Stereochemistry of Ion-Pair Return Associated with Solvolysis of Para-Substituted Benzhydryl *p*-Nitrobenzoates[1]

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Abstract: Solvolysis of *p*-methylbenzhydryl and *p*-methoxybenzhydryl *p*-nitrobenzoates in aqueous acetone involves alkyl–oxygen cleavage (eq 1) and is accompanied by ion-pair return that results in randomization of the carboxyl oxygen atoms (eq 2) and racemization (eq 3) of the unsolvolyzed ester. Rate constants for eq 1–3 have been determined for the two esters for solvolysis in 90% acetone at various temperatures. Comparison with earlier data for benzhydryl and *p*-chlorobenzhydryl *p*-nitrobenzoates shows that at 100° k_t increases over 2500-fold as the para substituent is varied from chloro to methoxyl. Amounts of return, k_{eq}/k_t, remain steady over this range and racemization associated with return, k_{rac}/k_{eq}, increases gradually with increase in reactivity. Thus, substituents have a large effect on rate, a negligible effect on the amount of return, and a small consistent effect on the stereochemistry of return. In the *p*-methylbenzhydryl system sodium azide causes what appears to be a special salt effect that eliminates part, but not all, of the ion-pair return. The salt has little effect on the stereochemistry of return, which indicates that in this system the stereochemistry is similar for internal and external ion-pair return.

In recent papers we have reported investigations of ion-pair return associated with solvolysis of several alkyl *p*-nitrobenzoates that do not rearrange. These include benzhydryl,[2] *p*-chlorobenzhydryl,[3] α-phenylethyl,[4] α-*p*-anisylethyl,[4] α-methyl-γ-phenylallyl,[5] and 2-phenyl-2-butyl *p*-nitrobenzoates.[6] Cyclopropylmethylcarbinyl[7a] and *tert*-butyl *p*-nitrobenzoate[7b] have also been investigated. These investigations involve comparison of the rates of reactions 1–3.[2–8] In these systems solvolysis (eq 1) involves alkyl–oxygen cleavage; the titrimetric rate constant, k_t, is determined from the rate of formation of acid. Reactions 2 and 3 are intramolecular first-order transformations of the unsolvolyzed ester. Either ether-^{18}O or carbonyl-^{18}O labeled ester is used to determine k_{eq}. The rate constant for racemization, k_{rac}, is determined from the rotations of isolated samples of unsolvolyzed ester or from the first-order rate constants for loss of optical activity (polarimetric rate constant, k_α) and k_t, *i.e.*, $k_{rac} = k_\alpha - k_t$.[8,9]

$$\overset{\curvearrowright}{\mathrm{R{-}OCOAr}} \xrightarrow{k_t} \mathrm{ROH + ArCO_2H} \qquad (1)$$

$$\mathrm{R^{18}OCOAr} \xrightarrow{k_{eq}} \mathrm{R^{18}OC^{18}OAr} \qquad (2)$$

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

Evidence that return results in substantial, if not complete, oxygen equilibration in resonance-stabilized systems such as the benzhydryl system has been discussed elsewhere.[5,8b] Providing equilibration is complete, $k_{eq} + k_t$ is the rate constant for total ionization (*i.e.*, k_i in eq 4) and k_{eq}/k_t is the return to solvolysis ratio (k_i/k_s in eq 4). The k_{rac}/k_{eq} ratio is a measure of the stereochemistry of return. This ratio corresponds to the fraction of return that results in loss of optical configuration; the rest proceeds with retention of optical activity.

$$\mathrm{ROCOAr} \underset{k_i}{\overset{k_i}{\rightleftharpoons}} \left[\begin{matrix}\text{ion-pair} \\ \text{intermediate(s)}\end{matrix}\right] \xrightarrow{k_s} \text{products} \qquad (4)$$

This paper reports an investigation of the amount (k_{eq}/k_t) and stereochemistry (k_{rac}/k_{eq}) of return involved in solvolysis of *p*-methylbenzhydryl and *p*-methoxybenzhydryl *p*-nitrobenzoates in 90% aqueous acetone.[10] The effect of sodium azide on ion-pair return in the *p*-methylbenzhydryl system was also investigated. Similar data for *p*-chlorobenzhydryl *p*-nitrobenzoate were reported earlier.[3] Thus data are now available for three para-substituted benzhydryl esters and for the parent benzhydryl *p*-nitrobenzoate.[2]

Results

Results for the solvolysis of *p*-methylbenzhydryl and *p*-methoxybenzhydryl *p*-nitrobenzoates in 90% acetone are presented in Table I together with earlier results for the *p*-chlorobenzhydryl and parent benzhydryl systems.

The titrimetric (k_t) and polarimetric (k_α) rate constants were determined as described earlier.[2–8] Reactions were followed to at least 75% completion and good first-order behavior was observed in all cases except for a small consistent upward trend in k_t—the integrated constants at 50% reaction were about 3% higher than the initial values. Independent experiments showed that the upward drift results from the *p*-nitrobenzoic acid produced by solvolysis.

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(10) Solvent composition based on volumes of pure components at 25° prior to mixing.

Table I. Rate Constants for Solvolysis (k_t), Equilibration of Carboxyl Oxygen Atoms (k_{eq}), and Racemization (k_{rac}) for Solvolysis of Para-Substituted Benzhydryl *p*-Nitrobenzoates in 90% Acetone

Substituent	Temp, °C	10^3k_t, hr^{-1}	10^3k_{eq}, hr^{-1}	10^3k_{rac},[a] hr^{-1}
p-Cl	99.6[b]	0.50 ± 0.02	1.27 ± 0.01[c]	0.46 ± 0.03
				0.48 ± 0.03[d]
None	99.5[e]	1.01 ± 0.01	2.97 ± 0.06[c]	
	118.6[f]	6.4 ± 0.3	18.7 ± 0.1[c]	
p-CH_3[e]	48.8[g]	0.036	0.105	0.018
	60.0	0.153 ± 0.002	0.44 ± 0.02[g]	0.134 ± 0.009
	79.0	1.30 ± 0.03	4.10 ± 0.05[h]	1.52 ± 0.08
	99.5	11.20 ± 0.20	32.3 ± 0.9[h]	19.2 ± 0.7
				19.2 ± 0.6[d]
	99.6[i]	11.43 ± 0.15	33.4 ± 0.7[c]	21.2 ± 1.4
	120.0	70.0 ± 1.1	237 ± 4[h]	148 ± 5
p-CH_3O[e]	48.8	12.9 ± 0.2	31.0 ± 1.4[c]	8.5 ± 0.6
	59.9	39.4 ± 0.8[j]		
	65.0	64.2 ± 1.0		35 ± 1
	99.5[d]	>1300	>3300[k]	473[c]

[a] Unless otherwise noted, determined from the titrimetric and polarimetric rate constants, *i.e.*, $k_{rac} = k_\alpha - k_t$. [b] Data taken from ref 3a. [c] Determined with carbonyl-^{18}O labeled ester. [d] Determined from rotations of isolated samples of unsolvolyzed ester. [e] Data obtained in present investigation. [f] Data taken from ref 2. [g] Determined by extrapolation of data for other temperatures. [h] Determined with ether-^{18}O labeled ester. [i] Taken from ref 7b. [j] Taken from ref 2b. [k] Estimated assuming k_{eq}/k_t is the same for 99.5° as for 48.8°.

Rate constants for racemization of the unsolvolyzed ester (k_{rac}) were determined from k_α and k_t. In one case k_{rac} was determined from the rotations of isolated samples of the ester—control experiments showed that isolation and purification of the unsolvolyzed ester (chromatography on neutral silicic acid) does not result in racemization or optical fractionation. As shown in Table I the constants determined by the two methods are in excellent agreement.

Rate constants for carboxyl–oxygen equilibration (k_{eq}) were determined as described earlier[5,8] using either ether-^{18}O or carbonyl-^{18}O labeled ester. Good first-order behavior was observed and in all cases the total ^{18}O content of the unsolvolyzed ester remained constant—enrichment of ^{18}O due to isotopic fractionation, as observed earlier in another system,[8b] could not be detected.

Oxygen equilibration (eq 2) and racemization (eq 3) are first order which shows that these processes are intramolecular. This was confirmed by exchange experiments.[2] Second-order rate constants for exchange between unsolvolyzed ester and *p*-nitrobenzoic acid-^{14}C in 90% acetone are 40.1 ± 0.8 × 10^{-3} l. mol^{-1} hr^{-1} at 99.5° for *p*-methylbenzhydryl *p*-nitrobenzoate and 30.0 ± 0.2 × 10^{-3} l. mol^{-1} hr^{-1} at 48.8° for *p*-methoxybenzhydryl *p*-nitrobenzoate. From these constants it can be determined[2] that *p*-methylbenzhydryl *p*-nitrobenzoate undergoes <1% exchange with the acid produced by solvolysis during the first 27% solvolysis (60% equilibration and 42% racemization). Similarly, the *p*-methoxybenzhydryl ester undergoes <1% exchange during the first 31% solvolysis (60% equilibration and 23% racemization). From these experiments it is clear that external return does not contribute to racemization or equilibration.

As shown earlier,[11] rates of solvolysis of substituted benzhydryl *p*-nitrobenzoates in aqueous acetone are correlated by the Hammett equation using δ^+ substituent constants.[12] The data in Table I give linear plots and ρ values are −3.9 ± 0.4 for k_t, −3.8 ± 0.2 for k_α, and −4.0 ± 0.4 for k_{eq}. These large negative values are typical of SN1 reactions of benzyl and benzhydryl systems[11-13] and clearly show that solvolysis involves alkyl–oxygen cleavage because ρ would be expected to be very small for acyl–oxygen cleavage. The large substituent effect results primarily from a decrease in activation energy as δ^+ decreases.[11]

Table II shows the relative solvolytic reactivities (k_t) and the ion-pair return to solvolysis ratios (k_{eq}/k_t) for the four benzhydryl *p*-nitrobenzoates. The racemization to return ratios for the three asymmetric esters are included in Table II. The four esters span a reactivity range of over 2500. However, the k_{eq}/k_t ratios remain steady as structure is varied. The amount of return is also temperature independent for the *p*-methylbenzhydryl ester over a temperature range (48–120°) that results in a more than 200-fold change in rate. Negligible temperature effects on the amount of return have been observed in other systems[5,14] and seem to be general for solvolysis of *p*-nitrobenzoates.

Table II. Relative Rates, Return to Capture Ratios (k_{eq}/k_t), and Stereochemistry of Return (k_{rac}/k_{eq}) for Solvolysis of Para-Substituted Benzhydryl *p*-Nitrobenzoates in 90% Aqueous Acetone

Substituent	Temp, °C	Rel rates[a]	k_{eq}/k_t[b]	k_{rac}/k_{eq}[b]
p-Cl	99.6	1	2.4 ± 0.2	0.35 ± 0.03
None	99.5	2	2.9 ± 0.1	
p-CH_3	48.8		3.0[c]	0.17[c]
	60.0		2.9 ± 0.2	0.30 ± 0.04
	79.0		3.2 ± 0.1	0.37 ± 0.03
	99.5	22	2.9 ± 0.1	0.60 ± 0.04
	120.0		3.4 ± 0.1	0.63 ± 0.04
p-CH_3O	48.8		2.4 ± 0.1	0.28 ± 0.03
	99.5	>2500		

[a] Relative titrimetric rates of solvolysis. [b] Uncertainties estimated from limiting values of rate constants in Table I. [c] Ratio obtained by extrapolation of Arrhenius plots.

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The amount of racemization associated with return (k_{rac}/k_{eq}) varies with structure and temperature. In all cases the ratio is less than one which means that return involves predominating retention of configuration. Comparison of the ratios for the *p*-chlorobenzhydryl and *p*-methylbenzhydryl esters at 99.5° and for the *p*-methylbenzhydryl and *p*-methoxybenzhydryl esters at 48° shows that k_{rac}/k_t increases with increase in reactivity (carbonium ion stability). This suggests that attractive forces that preserve optical configuration in ion-pair intermediates become weaker as delocalization of the charge in the cation increases.

Similar behavior was observed in the α-arylethyl system.[4] Return involved in solvolysis of α-phenylethyl *p*-nitrobenzoate in 70% acetone does not result in detectable racemization. On the other hand, in the α-*p*-anisylethyl system (>30,000 times more reactive) return results in considerable racemization, *e.g.*, k_{rac}/k_{eq} is 0.71 in 70% acetone.

The k_{rac}/k_{eq} ratios for *p*-methylbenzhydryl *p*-nitrobenzoate increase with temperature. This means that the activation energy for reformation of substrate with inversion is higher than for return with retention of configuration. Arrhenius plots of k_α and k_t converge at about 20° which indicates that at this temperature, and below, return would proceed with negligible racemization. The rate constant for return with inversion is $(1/2)k_{rac}$ and that for return with retention is $k_{eq} - (1/2)k_{rac}$. An Arrhenius plot of the ratio of these constants shows that the difference in activation energies for return with inversion and retention is 4.6 ± 1.2 kcal mol^{-1}. Presumably this difference results from the additional relocation of the ions and solvating solvent molecules required for interconversion of enantiomeric ion-pair intermediates.

From the effects of varying structure and temperature on the rates and relative rates it is evident that reactions 1–3 are mechanistically related instead of being independent parallel reactions. The large effects of changing structure and temperature on k_t and k_{eq} are essentially identical as shown by the constant k_{eq}/k_t ratios. The effect of varying structure on the rate of reaction 3 is also about the same as for reactions 1 and 2. If comparisons are made for the same temperature k_{rac}/k_t varies less than a factor of 3 while k_t varies by a factor of over 2500. This indicates that change in structure or temperature changes the rate of ionization which is the common initial step for each of the three reactions. Activation barriers for solvent capture, racemization, and return of ion-pair intermediates are small and thus cannot differ greatly. Hence, the ion-pair mechanism for reactions 1–3 predicts that the relative rates of the three reactions will be much less sensitive to change in temperature and structure than the absolute rates.

The effect of azide ion on the amount and stereochemistry of return involved in solvolysis of *p*-methylbenzhydryl *p*-nitrobenzoate in 90% acetone was also investigated. In another investigation[3] it was found that solvolysis of *p*-chlorobenzhydryl *p*-nitrobenzoate in 90% acetone is accompanied by intramolecular oxygen equilibration and partial racemization of the unsolvolyzed ester. Addition of 0.14 *M* sodium azide eliminates detectable racemization; however, carboxyl-oxygen equilibration still occurs.[3b,4] This shows that two types of return are involved; one which leads to racemic ester and can be suppressed by sodium azide and another that gives ester with preservation of optical configuration. These results were interpreted in terms of the Winstein mechanism[9] for solvolysis outlined by eq 5. According to this interpretation, internal return from the intimate ion pair (I) proceeds with retention of configuration and external ion-pair return from II involves partial or complete loss of optical configuration. The latter is eliminated by 0.14 *M* sodium azide.

$$\mathrm{R{-}X} \rightleftharpoons \underset{\mathrm{I}}{[\mathrm{R^+X^-}]} \rightleftharpoons \underset{\mathrm{II}}{[\mathrm{R^+}\,|\,\mathrm{X^-}]} \longrightarrow \text{products} \qquad (5)$$

Different behavior was observed[4] for solvolysis of α-*p*-anisylethyl *p*-nitrobenzoate in 90% acetone. In this case 0.12 *M* sodium azide or 0.180 *M* tetrabutylammonium azide reduce the amount of return (k_{eq}/k_t) but have very little effect on the stereochemistry of return (k_{rac}/k_{eq}). However, tetrabutylammonium azide shows a "special" salt effect[9] on k_t at low salt concentrations and this is followed by a normal salt effect at concentrations over 0.1 *M*. Evidently two kinds of return are involved. One that is eliminated by azide ion (cause of the special salt effect) and another which is not (return also occurs in the normal salt effect region). Where this system differs from the *p*-chlorobenzhydryl system is in the stereochemistry of that part of the return that is not eliminated by azide ion. In this case k_{rac}/k_{eq} is only slightly lower in the normal salt effect region (external ion-pair return eliminated) than in the absence of salt (combination of 54% internal and 46% external ion-pair return).

The effects of varying amounts of sodium azide on k_t, k_{eq}, and k_{rac} for solvolysis of *p*-methylbenzhydryl *p*-nitrobenzoate in 90% acetone[10] at 99.5° are presented in Table III. The highest salt concentration, 0.116 *M*, corresponds to a saturated solution at room temperature. In the presence of azide ion, solvolysis gives a mixture of alcohol (solvent capture) and alkyl azide (azide ion capture). Solvent capture results in formation of an equivalent of acid; however, azide ion capture does not generate acid. The ratio of alkyl azide to alcohol in the product can be determined from

Table III. Rate Constants for Solvolysis (k_t), Carboxyl Oxygen Equilibration (k_{eq}), and Racemization (k_{rac}) for Solvolysis of *p*-Methylbenzhydryl *p*-Nitrobenzoate in 90% Acetone at 99.5° in the Presence of Sodium Azide[a]

$[NaN_3]$, 10^2M	10^3k_t,[b] hr^{-1}	10^3k_{eq}, hr^{-1}	10^3k_{rac}, hr^{-1}
None	11.1 ± 0.2	32.3 ± 0.9	19.2 ± 0.7
1.00	10.9 ± 0.2		
3.00	13.8 ± 0.3	34.7 ± 0.8[c]	19.2 ± 0.6
5.03	22.7 ± 0.8		
6.55	32.1 ± 1.0	32.7 ± 1.2[c]	19.6 ± 0.3[c]
8.10	41.0 ± 1.1		
11.55	47.0 ± 0.5	25.8 ± 0.4[d]	13.3 ± 0.7[e]
11.67	46.0 ± 1.0		
11.67	46.5 ± 0.6		

[a] Initial ester concentration 0.027 *M*. [b] Average and average deviation of up to eight integrated first-order constants. [c] Average and average deviation of two independent determinations. [d] Average and average deviation of three integrated rate constants. [e] Average and average deviation of four independent experiments.

the amount of acid generated. Observed infinity titers were used to determine the rate constants for disappearance of ester (k_t).

Rate constants for solvolysis in the presence of sodium azide were determined as described earlier.[3b,4] In these experiments k_{rac} was determined from rotations of isolated samples of the unsolvolyzed ester. Control experiments showed that isolation and purification of the unsolvolyzed ester does not result in detectable racemization, optical fractionation, or carboxyl–oxygen equilibration. Reactions were followed to at least 50% completion except for racemization and equilibration at the highest sodium azide concentration (0.116 *M*). Under these conditions k_{eq}/k_t and k_{rac}/k_t ratios are low and as a result equilibration and racemization were followed only to 33 and 15% completion, respectively. However, as indicated in Table III, these constants were reproducible to within about 5% in independent experiments.

Under the conditions of the experiments in Table III both oxygen equilibration and racemization are intramolecular. This was established by exchange experiments with added ^{14}C-labeled *p*-nitrobenzoic acid.[2] In the absence of sodium azide, *p*-nitrobenzoic acid is largely undissociated and as shown above, exchange with *p*-methylbenzhydryl *p*-nitrobenzoate is negligible. In the presence of excess sodium azide, *p*-nitrobenzoic acid is converted to sodium *p*-nitrobenzoate. The second-order rate constant for exchange[2] between ester and added labeled acid in 90% acetone containing 0.116 *M* sodium azide at 99.5° is $46 \pm 3 \times 10^{-3}$ l. mol^{-1} hr^{-1}. This is only slightly larger than the value observed in the absence of sodium azide. From the second-order constant for exchange it can be shown[2] that for the conditions of the experiments in Table III the maximum amount of equilibration or racemization that results from exchange is less than experimental errors of the observations.

Evidently the increase in k_t with sodium azide concentration results from a salt effect instead of from azide-ion promoted acyl–oxygen cleavage or an SN2 displacement by azide ion. Azide-ion promoted acyl–oxygen cleavage of the type observed in the *p*-chlorobenzhydryl system[3b] would not be expected to compete in the present case because of the higher level of reactivity of the *p*-methylbenzhydryl system. Also, presumably this would lead to *p*-nitrobenzoyl azide. Control experiments showed that under the conditions of solvolysis, *p*-nitrobenzoyl azide (prepared from *p*-nitrobenzoic acid hydrazide)[15] is converted to *p*-nitroaniline in good yields. Solvolysis products were carefully examined by tlc and *p*-nitroaniline could not be detected

There is also evidence that an SN2 displacement by azide ion does not contribute to k_t. In the first place, benzhydryl systems are quite unreactive in SN2 reactions.[16] Moreover, the effect of 0.12 *M* sodium azide on k_t in the present case is about the same as that for solvolysis of α-*p*-anisylethyl *p*-nitrobenzoate[4] which is about 25 times more reactive. It seems unlikely that an SN2 displacement would compete to the same extent in systems of different reactivities. It should also be noted that the effects of sodium azide on the solvolysis of benzhydryl and *p-tert*-butylbenzhydryl chlorides in 90% acetone[17] and *p*-methoxybenzyl chloride in 70% acetone[18] are similar to those observed in the present work.

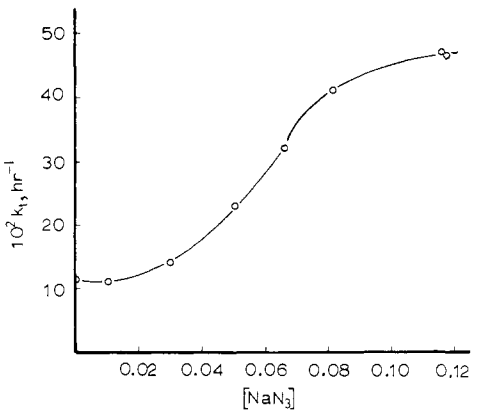

Figure 1. Plot of titrimetric rate constant (k_t) *vs.* sodium azide concentration (*M*) for solvolysis of *p*-methylbenzhydryl *p*-nitrobenzoate in 90% acetone at 99.5° (data taken from Table III).

The effect of sodium azide on the amount and stereochemistry of return for solvolysis of *p*-methylbenzhydryl *p*-nitrobenzoate in 90% acetone is shown in Table IV. The alkyl azide–alcohol ratio, determined from the amount of acid produced, is included in the table. These data show that sodium azide decreases the amount of return (note decrease in k_{eq}/k_t) but has little effect on the stereochemistry of return.

Table IV. Return to Capture Ratios (k_{eq}/k_t), Stereochemistry of Return (k_{rac}/k_{eq}), and Alkyl Azide to Alcohol Product Ratios (RN_3/ROH) for Solvolysis of *p*-Methylbenzhydryl *p*-Nitrobenzoate[a]

[NaN$_3$], 10^2M	[RN$_3$]/[ROH][b]	k_{eq}/k_t[c]	k_{rac}/k_{eq}
None	Zero	2.90 ± 0.10	0.59 ± 0.04
3.00	0.79	2.51 ± 0.12	0.55 ± 0.03
6.55	1.93	1.02 ± 0.07	0.60 ± 0.03
11.55	2.03	0.55 ± 0.02	0.52 ± 0.05

[a] 90% acetone at 99.5° in the presence of sodium azide. [b] Determined from the amount of acid produced by solvolysis. [c] Uncertainties estimated from limiting values of rate constants.

As shown in Figure 1, the effect of sodium azide on k_t is not linear in salt concentration. At low concentrations there is an apparent small effect followed by a steep rise in k_t for the range of 0.03–0.08 *M*. This is followed by what appears to be the beginning of a linear normal salt effect. Because of the limited solubility of sodium azide this region could not be investigated in more detail.

It appears that this remarkable salt effect results from alteration of ion-pair return. Except for the initial level portion, this plot has the characteristic features of a "special" salt effect.[9,19] The apparent small effect at low concentrations probably results from consumption

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of much of the azide ion early in the reaction. Solvent capture, as well as capture by azide ion, leads to consumption of azide ion because the *p*-nitrobenzoic acid produced by solvolysis liberates the weaker undissociated hydrazoic acid from the salt. Thus an equivalent of azide ion is consumed for each equivalent of reaction. In these experiments the initial ester concentration was 0.03 *M*. Thus 0.015 *M* azide ion is consumed at 50% solvolysis. The salt concentrations in Table III and Figure 1 are initial values and have not been corrected for consumption by the reaction. If each of the points in Figure 1 is shifted 0.015 concentration unit to the left (this corresponds to the salt concentration at 50% reaction) much of the initial level portion vanishes.

The salt effects on k_t and k_{eq} indicate that two types of return are involved, one that is eliminated by sodium azide (this is indicated by the apparent special salt effect) and another which is not. The k_{eq}/k_t ratios in Table IV show that much, but not all, of the return is eliminated by 0.12 *M* sodium azide.

The present results parallel those reported recently[4] for solvolysis of α-*p*-anisylethyl *p*-nitrobenzoate in 90% acetone. The effects of sodium azide on the rates and relative rates of reactions 1–3 are similar for the two systems and apparent special salt effects are observed in each case. In the anisylethyl system, 0.12 *M* sodium azide reduces k_{eq}/k_t from 2.2 to 0.55 and only changes k_{rac}/k_{eq} from 0.54 ± 0.03 to 0.43 ± 0.04. These are nearly the same as the changes in Table III for the *p*-methylbenzhydryl system.[20]

Evidently, in both of these systems internal return (return not eliminated by sodium azide), as well as external ion-pair return, results in partial racemization of the unsolvolyzed ester. This is in striking contrast to the *p*-chlorobenzhydryl system[3b,4] in which internal return (oxygen equilibration in the presence of 0.14 *M* sodium azide) in 80% acetone does not result in detectable racemization but external ion-pair return (absence of sodium azide) does. In this connection it is of interest that return associated with solvolysis of optically active α-phenylethyl *p*-nitrobenzoate in 70% acetone does not result in detectable racemization.[4]

If the present mechanistic interpretation is correct, in the α-phenylethyl and *p*-chlorobenzhydryl systems the attractive forces in the intimate ion pair (I) are strong enough to preserve optical configuration. The attractive forces in I are weaker in the α-*p*-anisylethyl and *p*-methylbenzhydryl systems (presumably because of the additional charge dispersion in the cations) and as a result, configuration is no longer fully preserved.

The stereochemistry of solvolysis of optically active *p*-methylbenzhydryl *p*-nitrobenzoate in 90% acetone[10] at 99.5° was also investigated. Under the conditions of the kinetic experiments in Table I *p*-methylbenzhydrol is not optically stable—solvolysis of racemic *p*-nitrobenzoate racemizes optically active *p*-methylbenzhydrol added at the outset. If 0.12 *M* 2,6-lutidine is added to neutralize the acid produced by solvolysis, racemization of added active *p*-methylbenzhydrol cannot be detected at 50% reaction for solvolysis of 0.04 *M* ester.

Solvolysis of 0.04 *M* (−)-*p*-methylbenzhydryl *p*-nitrobenzoate, $[\alpha]^{25}_{435}$ −14.52°,[21] in 90% acetone containing 0.12 *M* 2,6-lutidine, for 62 hr (50% solvolysis) gave *p*-methylbenzhydrol which was reconverted to (−)-*p*-methylbenzhydryl *p*-nitrobenzoate, $[\alpha]^{25}_{435}$ −0.35°. Control experiments showed that isolation and purification of the product and conversion to the *p*-nitrobenzoate derivative does not alter the optical purity. Thus, product is formed with about 2.5% retention of configuration. The average optical purity of the ester during the first 50% reaction (determined from k_α and k_t)[22] is 62% of the initial value. This means that for this period 38% of the product is derived from ester subsequent to racemization by ion-pair return. Thus, solvolysis proceeds with about 2.5/0.62 = 4% retention of configuration.

In an earlier investigation[3] it was shown that solvolysis of *p*-chlorobenzhydryl *p*-nitrobenzoate in 90% acetone proceeds with 10% retention of configuration and involves exclusive alkyl–oxygen cleavage. The present system solvolyzes 25 times faster and from this we conclude that the observed 4% retention does not result from acyl–oxygen cleavage.

Predominating retention of configuration has also been observed for solvolysis of 2-phenyl-2-butyl (38% retention)[6] and α-*p*-anisylethyl (8% retention)[4] *p*-nitrobenzoates in 90% acetone. Solvolysis (alkyl–oxygen cleavage) of optically active 2-phenyl-2-butyl *p*-nitrobenzoate proceeds with 65% retention in 95% acetone, 42% retention in an 8:1 acetone–methanol mixture,[10] and 9% retention in a mixture of 71% cyclohexane and 29% methanol.[10,23] We presume that retention results from favored capture (probably of a solvent-separated ion pair) by solvent molecules that are hydrogen bonded to the anion and as a result are more nucleophilic than the rest of the solvating molecule.[3a,6]

There is indirect evidence that azide ion capture, unlike solvent capture, proceeds with excess inversion of configuration. Solvolysis of (−)-*p*-methylbenzhydryl *p*-nitrobenzoate, $[\alpha]^{25}_{435}$ −13.6°[21] (derived from (−)-*p*-methylbenzhydrol, $[\alpha]^{25}_{435}$ −10.13°) in 90% acetone containing 0.116 *M* sodium azide at 99.5° gave (+)-*p*-methylbenzhydryl azide, $[\alpha]^{25}_{435}$ 5.60°, which was converted to (+)-*p*-methylbenzhydrylamine, $[\alpha]^{24}_{589}$ 1.10°, by reduction with lithium aluminum hydride. As shown by the last experiment in Table IV, under these conditions solvolysis gives 67% azide and 33% alcohol. In this multistep conversion of (−)-*p*-methylbenzhydrol to (+)-*p*-methylbenzhydrylamine, the only step in which the asymmetric center is involved is the conversion of the (−)-*p*-nitrobenzoate to the (+)-azide.

Evidence that (−)-*p*-methylbenzhydrol and (+)-*p*-methylbenzhydrylamine have opposite configurations is as follows. Deamination of (−)-*p*-methylbenzhydryl amine hydrochloride with excess sodium nitrite in water at 50° gave (−)-*p*-methylbenzhydrol. Deaminations of α-phenylethylamine and 2-phenyl-2-butylamine proceed with substantial retention of configuration[24] and a

(20) Similar behavior has been observed for solvolysis of optically active *p*-chlorobenzhydryl chloride in 80% acetone at 25°.[9] Addition of sodium azide reduces, but does not eliminate, racemization. In this case there is no way to measure total return because return with preservation of configuration cannot be detected. Thus it cannot be determined if the stereochemistry of return is changed by the sodium azide.

(21) Optical rotations are for chloroform solutions.

(22) S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, 74, 1154 (1952).

(23) S. Chang, Ph.D. Thesis, The University of Wisconsin, Madison, Wis., 1966.

(24) E. H. White and D. J. Woodcock in "Chemistry of the Amine Group," S. Patai, Ed., Wiley, New York, N. Y., 1968, pp 461–471.

similar result would be expected in the present case. Thus, evidently, in the *p*-methylbenzhydryl system alcohol and amine with the same configuration have rotations with the same sign.

In connection with this correlation it is significant that optical configurations of several secondary alcohols and azides have been related and in every case azides and alcohols of the same configuration have rotations with the same sign.[25] Thus all of the evidence points to an inversion in the transformation of (−)-*p*-methylbenzhydryl *p*-nitrobenzoate to (+)-*p*-methylbenzhydryl azide.

For reasons outlined above it appears that alkyl azide results from capture of an ion-pair intermediate, probably the solvent-separated ion pair (II), rather than from an SN2 displacement. The difference in the stereochemistry for azide ion capture and solvent capture may be due to the different charge types of the two reactions. Backside approach (leading to inversion) by azide ion keeps the two negative ions separated as far as possible during the capture step. On the other hand, frontside capture by hydroxylic solvent locates the solvent molecule that is developing a positive charge next to the departing *p*-nitrobenzoate ion to which it is hydrogen bonded.

Experimental Section

Materials. ***dl*-*p*-Methylbenzhydryl *p*-nitrobenzoate,** mp 92–94° (lit.[11] mp 90–93°), and ***dl*-*p*-methoxybenzhydryl *p*-nitrobenzoate,** mp 83–84.5° (lit.[11] mp 79–82°), were prepared by a standard method.[26]

Attempts to resolve *p*-methylbenzhydrol by a reported procedure[27] were unsuccessful—under these conditions the acid phthalate decomposes and the brucine salt of phthalic acid is the only isolable product. *p*-Methylbenzhydrol was resolved as follows. To a warm solution of 70 g (0.2 mol) of *p*-methylbenzhydryl acid phthalate, mp 121.5–123° (lit.[27] 120–122°), in 1.4 l. of acetone was added 75 g (0.23 mol) of quinidine. The solution was placed in a refrigerator overnight and the white precipitate was separated. Four recrystallizations of the first crop from acetone gave 10 g of quinidine salt. The acid phthalate derived from the salt (cold dilute HCl) had mp 114–119° and $[\alpha]^{24}_{589}$ −8.08° (*c* 0.62).[21] Reduction of the acid phthalate in ether with lithium aluminum hydride followed by four recrystallizations from pentane gave 0.92 g of **(−)-*p*-methylbenzhydrol,** mp 57–68° (mp 50–52° for racemic material), $[\alpha]^{24}_{435}$ −8.18° (*c* 0.409). (−)-*p*-Methylbenzhydrol, $[\alpha]^{24}_{435}$ −13.13° (*c* 0.63), obtained from another resolution was converted[26] to **(−)-*p*-methylbenzhydryl *p*-nitrobenzoate,** $[\alpha]^{24}_{435}$ −18.12° (*c* 0.441).[21,28]

The *p*-methoxybenzhydryl system was resolved as follows. A slurry of 100 g (0.278 mol) of *p*-methoxybenzhydryl acid phthalate, mp 98–99° (lit.[29] mp 102–103°), in 320 ml of warm ethyl acetate was added to a stirred suspension of 83.9 g (0.285 mol) of cinchonidine in 50 ml of ethyl acetate. The resulting clear solution was allowed to stand at room temperature for 3 days during which time the first crop of cinchonidine salt separated. Four recrystallizations from ethyl acetate gave 55 g of salt which was converted (ice-cold 4% HCl and rapid extraction with ether) to (−)-*p*-methoxybenzhydryl acid phthalate, mp 103–104°, $[\alpha]^{24}_{435}$ −33.5° (*c* 0.9).[21] Reduction of active acid phthalate with lithium aluminum hydride and purification of the product by column chromatography (Mallinckrodt SilicAR-CC-7; chloroform as solvent and eluent) gave **(−)-*p*-methoxybenzhydrol,** mp 45–56° (mp 66–67° for racemic material), $[\alpha]^{24}_{435}$ −20.02° (*c* 1.38). The active *p*-methoxybenzhydrol was converted[26] to (−)-*p*-methoxybenzhydryl *p*-nitrobenzoate, mp 73–80° (mp 79–82° for racemic material), $[\alpha]^{24}_{435}$ −23.75° (*c* 1.42).[21,28]

***p*-Methylbenzhydryl *p*-nitrobenzoate-*ether*-^{18}O,** 3.96% ^{18}O,[30] was prepared from ^{18}O-labeled alcohol prepared from phenyl Grignard and *p*-tolualdehyde-^{18}O. The latter was prepared by stirring a mixture of pure *p*-tolualdehyde and a threefold molar excess of ^{18}O-enriched water containing a trace of toluenesulfonic acid for 18 hr under nitrogen. The aldehyde was extracted with ether and dried ($MgSO_4$). Distillation gave a 65% yield of pure ^{18}O-labeled tolualdehyde.

***p*-Methoxybenzhydryl *p*-nitrobenzoate-*carbonyl*-^{18}O,** 5.52% ^{18}O,[30] was prepared in the usual way[26] using ^{18}O-labeled *p*-nitrobenzoyl chloride.[8]

(−)-*p*-Methylbenzhydrylamine, $[\alpha]^{24}_{589}$ −1.31° (*c* 3.67),[21] was prepared from (+)-phenyl-*p*-tolylacetic acid, $[\alpha]^{24}_{589}$ 12.77° (*c* 1.68, acetone), using a variation[31] of the Curtius rearrangement. Phenyl-*p*-tolylacetic acid,[32] mp 111–113°, was resolved by recrystallization of the cinchonidine salt six times from ethanol.[32] The active amine hydrochloride, mp 246°, $[\alpha]^{24}_{589}$ −4.14° (*c* 1.33 ethanol), was converted to the above (−)-amine which in contrast to racemic material (mp 35°, lit.[33] 40°) did not solidify at room temperature. Spectral properties were the same as for authentic racemic amine and tlc indicated the active amine was homogeneous.

Kinetic Experiments.[34] **A. Titrimetric Rates.** The ampoule technique was used. Ampoules were flushed with dry nitrogen prior to filling. For experiments without added sodium azide, reactions were followed by titration of 5-ml aliquots with aqueous sodium hydroxide to the bromthymol blue endpoint. Observed and calculated infinity titers were within experimental error (<1%). The results are presented in Table I. Reactions with added sodium azide were followed potentiometrically as described earlier.[4]

B. Rates of Racemization. Some of the rate constants (k_{rac}) were determined from the polarimetric (k_α) and titrimetric (k_t) rate constants as described earlier.[8] In other experiments k_{rac} was determined directly from rotations of isolated samples of unsolvolyzed ester.

In a typical experiment 100-, 110-, 130-, and 160-ml portions of 0.04231 *M* (−)-*p*-methylbenzhydryl *p*-nitrobenzoate, $[\alpha]^{24}_{435}$ −10.44° (*c* 1.138),[21] were sealed in heavy-walled ampoules. The ampoules were flushed with nitrogen prior to filling and sealing. After heating at 99.5° for appropriate times (up to 47% solvolysis and about 65% racemization) the unsolvolyzed ester was isolated as follows. The reaction mixture was treated with enough benzene to form two layers. The upper layer was washed with 5% aqueous sodium bicarbonate and evaporated under reduced pressure. The residual mixture of unsolvolyzed ester and *p*-methylbenzhydrol solidified on standing and was separated by column chromatography on silica gel using hexane containing 7% ether as eluent. Control experiments showed that this method of isolation and purification does not alter the optical purity of the unsolvolyzed *p*-methylbenzhydryl *p*-nitrobenzoate. The isolated ester was shown to be pure by tlc and ir spectroscopy.

The following modification was used to isolate and purify the unsolvolyzed ester for solvolysis in the presence of sodium azide. The *p*-methylbenzhydryl azide was removed from the residual yellow oil (neutral fraction obtained as described in the preceding paragraph) by high-vacuum sublimation (2 days, 30°, 3×10^{-6} mm) and the remaining mixture of alcohol and unsolvolyzed ester was separated by column chromatography as described above.

C. Rates of Carboxyl Oxygen Equilibration. Equilibration rate constants (k_{eq}) were determined as described earlier.[2-5] For solvolysis of *p*-methylbenzhydryl *p*-nitrobenzoate ether-^{18}O the unsolvolyzed ester was isolated and purified as described in the preceding section. Control experiments showed that the starting ester was discretely labeled and that isolation and purification does not alter the ^{18}O distribution in the unsolvolyzed ester.

A different method was required for isolating and purifying the more reactive *p*-methoxybenzhydryl *p*-nitrobenzoate without altering the ^{18}O distribution. In this case discretely labeled carbonyl-^{18}O

(25) E. D. Hughes and F. Hiron, *J. Chem. Soc.*, 795 (1960).
(26) H. L. Goering and J. P. Blanchard, *J. Amer. Chem. Soc.*, 76, 5405 (1954).
(27) A. G. Davies, J. Kenyon, B. J. Lyons, and T. A. Rohan, *J. Chem. Soc.*, 3474 (1954).
(28) Infrared and nmr spectra of active compounds were indistinguishable from those of corresponding authentic racemic samples. Active *p*-nitrobenzoate derivatives used in the product studies were shown to be uncontaminated by active alcohol by tlc. The presence of as little as 0.3% alcohol can readily be detected by this technique.
(29) M. P. Balfe, M. A. Doughty, J. Kenyon, and R. Poplett, *J. Chem. Soc.*, 605 (1942).
(30) Oxygen-18 contents are atom per cent excess ^{18}O.
(31) J. Weinstock, *J. Org. Chem.*, 26, 3511 (1961).
(32) A. McKenzie and S. T. Widdows, *J. Chem. Soc.*, 702 (1915).
(33) P. Billon, *Justus Liebigs Ann. Chem.*, 7, 314 (1927).
(34) Concentrations are for 25° and aliquots were measured at 25°. The solvent was prepared from purified acetone and conductivity water.

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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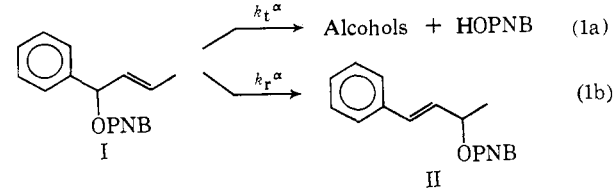
Abstract: Ion-pair return from the ion-pair intermediate(s) common to *trans*-α-phenyl-γ-methylallyl and *trans*-α-methyl-γ-phenylallyl *p*-nitrobenzoates (I and II) gives the γ-phenylallyl isomer (II). In aqueous acetone the α-phenylallyl isomer (I) undergoes simultaneous solvolysis and allylic isomerization 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



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