Stereochemistry of Allylic Rearrangements. XV. Ion-Pair Return Associated with the Solvolysis of *trans*-α-Methyl-γ-phenylallyl *p*-Nitrobenzoate in Aqueous Acetone[1]

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Abstract: Ion-pair return associated with solvolysis (alkyl–oxygen cleavage) of *trans*-α-phenyl-γ-methylallyl *p*-nitrobenzoate (IV) in aqueous acetone results in allylic rearrangement to the less reactive (about 300 times) γ-phenylallyl isomer VI. Both reactions are first order and the rearrangement is intramolecular. The rearrangement to solvolysis ratio, $k_r^{\alpha}/k_t^{\alpha}$, corresponds to the return (to VI) to solvolysis ratio, k_2/k_3 (Chart I). Solvolysis of the γ-phenylallyl isomer (VI) does not involve rearrangement—the much more reactive α-phenylallyl isomer would not accumulate if formed. In this case ion-pair return results in re-formation of VI with the carboxyl oxygen atoms randomized. To determine if ion-pair return results in complete oxygen equilibration (eq 2) the ratio of oxygen equilibration (k_{eq}^{γ}) to solvolysis (k_t^{γ}) for the γ-phenylallyl isomer has been compared to the $k_r^{\alpha}/k_t^{\alpha}$ ratio for the α-phenylallyl isomer for solvolysis in 70%, 80%, and 90% acetone. Oxygen equilibration is intramolecular and the $k_{eq}^{\gamma}/k_t^{\gamma}$ ratios are only slightly smaller than the $k_r^{\alpha}/k_t^{\alpha}$ ratios which means that ion-pair return involved in solvolysis of the γ-phenylallyl isomer VI results in almost complete oxygen equilibration. As predicted by this result, rearrangement of carboxyl ^{18}O-labeled IV gives VI with the label almost completely randomized.

In nonrearranging systems such as benzhydryl,[3] substituted benzhydryl,[4] α-arylethyl,[5] 2-phenyl-2-butyl,[6] and cyclopropylmethylcarbinyl[7] *p*-nitrobenzoates, ion-pair return associated with solvolysis in aqueous acetone results in equilibration of the carboxyl oxygen atoms (eq 2) and in partial racemization of optically active substrates (eq 3). In these systems solvolysis (eq 1) involves alkyl–oxygen cleavage and the three transformations are first order.

$$\text{R—OCOAr} \xrightarrow[+H_2O]{k_t} \text{ROH} + \text{ArCO}_2\text{H} \quad (1)$$

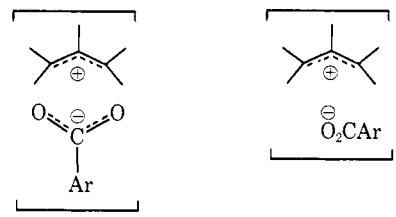
$$\text{R-}^{18}\text{OCOAr} \xrightarrow{k_{eq}} \text{R-}^{18}\text{OC-}^{18}\text{OAr} \quad (2)$$

$$(d \text{ or } l)\text{-R-OCOAr} \xrightarrow{k_{rac}} dl\text{-ROCOAr} \quad (3)$$

In each of the several cases thus far examined[4-7] $k_{eq} > k_{rac}$ which means that return proceeds with partial racemization (predominating retention of configuration). The amount of racemization associated with equilibration varies from considerable in the case of cyclopropylmethylcarbinyl *p*-nitrobenzoate ($k_{rac}/k_{eq} = 0.7$; 80% acetone)[7] to small for 2-phenyl-2-butyl ($k_{rac}/k_{eq} = 0.1$; 80% acetone)[6] and α-phenylethyl *p*-nitrobenzoate ($k_{rac}/k_{eq} = 0.04 \pm 0.04$; 70% acetone).[5] From this it is clear that in such systems racemization measures only a fraction of total return.

Whether or not ion-pair return results in complete randomization of carboxyl oxygen atoms is a long-standing[3,8-10] and important question in connection with using oxygen equilibration as a measure of ion-pair return. Providing equilibration is complete k_{eq} measures total return and $k_t + k_{eq}$ corresponds to total ionization. Otherwise, the total ionization rate remains undeterminable for nonrearranging systems.

To obtain information about this question we have examined oxygen equilibration in several systems in which ion-pair return can be determined by an independent method. For example, in symmetrical allylic systems, *i.e.*, systems in which allylic isomers are enantiomers, ion-pair return results in racemization. In this case the cation is symmetrical and providing the ion-pair intermediate as a whole is symmetrical (*e.g.*, I or II), k_{rac} will correspond to total return. In earlier work we compared k_{eq} and k_{rac} for several such systems. The



I II

two rates are equal for *trans*-α,γ-dimethylallyl[11] and *cis*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate[9] which suggests that in these cases k_{rac} and k_{eq} are independent measures of total return. This, however, does not establish if return without rearrangement results in equilibration. To determine if return to the original carbon atom (*i.e.*, without rearrangement) involves oxygen equilibration it is necessary to distinguish between orientations I and II for the symmetrical intermediate.

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

(2) National Institute of Health, Predoctoral Fellow, 1965–1968.

(3) H. L. Goering and J. F. Levy, *J. Amer. Chem. Soc.*, **84**, 3853 (1962).

(4) (a) H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, **85**, 3059 (1963); H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964); (b) H. Hopf, Ph.D. Thesis, The University of Wisconsin, Madison, Wisconsin, 1967.

(5) Unpublished work by Dr. G. Sandrock.

(6) H. L. Goering and S. Chang, *Tetrahedron Lett.*, 3607 (1965).

(7) K. E. Rubenstein, Ph.D. Thesis, The University of Wisconsin, Madison, Wisconsin, 1967.

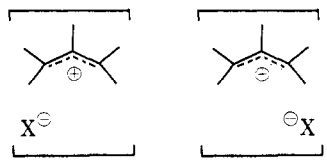
(8) S. Winstein and G. C. Robinson, *J. Amer. Chem. Soc.*, **80**, 169 (1958).

(9) H. L. Goering, J. T. Doi, and K. D. McMichael, *ibid.*, **86**, 1951 (1964).

(10) A. F. Diaz, and S. Winstein, *ibid.*, **88**, 1318 (1966); E. H. White and C. A. Elliger, *ibid.*, **89**, 165 (1967). G. J. Frisone and E. R. Thornton, *ibid.*, **90**, 1211 (1968).

(11) H. L. Goering, M. M. Pombo, and K. D. McMichael, *ibid.*, **85**, 965 (1963); H. L. Goering and M. M. Pombo, *ibid.*, **82**, 2515 (1960).

In each case the allylic carbon atoms, as well as the carboxyl oxygen atoms, are equivalent and thus $k_{rac} = k_{eq}$. For orientation I equilibration does not occur (or will be incomplete) for return to the original carbon atom whereas in the other case, II, return either with or without rearrangement results in complete equilibration. To distinguish between these possibilities it is necessary to examine the individual enantiomers of the ion-pair return product and determine if equilibration is complete in each, II, or if the enantiomers tend to remain discretely labeled, I. In the *cis*-5-methyl-2-cyclohexenyl system oxygen equilibration is complete in both enantiomers.[9] Therefore, in this case return to the original carbon atom results in complete equilibration. In the case of *trans*-α,γ-dimethylallyl *p*-nitrobenzoate, return to the original enantiomer results in incomplete equilibration (42% in 60% acetone and 34% in 90% acetone).[11] In two other allylic systems, *trans*-5-methyl-2-cyclohexenyl[12] and *exo*-bicyclo[3.2.1]oct-3-en-2-yl[13] *p*-nitrobenzoate, $k_{eq} > k_{rac}$. This remarkable result shows that even though the unperturbed cations are symmetrical k_{rac} does not measure total return. In these cases apparently enantiomeric[14] intermediates (III) are involved and as a result oxygen equilibration detects more return than racemization does.



III

We now report an investigation of oxygen equilibration (eq 2) associated with solvolysis of *trans*-α-methyl-γ-phenylallyl *p*-nitrobenzoate (VI) in 70%, 80%, and 90% aqueous acetone. In this work we have compared oxygen equilibration in the unsolvolyzed ester with an independent measure of ion-pair return to determine if return results in complete equilibration.

In an earlier study Sneen[15a] observed that solvolysis of *trans*-α-phenyl-γ-methylallyl *p*-nitrobenzoate (IV) in aqueous dioxane is accompanied by concurrent allylic rearrangement to the γ-phenylallyl isomer VI. Both reactions are first order and the rearrangement is intramolecular. The rearrangement product, VI, is about 300 times less reactive than IV and solvolyzes to only a slight extent under the reaction conditions. Thus, the rearrangement to solvolysis ratio, $k_r^{\alpha}/k_t^{\alpha}$, can be determined directly from the amount of acid produced by solvolysis. From the effects of varying solvent composition and temperature on k_t^{α} and k_r^{α}, it is apparent that rearrangement involves ion-pair return as illustrated in Chart I.[15] At higher temperatures the γ-phenylallyl isomer VI solvolyzes by a first-order process (alkyl–oxygen cleavage[15]) without rearrangement—the much more reactive α-phenylallyl isomer would not accumulate if formed. Thus, the only detectable return from V gives VI.

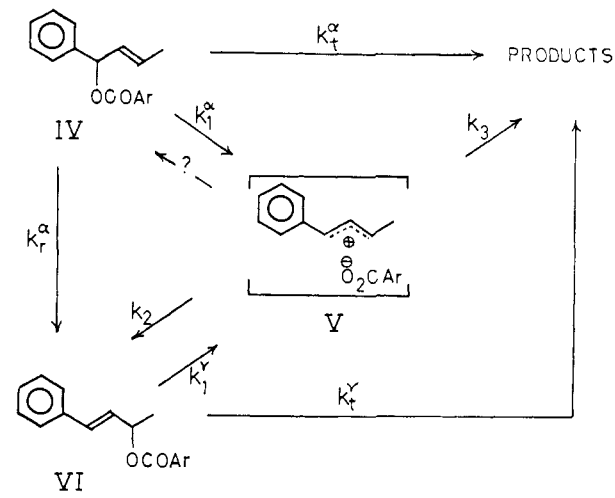
(12) H. L. Goering and J. T. Doi, *J. Amer. Chem. Soc.*, 82, 5850 (1960).

(13) R. P. Anderson, Ph.D. Thesis, University of Wisconsin, Madison, Wisconsin, 1966.

(14) As pointed out elsewhere[9] the anion is not in the plane of the cation and thus the partners in III are asymmetric.

(15) (a) R. A. Sneen, *J. Amer. Chem. Soc.*, 82, 4261 (1960); (b) R. A. Sneen and A. M. Rosenberg, *ibid.*, 83, 895, 900 (1961).

Chart I



Providing that ion-pair return associated with solvolysis of the γ-phenylallyl isomer VI results in complete randomization of the carboxyl oxygen atoms the oxygen equilibration (eq 2) to solvolysis (eq 1) ratio, $k_{eq}^{\gamma}/k_t^{\gamma}$, will correspond to the return to solvolysis ratio, k_2/k_3.[3,6] It can be shown[15a] that the $k_r^{\alpha}/k_t^{\alpha}$ ratio for the α-phenylallyl isomer (determined from the amount of acid produced) also corresponds to k_2/k_3 and thus is an independent measure of the return to solvolysis ratio. Thus the amount of equilibration associated with return for solvolysis of VI can be determined by comparing the $k_{eq}^{\gamma}/k_t^{\gamma}$ and $k_r^{\alpha}/k_t^{\alpha}$ ratios.

Results

The solvolytic behavior of the isomeric methylphenylallyl *p*-nitrobenzoates (IV and VI) in aqueous acetone is similar to that reported for aqueous dioxane[15a] and methanol[15b] in that the α-phenylallyl isomer IV undergoes simultaneous solvolysis and rearrangement to VI and at a much slower rate (about 300 times), the γ-phenylallyl isomer VI solvolyzes without rearrangement.

Solvolysis of *trans*-α-methyl-γ-phenylallyl *p*-nitrobenzoate (VI) in 70%, 80%, and 90% aqueous acetone (per cent by volume before mixing) is accompanied by randomization of the carboxyl oxygen atoms (eq 2). The titrimetric (k_t^{γ}) and oxygen equilibration (k_{eq}^{γ}) first-order rate constants are given in Table I. These

Table I. Rate Constants for Solvolysis (k_t^{γ})[a] and Oxygen Equilibration (k_{eq}^{γ})[a] for Solvolysis of *trans*-α-Methyl-γ-phenylallyl *p*-Nitrobenzoate (VI) in Aqueous Acetone

Solvent, % acetone[b]	Temp, °C	$10^2 k_t^{\gamma}$,[c] hr^{-1}	$10^2 k_{eq}^{\gamma}$,[c] hr^{-1}
90	99.41	5.16 ± 0.11	10.88 ± 0.34[d]
90	78.47	0.662 ± 0.013	1.38[e]
80	78.47	6.91 ± 0.10	7.15 ± 0.10[d]
80	49.04	0.244 ± 0.008	
70	49.04	1.06 ± 0.01	0.70 ± 0.01[d]

[a] Ester concentration: 0.015–0.05 *M* for k_t and 0.04 *M* for k_{eq}. [b] Per cent by volume (25°) before mixing. [c] Average (and average deviation) of 2 to 4 independent kinetic experiments. [d] Carbonyl-^{18}O- and ether-^{18}O-labeled substrates used in duplicate experiments. [e] Single kinetic experiment.

constants were determined by methods described earlier.[9,11] Most of the values in Table I are averages of three or four independent kinetic experiments. Both

Table II. Oxygen-18 Equilibration to Solvolysis Ratio ($k_{eq}^{\gamma}/k_t^{\gamma}$) for *trans*-α-Methyl-γ-phenylallyl *p*-Nitrobenzoate (VI), Rearrangement to Solvolysis Ratios ($k_r^{\alpha}/k_t^{\alpha}$) for *trans*-α-Phenyl-γ-methylallyl *p*-Nitrobenzoate (IV), and ^{18}O Equilibration for the IV → VI Rearrangement

Solvent, % acetone[a]	Temp, °C	$k_{eq}^{\gamma}/k_t^{\gamma}$[b]	$k_r^{\alpha}/k_t^{\alpha}$[c]	$\frac{100\,(k_{eq}^{\gamma}/k_t^{\gamma})^{d}}{(k_r^{\alpha}/k_t^{\alpha})}$	% ^{18}O equilibration for IV → VI rearrangement
90	99.41	2.10 ± 0.12	2.50 ± 0.05	84 ± 7	90
90	78.47	2.08[e]	2.46[e]	85[e]	
80	78.47	1.03 ± 0.03	1.10 ± 0.05	94 ± 6	97
80	49.04		1.12 ± 0.02		
70	49.04	0.66 ± 0.02	0.73 ± 0.01	90 ± 5	100

[a] Per cent by volume (25°) before mixing. [b] Data taken from Table I; uncertainties determined from limiting values of the two constants. [c] Average (and average deviations) of two or three independent determinations. [d] Indicated uncertainties determined from limiting values of the two ratios. [e] No independent duplicate data in this case.

carbonyl and ether ^{18}O-labeled VI were used in the equilibration experiments and gave the same results within experimental error. The oxygen equilibration experiments were followed to up to 70% completion and no loss of label was detected.

From the high reactivity it is clear that solvolysis involves exclusive alkyl–oxygen cleavage[15a] and from the kinetic behavior it is apparent that oxygen equilibration is intramolecular. This was confirmed by exchange experiments in which 0.035 *M* VI was solvolyzed in 80% acetone containing 0.035 *M* ^{14}C-labeled *p*-nitrobenzoic acid. The second-order exchange constant was determined as described earlier[3] (at 78.47° k_{exc} = 0.0250 l mol^{-1} hr^{-1}) and from this it can be shown[3] that at 50% equilibration (also about 50% solvolysis) the unsolvolyzed ester has undergone less than 1% exchange with the acid produced by solvolysis. This shows that intermolecular exchange does not contribute to the observed equilibration.

Under the conditions for the experiments in Table I the α-phenylallyl isomer IV undergoes rapid simultaneous solvolysis and irreversible rearrangemtent to the γ-phenylallyl isomer. The rearrangement to solvolysis ratios for IV, $k_r^{\alpha}/k_t^{\alpha}$, is presented in Table II together with the $k_{eq}^{\gamma}/k_t^{\gamma}$ ratios for VI. The α-phenylallyl isomer is over 300 times more reactive than VI and thus solvolysis of the rearrangement product is not significant during the solvolysis and rearrangement of IV, *e.g.*, ten half-lives for IV correspond to ~2% reaction for VI.

The $k_r^{\alpha}/k_t^{\alpha}$ ratios for IV were determined from the fraction of *p*-nitrobenzoic acid generated by the initial rapid solvolytic reaction. This corresponds to the amount of solvolysis of IV and the remainder of the acid, which is liberated at a slow rate corresponding to k_t^{γ}, gives the amount of rearrangement. The ratios were calculated from titers at a time corresponding to 8 to 10 half-lives for solvolysis of IV and a small correction was made for the acid liberated by the rearrangement product during this period (1–2% of the observed titer). Because of the high reactivity of IV appreciable reaction occurred during the warm-up period and thus the ratios are not for total reaction at the indicated temperatures for the experiments in 80% and 90% acetone—in the case of 70% acetone IV was added to preheated solvent. However, it was found that the $k_r^{\alpha}/k_t^{\alpha}$ ratio is insensitive to temperature variations. For example, the same value was obtained for 80% acetone when most of the reaction occurred >80° as when all of the reaction occurred <50°.

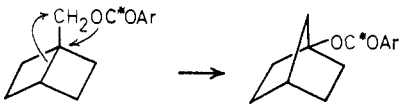
The data in Table II show that the $k_{eq}^{\gamma}/k_t^{\gamma}$ and $k_r^{\alpha}/k_t^{\alpha}$ ratios are similar. The latter correspond to k_2/k_3 in Chart I. This comparison shows that ion-pair return associated with solvolysis of IV results in almost complete oxygen equilibration. We believe that the small differences in the ratios are real in which case equilibration is not quite complete. The calculated per cent equilibration associated with total return is given in the penultimate column in Table II.

Also included in Table II is the amount of carboxyl oxygen equilibration for the IV → VI rearrangement associated with solvolysis of ^{18}O-labeled IV. In these experiments carbonyl-^{18}O IV was solvolyzed and the distribution of the label in the rearrangement product VI was determined. The results are shown in the last column of Table II. Under the conditions of these experiments the rearrangement product VI does not undergo detectable oxygen equilibration. Thus these results correspond to the amount of scrambling that occurs for a single pass through the intermediate(s) separating the allylic isomers. The amount of scrambling involved in the IV → VI rearrangement is in excellent agreement with that observed for return associated with solvolysis of VI. Or to put it another way, the same amount of scrambling occurs when the intermediate V is generated from either allylic isomer.

The $k_r^{\alpha}/k_t^{\alpha}$ ratios correspond to return from an intermediate common to the allylic isomers. Return from an intermediate between VI and the common intermediate V would not be involved in this ratio. For that matter, return from isomeric allylic ion-pair intermediates such as III, to the corresponding allylic esters without oxygen equilibration or racemization would not be detected by the present or other known techniques. However, it should be pointed out that the only way that isomeric allylic ion-pair intermediates of this type have been detected[12,13] is by excess oxygen equilibration and for reasons given below excess equilibration would be expected in this system if such intermediates were involved.

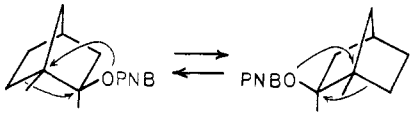
Evidence is beginning to emerge that indicates that the amount of equilibration associated with return in *p*-nitrobenzoate systems is related to the stability of the ion-pair intermediate; *i.e.*, the more stable or longer lived the intermediate, the more equilibration. In this connection it is of interest to compare the *trans*-α,γ-phenylmethylallyl and *trans*-α,γ-dimethylallyl systems. As noted above, in the latter case return to the original carbon atom results in partial equilibration.[11] The present work shows that replacement of a methyl by a phenyl group, which provides additional stabilization of the cation and presumably increases the life time of the intermediate, results in an increase in equilibration from ~35[11] to ~85% for return in 90% acetone.

Another instructive comparison involves two tertiary systems. The ion-pair related to 1-norbornyl *p*-nitrobenzoate (VIII) cannot be generated from the corresponding ester because this unreactive system would undergo acyl–oxygen cleavage instead of alkyl–oxygen cleavage. This ion pair can however be generated by rearrangement. Ion-pair return involved in the solvolysis of bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate (VII) in aqueous acetone results in isomerization to VIII without equilibration of the carboxyl oxygen atoms.[16] Thus in this case in which the cation is destabilized by ring strain, return does not result in detectable equilibration.



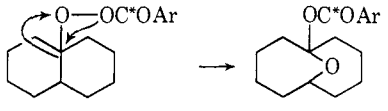
VII VIII

On the other hand, in the 1,2-dimethyl-*exo*-2-norbornyl system IX, a typical unactivated tertiary system, return results in partial equilibration. In this case return results in racemization;[17] however, k_{rac} does not measure total return because ionization gives, at least in part, an asymmetric intermediate (active IX gives active products).[16] Presumably substrate reformed by return is at least as active as the most active product (~65%) in which case total return is about three times larger than racemization. For solvolysis in 90% acetone $k_{eq}/k_{rac} = 0.5$.[18] From this we estimate an upper limit of 20% equilibration for this tertiary system. This suggests that in unactivated tertiary alkyl systems, return at best only results in partial equilibration and points up that equilibration is not a reliable criterion for ion-pair return in such systems.



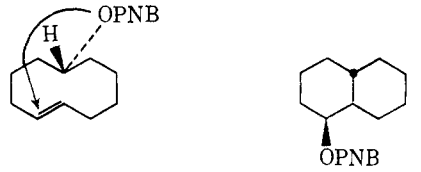
IX

The isomerization of 9-decalyl perbenzoate X to the hemiketal ester XI is similar to the VII → VIII rearrangement. This rearrangement involves ion-pair return[19] and proceeds with little, if any, equilibration.[20] In this case the cation is also destabilized by ring strain.



X XI

There is evidence that return in unactivated secondary alkyl systems results in incomplete equilibration. A remarkable example involves the isomerization of *trans*-5-cyclodecen-1-yl *p*-nitrobenzoate (XII) to *trans,cis*-1-decalyl *p*-nitrobenzoate (XIII) in aqueous acetone. This isomerization involves ion-pair return[21] and proceeds with the indicated stereochemistry.[21b] In spite of the long migration route of the anion, oxygen equilibration is incomplete.[21] From this it is clear that the ion pair related to XIII returns with little, if any, oxygen equilibration.



XII XIII

From the essentially complete equilibration in the α-methyl-γ-phenylallyl (VI) and cyclic and bicyclic allylic systems mentioned above, we tend to feel that in resonance stabilized systems such as the α-anisylethyl,[5] 2-phenyl-2-butyl,[6] and benzhydryl[3,4] systems (all more reactive than VI) return results in complete equilibration and k_{eq} and $k_t + k_{eq}$ correspond to ion-pair return and ionization, respectively. In this connection it is significant that for a series of *p*-substituted benzhydryl *p*-nitrobenzoates ranging from *p*-chloro to *p*-methoxy, the k_{eq}/k_t ratios for solvolysis in 90% acetone remain remarkably constant (random scatter from 2.4 to 2.9) even though total rates vary by 2,500.[4b] This suggests that equilibration is complete in each case.

Experimental Section

α-Methyl-γ-phenylallyl *p*-nitrobenzoate VI, mp 57.5–59.5° (lit.[15] mp 59–60°), and α-phenyl-γ-methylallyl *p*-nitrobenzoate IV, mp 97.2–98.9° (lit.[15] mp 99.5–100.5°), were prepared[22] from the corresponding alcohols.[15,23] Carbonyl ^{18}O-labeled IV (3.67% ^{18}O)[24] and VI (2.98 to 3.41% ^{18}O) were prepared from the corresponding pure alcohols and *p*-nitrobenzoyl chloride-^{18}O.[11] Ether ^{18}O-labeled IV (4.36% ^{18}O) was prepared from α-methyl-γ-phenylallyl alcohol-^{18}O which was prepared[23] from cinnamaldehyde-^{18}O and methylmagnesium bromide. Cinnamaldehyde-^{18}O was prepared by stirring a mixture of 29.7 g (0.25 mol) of purified cinnamaldehyde,[23] 10 ml of $H_2{}^{18}O$ (0.56 mol; 6.18% ^{18}O)[24] and a trace of *p*-toluenesulfonic acid at room temperature for 24 hr. The labeled aldehyde was extracted with ether. After drying (Na_2SO_4) and removal of ether the residual product was distilled, bp 80° (1.2 mm).

Kinetic Experiments.[25] **(A) Titrimetric Rates.** The initial ester concentrations for most of these experiments was 0.015 *M*. The same rate constants, within experimental error, were obtained with 0.05 *M* solutions. The ampoule technique was used and the ampoules containing reaction mixture were flushed with nitrogen prior to sealing. The reactions were followed as described earlier.[9–11]

(B) Rates of Carboxyl Oxygen Equilibration. Enough 0.05 *M* solution of carbonyl or ether ^{18}O-labeled VI so that about 1 g of unsolvolyzed ester would remain when the reaction was quenched, was transferred to nitrogen-flushed heavy-walled ampoules which were chilled and sealed. The ampoules were immersed in a constant temperature bath with vigorous shaking to hasten temperature equilibration. At appropriate times (determined from $k_{eq}\gamma$ for a preliminary experiment) the reaction was quenched by placing the ampoules in ice water. The solvent was evaporated at room temperature and the residual mixture of oil and water was extracted with ether. The organic extract was washed with several portions of 5% Na_2CO_3 and then with water. After drying (Na_2SO_4), the ether was removed by evaporation and the allylic alcohols were removed under high vacuum (<0.02 μ). The infrared spectrum of the residual *p*-nitrobenzoate corresponded to that for pure VI

(16) W. G. Dauben and J. L. Chitwood, *J. Org. Chem.*, **34**, 726 (1969).
(17) H. L. Goering and K. Humski, *J. Amer. Chem. Soc.*, **90**, 6213 (1968).
(18) Unpublished work by Dr. K. Humski.
(19) P. D. Bartlett and J. L. Kice, *J. Amer. Chem. Soc.*, **75**, 5591 (1953); H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).
(20) D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957).
(21) (a) H. L. Goering and W. D. Closson, *ibid.*, **83**, 3511 (1961); (b) H. L. Goering and R. F. Myers, *ibid.*, **91**, 3386 (1969).
(22) H. L. Goering and J. P. Blanchard, *ibid.*, **76**, 5405 (1954).
(23) O. Grummitt and E. I. Becker in "Organic Synthesis," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 771.
(24) Oxygen-18 contents are atom per cent excess ^{18}O.
(25) All concentrations are for 25° and all aliquots were measured at 25°.

and there was no indication of the presence of alcohols (solvolysis products). Two recrystallizations from pentane gave pure VI. The ^{18}O content of this material was the same as that of the starting material.

The purified recovered unsolvolyzed ester (about 0.5 g) was reduced with $LiAlH_4$ and the resulting solid α-methyl-γ-phenylallyl alcohol was purified by vacuum distillation. The *p*-nitrobenzoate derivative was prepared in the usual manner and purified by recrystallization from pentane. The ^{18}O content of this ester corresponds to that of the ether position in the unsolvolyzed ester. The ^{18}O content was determined as described earlier[11] except that the train was packed with 50% platinized carbon[26] at 920°[27] instead of carbon at 1100°, and helium, instead of nitrogen, was used as the carrier gas. Also, the ^{18}O content of the CO_2 was determined with a Nuclide Isotope Ratio mass spectrometer 6-60.

The rate constant, k_{eq}^{γ}, was determined as described earlier.[3,11] The time intervals were corrected for the warm-up period as follows. After complete temperature equilibration was certain (~1 hr), a sample was titrated and the time that would be required for the observed amount of reaction to occur at the bath temperature was determined from k_t^{γ}. For example, in one case an ampoule containing 90 ml of reaction mixture (a typical amount) was placed in a 99.41° bath and 90 min after immersion the reaction was quenched and titrated. From k_t it was determined that at 99.41° the observed amount of reaction would occur in 73 min. Thus in this case, zero time for calculating k_{eq} would be 17 min after placing the ampoule in the bath. This time correction changes the rate constant by an amount that is likely less than the experimental error.

Control experiments showed that the methods used for isolation, purification, and determination of the ^{18}O distributions do not result in loss or scrambling of the ^{18}O label.

(C) Exchange of VI and *p*-Nitrobenzoic Acid-^{14}C. A solution of 2.6238 g (88 mmol) of VI and 1.4716 g (88 mmol) of *p*-nitrobenzoic acid-α-^{14}C[3] in 250 ml of 80% aqueous acetone was distributed in three ampoules. The reaction was quenched and the unsolvolyzed ester was isolated as described above and the radioactivities of the unsolvolyzed ester were determined as described earlier.[3] The activity of the labeled acid was determined as the α-methyl-γ-phenylallyl ester and was 432×10^{-3} μCi/mmol. Thus, all determinations were for the same derivative. The pertinent results are given in Table III.

Oxygen-18 Scrambling for the IV → VI Rearrangement. In a typical experiment 2.726 g of α-phenyl-γ-methylallyl *p*-nitrobenzoate (IV)-carbonyl-^{18}O (3.67% ^{18}O)[24] in 250 ml of 80% acetone (0.036 *M*) in a heavy-walled ampoule was placed in a 78.47° bath and shaken to hasten temperature equilibration. After 45 min the reaction was quenched and the rearranged ester VI was isolated and purified as described above and the total ^{18}O content was 3.70 atom per cent excess. The distribution of the label was determined as indicated above. The results of these experiments are given in the last column of Table II.

Table III. Exchange between α-Methyl-γ-phenylallyl *p*-Nitrobenzoate and *p*-Nitrobenzoic Acid-α-^{14}C in 80% Aqueous Acetone at 78.47°[a]

Time, hr	αRX,[b] 10^3 μCi/mmol	$10^2 k_{exc}$,[c] hr^{-1} M^{-1}	Ester exchanged,[d] %	Equilibration, % reacted[e]
5	1.815	2.40	0.49	30
8	3.013	2.47	0.86	44
10	3.945	2.62	1.19	51

[a] Initial ester concentration was 0.0353 *M* and initial acid concentration was 0.0352 *M*. [b] Average activity of recovered unsolvolyzed ester determined in triplicate; the activity of starting acid was determined as the α-methyl-γ-phenylallyl ester derivative, μCi/mmol = 432×10^{-3}. [c] Second-order rate constant for exchange. [d] Per cent of ester which has undergone exchange at time *t*. [e] Percentage of unsolvolyzed ester which has undergone oxygen equilibration at this time.

Solvolysis and Rearrangement of α-Phenyl-γ-methylallyl *p*-Nitrobenzoate (IV). The rearrangement to solvolysis ratios, $k_r^{\alpha}/k_t^{\alpha}$, for IV in Table II was determined as follows. In a typical experiment a 0.01896 *M* solution[25] of pure IV was distributed into ampoules. The IV used in these experiments was shown to be uncontaminated by VI by physical properties including ir and nmr spectra. Also, the uv spectrum of the alcohol from which the ester was prepared and the alcohol derived from the ester by $LiAlH_4$ reduction (or alcoholic KOH saponification)[15b] showed that contamination by the γ-phenylallyl isomer was negligible; α-methyl-γ-phenylallyl alcohol has λ_{max} 251 mμ, ϵ 1.95×10^4 (ethanol), and the unconjugated α-phenylallyl isomer has ϵ 450 at this wavelength.[15b]

The ampoules were placed in a 99.41° bath. Ampoules were withdrawn after 0.30, 0.45, and 0.70 hr and the titers determined for titration of 5.319-ml aliquots[25] with 0.02469 *N* aqueous sodium hydroxide. These titers showed that the initial rapid solvolysis of IV was complete by 0.45 hr. The observed titer at this point was 1.224 ml and the observed infinity titer after complete solvolysis of the rearranged ester VI was 4.171 ml. From k_t^{γ} (Table I) it can be estimated that solvolysis of the rearranged ester contributed about 0.030 ml to the titer at 0.45 hr. Thus the corrected titer for solvolysis of IV is 1.19 ml and the titer for the subsequent solvolysis of the less reactive γ-phenylallyl isomer is 4.17 − 1.19 = 2.98 ml. The $k_r^{\alpha}/k_t^{\alpha}$ ratio for this case is (2.98/1.19) = 2.50.

The observed rate constant for solvolysis of the rearrangement product (*i.e.*, using 0.45 hr as zero time) was 5.29×10^{-2} hr^{-1} which is in good agreement with the constant for VI in Table I for these conditions.

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