The Solvolysis of Linalyl *p*-Nitrobenzoate and the Stereochemical Aspects of the Resulting 1–3 and 1–5 Rearrangements[1]

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Abstract: The solvolysis of linalyl *p*-nitrobenzoate (L-PNB) in 70% aqueous acetone at 50, 75, and 100° is accompanied by ester rearrangement to geranyl *p*-nitrobenzoate (G-PNB), neryl *p*-nitrobenzoate (N-PNB), and α-terpinyl *p*-nitrobenzoate (T-PNB). Apart from 1–3 allylic rearrangements, a major contribution of 3–7 rearrangement with ring closure was found to operate in this terpene system. When optically active ester was hydrolyzed, 20% retention of activity at the unrearranged center was observed. The T-PNB and the α-terpineol (T-OH) formed as a result of 3–7 rearrangement were 50–90% optically active (temperature dependent). These findings indicate that L-PNB occupies a pivotal position in the overall reaction and that the 1–3 and 3–7 rearrangements proceed intramolecularly.

Stephan in 1898[5] reported that linalool (L-OH) and its esters rearrange to give, among other hydration and dehydration products, the isomeric alcohols geraniol (G-OH), nerol (N-OH), and α-terpineol (T-OH) and their esters when treated with acidic media. Remarkably, Stephan observed that optically active linalool led to active α-terpineol even though the transformation was carried out under conditions that might easily have racemized the starting alcohol.

This study was initiated to examine the solvolytic participation of remote double bonds although it soon became clear that it had implications about the geometric integrity of ion pairs as well.[6] The work subsequently assumed a still broader significance because of the special role that has been assigned to geranyl and linalyl esters in the biosynthesis of terpenoids and steroids.[7]

Results

Solvolyses. The *p*-nitrobenzoate esters of linalool (L-PNB), geraniol (G-PNB), nerol (N-PNB), and α-terpineol (T-PNB) were prepared and solvolyzed in 70% aqueous acetone. The simple first-order rate constants found for G-PNB, N-PNB, and T-PNB are recorded in Table I. Also given are the first-order rate constants for the reference *p*-nitrobenzoate esters of *tert*-butyl alcohol and γ,γ-dimethylallyl alcohol. The linalool ester showed a dropping solvolysis rate, which could be analyzed in terms of a simple first-order rate process accompanied by a competitive rearrangement to a material with a lower rate constant (a mixture of G-PNB, N-PNB, and T-PNB). The initial solvolysis rate constants, the final rate constants, and the sum of the initial rate constant plus the rearrangement rate constant are recorded in Table II. Also recorded are the data for the reference *p*-nitrobenzoate ester of α,α-dimethylallyl alcohol, which undergoes a similar solvolysis with partial rearrangement. Unless indicated by an appended average uncertainty the reported rate constants are for a single run.

The products of the L-PNB solvolysis in 70% aqueous acetone were examined mainly at 75° and to a lesser extent at 100°. The olefinic and hydroxylic

Table I. Solvolysis Rate Constants of Esters Giving Simple First-Order Kinetics in 70% Aqueous Acetone

	Rate constants, $sec^{-1} \times 10^5$	
Ester	75°	100°
G-PNB	0.0363	0.503 ± 0.020[a]
N-PNB		0.571
T-PNB		1.14 ± 0.01
tert-B-PNB[b]		0.63
γ,γ-DMA-PNB[c]	0.084	1.17[d]

[a] $\Delta H(50°) = 26.5$ kcal/mol, $\Delta S(50°) = -10.3$ eu. [b] *tert*-Butyl *p*-nitrobenzoate. [c] γ,γ-Dimethylallyl *p*-nitrobenzoate. [d] $\Delta H(50°) = 26.6$ kcal/mol, $\Delta S(50°) = -10.3$ eu.

Table II. Solvolysis Rate Constants for Esters Showing Competitive Rearrangement in 70% Acetone

	Rate constant, $sec^{-1} \times 10^5$		
Ester	Initial	Final	Initial and rearrangement
L-PNB			
75°	2.31	0.0549	3.81
	2.35[a]		3.79[a]
100°	21.5 ± 0.1	0.741	34.6 ± 0.4
100°, 0.022 *M* lithium *p*-nitrobenzoate	21.4	(0.741)[b]	34.7
100°, 0.022 *M* *p*-nitrobenzoic acid	21.4	(0.741)[b]	36.9
100° optically active L-PNB			34.7[c]
α,α-DMA-PNB[d]			
75°	3.70	0.084	5.73
100°	36.1	1.17	52.3

[a] Determined independently by G. V. [b] Final rate constant without added acid or salt used in calculating rearrangement rate. [c] Rate constant for first-order loss of optical activity. [d] α,α-Dimethylallyl *p*-nitrobenzoate.

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[1] This work was mainly conducted in the Department of Chemistry of the University of California at Los Angeles. The kinetic aspects are taken largely from the Ph.D. Dissertation of C. F. W., Jr., and the detailed product analysis and interpretation are based on the postdoctoral work of G. V.

[2] Deceased Nov 23, 1969.

[3] Postdoctoral Fellow, 1959–1960.

[4] National Science Predoctoral Fellow, 1952–1953, 1954–1955.

[5] W. Stephan, *J. Prakt. Chem.*, **58**, 109 (1898).

[6] A preliminary account of the kinetic aspects of this study has been reported: S. Winstein, *Experientia Suppl.*, No. **2**, 137 (1955).

[7] F. Lynen, H. Eggerer, U. Henning, and I. Kessel, *Angew. Chem.*, 738 (1958); R. B. Clayton *Quart. Rev. Chem. Soc.*, **19**, 201 (1965); F. Cramer and W. Rittersdorf, *Tetrahedron*, **23**, 3015 (1967).

Table III. Alcohol Products from the Solvolysis of L-PNB in 70% Acetone at 75.0°

[L-PNB], $10^2 M$	Time, min	% rxn	% ROH composition L-OH	T-OH	N-OH	G-OH
3.3	190	28.5	52.3	21.5	8.7	17.5
2.7[a]	340	45.0	54.6	21.2	7.9	16.9
3.3[b]	360	48.0	57.7	18.7	6.4	17.5
3.2	500	59.0	57.3	21.5	5.9	15.3
2.7[a]	600	69.5	53.8	19.5	9.0	18.2
3.3	670	70.2	53.5	20.8	7.4	18.3
3.3[b]	1200	89.5	57.9	18.1	6.5	17.5
3.3	1605	95.0	51.3	21.0	7.3	19.2
3.3	1895	98.0	55.7	31.4	5.9	17.0
4.0	1963	98.5	54.7	20.5	6.8	18.0
3.3	2800		56.0	21.0	5.9	17.1
		Mean	55.0 ±1.7	20.5 +0.8	7.0 +0.7	17.5 ±1.0

[a] 0.0264 M Et_3N. [b] 0.0340 M Et_3N.

Table IV. Solvolysis Products of Linalyl *p*-Nitrobenzoate in 70% Acetone

L-PNB[a]	% dehydration products	% ROH composition L-OH	T-OH	N-OH	G-OH
50° [a]	36.8	54.0	22.6	5.9	17.5
75° [a]	43.4	55.0	20.5	7.0	17.5
100° [b]	49.8	56.6	17.1	6.2	20.1

[a] Mean values. [b] Extrapolated initial values.

Table V. Summary of Olefins from Linalyl *p*-Nitrobenzoate in 70% Acetone

	Myrcene	Limonene	γ-Terpinene	Terpinolene
50° [a]	48.1	4.3	15.7	31.9
75° [b]	46.4	4.25	17.85	31.5
100° [c]	44.0	3.0	23.5	30.5

[a] Estimated at 9.70% reaction. [b] Estimated at 28.5% reaction. [c] Extrapolated initial values.

Table VI. Solvolysis and Rearrangement Products of L-PNB in 70% Acetone at 75.0° [a]

[L-PNB], $10^2 M$	Time, min	% rxn	Rearranged ester composition, % T-PNB	N-PNB	G-PNB
4.13	1050	81.0	13.2	29.6	57.1
4.13	1250	90.5	12.3	30.4	57.3
2.72[b]	1370	92.5	15.6	31.3	53.1
2.72[b]	1370	92.5	11.3	30.5	58.2
3.97	1460	93.5	11.9	28.9	59.2
3.77	1470	94.0	14.2	27.1	58.7
3.77	1470	94.0	13.5	28.1	58.4
		Mean	13.1 ±1.2	29.4 ±1.2	57.5 ±1.5

[a] In these runs the following mean percentage compositions were found: dehydration products, 42.8 ± 1.2; L-OH, 55.0 ± 1.5; T-OH, 19.9 ± 0.5; N-OH, 7.2 ± 1.4; G-OH, 17.9 ± 0.8. [b] 0.0272 M Et_3N.

Table VII. Rearrangement Products of L-PNB in 70% Acetone

Temp, °C	Rearrangement, %[a]	% R-PNB composition[b] T-PNB	N-PNB	G-PNB
50	39.0	19	26	55
75	38.0	13	29	58
100	37.0	10	31	59

[a] Of total reaction. [b] Mean values.

product composition was determined by glpc on samples that had been washed to remove *p*-nitrobenzoic acid. The composition of the rearranged esters was calculated from the compositions of the alcohol product mixture before and after reduction with lithium aluminum hydride coupled with the fraction of unreacted linalool ester remaining. The details of the experimental procedure are given in the Experimental Section with a description of the controls employed.

From the kinetic data at 75° it could be calculated that 38% of the initial L-PNB rearranged to a mixture of the other three esters. From the glpc analysis of the remaining products it could be calculated that 27% of the L-PNB gave dehydration products and 35% gave a mixture of the four alcohols. The composition of the alcohol mixture determined for several fractions of reaction is recorded in Table III. The constancy of composition should be noted, particularly its insensitivity to added base. Table IV summarizes the alcohol data obtained over the 50–100° temperature range. Table V records the composition of the olefin fraction for the same runs.

The solvolysis product composition shows a small but definite temperature dependence. As the reaction temperature increases, elimination increases from 36.5% of hydrolysis products at 50° to 49.8% at 100°. The increase in dehydration products is probably not a consequence of tertiary alcohol dehydration, because the relative L-OH composition increases as the temperature increases. Although the T-OH is produced in smaller amounts at higher temperatures, the decrease is insufficient to account for the increase in dehydration products (Table V) or the particular olefins formed. The relative amount of γ-terpinene (VII) increases as the temperature increases, whereas the relative amounts of the other terpenes, myrcene (V), limonene (IX), and terpinolene (VIII), do not change among themselves. It is interesting that the decreased formation of T-PNB and T-OH as the reaction temperature increases does not lead to limonene and terpinolene, which are their normal elimination products,[8] but to γ-terpinene, the formation of which would appear to be connected with the collapse of the intermediate involved in the 1–5 migration.

The rearranged ester composition (Tables VI and VII) does not follow the composition of the corresponding alcohols. Among the rearranged esters G-PNB comprises 55–59% of the total esters and T-PNB 19–10%. Comparison with the alcohol composition indicates that in the case of 1–5 ester rearrangement, alcohol formation is much preferred. As the reaction temperature increases, from 50 to 100°, there is a decrease in both G-PNB and N-PNB but a substantial decrease in the tertiary ester T-PNB.

Optical Activity Measurements. Similar kinetic and product analyses were also carried out with optically active linalyl *p*-nitrobenzoate. From preparative glpc isolations of the resulting L-OH and T-OH the activities recorded in Table VII were observed. Lithium aluminum hydride reduction of the alcohol–ester mixture (described in the Experimental Section) gave, after appropriate combination of the activity and composition data, the activities of the alcohol portions of the cyclized T-PNB and unrearranged L-PNB. These

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[8] G. Valkanas, unpublished results.

Table VIII. Optical Activity of Products from Active L-PNB in 70% Acetone

Temp, °C	% rxn	$[\alpha]^{25}\text{D}$ values L-OH	L′-OH	T-OH	T′-OH
50	72.0	−5.05	−23.5	+87.0	+86.0
50	97.0			+71.0	+72.0
75	72.0	−4.85	−22.8	+78.0	+79.0
75	75.0	−4.75	−18.4	+77.5	+77.3
75	99.0	−4.58		+63.1	+60.2
100	68.0	−4.58	−20.2	+54.3	+50.0
100	89.0	−4.16	−12.5	+52.3	+46.0
			−25.0[a]	+100.5[b]	

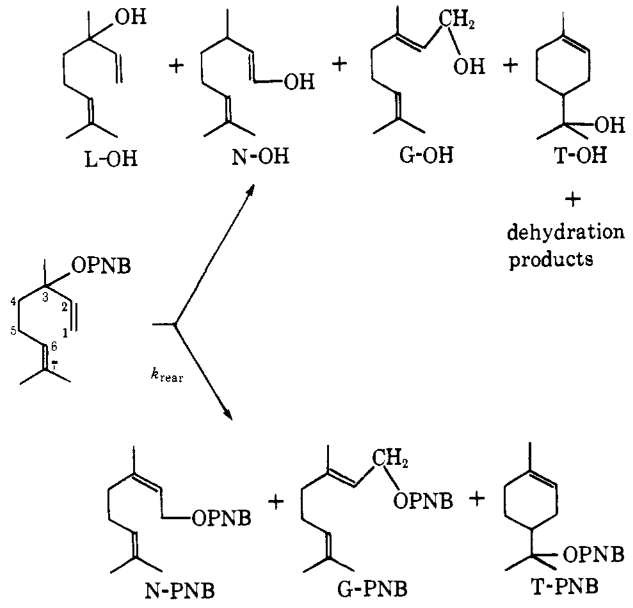
[a] Control on method of $LiAlH_4$ reduction of active L-PNB and separation of active L-OH. [b] Specific rotation of pure (+)-T-OH.

activities are listed in Table VIII as T′-OH and L′-OH values. The data yield the following important conclusions. The T-OH and T-PNB are formed with high optical purities, both at nearly equal specific rotations, which decrease as the reaction proceeds and the activity of the remaining L-PNB decreases. At 50° the cyclization gives T-OH and T-PNB with *ca.* 90% stereospecificity. At 75° the apparent specificity decreased to 78% but the T-OH and T-PNB arose from L-PNB that had an average optical purity during the cyclization of *ca.* 90%. At 100° and 68% reaction the T′-OH had an apparent stereospecificity of 50% arising from L-PNB with an average activity of 90%; at 100° and 89% reaction the apparent stereospecificity was 46% from material with an average activity of 75%. It appears that at higher temperatures the rearrangement process produces increasing racemization although a remarkable degree of specificity is retained even at 100°.

Discussion

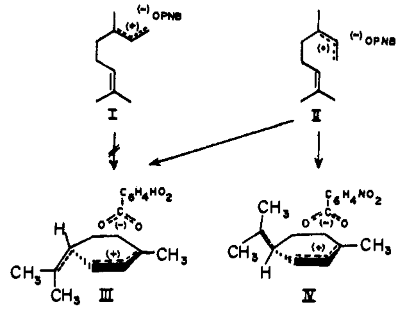
The kinetic and product data for the solvolysis of linalyl *p*-nitrobenzoate (L-PNB) in 70% aqueous acetone can be interpreted in terms of the scheme outlined in Chart I. One observation not embodied in the kinetic scheme is the slow racemization of the L-PNB (Table VIII). This could arise either by leakage of an L-PNB ion pair intermediate to its enantiomer or by reverse rearrangement of inactive N-PNB and G-PNB. The rapid decrease in the optical activity of unreacted L-PNB at higher percentage solvolysis is more in accord with the reverse rearrangement. A further complication not shown in Chart I is the observation that added *p*-nitrobenzoic acid accelerates slightly the rearrangement rate of L-PNB (Table II) as is found typically for solvolysis of allylic esters.[9] Added lithium *p*-nitrobenzoate had only a small (salt) effect.

Chart I



Two possible ion pairs can be formed from L-PNB depending on the relative orientation of the sickle-shaped allylic cation relative to the isohexenyl side chain. Intermediate I, after a C_3–C_1 allylic shift, would produce G-PNB. Other possible fates for I are solvolysis to the alcoholic products L-OH and G-OH and proton loss. Intermediate II can, similarly, form N-PNB, L-OH, and N-OH as well as dehydration products.

A further possibility open to the cisoid configuration II and not available to I is the formation of delocalized ion pairs III and IV. It might have been expected that IV would have been favored over III because of the ability of the *p*-nitrobenzoate counterions to interact favorably with that portion of charge delocalized to the remote tertiary center (C_7). In this way ion pair IV could be envisioned to collapse readily with the counterion and thereby account for the large amount of T-PNB formed. Ion pair IV was proposed[6] and the early assignments of absolute configuration of L-OH[10] and T-OH[11] were consistent with it. Subsequently, however, the absolute configurational assignment of L-OH was reversed;[12] the new assignment requires that the contribution of paths through III ,dominate. Rittersdorf and Cramer[13] in an investigation of the solvolysis of the phosphates of L-OH, G-OH, and N-OH have drawn an intermediate ion analogous to III. In comparing the relative importance of III and IV it should be borne in mind that the stereochemistry of the T-OH and T-PNB formed is determined by the face of the C_6–C_7 double bond that is attacked and not by the face of the C_1–C_2–C_3 allylic ion. By analogy[14] with the stereochemical behavior of other SN2′ reactions on allylic compounds, however, it can be supposed that attack at C_1 comes from the same side as the *p*-nitrobenzoate group departs.



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[9] R. H. Dewolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956).

[10] V. Prelog and E. Watanable, *Justus Liebigs Ann. Chem.*, **603**, 1 (1957).

[11] K. Freundenberg and W. Lwowski, *ibid.*, **594**, 76 (1955).

[12] R. H. Cornforth, J. W. Cornforth, and V. Prelog, *ibid.*, **634**, 197 (1960); G. Ohloff and E. Klein, *Tetrahedron*, **18**, 37 (1962); R. H. Cornforth, J. W. Cornforth, and G. Popjak, *ibid.*, **18**, 1351 (1962).

[13] W. Rittersdorf and F. Cramer, *ibid.*, **24**, 43 (1968).

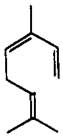
[14] G. Stark and W. N. White, *J. Amer. Chem. Soc.*, **78**, 4609 (1956).

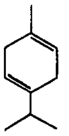
The intermediates I, II, and III are best formulated as internal ion pairs in which the migrating group remains firmly bound to the electron-deficient carbon center rather than being solvent separated. The unreacted L-PNB isolated in runs at 50, 75, and 100° shows no appreciable racemization until *ca.* 70% reaction. Racemization speeds up after 70% reaction most probably because of the presence of increased liberated acid. Higher temperatures seem to promote the racemization of L-PNB (Table VIII) as would be expected.

Solvent collapse at the 1, 3, and 7 positions to yield G-OH, N-OH, L-OH, and T-OH accompanies rearrangement. As shown in Table III, formation of the tertiary alcohols is somewhat preferred even though solvent collapse at the tertiary centers must compete with proton elimination.[15] Myrcene (V) is the only acyclic elimination product isolated, indicating that proton abstraction around the C_3 cationic center comes exclusively from the CH_3 group. The isomeric diene ocimene (VI) which was a main product of linalool dehydration under alkaline or neutral conditions,[16] and would arise from proton removal from the adjacent CH_2 group of the isohexenyl chain, was not detected. This might reflect the steric inaccessibility of the adjacent CH_2 group in the dominant conformations taken by the noninteracting isohexenyl side chain in ion pairs I and II. Alternatively it might reflect an acidity enhancing mesomeric (hyperconjugative) release of electrons to the allylic cations by the CH_3 group relative to a geometrically inhibited release by a misoriented adjacent CH_2 group.

It is interesting to note that although large amounts of cyclized olefins are formed, the major monocyclic olefins observed are γ-terpinene (VII) and terpinolene (VIII) rather than limonene (IX), the dominant elimination product formed in the solvolysis of T-PNB.[8] This discrepancy could be interpreted in terms of the intermediacy of ion pairs such as III or IV not immediately accessible to the first-formed ion pairs from T-PNB.


V


VI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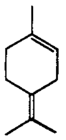
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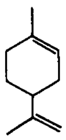
IX

The linalool formed during solvolysis of the active L-PNB is *ca.* 20% active (Table VIII) and of the same configuration as the starting ester. Goering and coworkers[17] have observed partial retention of configuration in the solvolysis products of a number of optically active alkyl *p*-nitrobenzoates which they ascribe to preferential reaction with the solvation shell of the solvent separated ion pair. They have also observed partial retention of configuration of the ester formed from collapse of the internal ion pair and noted that this is generally more stereospecific than solvent collapse. On this basis the *ca.* 20% activity of the linalool product suggests a much higher stereospecificity for the (unmeasured) return from the ion pair to LPN.[18]

Examination of the cyclized products reveals that both the T-OH and the T-PNB formed after the 3–7 ester rearrangement have a similar high optical purity, even at the highest temperature studied. This suggests a common pathway for T-OH and T-PNB formation, which is likely to include either the pair of ions pictured as III and IV or possibly solvent-separated variants of them. The optical purities of the T-OH and T-PNB were markedly temperature dependent. The data of Table IV provide a rough estimate of the difference in activation parameters of III and IV as $\Delta H^{\ddagger}{}_{\text{III}} - \Delta H^{\ddagger}{}_{\text{IV}} = -7 \pm 3$ kcal/mol and $\Delta S^{\ddagger}{}_{\text{III}} - \Delta^{\ddagger}{}_{\text{IV}} = 17 \pm 7$ eu. In our original proposal[6] intermediate IV was visualized as being more stable than III as a result of the extra electrostatic stabilization available to IV. The apparently lesser stability of IV may arise from the unfavorable steric interactions of the isopropenyl side chain with the counterion or, more probably, its solvation shell. The more favorable entropy of activation of IV would be consistent with a loosening of the solvation shell. Whatever the basis of preference for III over IV it remains clear that participation of the remote C_6–C_7 double bond competes well with solvent for attack on the developing allylic cation.

Experimental Section

Esters. The esters were prepared by the common Tipson procedure[19] using *p*-nitrobenzoyl chloride, alcohol, and pyridine. The linalool (Fritzsche Brothers, Inc.) was 93.5% pure by glpc; the impurities were terpene hydrocarbons. Active (−)-linalool of 98% compound purity was obtained from alkaline hydrolysis of Mexican Linaloe Wood Oil (Fritzsche Brothers, Inc.) and converted into its *p*-nitrobenzoate which was then recrystallized at −15° to constant melting point and optical activity from Skelly B and *n*-pentane. Lithium aluminum hydride gave optically active alcohol, $[\alpha]^{25}\text{D}$ −25.0° (*c* 4, acetone).

The esters of geraniol, α,α-dimethylallyl alcohol, and *tert*-butyl alcohol were prepared by the standard procedure.[16]

Nerol was obtained by saponification of the oil of *Helichrysum angustifolium* D.C. (Fritzsche Brothers, Inc.) and converted to the *p*-nitrobenzoate by the standard method. After recrystallization from methanol and then Skelly B (bp 60–70°) the ester gave depressed mixture melting points with both *d,l*-linalyl ester and geranyl ester. The *p*-nitrobenzoate of α-terpineol was prepared from redistilled α-terpineol (Fritzsche Brothers, Inc.); it gave two crystalline modifications, mp 108 and 139°. Both forms gave the correct analyses and identical rate constants.

γ,γ-Dimethylallyl was prepared from α,α-dimethylallyl alcohol (kindly donated by C. Shee) by rearrangement in acetic anhydride and 85% phosphoric acid at room temperature for 18 hr followed by saponification of the acetate. The rearranged primary alcohol was converted to the *p*-nitrobenzoate ester in the standard manner. Analytical data for these esters are recorded in Table IX.

Kinetics. The solvolysis rates of the *p*-nitrobenzoates were determined in the usual manner by sampling aliquots at appropriate time intervals and titrating them with methanolic sodium methoxide against Brom Thymol Blue.

Product Analyses. In a typical determination a solution of the ester (*ca.* 1.2 wt %) was divided into five or six ampoules holding 8 ml and one holding 80 ml. The 8-ml ampoules were used to follow the alcohol composition during the solvolysis; the 80-ml ampoule was used to determine the composition of rearranged esters at the end of the solvolysis.

The contents of an 8-ml ampoule was withdrawn from the kinetic bath, thermally quenched, and poured into 20 ml of purified *n*-pentane. The solution was washed with 10% aqueous

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[15] D. Semenow, Chin-Hua Shih, and W. G. Young, *ibid.*, **80**, 5472 (1958).

[16] M. Gunzl-Schumacher and U. Wicker, *Chem. Ber.*, **93**, 974 (1960).

[17] H. L. Goering and H. Hopf, *J. Amer. Chem. Soc.*, **93**, 1224 (1971), and references contained therein.

[18] Rittersdorf and Cramer[13] in their study of the phosphates of L-OH found no activity in the L-OH product and from this and other evidence concluded that internal return was unimportant.

[19] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

Table IX

Alcohol	Mp of *p*-nitrobenzoate, °C	Anal., %		
		Calcd	Compd	Found
d,*l*-Linalool	65.5–65.8 65.6–66[a]	C 67.31; H, 6.98; N, 4.62	$C_{17}H_{21}O_4N$	C, 67.5; H, 7.17
(−)-Linalool	72.0–72.6 72.4–73.0[a]			C, 67.4; H, 6.91; N, 4.65
Geraniol	37.8–38.2[c] 35.0[b]	C, 67.31; H, 6.98	$C_{17}H_{21}O_4N$	C, 67.0; H, 6.60
Nerol	25.0	C, 67.31; H, 6.98	$C_{17}H_{21}O_4N$	C, 67.6; H, 6.71
α-Terpineol	107–108, 139 139[d]	C, 67.31; H, 6.98	$C_{17}H_{21}O_4N$	C, 67.3; H, 7.21[e] C, 67.2; H, 7.25[f]
α,α-Dimethylallyl alcohol	113–114	C, 61.27; H, 5.57	$C_{12}H_{13}O_4N$	C, 61.2; H, 5.54
γ,γ-Dimethylallyl alcohol	61.0–61.6	C, 61.27; H, 5.57	$C_{12}H_{13}O_4N$	C, 61.1; H, 5.47

[a] Results of G. V. [b] E. H. Huntress and S. P. Milliken, "Identification of Pure Organic Compounds," Wiley, New York, N. Y., 1941. [c] Saponification equivalent, 184.9; calcd, 184.9. [d] E. Huckel, *Justus Liebigs Ann. Chem.*, **528**, 69 (1937). [e] 108° form. [f] 139° form.

sodium bicarbonate and then with water, then dried (potassium carbonate) and carefully concentrated to 1 ml. The pentane solution was analyzed by glpc.

The contents of the 80-ml ampoule was diluted with ether and then reduced with lithium aluminum hydride. After hydrolysis with saturated aqueous ammonium chloride, the ether layer was washed with water and dried over potassium carbonate and the ether evaporated. The residue was taken up in pentane and analyzed by glpc.

The alcohol compositions were determined by glpc (Perkin-Elmer Model 154B vapor fractometer) using 1.2–1.5-m Carbowax 1540 or 4000 on Chromosorb W columns at 120–130°. Dehydration of the alcohols was negligible under these conditions. Columns were replaced after 20 analyses. The concentration of each component was calculated by multiplying the peak height by the half-width without correction for relative detector response. In a careful series of control experiments it was established that synthetic alcohol mixtures could be analyzed with an average error in per cent composition of 0.6 and that mixtures of pure esters as well as mixtures of esters and alcohols could be put through the reduction and analysis scheme with an average error in per cent composition of 1.1.

The olefins were analyzed on 3 m × 1/4 in. 30% 3-nitro-3-methylpimelonitrile on Chromosorb W columns using known terpenes as retention standards. The observed peak areas of olefin–alcohol mixtures were corrected for the relative dectector response (1:1.1) determined by analysis of mixtures of known composition. Bromobenzene was used as the internal standard in both the alcohol and olefin determinations.

The optical activity of the L-PNB, L-OH, T-PNB, and T-OH in the solvolysis of active L-PNB was determined by isolating appropriate samples in the fashion described above and collecting the L-OH and T-OH by preparative glpc.

Calculations. The ester composition can be calculated from the composition of the alcohol mixture before and after reduction with hydride combined with a knowledge of the fractions of starting ester giving either rearranged esters or rearranged alcohols. The expression for the fraction of total rearranged ester mixture that is one of the three esters is

$$f_{\mathrm{R-PNB}} = \frac{f^{+}_{\mathrm{R-OH}}(F_{\mathrm{R-OH}} + F_{\mathrm{R-PNB}})}{F_{\mathrm{R-PNB}}} - \frac{f_{\mathrm{R-OH}}(F_{\mathrm{ROH}})}{F_{\mathrm{R-PNB}}}$$

where the lower case $f_{\mathrm{R-PNB}}$, $f_{\mathrm{R-OH}}$, and f^{+}_{ROH} represent the fractions of particular ester, alcohol before reduction, and alcohol after reduction. The capital $F_{\mathrm{R-OH}}$ and $F_{\mathrm{R-PNB}}$ represent the fractions of reacted L-PNB giving rearranged alcohols and esters, respectively.