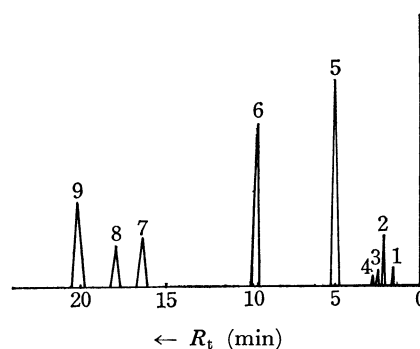

← R_t (min)

Fig. 1.   A typical gas chromatograms of the products in a rearrangement.
1: myrcene, 2: limonene, 3: ocimene, 4: terpinolene, 5: methyl caprylate, 6: LA, 7: terpinylacetate, 8: neryl acetate, 9: geranyl acetate.

such as LA, terpinyl-, neryl-, geranyl acetates and terpene hydrocarbons (the mixture of myrcene, limonene, ocimene and terpinolene was found to have the ratio of 1 : 2 : 1 : 0.2), were obtained by the usual way. All the curves referring to the area ratio against the weight ratio of these compounds to methyl caprylate showed a linear relationship. The products estimated from the gas chromatograms (Fig. 1) were as follows: partially racemized (10—15%) LA, acetates of geranyl, neryl, and the more racemized (65—70%) d-α-terpinyl, myrcene, limonene, β-trans-ocimene and terpinolene. The degrees of racemization in the LA and terpinyl acetate separated by preparative glc were estimated by the loss of optical purity (Table 1). The partial racemization of LA suggests a much higher stereospecificity for the return from the carbonium-ion pair to LA than for the solvent (HOAc) collapes.[4] On the other hand, the remarkable racemization of terpinyl acetate ($[\alpha]_D^{25}$ of pure acetate, +52.5°) shows a preferential collapse of the terpinyl-carbonium ion with the solvation shell of HOAc.

The amounts of acetates resulting from the allylic rearrangement were found to be in the following order:

geranyl > neryl > linalyl > terpinyl
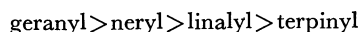
The acetates of geranyl (trans) and neryl (cis) were considered to be derived from the primary terpenoid carbonium ion and the d-α-terpinyl acetate, from the tertiary terpenoid carbonium ion. The product distribution is proportional to the instability of the following carbonium ions, disclosing that the labile carbonium ions are more reactive:[19]

carbonium ion   geranyl   linalyl   terpinyl
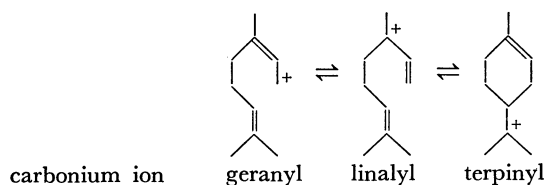
As the terpinyl carbonium ion is considered to be the most stable one of the four, the total energies of the other two typical carbonium ions (geranyl and linalyl) were calculated by Hoffmann's EHMO Method (Figs. 2—3). The instability of these carbonium ions was found to be in the following order;

carbonium ion	geranyl	linalyl
eV	−983.724	−984.322
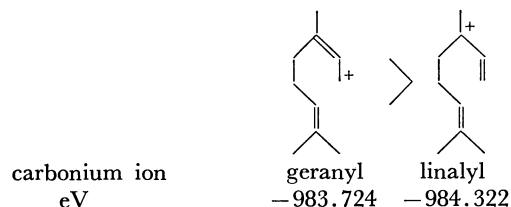
This order well agrees with the results mentioned above.

The acetates of geranyl, neryl, and terpinyl obtained were not further isomerized in HOAc under the same conditions (Table 1, Remarks column). This indicates that; 1) these acetates are directly formed by the alkyl fission of LA via carbonium ions, and 2) the rearrangement of LA may be promoted by the delocalization of the tertiary carbonium ions due to the allyl group.

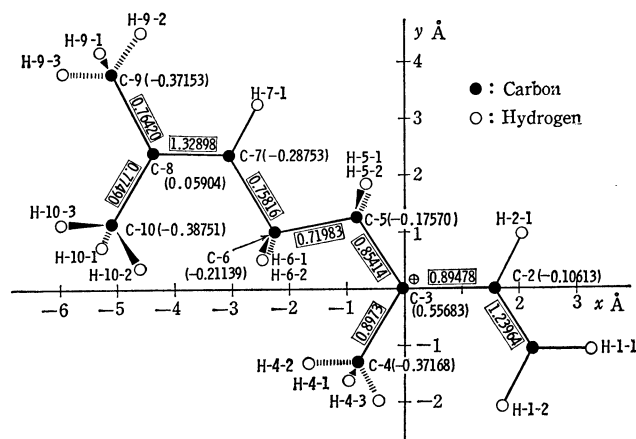An E_1-type elimination was found to be accompanied

Fig. 2. Calculation on the total energy of a linalyl carbonium ion.
Total energy: −984.3220 eV.
Numerals in ( ) refer to formal charge and those in [ ] to bond population.
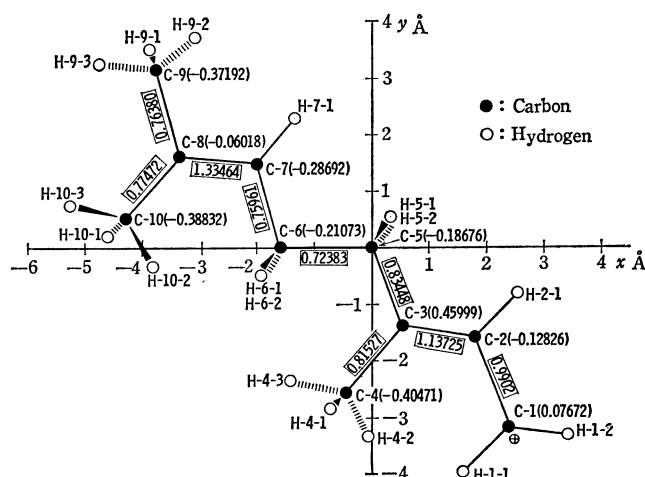

Fig. 3. Calculation on the total energy of a geranyl carbonium ion.
Total energy: −983.7244 eV.

by a S_N1-type solvolytic reaction. The elimination products amounted to as much as 20% of the total. They were terpene hydrocarbons, such as myrcene, limonene, ocimene, and terpinolene, which were also considered to be derived from the above carbonium ions. Even at relatively lower concentrations of HOAc as well as at lower reaction temperatures and in the eary stages of the rearrangement, a great deal of myrcene was found, together with a small amount of limonene, ocimene, and terpinolene. However, the amount of limonene nearly increased with the concentration of HOAc as well as with the advance of the reaction. As a result, the main product under the conditions of an S_N1-type solvolytic reaction was found to be the above-described primary acetates (geranyl and neryl), while the main products of an E_1-type elimination was myrcene. The latter result agrees well with the fact that acetates of geranyl and neryl are broken down to form myrcene in an electron-impact elimination.[12]

For studying the common ion effect charcteristic of the S_N1-type solvolytic reaction, LA was isomerized

Table 3. Rearrangement of LA in the medium of HOAc containing sodium acetate

| Reaction time (hr) | Composition of products (%) | | | | | | Yield (%) |
	TH	LA	TA	NA	GA	Residue	
A 0.5	15.0	54.1	8.8	4.1	15.4	2.6	89.0
1.0	18.5	45.3	10.8	6.7	14.0	4.7	88.1
		$[\alpha]_D^{25}$ $-7.2°$					
B 0.5	10.1	76.4	3.4	2.8	6.2	1.1	92.0
1.0	10.6	74.0	4.5	2.8	6.3	1.8	91.2
		$[\alpha]_D^{25}$ $-7.4°$					
C 0.5	15.7	52.7	7.4	5.4	15.0	3.8	90.1
1.0	19.7	30.1	9.3	7.1	27.5	6.5	89.1
		$[\alpha]_D^{25}$ $-7.0°$					

Remarks: Reaction temperature; 120 °C. A; LA (1.0 mol)-HOAc (3.34 mol)-sodium acetate (0.5 mol). B; LA (1.0 mol)-HOAc (3.34 mol)-sodium acetate (1.5 mol). C; LA (1.0 mol)-HOAc (3.34 mol). Inscriptions for terpene hydrocarbons, TH; for acetates; linalyl acetate, LA; terpinyl acetate, TA; neryl acetate, NA; geranyl acetate, GA.

in the medium of HOAc containing sodium acetate, and was estimated by glc on the basis of the product distribution. The effect seems to suppress the ionization of LA to carbonium ion pairs qualitatively. Table 3 shows the results obtained. The optical purity of LA was almost the same before and after the reaction. It may be postulated that nucleophilic acetate anions dissociated from sodium acetate are attracted to coordinate intimately with the carbonium ion of LA, resulting in the prevention of coordination with the neutral HOAc molecules.

(2) Rearrangement of LA in the Medium of HOAc containing Dioxane.   It is well known that a carbonium ion is coordinated from the back with a dioxane molecule.[3] Consequently, dioxane is considered to be a suitable solvent for studying the specific solvation of HOAc. The rearrangement of LA in the medium of HOAc containing dioxane was found to be of the first order with respect to the concentration of LA. The rates constants and the product distributions estimated in the same manner as (1) are summarized in Tables 4 and 5. In the straight lines giving the correlation between the logarithm of the concentration of HOAc and that of the rate constant, the slopes of the lines ranged from 7.3 to 7.5 (the value corresponds to the order of solvent participation).[3] Thus, the rearrangement in this case can be classified as an S_N1-type solvolytic reaction. The plots of the Arrhenius equation relating to log k_1 and $1/T$ gave straight lines. The estimated activation energy changed from -15.41 to -20.63 kcal/mol; however, no linearity was found with the concentration of HOAc as follows:

| HOAc vol% | Dioxane vol% (mol. fr.) | ΔE kcal/mol | ΔS^* (e.u.) | | |
			100 °C	90 °C	80 °C
45	5 (0.07)	15.41	-34.1	-34.5	-33.7
40	10 (0.14)	20.63	-22.1	-21.7	-21.9
35	15 (0.21)	19.67	-25.7	-26.2	-25.6

LA, 1 vol%, 0.0046 mol.

The value increased nearly parallel with the increase in the molar fraction (up to 0.14) of dioxane, and then decreased. This may be explained in terms of the

specific solvation of a polar solvent, HOAc, in the mixed system.[4] In spite of the presence of an actual rearrangement, the well reservation in the optical purity of LA proves that the coordination of dioxane to a carbonium ion eventually occurred from the back alone (Table 4). The entropy of activation, which ranged from -34.5 to -21.7 e.u., also discloses that the solvation of HOAc to a carbonium ion is much stronger than that of dioxane. The smaller effect of dioxane on the solvation in the medium of HOAc containing dioxane resulted also in a product distribution similar to that in the medium of HOAc (Table 4).

(3) Rearrangement of LA in Propionic Acid. There is no available means to prove the reverse reaction, in which a LA molecule returns via the carbonium ion or the ion pairs to the original LA in the foregoing system (1)—(2). Thus, the rearrangement of LA in propionic acid was examined. Table 6 gives the results obtained. The kinetics of the rearrangement were found to follow the first-order rate law with respect to the concentration of LA. As products, not only propionates of linalyl, geranyl, neryl, and terpinyl, but also acetates of the same terpene alcohol, were obtained, together with some terpene hydrocarbons. Among the products, only linalyl
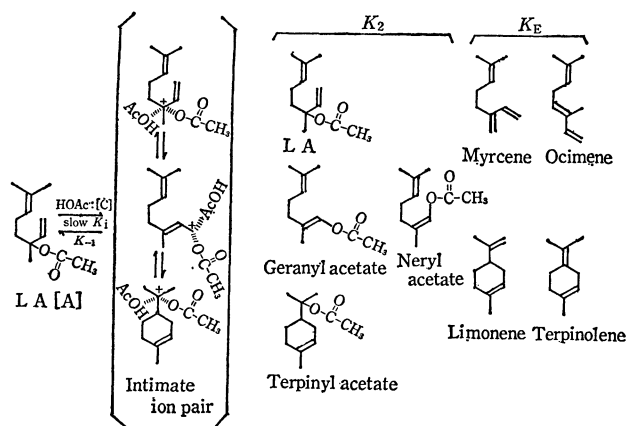

Fig. 4. Postulated mechanism on the rearrangement of LA in HOAc.

TABLE 4. REARRANGEMENT OF LA IN THE MEDIUM OF HOAc CONTAINING DIOXANE

Reaction time (min)	TH Total	TH Comp.	LA (a)	TA	NA	GA	Dist. residue	Total yield (%) (b)	LA theor. (a)×(b)	Remarks
7	2.1	M 1.9 / L 0.1 / O 0.1 / T 0	78.9	4.1	3.5	10.5	1.0	92.3	72.8	Conc.; vol% mol / HOAc 45 15.57 / Dioxane 5 1.13
14	3.0	M 2.2 / L 0.4 / O 0.4 / T 0	58.0	7.1	6.7	22.9	2.3	88.8	51.5	LA 1 0.0046 / Reaction temp.; 100 °C. / $H_0 = +0.84$. log C (HOAc) = 1.19.
21	6.8	M 4.8 / L 1.2 / O 0.6 / I 0.2	41.2	13.4	10.7	24.9	3.0	89.6	36.1	Optical purity $[\alpha]_D^{25}$: / LA $(-7.0°)$; TA $(+17.2°)$. / k_1 (mean) $=0.000785$ l/s.
10	1.2	M 1.0 / L 0.1 / O 0.1 / T 0	88.9	1.9	1.9	5.8	0.3	94.1	83.9	Conc.: vol% mol / HOAc 40 13.84 / Dioxane 10 2.27
20	2.0	M 1.2 / L 0.4 / O 0.4 / T 0	79.6	3.6	5.4	8.2	1.0	94.0	74.8	LA 1 0.0046 / Reaction temp.; 100 °C / $H_0 = +0.96$. log C (HOAc) = 1.14.
30	3.9	M 2.6 / L 0.7 / O 0.5 / T 0.1	69.8	5.0	7.0	12.7	1.6	92.2	64.4	Optical purity $[\alpha]_D^{25}$: / LA $(-7.2°)$. / k_1 (mean) $=0.000260$ l/s.
10	1.0	M 0.8 / L 0.1 / O 0.1 / T 0	95.9	0.5	1.0	1.3	0.3	94.3	90.4	Conc.: vol% mol / HOAc 35 12.11 / Dioxane 15 3.40
20	4.3	M 3.6 / L 0.4 / O 0.3 / T 0	88.1	1.1	1.6	4.6	0.3	94.4	83.2	LA 1 0.0046 / Reaction temp.; 100°C. / $H_0 = +1.04$. log C (HOAc) = 1.08.
40	6.2	M 5.1 / L 0.6 / O 0.5 / T 0	79.9	2.1	3.0	8.2	0.5	90.6	72.2	Optical purity $[\alpha]_D^{25}$: / LA $(-7.3°)$; TA $(+18°)$. / k_1 (mean) $=0.000150$ l/s.
80	10.9	M 9.1 / L 1.0 / O 0.6 / T 0.2	55.1	4.6	7.8	19.5	2.0	91.0	50.1	

Inscriptions for terpene hydrocarbons and acetates are the same as those in Table 1.
Product distributions at 80 and 90 °C are abbreviated owing to the same tendency as those at 100 °C.

TABLE 5. REARRANGEMENT RATE CONSTANTS k_1 (1/s) OF LA IN THE MEDIUM OF HOAc CONTAINING DIOXANE

HOAc vol%	HOAc mol	Dioxane vol%	Dioxane mol	LA vol%	LA mol	80	90	100
45	15.57	5	1.13	1	0.0046	2.45×10^{-4}	3.10×10^{-4}	7.85×10^{-4}
40	13.84	10	2.27	1	0.0046	5.48×10^{-5}	1.40×10^{-4}	2.60×10^{-4}
35	12.11	15	3.40	1	0.0046	3.40×10^{-5}	5.64×10^{-5}	1.50×10^{-4}

(Medium) — (Reaction temperature (°C))

propionate was found to be racemized. This fact suggests that a leaving-group acetate anion was rather closely associated with a carbonium ion (linalyl) to form an intimate ion pair, and that a selective internal return[6] resulted in the products obtained. This interesting finding reflects the structure of the intimate ion pairs as well as the varieties of the activated intermediate in the transition state.

The same phenomenon can be expected to occur in the rearrangement of LA in the medium of HOAc, because the former system has a dielectric constant and pk_a similar to those in the medium of propionic acid.

Based on the preceding results, the kinetic and mechanism of the rearrangement of LA in HOAc can be postulated to be as follows (Fig. 4):

$$v = k_1(C)^x(A)k_2(C)/(k_{-1}+k_2(C)+k_E)$$
$$k_{-1} \text{ or } k_E = \text{very small} \ll k_2(C).$$
$$v = k_1(C)^x(A).$$

TABLE 6. REARRANGEMENT OF LA IN PROPIONIC ACID

Reaction time (min)	Total	TH Compos.	Composition of products (%)								Yield total (b) (%)	LA theor. (a×b)
			LA (a)	LP	TA	NA	GA	TP	NP	GP		
45	4.1	M 1.5 L 2.5 O 0.2 T 0	77.3	3.3	0.4	3.4	5.7	0.2	1.5	4.0	94.2	72.9
90	11.4	M 4.4 L 6.5 O 0.3 T 0.2	65.0	3.8	0.7	3.9	6.1	0.5	2.0	4.6	90.0	58.5
180	17.2	M 7.5 L 8.9 O 0.7 T 0.4	40.4	5.9	1.8	6.3	14.1	1.6	4.3	8.1	85.2	35.4

Remarks: Reaction temp; 100 °C. Propionic acid; 90 vol% (12.16 mol). LA; 10 vol% (0.5 mol).
Inscriptions for tepene hydrocarbons–TH; myrcene–M, limonene–L, ocimene–O, terpinolene–T, for acetates; linalyl acetate–LA, terpinyl acetate–TA, neryl acetate–NA, geranyl acetate–GA for propionates; linalyl propionate–LP, terpinyl propionate–TP, neryl-propionate–NP, geranyl propionate–GP. Optical purity $[^{25}_D]$ of the composition of products (180 min); (−7.3), LP (0 °). k_1 (mean) = 0.00010 l/s.

TABLE 7. REARRANGEMENT OF LA IN THE MEDIUM OF HOAc CONTAINING SULFURIC ACID

Reaction time (s)	Total	TH Comps.	Composition of products (%)						Yield (%)		Remarks
			L	LA (a)	T	TA	NA	GA	Total (b)	LA theor. (a)×(b)	
35	10.6	M 4.0 L' 5.6 O 0.3 T' 0.7	9.6	58.9	3.8	5.0	3.2	8.9	92.4	54.4	Reaction temp.; 0 °C. Medium; 90% HOAc-0.8 mol H_2SO_4. H_0; −1.53 LA; 0.0046 mol.
60	12.5	M 4.6 L' 6.3 O 0.6 T' 1.0	16.7	43.1	5.7	9.1	3.1	9.8	90.4	38.9	Optical purity $[\alpha]^{25}_D$ L (0°). T (+12.9°) k_1 (mean) = 0.01674 l/s.
90	12.8	M 4.7 L' 6.5 O 0.6 T' 1.0	26.0	23.8	7.0	15.1	5.3	10.0	90.3	21.9	

Inscriptions for terpene hydrocarbons–TH; myrcene–M, limonene–L', ocimene–O, terpinolene–T'., for alcohols; linalool–L, terpineol–T, and for acetates; linalyl acetate–LA, terpinyl acetate–TA, neryl acetate–NA, geranyl acetate–GA
Product distributions in 90% HOAc-0.6 mol H_2SO_4 and 90% HOAc-0.4 mol H_2SO_4 are abbreviated owing to the same tendency as the above one.

(4) Rearrangement of LA in the Medium of HOAc Containing Sulfuric Acid, The rearrangement was found to follow the first-order rate law with respect to the concentration of LA. It corresponds to a typical acid-catalyzed A1 reaction, because it shows such a linearity as gives a slope of 1.0 based on the correlation of log k_1 against H_0.[8–10] The following products were obtained: racemized linalool ([α]$^{25}_D$ = 0°), d-α-teripneol ([α]$^{25}_D$ = +12.9°), acetates of linalyl, terpinyl, neryl and geranyl, myrcene, limonene, ocimene, and terpinolene (Tables 7, 8, and Fig. 5). The amount of cyclized products, such as terpinyl acetates, terpineol, limonene, and terpinolene, which are considered to be derived via a cyclized tertiary carbonium (terpinyl), exceeded that obtained in other solvents. The results agree with the fact that monoterpenoids are readily cyclized in a strong acid.[20,21] No primary terpene alcohols, such as geraniol or nerol, could be found. This proves that the behavior of carbonium

ions in a strong acid undoubtedly differs from that in a weak acid, and that a tertiary carbonium ion in a strong acid medium is more stable and reactive than in a weak one.

Lately, Winstein et al.[22] reported that the solvolysis of optically-active linalyl p-nitrobenzoate in 70% aqueous acetone at 50, 75, and 100 °C was accompanied by a S_N2' reaction to geranyl p-nitrobenzoate, neryl p-nitrobenzoate, and d-α-terpinyl p-nitrobenzoate (50—90% optical active, temperature-dependent) as well as terpene hydrocarbons (myrcene, limonene, γ-terpinene, and terpinolene), and that the linalool formed during the solvolysis of the optical active ester was ca. 20% active.

However, it might have been expected that the S_N1-type rearrangement of linalyl esters would have been favored over S_N2' reaction because of ability of the intermediates, the carbonium ions, to dissociate favorably in acidic media.
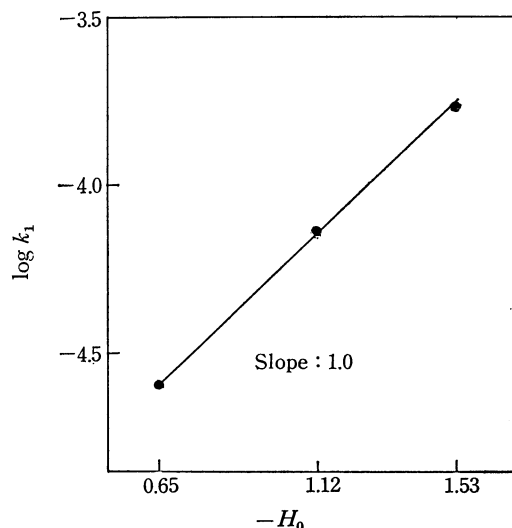
Fig. 5. Effect of the acidity function on the rearrangement rate constant of LA in the medium of HOAc containing sulfuric acid.

Table 8. Rate constants k_1 (1/s) of rearrangement of LA in the medium of HOAc containing sulfuric acid

HOAc–H₂SO₄	H_0	Reaction temperature, 0 °C k_1 (1/s)
90% HOAc-0.8 mol H₂SO₄	−1.53	1.67×10^{-2}
90% HOAc-0.6 mol H₂SO₄	−1.12	7.35×10^{-3}
90% HOAc-0.4 mol H₂SO₄	−0.65	2.45×10^{-3}

The present authors produced racemized linalyl propionate ($[\alpha]_D^{25}=0°$), together with myrcene, ocimene, limonene, and terpinolene, in the rearrangement of LA in propionic acid, and racemized linalool ($[\alpha]_D^{25}= 0°$) in that of LA in the medium of HOAc containing sulfuric acid. In addition to these facts, the aforementioned kinetic and product data for the allylic rearrangement of LA in the medium of acetic, propionic acid, or acetic acid containing dioxane or sulfuric acid indicate that intermediate carbonium ions occupy a pivotal position in the rearrangements.

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