labeled ester was partially solvolyzed and the remaining ester was isolated as follows. The oily residue derived from the benzene extract (consisting of unsolvolyzed ester and *p*-methoxybenzhydrol) was separated by high-vacuum sublimation instead of by column chromatography. After 3 days at 48° and 3×10^{-6} mm all of the alcohol had sublimed and tlc showed that the residue was pure unsolvolyzed *p*-methoxybenzhydryl *p*-nitrobenzoate. Control experiments showed that this method of isolation does not alter the ^{18}O distribution. The ^{18}O distributions were determined as described earlier.[4]

In all of the oxygen equilibration experiments the total ^{18}O content of the ester remained steady throughout the solvolysis.

D. Rates of Exchange. Second-order rate constants for exchange between unsolvolyzed ester and *p*-nitrobenzoic acid-α-^{14}C were determined as described earlier.[2,5] The activity of the labeled acid was determined as the corresponding ester derivative and thus, in each case, all activities were for the same derivative. Samples of unsolvolyzed esters were isolated and purified as described above. The activity of the *p*-methylbenzhydryl derivative of the added labeled acid was 0.517 μCi/mmol and that of the *p*-methoxybenzhydryl derivative was 0.458 μCi/mmol. All activities were determined in triplicate. Reactions were followed for about two solvolytic half-lives and second-order rate constants[2] were steady.

Product Studies. A. *p*-Methylbenzhydrol Derived from (−)-*p*-Methylbenzhydryl *p*-Nitrobenzoate. A 0.036 *M* solution of (−)-*p*-methylbenzhydryl *p*-nitrobenzoate, $[\alpha]^{24}_{435}$ −14.52° (*c* 1.53),[21,28] in 90% acetone containing 0.12 *M* 2,6-lutidine was sealed in a heavy-walled ampoule and placed in a 99.5° thermostat for 62 hr (one solvolytic half-life). The reaction mixture was treated with ether and extracted with 5% aqueous sodium carbonate and water. After drying (Na_2SO_4) the ether was removed under reduced pressure and the residue was placed under high vacuum (3×10^{-6} mm) overnight to remove the lutidine. The residue was extracted with warm pentane in which the alcohol is much more soluble than the unsolvolyzed ester. Removal of the pentane gave a slightly yellow residue which was purified by chromatography (Mallinckrodt SilicAR-CC-7 with chloroform as solvent and eluent). The pure alcohol (tlc) was converted to (−)-*p*-methylbenzhydryl *p*-nitrobenzoate, $[\alpha]^{24}_{435}$ −0.35 (*c* 1.57).[21] Control experiments showed that isolation and purification of the alcohol and conversion to the *p*-nitrobenzoate derivative does not alter the optical purity.

B. *p*-Methylbenzhydryl Azide Derived from (−)-*p*-Methylbenzhydryl *p*-Nitrobenzoate. A solution of 1.22 g (3.5 mmol) of (−)-*p*-methylbenzhydryl *p*-nitrobenzoate, $[\alpha]^{25}_{435}$ −13.59° (*c* 1.236),[21] in 100 ml of 90% acetone containing 0.1155 *M* sodium azide was heated at 99.5° for 17 hr. After cooling, the mixture was dissolved in ether and washed twice with 5% aqueous sodium carbonate and several times with water. The ether solution was dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography (Mallinckrodt SilicAR-CC-7; benzene–hexane eluent) gave nearly pure azide. This was purified by chromatography on silicic acid (benzene–hexane eluent). The resulting (+)-*p*-methylbenzhydryl azide, $[\alpha]^{24}_{435}$ 5.60° (*c* 1.78),[21] had the same ir and nmr spectra as an authentic racemic sample.

Reduction of the above (+)-azide with lithium aluminum hydride in ether gave (+)-*p*-methylbenzhydrylamine, $[\alpha]^{24}_{589}$ 1.1° (*c* 1.23). Spectra of this material were identical with those of the enantiomer described above and racemic *p*-methylbenzhydrylamine.

Deamination of (−)-*p*-Methylbenzhydrylamine. A solution of 0.230 g (0.98 mmol) of (−)-*p*-methylbenzhydrylamine hydrochloride, $[\alpha]^{24}_{589}$ −4.14° (*c* 1.33 ethanol), and 0.16 g (2.3 mmol) of sodium nitrite in 5 ml of water was heated to 60° for 1 hr. The mixture was extracted with ether and dried ($MgSO_4$). Removal of the ether followed by purification by chromatography as described above, gave 0.084 g (43%) of (−)-*p*-methylbenzhydrol, $[\alpha]^{24}_{589}$ −1.525° (*c* 4.4). An impurity was indicated by tlc so the alcohol was converted to pure (−)-*p*-methylbenzhydryl *p*-nitrobenzoate, $[\alpha]^{24}_{589}$ −0.93° (*c* 1.75).

Stereochemistry of Allylic Rearrangements. XVI. Stereochemistry of Ion-Pair Return in the *trans*-α,γ-Methylphenylallyl *p*-Nitrobenzoate System[1]

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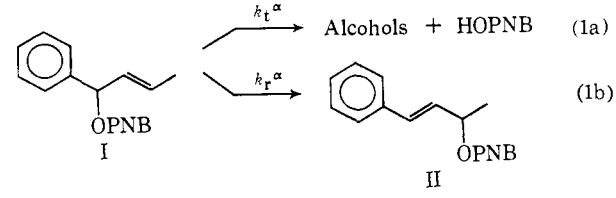
Abstract: Ion-pair return from the ion-pair intermediate(s) common to *trans*-α-phenyl-γ-methylallyl and *trans*-α-methyl-γ-phenylallyl *p*-nitrobenzoates (I and II) gives the γ-phenylallyl isomer (II). In aqueous acetone the α-phenylallyl isomer (I) undergoes simultaneous solvolysis and allylic isomerization to II which is less reactive than I and accumulates. At higher temperatures the γ-phenylallyl isomer (II) solvolyzes without rearrangement. In this case the amount of return from the common intermediate(s) (III) can be determined by carboxyl oxygen equilibration (eq 3). Ion-pair return results in partial loss of optical configuration. The amount lost starting with I was determined from the relative optical purities for the I → II isomerization and the amount lost starting with II (in this case racemization) was determined from the amount of racemization (eq 4) associated with return, *i.e.*, from the k_{rac}/k_{eq} ratio. Within experimental error the stereochemistry of return is the same starting with either I or II. In 90% acetone at 100° return results in about 65% loss of optical configuration.

In aqueous acetone,[3] aqueous dioxane,[4] or methanol[4b] α-phenyl-γ-methylallyl *p*-nitrobenzoate (I) undergoes simultaneous solvolysis (eq 1a) and isomeric rearrangement (eq 1b) to the α-methyl-γ-phenylallyl isomer (II). The latter is relatively unreactive (~300 times less reactive than I) and accumulates. The fraction of



(1) This work was supported by grants from the Air Force Office of Scientific Research (AFOSR-847-67) and the National Science Foundation (GP6555X).

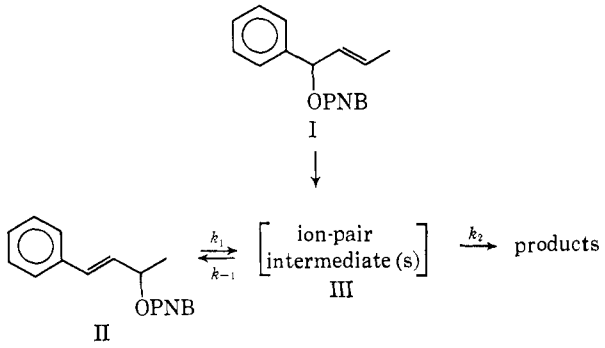
(2) (a) National Institutes of Health, Predoctoral Fellow, 1968–1971; (b) National Institutes of Health, Predoctoral Fellow, 1965–1968.

(3) H. L. Goering and E. C. Linsay, *J. Amer. Chem. Soc.*, 91, 7435 (1969).

(4) (a) R. A. Sneen, *ibid.*, 82, 4261 (1960); (b) R. A. Sneen and A. M. Rosenberg, *ibid.*, 83, 895, 900 (1961).

I that solvolyzes gives 1 equiv of acid and the ratio of rearrangement (ion-pair return) to solvolysis (k_r^α/k_t^α) can be determined directly from the amount of acid generated. Only a small correction is required for solvolysis of the rearrangement product (<2%) during the solvolysis and rearrangement of I.[3] The titrimetric rate constant (k_t, eq 2) is the rate constant for disappearance of substrate. Thus, in this case, $k_t = k_t^\alpha + k_r^\alpha$. From the high reactivity and the effects of varying structure, solvent, and temperature on the rates and relative rates it is apparent that solvolysis involves alkyl–oxygen cleavage and the I → II isomerization results from ion-pair return as illustrated in Chart I.[3,4]

Chart I



At higher temperatures the γ-phenylallyl isomer (II) solvolyzes without rearrangement.[3,4] In this case alkyl–oxygen cleavage leads to the common intermediate(s) (III) and return results in re-formation of unrearranged ester—the much more reactive α-phenylallyl ester (I) cannot accumulate under conditions for solvolysis of II.

In an earlier paper[3] it was shown that in this system the attractive forces in the common intermediate (III) are weak enough so that the carboxyl oxygen atoms are essentially equivalent. This means that for the first-order solvolysis of II (eq 2), oxygen equilibration (eq 3) measures most, if not all, of the re-formation of II by ion-pair return. We have now investigated the stereochemistry of return to determine to what extent optical configuration is preserved in the ion-pair intermediate(s) III.

In all of the asymmetric nonrearranging systems that we have investigated thus far,[5–8] the unsolvolyzed ester undergoes carboxyl–oxygen equilibration faster than racemization. This means that return (oxygen equilibration) proceeds with predominating retention of configuration. Two cases have been reported[6a,7] in which oxygen equilibration does not result in detectable racemization. Thus, evidently weaker attractive forces are required for loss of configuration than for randomization of carboxyl oxygen atoms. Evidence has been presented elsewhere[3,8] that in *p*-nitrobenzoate systems attractive forces in ion-pair intermediates seem to decrease with increase in charge delocalization in the cation.

(5) H. L. Goering and S. Chang, *Tetrahedron Lett.*, 3607 (1965).
(6) (a) H. L. Goering and J. F. Levy, *J. Amer. Chem. Soc.*, **86**, 120 (1964); (b) H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, **84**, 3059 (1968).
(7) H. L. Goering, R. G. Briody, and G. Sandrock, *ibid.*, **92**, 7401 (1970).
(8) H. L. Goering and H. Hopf, *ibid.*, **93**, 1224 (1971).

Evidence that return involved in the solvolysis of II in aqueous acetone results in essentially complete oxygen equilibration is as follows. Providing oxygen equilibration is complete, k_{eq}/k_t corresponds to the return to solvolysis ratio, k_{-1}/k_2 in Chart I. The k_{-1}/k_2 ratio can be determined independently because this corresponds to the k_r^α/k_t^α ratio for the α-phenylallyl ester (I).[3] It has been found[3] that the k_{eq}/k_t ratio for II is nearly as large as the k_r^α/k_t^α ratio for I for solvolysis in 70, 80, and 90% aqueous acetone. This means that return from III associated with the solvolysis of II results in essentially complete oxygen equilibration. The amount of carboxyl–oxygen scrambling for the I → II isomerization (single pass through III) was also investigated[3] and found to be essentially complete (90–100%). Thus the same amount of scrambling is observed when the intermediate (III) is generated from either ^{18}O-labeled I or II.

In the present study we have determined the amount of racemization associated with return for solvolysis of α-methyl-γ-phenylallyl *p*-nitrobenzoate (II) in aqueous acetone. The method involves comparison of the rates of oxygen equilibration (eq 3) and racemization (eq 4) of the unsolvolyzed ester. The k_{rac}/k_{eq} ratio is a measure of the amount of racemization associated with return. For comparison, the amount of optical configuration lost for the I → II isomerization was also determined.

$$R\overset{\curvearrowright}{-}OCOAr \xrightarrow[H_2O]{k_t} ROH + ArCO_2H \qquad (2)$$

$$R^{18}OCOAr \xrightarrow{k_{eq}} R^{18}OC^{18}OAr \qquad (3)$$

$$(d \text{ or } l)\text{-ROCOAr} \xrightarrow{k_{rac}} dl\text{-ROCOAr} \qquad (4)$$

Results

Solvolysis of *trans*-α-methyl-γ-phenylallyl *p*-nitrobenzoate (II) in 70, 80, and 90% aqueous acetone[9] is accompanied by oxygen equilibration of the unsolvolyzed ester (eq 3). Solvolysis and oxygen equilibration are first order and the latter is intramolecular (no exchange between unsolvolyzed ester and ^{14}C-labeled *p*-nitrobenzoic acid).[3] The titrimetric (k_t) and oxygen equilibration (k_{eq}) rate constants were reported earlier.[3]

Polarimetric rate constants (k_α) were determined as described earlier[10] from the rate of loss of optical activity for solvolysis of active II. Reactions were followed to 80% completion and in all cases k_α was steady. In these experiments the change in observed rotation during the reaction was >1° and rotations were determined with a precision of ±0.002°. Thus k_α as well as k_t can be determined with high precision.

Under all of the conditions investigated $k_\alpha > k_t$ which shows that ion-pair return results in racemization. Rate constants for racemization were determined from k_α and k_t, *i.e.*, $k_{rac} = k_\alpha - k_t$.[10,11] The polarimetric (k_α) and racemization (k_{rac}) constants are shown in Table I together with the titrimetric (k_t) and oxygen equilibration (k_{eq}) constants. For each of the

(9) Solvent composition determined from volumes of pure components at 25° prior to mixing.
(10) (a) H. L. Goering, M. M. Pombo, and K. D. McMichael, *J. Amer. Chem. Soc.*, **85**, 956 (1963); (b) H. L. Goering and J. T. Doi, *ibid.*, **82**, 5850 (1960).
(11) S. Winstein, B. Appel, R. Baker, and A. Diaz, *Chem. Soc., Spec. Publ.*, **No. 19**, 109 (1965).

Table I. Rate Constants for Solvolysis (k_t), Loss of Optical Activity (k_α), Racemization (k_{rac}), and Carboxyl Oxygen Equilibration (k_{eq}) for Solvolysis of α-Methyl-γ-phenylallyl *p*-Nitrobenzoate in Aqueous Acetone[a]

% acetone[b]	Temp, °C	10^2k_t,[c] hr^{-1}	10^2k_α, hr^{-1}	10^2k_{rac},[d] hr^{-1}	10^2k_{eq},[c] hr^{-1}
90	99.41	5.16 ± 0.11	12.20 ± 0.07[e]	7.04 ± 0.18	10.88 ± 0.34
90	78.47	0.662 ± 0.01	1.50 ± 0.01	0.84 ± 0.02	1.38
80	78.47	6.91 ± 0.10	10.44 ± 0.20[f]	3.53 ± 0.30	7.15 ± 0.10
80	49.04	0.244 ± 0.01	0.330 ± 0.004	0.086 ± 0.014	0.252[g]
70	49.04	1.06 ± 0.01	1.17 ± 0.02[e]	0.11 ± 0.03	0.70 ± 0.01

[a] Ester concentrations: 0.015–0.05 *M* for k_t, 0.04–0.10 *M* for k_α, and 0.04 *M* for k_{eq}. [b] Per cent by volume at 25° before mixing. [c] Taken from ref 3. [d] Determined from k_α and k_t, *i.e.*, $k_{rac} = k_\alpha - k_t$, uncertainties determined from limiting values of k_α and k_t. [e] Average of two independent kinetic experiments. [f] Average of three independent kinetic experiments. [g] Calculated assuming k_{eq}/k_t is temperature independent.

three solvents all rate constants were determined with solvent taken from the same batch. Thus solvent variations do not contribute to the differences in the constants in each line.

Return to solvolysis ratios (k_{eq}/k_t) and racemization to return ratios (k_{rac}/k_{eq}) for each condition are shown in Table II. The k_{rac}/k_{eq} ratio is the fraction of return

Table II. Return to Capture Ratios (k_{eq}/k_t) and Racemization to Return Ratios (k_{rac}/k_{eq}) for Solvolysis of α-Methyl-γ-phenylallyl *p*-Nitrobenzoate in Aqueous Acetone

% acetone	Temp, °C	k_{eq}/k_t[a]	k_{rac}/k_{eq}[a]
90	99.41	2.10 ± 0.12	0.65 ± 0.04
90	78.47	2.08	0.61 ± 0.03
80	78.47	1.03 ± 0.03	0.49 ± 0.05
80	49.04	1.03	0.34 ± 0.05
70	49.04	0.66 ± 0.02	0.16 ± 0.07

[a] Uncertainties estimated from limiting values of rate constants in Table I.

that results in racemization, the rest proceeds with retention of configuration. The exchange experiments reported earlier[3] establish that racemization, as well as oxygen equilibration, is intramolecular.

From the k_{rac}/k_{eq} ratios it is apparent that return (oxygen equilibration) results in considerable racemization, *e.g.*, from 16% in 70% acetone at 49° to 65% in 90% acetone at 99°. This means that in III the counterions achieve sufficient separation so that configuration is lost (this requires migration of the anion to the opposite side of the allylic cation). It is remarkable that the ions retain their identities for periods that allow this much separation and relocation—presumably protonation of the anion, as well as solvent capture of the cation, would divert ion-pair return.

The amount of return (k_{eq}/k_t) decreases as the solvent becomes more aqueous. Similar behavior has been observed in other cases[5–7,10] and seems to be general. This may be due to an increase in ionizing power of the medium which facilitates dissociation relative to return. An alternate interpretation is that nucleophilic attack on III by water competes with return and increase in water concentration favors solvent capture. Knowledge of the mechanistic details of the product-forming step that would enable distinguishing between these alternate interpretations is lacking.[12] In any case, the net result is that solvent capture increases relative to return as the water content of the solvent increases.

In this connection it is interesting that the amount of racemization associated with return (k_{rac}/k_{eq}) decreases with the amount of return as the water content increases. This suggests the possibility that more than one ion-pair species may be involved which differs in capturability and stereochemistry. If the more capturable one(s) return(s) with the most racemization, as seems reasonable, the k_{rac}/k_{eq} ratio would decrease with increase in solvent capture as is in fact observed. The k_{rac}/k_{eq} ratios decrease with temperature and this should be taken into account when comparing ratios for the different solvents. A similar temperature dependence of k_{rac}/k_{eq} was recently reported for the *p*-methylbenzhydryl system.[8] This results from a higher activation energy for return with inversion than for return with retention.[8]

Starting with the α-phenyl-γ-methylallyl isomer (I), return results in isomerization to the γ-phenylallyl isomer (II). If, as indicated in Chart I, only intermediates common to the two isomers are involved in solvolysis and return, the stereochemistry of return should be the same starting with either optically active I or II. To investigate this point the loss of optical configuration for the I → II isomerization was compared with the stereochemistry of return for solvolysis of II. This comparison was made for solvolysis in 90% acetone. As shown by Table II the return to capture ratio (k_{eq}/k_t) is favorable in this solvent (k_r^α/k_t^α for I is 2.5),[3] and, the stereochemistry of return (k_{rac}/k_{eq}) is not very temperature sensitive. This is important because due to the large difference in reactivities it is not practical to compare the two isomers at the same temperature. As shown in Tables I and II the less reactive γ-phenylallyl isomer (II) was solvolyzed at 78.5 and 99.4°. In the case of I the reaction mixture was placed in a 100° bath; however, most of the reaction occurs during the warm-up period and an exact temperature cannot be specified. The half-life for I is ~20 min at 80° and <3 min at 100°. From this we estimate that most of the reaction occurs in the 80–100° range.

The *trans*-α-phenyl-γ-methylallyl[13] and *trans*-α-methyl-γ-phenylallyl[14] systems were resolved as described earlier. Spectral properties of the alcohols and

(12) What is known (from the exchange experiments[3]) is that external return is not involved. Thus, if dissociation of III is involved this dissociation is irreversible. This would not be surprising because the *p*-nitrobenzoate ion concentration remains low throughout the reaction because of the low dissociation of *p*-nitrobenzoic acid.

(13) (a) J. Kenyon, S. M. Partridge, and H. Phillips, *J. Chem. Soc.*, 207 (1937); (b) Y. Pocker and M. Hill, *J. Amer. Chem. Soc.*, 91, 3243 (1969).

(14) J. Kenyon, S. M. Partridge, and H. Phillips, *J. Chem. Soc.*, 85 (1937).

various derivatives indicated that the two isomers were free of intercontamination.

Optical purities of partially resolved *trans*-α-phenyl-γ-methylallyl alcohol and *trans*-α-methyl-γ-phenylallyl alcohol were determined by the nmr method of Raban and Mislow.[15] This involves esterification of active alcohol with excess optically pure *O*-methylmandelyl chloride and determining the ratio of the resulting diastereoisomers (which corresponds to the ratio of enantiomers in the active alcohol) by nmr analysis. For the α-phenyl-γ-methylallyl ester the chemical shifts of the γ-methyl doublet and *O*-methyl singlet differ for the two diastereoisomers by 0.086 and 0.017 ppm, respectively (pyridine solution). In the case of the α-methyl-γ-phenylallyl ester the chemical shifts of the α-methyl doublet were separated 0.079 ppm (benzene) for the diastereoisomers. Two samples of active α-phenyl-γ-methylallyl alcohol used in the isomerization experiments were found to be 60 ± 4 and 63 ± 4% optically pure. Absolute rotations for the two allylic alcohols are presented in Table III.[16]

Table III. Absolute Rotations of α-Phenyl-γ-methylallyl Alcohol (I-OH) and α-Methyl-γ-phenylallyl Alcohol (II-OH)

λ, Å	I-OH, α,[a] deg	II-OH, [α],[b] deg
589	80 ± 5	78 ± 6
578	84 ± 5	82 ± 6
546	97 ± 5	96 ± 7
436	183 ± 11	191 ± 14

[a] Rotation for neat sample at 30° (1 = 1 dm). [b] Specific rotation for chloroform solution at 30° (*c* 5.04).

(−)-*trans*-α-Phenyl-γ-methylallyl alcohol of known optical purity was converted to (−)-*trans*-α-phenyl-γ-methylallyl *p*-nitrobenzoate ((−)-I) by a method that does not result in change of optical purity. This was established by reconverting the active I to alcohol (reduction with lithium aluminum hydride) with the original optical activity. A 0.2 *M* solution of (−)-I in 90% acetone was placed in a 100° bath for 27 min. This corresponds to about five half-lives for solvolysis of the α-phenylallyl ester.[3] The difference in reactivities of I and II is large enough so that under these conditions II produced by ion-pair return does not react to any significant extent.[17]

The rearrangement product, (−)-II, was isolated and converted to (+)-α-methyl-γ-phenylallyl alcohol by reduction with lithium aluminum hydride. The alcohol was purified by sublimation and the optical purity was determined by the above described nmr method. In one experiment 60 ± 4% optically pure (−)-I gave 18 ± 4% optically pure (−)-II. In another case 63 ± 4% optically pure (−)-I gave 22 ± 4% optically pure (−)-II. From this it can be seen that the I → II isomerization involves 67 ± 8% loss of configuration. Comparison of this result with the first two entries in Table II shows that within experimental error loss of configuration associated with return is the same for the two allylic isomers.

In this system loss of optical configuration involves rebonding of the anion on the opposite side of the planar allylic cation from which it departed. The amount of inversion is one-half the amount of optical activity lost. Thus in 90% acetone in the temperature range of 80–100°, return proceeds with about one-third inversion of configuration.

Return with inversion in this allylic system is in sharp contrast to the stereospecific ion-pair return in the 5-methyl-2-cyclohexenyl system. In the latter case the carbonium ion is symmetrical and ion-pair return results in re-formation of racemic substrate. Considerable return is associated with solvolysis of *cis*- and *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoates (aqueous acetone),[10b,18] acid phthalates (aqueous acetone),[19] and chlorides (ethanol and acetic acid).[20] However, return does not result in detectable interconversion of geometric isomers. This shows that there is no leakage between the cis and trans ion-pair intermediates. Or to put it another way, in this case return involves exclusive rebonding of the anion to the original side of the allylic cation.

Originally the results for the 5-methyl-2-cyclohexenyl system were taken to mean that in allylic systems ion-pair return in general is stereospecific in that the anion remains on the side of the planar cation from which it departed (*i.e.*, no inversion or epimerization).[21] Later it was recognized that conformational factors, rather than inherent structural properties of allylic ion-pair intermediates, might be responsible for stereospecific ion-pair return in the 5-methyl-2-cyclohexenyl system.[22,23]

The present results suggest that the stereospecificity in the cyclohexenyl system is indeed due to conformational factors because we now see that return in the *trans*-α,γ-methylphenylallyl system results in substantial inversion of configuration.

In this connection it is significant that ion-pair return associated with solvolysis of *exo*- and *endo*-bicyclo[3.2.1]oct-3-en-2-yl *p*-nitrobenzoates in aqueous acetone results in considerable interconversion of geometric isomers.[24] In this bicyclic system the cyclohexenyl cation is conformationally rigid. Thus, unlike in the 5-methyl-2-cyclohexenyl system,[23] the carbonium ion cannot differ conformationally in intermediates derived from the geometric isomers.

(15) M. Raban and K. Mislow, *Top. Stereochem.*, 2, 199 (1967).

(16) After this phase of the work was complete it was found that the chemical-shift differences for the diastereoisomers are increased substantially by addition of one-third of a molar amount of tris(dipivalomenthanato)europium. This technique would enable determination of optical purities and absolute rotations of the allylic alcohols with higher precision than obtained in this work. See J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

(17) The rate constant for disappearance of I is over 220 times larger than that for racemization of II. Thus, five half-lives for solvolysis and isomerization of I corresponds to ~3% racemization of II.

(18) H. L. Goering, J. T. Doi, and K. D. McMichael, *J. Amer. Chem. Soc.*, 86, 1951 (1964); H. L. Goering and E. F. Silversmith, *ibid.*, 77, 6249 (1955).

(19) H. L. Goering and E. F. Silversmith, *ibid.*, 77, 1129 (1955).

(20) H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *ibid.*, 77, 5026 (1955).

(21) H. L. Goering, *Rec. Chem. Progr.*, 21, 109 (1960).

(22) H. L. Goering and R. R. Josephson, *J. Amer. Chem. Soc.*, 84, 2779 (1962).

(23) Evidently the 5-methyl-2-cyclohexenyl carbonium ion differs conformationally in the ion-pair intermediates related to the geometric isomers.[22] To interconvert these intermediates requires conformational interconversion of the cation as well as relocation of the anion. Presumably the required conformational change contributes enough to the energy barrier for interconversion to preserve geometric configuration.

(24) R. P. Anderson, Ph.D. Thesis, The University of Wisconsin, Madison, Wis., 1966.

Experimental Section

Materials. ***dl*-α-Phenyl-γ-methylallyl acid phthalate,** mp 93–94° (lit.[13b] mp 93–94°), was prepared[13] from pure α-phenyl-γ-methylallyl alcohol.[3] The uv spectrum of this material showed only slight absorption in the 250-mμ region. Saponification with 5 *M* sodium hydroxide in 95% ethanol gave α-phenyl-γ-methylallyl alcohol that had λ_{max} 251 mμ (ε 490; ethanol)—the α-methyl-γ-phenylallyl isomer has λ_{max} 251 mμ (ε 1.95 × 10⁴; ethanol).[4b] From this we conclude that the acid phthalate derivative contained only a trace, if any, of the conjugated α-methyl-γ-phenylallyl isomer.

The acid phthalate was resolved by recrystallization of the quinidine salt as described earlier.[13] Regeneration of the acid phthalate with dilute acid resulted in partial allylic rearrangement to the conjugated γ-phenylallyl isomer. Thus the quinidine salt was saponified directly with 5 *N* sodium hydroxide in 95% ethanol as reported earlier.[13b] One resolution gave **(−)-α-phenyl-γ-methylallyl alcohol,**[25] α^{30}_{589} −50.415° (neat), α^{30}_{436} −114.80° (neat). This sample was shown to be 63 ± 4% optically pure by the method outlined below.

***dl*-α-Methyl-γ-phenylallyl acid phthalate,** mp 95.0–96.8° (lit.[14] 92.0–93.5°), was obtained in 57% yield by heating a stirred solution of 55 g (0.37 mol) of pure α-methyl-γ-phenylallyl alcohol[3] and 55 g (0.42 mol) of recrystallized ($CHCl_3$) phthalic anhydride in 64 ml of anhydrous pyridine on a steam bath for 2 hr. After cooling, the reaction mixture was added to a mixture of ice and concentrated hydrochloric acid to remove the pyridine. The resulting oil was dissolved in aqueous sodium carbonate and the basic solution was extracted with chloroform to remove neutral impurities. Acidification caused the acid phthalate to separate as an oil. The product was purified by recrystallization from a 2:1 pentane–ether mixture.

The acid phthalate was converted to the cinchonidine salt[14] which was only slightly soluble in refluxing ethyl acetate. The solid salt was extracted repeatedly with refluxing ethyl acetate until the residue amounted to about 40% of the original amount. This was converted to the acid phthalate derivative which was hydrolyzed with 5 *N* sodium hydroxide.[14] One resolution gave **(+)-α-methyl-γ-phenylallyl alcohol,** $[\alpha]^{30}_{589}$ 34.7°, $[\alpha]^{30}_{385}$ 170.6° (*c* 5.04, $CHCl_3$).[25] This was shown to be 44 ± 4% optically pure by the method outlined below. **(−)-α-Methyl-γ-phenylallyl *p*-nitrobenzoate**[25] was prepared from the (+)-alcohol by a standard procedure.[26]

Determination of Optical Purity of α-Phenyl-γ-methylallyl and α-Methyl-γ-phenylallyl Alcohols. α-Phenyl-γ-methylallyl *O*-methylmandelate was prepared from (−)-α-phenyl-γ-methylallyl alcohol and optically pure *O*-methylmandelyl chloride by a procedure reported earlier.[27] Each batch of acid chloride was shown to be optically pure by the nmr spectrum of the L-menthyl derivative.[27] The two diastereoisomers resulting from esterification of racemic α-phenyl-γ-methylallyl alcohol with racemic acid chloride have different chemical shifts for the *O*-methyl singlet and *C*-methyl doublet. The nmr spectrum of a pyridine solution has *O*-methyl singlets at δ 3.30 and 3.32 and *C*-methyl doublets centered at δ 1.43 and 1.52 for the two diastereoisomers. The optical purity of partially resolved (−)-alcohol was determined from the relative peak areas (100-MHz spectra) of expanded sweep widths of these signals. Results using the *C*-methyl and *O*-methyl signals were within one percentage unit.

The optical purity of partially resolved (+)-α-methyl-γ-phenylallyl alcohol was determined in the same way. In this case the two diastereoisomers obtained by esterification of racemic alcohol with racemic *O*-methylmandelyl chloride have different chemical shifts for the *C*-methyl doublet. The nmr spectrum of a benzene solution has *C*-methyl doublets centered at δ 0.90 and 0.98. The optical purity of the (+)-alcohol was determined from the relative peak areas (60-MHz spectra) of expanded sweep widths of these two doublets. For both allylic alcohols, the results of several independent determinations were within ±4 percentage units.[16]

Polarimetric Rates. Polarimetric rates of solvolysis of (−)-α-methyl-γ-phenylallyl *p*-nitrobenzoate were followed with either an O. C. Rudolph and Sons Model 80 polarimeter (with Model 200A oscillating polarizer) or a Perkin-Elmer Model 141 polarimeter. The ampoule technique was used in most cases. In these experiments all rotations were determined at 25°. The procedure was modified for solvolysis in 70% acetone. In this case the unsolvolyzed ester oiled out when the reaction mixture was cooled to 25°. To avoid this, aliquots were diluted with an equal volume of acetone.

The reaction in 70% acetone at 49.04° was also carried out in a thermostated jacketed polarimeter cell. The rate constant obtained in this manner was in excellent agreement (within 4%) with that obtained by the ampoule technique. In these experiments the solvent was taken from the same batch as was used for the titrimetric and oxygen equilibration experiments described earlier.[3] In all cases loss of optical activity was complete and the first-order rate constants were steady. Reactions were followed to about 80% completion. In most cases the change in the observed rotation during the experiment was >1°.

Solvolysis and Rearrangement of Optically Active α-Phenyl-γ-methylallyl *p*-Nitrobenzoate in 90% Acetone.[9] In a control experiment (−)-α-phenyl-γ-methylallyl alcohol, $[\alpha]^{30}_{589}$ −37.8° (*c* 0.041, CCl_4) was converted[26] to (−)-α-phenyl-γ-methylallyl *p*-nitrobenzoate[25] ((−)-I) which was isolated as a residue by evaporating an ether solution that had been extracted with 5% sodium carbonate and water and dried over potassium carbonate. To avoid optical fractionation the (−)-I was not recrystallized. Unreacted alcohol isolated from the reaction mixture had $[\alpha]^{20}_{589}$ −38.3° (*c* 0.018, CCl_4). Reduction of the (−)-I with lithium aluminum hydride gave (−)-α-phenyl-γ-methylallyl alcohol, $[\alpha]^{30}_{589}$ −38.8° (*c* 0.018, CCl_4).[25] These experiments show that optically active α-phenyl-γ-methylallyl alcohol can be converted to the *p*-nitrobenzoate derivative without rearrangement or change of optical activity.

The stereochemistry of the I → II isomerization was determined as follows. A 0.02 *M* solution (150 ml) of (−)-α-phenyl-γ-methylallyl *p*-nitrobenzoate (derived[26] from (−)-alcohol of known optical purity) in 90% acetone[9] was sealed under nitrogen in a heavy-walled ampoule. The ampoule was placed in a 100° bath for 27 min after which the reaction was quenched by immersing the ampoule in ice water. These conditions correspond to about 97% disappearance of the (−)-I.[3] The solvent was evaporated at room temperature under reduced pressure and the residual oil was taken up in ether. The organic extract was washed three times with 5% sodium carbonate and several times with water. After drying (K_2CO_3), the ether was removed and the allylic alcohols (solvolysis products) were removed under high vacuum (<5 × 10⁻⁶ mm).[3] The infrared spectrum indicated that the residue was alcohol free. The residual (−)-α-methyl-γ-phenylallyl *p*-nitrobenzoate[25] was converted to (+)-α-methyl-γ-phenylallyl alcohol by reduction with lithium aluminum hydride.[3] The (+)-alcohol was purified by sublimation and the optical purity of the (+)-γ-phenylallyl alcohol[25] was determined as described above. In one experiment (−)-I, derived from 60 ± 4% optically pure (−)-alcohol, gave (−)-II which was 18 ± 4% optically pure. In another case 63 ± 4% optically pure (−)-I gave 22 ± 4% optically pure (−)-II.[16]

(25) Infrared and nmr spectra of active compounds were indistinguishable from those of authentic racemic samples.

(26) H. L. Goering and J. P. Blanchard, *J. Amer. Chem. Soc.*, 76, 5405 (1954).

(27) H. L. Goering, C. Brown, S. Chang, J. V. Clevenger, and K. Humski, *J. Org. Chem.*, 34, 624 (1969).