Retentive Solvolysis. Part 14.[1] The Methanol-perturbed Phenolysis of Optically Active 2,2-Dimethyl-1-(*p*-methoxyphenyl)propyl *p*-Nitrobenzoate. The Mechanism and the Structure of the Second Ion-pair Intermediate†

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The polarimetric and titrimetric rate constants have been measured for the solvolysis of optically active 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) in phenol–methanol (97:3 w/w). The salt effect of added $(Bu^n)_4NClO_4$ indicates that all products are derived from the second ion-pair intermediate (Int-2), not from the first (Int-1), as for the phenolysis in pure phenol. Competitive solvolysis, *i.e.*, methanol-perturbed phenolysis, produced partially inverted ROPh, *o*- and *p*-RC_6H_4OH, and partially retained ROMe, whereas phenolysis in pure phenol afforded partially retained ROPh and *o*- and *p*-RC_6H_4OH. This stereochemical outcome demonstrates that Int-2, the key intermediate of these phenolyses, has an ion-pair structure shielded by a phenol molecule from the rear-side. The absolute configurations and the maximum rotations of all products have been determined.

In recent discussions on multiple, substantially two, ion-pair intermediates in S_N1 solvolysis,[1,2] various types of model have been proposed for the structure of ion-pair intermediates, especially of the second one (Int-2).[2–13] However, a few examples of solvolysis provide experimental evidence for the existence of the Int-2 as the product-forming intermediate; they are the acetolyses of *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl systems[3,14] and the phenolyses of 1-(*p*-methoxyphenyl)ethyl[15] and 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoates,‡[16] and in these solvolyses the salt effect on the polarimetric and titrimetric rate constants (k_p and k_t, respectively) has been examined.

Previously, we discussed the structure of Int-2 for the phenolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) on the basis of retentive ROPh formation alone.[16] However, the stereochemical results in pure phenol were not conclusive enough to determine the structure of Int-2 to be a rear-side shielded ion-pair,[1h,10,19] a four-centre ion-pair,[5,20] or a solvent-separated ion-pair.[2,3]

The additional information obtained from the perturbation of another competing nucleophile by adding azide,[4,21] ethanol,[22] methanol,[10,23] or water[24] is helpful in such cases.

In this paper we describe the stereochemical outcome of the phenolysis of ROPNB perturbed by added methanol, and propose an ion-pair model shielded by a phenol molecule from the rear-side to account for the structure of Int-2 and the stereochemical pathways for the formation of all solvolysis products.

Results and Discussion

The Pattern of Salt Effects on the Solvolysis Rate.—Measurements of k_p and k_t were carried out at variable concentrations (0.00—0.40M) of added tetra-n-butylammonium perchlorate for optically active ROPNB in phenol–methanol (97:3 w/w) at 75 °C. To the solvolysis media, 2,6-di-t-butyl-4-methylpyridine (1.0—1.1 equiv.) was added in order to neutralize the liberated acid which causes the rearrangement of the phenyl ether to the aralkylphenol.[1,25] Subsequently, k_p and k_t were plotted against the salt concentration (Table 1 and Figure 1).

Table 1. The solvolysis rates of 2,2-dimethyl-1-(*p*-methoxyphenyl)-propyl *p*-nitrobenzoate (ROPNB) in phenol–methanol (97:3 w/w) at 75 °C[a]

$Bu^n{}_4NClO_4$/M	k_t/s^{-1} [b]	k_p/s^{-1} [c]
0.000	8.38×10^{-5}	1.54×10^{-4}
0.030	8.76×10^{-5}	
0.060	9.64×10^{-5}	
0.100	1.06×10^{-4}	
0.200	1.18×10^{-4}	1.55×10^{-4}
0.300	1.19×10^{-4}	1.52×10^{-4}
0.400	1.25×10^{-4}	

[a] $[ROPNB]_0$ 0.100—0.110M; in the presence of 2,6-di-t-butyl-4-methylpyridine (0.100—0.122M; see text). [b] Accurate to within ±2%. [c] Accurate to within ±3%.

A special salt effect[2a,3,26] is observed on k_t. In addition k_p exceeds k_t over the whole range of added salt concentration and the k_p/k_t ratio is constant at higher salt concentrations (>0.2M). Such a pattern for the k_p–k_t profile is analogous to that for the phenolysis of ROPNB in pure phenol as solvent,[1] and indicates that the second, not the first, ion-pair intermediate interacts or reacts with the added nucleophile.[1]

Product Distribution.—The product distribution was assayed by g.l.p.c. for the methanol-perturbed phenolysis of ROPNB carried out under conditions identical with those employed in the rate measurements. Solvolysis produced a considerable amount of the methanol-perturbed product, *i.e.*, the aralkyl methyl ether (ROMe), together with the ordinary phenolysis products, *i.e.*, ROPh and *o*- and *p*-RC_6H_4OH (Figure 2). In some other solvolyses of neopentyl systems, products with a rearranged carbon skeleton have been found.[27] Thus, Winstein

† Presented in part at the 7th IUPAC Conference in Physical Organic Chemistry, Auckland, New Zealand, 1984.

‡ Although two other examples were previously reported for the phenolysis of 1-phenylethyl chloride[17] and for the acetolysis of 2-(*p*-methoxyphenyl)propyl tosylate,[18] re-examination of the k_p–k_t profiles for the systems has disclosed that all the products of both systems come from Int-1, not from Int-2.[1]

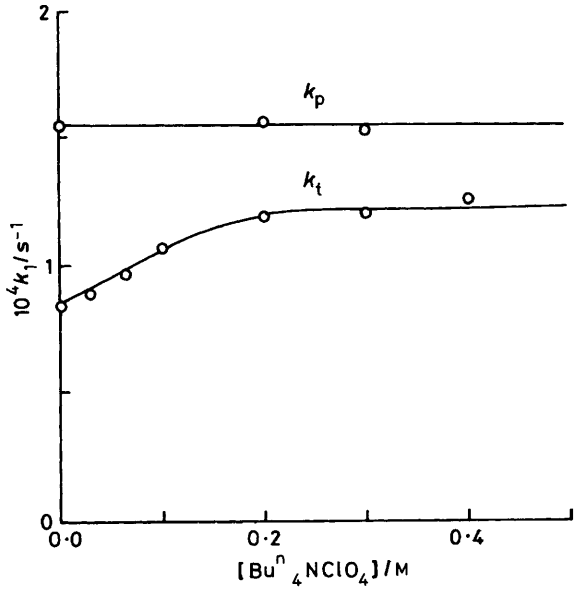


Figure 1. Effect of added $Bu^n_4NClO_4$ on the polarimetric and titrimetric rate constants (k_p and k_t) for the solvolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate in phenol–methanol (97:3 w/w) at 75 °C

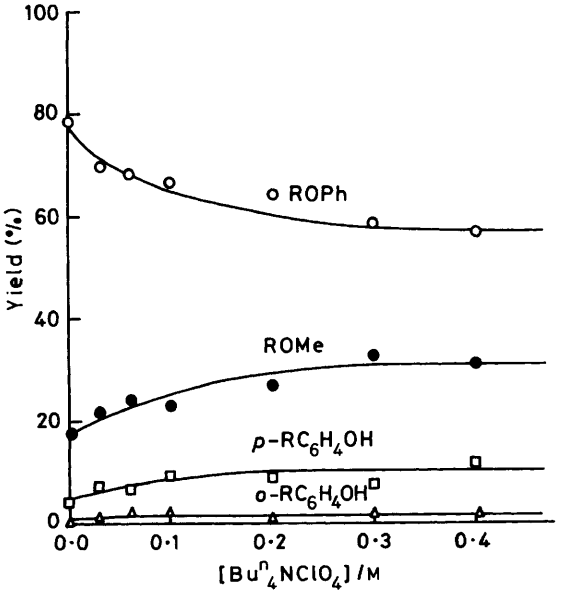


Figure 2. Product distribution in the solvolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate in the presence of tetra-n-butylammonium perchlorate in phenol–methanol (97:3 w/w) at 75 °C

and Morse reported that the acetolyses of 2,2-dimethyl-1-phenylpropyl systems also produced a small amount of rearranged product.[28] However, in the solvolysis of ROPNB in PhOH–MeOH, no rearranged products were detected. This was also true in pure phenol,*[,1] indicating little σ-participation[27] by a methyl group in the neopentyl moeity in these phenolysis media.

With an increase in the concentration of added salt, the product distribution exhibits a pattern similar to the special salt effect on k_t (Figure 1), *i.e.*, the yield of *p*-RC_6H_4OH and ROMe increases and that of ROPh decreases simultaneously, although that of *o*-RC_6H_4OH is almost constant (Figure 2). Analogous patterns except for ROMe were observed for phenolysis in the presence of NaOPh in pure phenol.[1] The constant product distribution at higher salt concentrations also means that almost all products are derived from the added salt, not from the solvent molecule, at such higher salt concentrations.

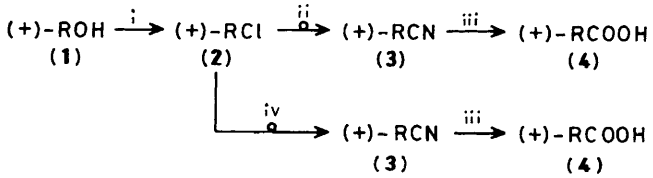
* The rearranged products were obtained by reaction of the carbocation, generated from RCl and $AgSbF_6$ in CH_2Cl_2–SO_2 (1:1 v/v), with phenol or methanol at −63 or −98 °C, respectively. Details on these will be reported in the near future.

Table 2. Maximum specific rotations of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl and 2,2-dimethyl-1-phenylpropyl derivatives (RX and R′X, respectively) with *R*-configuration

RX or R′X	Maximum specific rotation $[\alpha]_{D,max}(°)$[a]	
ROH (**1**)	+44.83	(±0.11)[b]
ROPNB	−161.4	(±0.3)
ROPh	−45.0	(±0.2)
o-RC_6H_4OH	+64.5	(±6.3)
p-RC_6H_4OH	−60.4	(±3.2)
ROMe	+133.9	(±0.5)
RCl (**2**)	⩾ +68.4	(±0.2)[c,d]
RCN (**3**)	−28.8	(±4.6)[c]
RCO_2H (**4**)	−62.2	(±0.2)[e]
$R'CO_2H$	−48.2[e,g]	
R′COMe (**10**)	−275[e,f]	

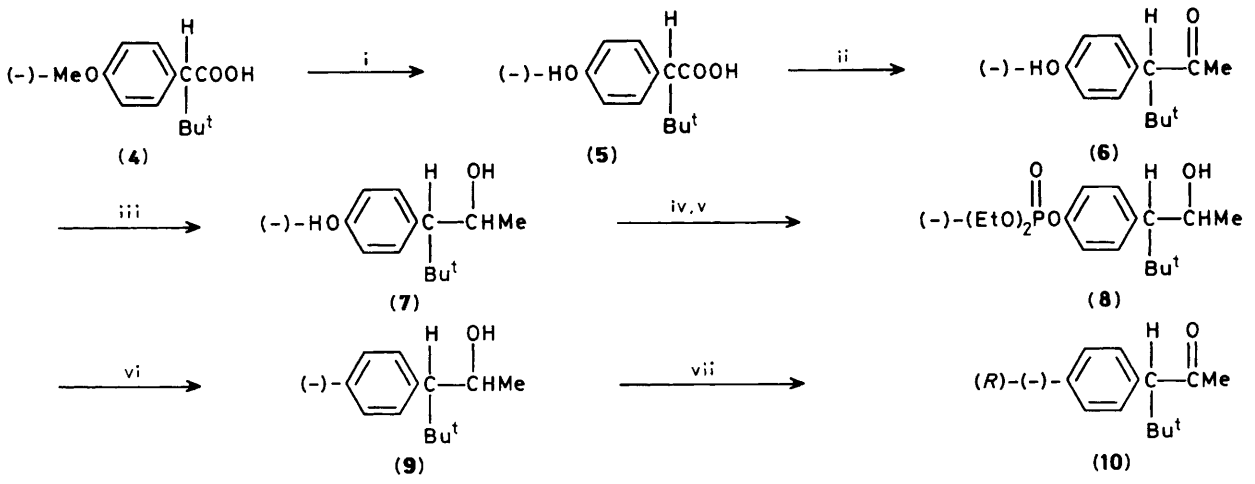
[a] In benzene. [b] Determined by the ^1H n.m.r. spectral method by the use of chiral shift reagent; see the text. [c] In CCl_4. [d] Owing to the possibility of racemization of the chloride under the synthetic reaction conditions, this is the lowest value. [e] In acetone. [f] Cited in ref. 29. [g] In ethanol.

Absolute Configurations and Maximum Rotations for Compounds Relevant to Phenolysis and Methanolysis.—Since the absolute configuration is not known for 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl systems, that of ROH (**1**) has been established by relating the system chemically to 4,4-dimethyl-3-phenylpentan-2-one (**10**) with a known absolute configuration,[29] *via* 3,3-dimethyl-2-(*p*-methoxyphenyl)butanoic acid (RCO_2H) (**4**) (Schemes 1 and 2). Then, RC_6H_4OH (*o* and *p*) and ROMe are chemically related to (**4**) (Scheme 3) and (**1**) (Scheme 4), respectively. The maximum specific rotation of ROPh has been also re-examined by a chemical method (Scheme 5). The absolute configurations and the maximum rotations of compounds relevant to the solvolyses are summarized in Table 2.



Scheme 1. *Reagents:* i, $SOCl_2$; ii, Me_3SiCN–$SnCl_4$; iii, 42% H_2SO_4; iv, aqueous NaCN, phase-transfer catalysis

2,2-*Dimethyl*-1-(p-*methoxyphenyl*)*propanol* (ROH) (**1**).— Alcohol (**1**) was converted into (**10**) by the nine reaction steps shown in Schemes 1 and 2. The chlorination of (**1**) by the use of $SOCl_2$–pyridine[30] proceeded with predominant retention of configuration, *i.e.*, from (+)-(**1**) to (+)-RCl (**2**), which was confirmed by comparison with a retentive chlorination using $SOCl_2$ at low temperature,[5,30] from (+)-(**1**) to (+)-(**2**), and a typical inverted chlorination using PCl_3–pyridine,[28,30] from



Scheme 2. *Reagents:* i, 47% HBr; ii, MeLi; iii, $LiAlH_4$; iv, NaH; v, $(EtO)_2POCl$; vi, Na–NH_3 (liquid); vii, CrO_3–C_5H_5N

(−)-(**1**) to (+)-(**2**). The cyanation of (+)-(**2**) was conducted under two different reaction conditions[31,32] to afford (+)-RCN (**3**) accompanied by a large amount of racemization, which seemed to be a result from the racemization of (**2**) itself under the reaction conditions. Neopentyl tosylate has been reported to undergo normal S_N2 substitution by cyanide and other nucleophiles with configurational inversion.[33] The acidic hydrolysis of (+)-(**3**) yielded (+)-(**4**). The MeO group of (−)-(**4**) was converted into HO by aqueous HBr[34] to produce (−)-(**5**), from which (−)-(**6**) was synthesized and then reduced to (−)-(**7**). The phenolic hydroxy group of (−)-(**7**) was replaced by hydrogen by the method of Kenner and Williams[35] to give (−)-(**9**), which was finally oxidized to (−)-(**10**) having the *R*-configuration by the use of chromium trioxide–pyridine complex.[36] Seven steps from (**3**) to (**10**) involve neither configurational inversion nor racemization because the reaction centres are different from the optical centres. Therefore, the absolute configuration (*R*) and the optical purity for (−)-(**3**) and (−)-(**10**) should be identical.

Thus, the absolute configurations of (**1**)—(**4**) have been established as (*R*)-(+), (*R*)-(+), (*R*)-(−), and (*R*)-(−), respectively.

The maximum rotation of (**1**) was re-examined by the ^1H n.m.r. chiral shift reagent method: instead of the previous tris[trifluoroacetyl-(+)-camphorato]europium(III),[16] tris-[3-heptafluoropropylhydroxymethylene-(+)-camphorato]europium(III) was used as an optically active shift reagent and an enantiomeric chemical shift difference was observed for the methine proton shifted downfield. From the specific rotation and the optical purity which was estimated from the relative peak-area ratios for each enantiomer, the maximum specific rotation of (**1**) has been determined as 44.83 ± 0.11° (acetone) (see Experimental section). The new value is considerably larger than the previous value (27.0°).[16] The discrepancy seems to be owing to more complete separation of enantiomeric proton peaks by the higher resolution (100 MHz) of the new n.m.r. instrument than that (60 MHz) of the previous one[16] and by the difference of the shift reagent.

o- *and* p-[2,2-*Dimethyl*-1-(p-*methoxyphenyl*)*propyl*]*phenols* (o- *and* p-RC_6H_4OH).—Optically active (−)-*o*- and (−)-*p*-RC_6H_4OH, which had been obtained by the phenolyses of optically active ROPNB, were subjected to permanganate oxidation[16,37,38] to be converted into (*S*)-(+)- and (*R*)-(−)-(**4**), respectively (Scheme 3), according to the method originally employed by Hart and Eleuterio[37] (see Experimental section).

The absolute configurations and the maximum rotations of *o*- and *p*-RC_6H_4OH have been determined as (*S*)-(−) 64.5 ± 6.3° (benzene) and (*R*)-(−) 60.4 ± 3.2° (benzene), respectively, from those of (**4**), which have been established above.

$$(-)\text{-}o\text{-}RC_6H_4OH \xrightarrow{KMnO_4} \underset{(4)}{(S)\text{-}(+)\text{-}RCOOH}$$

$$(-)\text{-}p\text{-}RC_6H_4OH \xrightarrow{KMnO_4} \underset{(4)}{(R)\text{-}(-)\text{-}RCOOH}$$

Scheme 3.

2,2-*Dimethyl*-1-(p-*methoxyphenyl*)*propyl Methyl Ether* (ROMe).—(*S*)-(−)-(**1**) was changed to the lithium alcoholate, then the alcoholate was treated with MeI to produce (−)-ROMe (Scheme 4). The absolute configuration of ROMe has been established as (*S*)-(−). Its maximum rotation has been estimated as 133.9 ± 0.5° (benzene), on the basis of the optical purity of (**1**).

$$\underset{(1)}{(S)\text{-}(-)\text{-}ROH} \xrightarrow{Bu^nLi} (S)\text{-}ROLi \xrightarrow{MeI} (S)\text{-}(-)\text{-}ROMe$$

Scheme 4.

2,2-*Dimethyl*-1-(p-*methoxyphenyl*)*propyl Phenyl Ether* (ROPh).—(*R*)-(+)-(**1**) was converted into the potassium alcoholate, which was refluxed with an excess of fluorobenzene to afford (*R*)-(−)-ROPh (Scheme 5). The maximum rotation of ROPh has been calculated as 45.0 ± 0.2° (benzene) on the basis of the optical purity of (**1**). The new value is considerably larger than the previous value (5.84°).[16] It can be attributed to (i) the lower previous value[16] for the maximum rotation of (**1**) and (ii) the accompanied racemization of trifluoroacetate of (**1**) in the previous synthetic reaction under S_N2 conditions.[16]

$$\underset{(1)}{(R)\text{-}(+)\text{-}ROH} \xrightarrow{K} (R)\text{-}ROK \xrightarrow{PhF} (R)\text{-}(-)\text{-}ROPh$$

Scheme 5.

Stereochemical Courses for the Solvolysis.—As for the stereochemical course of the solvolysis of the 1-aryl-2,2-dimethylpropyl system, the acetolyses of 2,2-dimethyl-1-phenylpropyl systems proceed with partial inversion of configuration,[28] whereas 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl chloride is solvolysed in 80% aqueous ethanol with partial retention of configuration.[39] These stereochemical outcomes suggest that, for the ion-pair intermediates (Int-1 or Int-2?)

Table 3. The stereochemical courses for the products of the phenolyses of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) in phenol at 75 °C[a]

Added salt	Concentration (M)	[ROPNB]/M $\{[\alpha]_D(°)\}$[b]	Net stereochemical course, α%[c] $\{[\alpha]_D(°)\}$[b] ROPh	*o*-RC_6H_4OH	*p*-RC_6H_4OH
None[d]	0.000	0.0973 {−46.39}[e]	1.09 ret. (±0.13) {−0.17}	20.4 ret. (±5.1) {+4.56}	3.57 ret. (±0.29) {−0.75}
NaOPh	0.102	0.0956 {−46.39}[e]	3.83 ret. (±0.13) {−0.60}	6.31 ret. (±0.81) {+1.41}	5.02 ret. (±0.76) {−1.05}
NaOPh	0.207	0.0966 {+77.94}[f]	2.68 ret. (±0.12) {+0.69}	6.91 ret. (±0.22) {−2.54}	5.85 ret. (±0.20) {+2.02}
NaOPh	0.383	0.0962 {−46.39}[e]	4.09 ret. (±0.26) {−0.64}	6.92 ret. (±1.47) {+1.55}	6.31 ret. (±0.29) {−1.32}
$Bu^n_4NClO_4$[d]	0.100	0.100 {−81.62}[g]	0.96 ret. (±0.24) {−0.20}	3.84 ret. (±0.77) {+1.14}	3.79 ret. (±0.11) {+1.05}

[a] The maximum specific rotations for the relevant compounds in this Table are shown in Table 2. [b] In benzene. [c] Calculated on the basis of the optical purity of the starting ROH, from which ROPNB was synthesized. [d] In the presence of 2,6-di-t-butyl-4-methylpyridine (0.1M; see the text). [e] Synthesized from (+)-ROH, $\{[\alpha]_D^{26.2}$ +15.55 ± 0.04° (benzene)}. [f] Synthesized from (−)-ROH, $\{[\alpha]_D^{26.5}$ −25.58 ± 0.04° (benzene)}. [g] Synthesized from (+)-ROH, $\{[\alpha]_D^{26.0}$ +20.56 ± 0.04° (benzene)}.

Table 4. The stereochemical courses for the products of the solvolyses of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate (ROPNB) in phenol–methanol (97:3 w/w) at 75 °C[a]

Added salt	Concentration (M)	[ROPNB]/M $\{[\alpha]_D(°)\}$[b]	Net stereochemical course, α%[c] $\{[\alpha]_D(°)\}$[b] ROPh	*o*-RC_6H_4OH	*p*-RC_6H_4OH	ROMe
None[d]	0.000	0.097 {+78.06}[e]	5.68 inv. (±0.16) {−1.46}	0.51 inv. (±0.75) {+0.19}	0.63 inv. (±0.37) {−0.22}	0.33 ret. (±0.09) {−0.25}
Bu_4NClO_4[d]	0.180	0.089 {+78.06}[e]	12.5 inv. (±0.2) {−3.21}	0.84 inv. (±0.43) {+0.31}	0.44 inv. (±0.18) {−0.15}	2.46 ret. (±0.05) {−1.88}

[a] The maximum specific rotations for the relevant compounds in this Table are shown in Table 2. [b] In benzene. [c] Calculated on the basis of the optical purity of the starting (−)-ROH, from which the (+)-ROPNB was synthesized. [d] In the presence of 2,6-di-t-butyl-4-methylpyridine (0.100M; see the text). [e] Synthesized from (−)-ROH, $\{[\alpha]_D^{26.5}$ −25.58 ± 0.04° (benzene)}.

generated from these substrates with a neopentyl group, a nucleophile can attack both from the front and the rear sides depending on the reaction conditions.

The products of solvolyses, under conditions identical with those in kinetic measurements, were isolated by m.p.l.c. and preparative t.l.c. The net stereochemical course was deduced for the formation of each product by comparing the absolute configuration and optical purity of the product with those of the substrate. The results are summarized in Tables 3 and 4.

The phenolysis of ROPNB in pure phenol gave rise to partially retained ROPh and *o*- and *p*-RC_6H_4OH with predominant racemization, respectively, in the presence of NaOPh, $Bu^n_4NClO_4$, or nothing (Table 3). The retention percentage for each product formation exhibits a pattern (Figure 3) similar to the special salt effect on k_t (Figure 1) and to the pattern of the product distribution (Figure 2) as the concentration of NaOPh increases. However, the values of the retention percentage are somewhat higher for RC_6H_4OH than for ROPh, and this suggests the coexistence of an inversive but minor pathway in the ROPh formation.

In marked contrast to the phenolysis in pure phenol, the methanol-perturbed phenolysis in the PhOH–MeOH afforded partially inverted ROPh, slightly inverted *o*- and *p*-RC_6H_4OH, and partially retained ROMe, respectively, with predominant racemization, in both the presence and absence of added $Bu^n_4NClO_4$ (Table 4). The extent of racemization is somewhat smaller for the ROPh formation than for the other products.

In both solvolyses, in pure phenol and in phenol–methanol, the added salts do not exert much influence to change the predominant stereochemical course, *i.e.*, inversion or retention, for each product.

Reaction Pathways and Intermediate Structures.—Behaviour of tetra-n-butylammonium perchlorate. For methanol-perturbed phenolysis in the presence of $Bu^n_4NClO_4$, the k_p–k_t profile (Figure 1) indicates that the second ion-pair intermediate (Int-2), not the first one (Int-1), is perturbed by an added nucleophile. For the nucleophile which reacts directly with Int-2, three possible species are presumed, (a) perchlorate, (b) phenoxide, or (c) methoxide. The latter two might be generated by addition of tetrabutylammonium perchlorate to the solvolysis medium.

The interaction of Bu_4NClO_4 and methanol in benzene gives an anion composed of the perchlorate ion and methanol with increased nucleophilicity of the methanol oxygen.[40] However, phenol neutralizes this anionic species because of the much higher acidity of phenol.[41] In addition, a special salt effect of Bu_4NClO_4 has been observed both in pure phenol[1] and in phenol–methanol (97:3). Thus, the possibility of induced formation of the methoxide ion is ruled out in the phenolysis media.

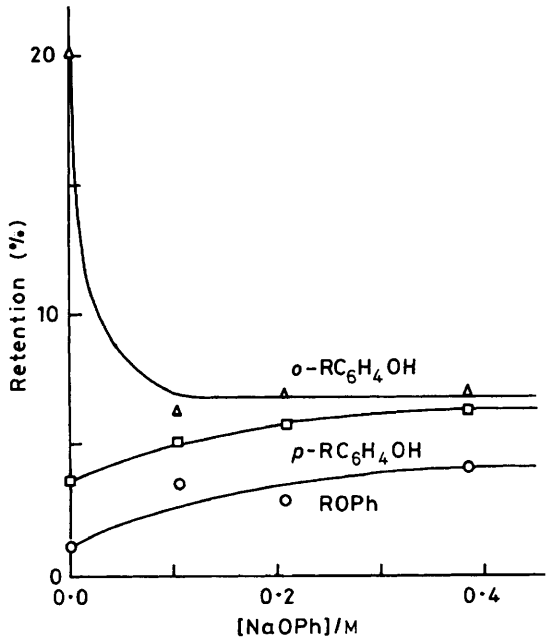
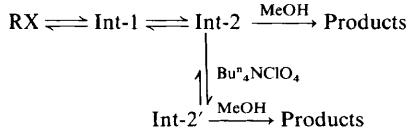


Figure 3. Stereochemical courses in the phenolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate in the presence of sodium phenoxide in phenol at 75 °C

Since reactions of some phenols with various nitrogen bases are promoted in benzene by adding quaternary ammonium salts,[42] tetrabutylammonium perchlorate might induce phenoxide formation from the added hindered nitrogen base. However, the perchlorate shows a special salt effect of a similar pattern regardless of the presence or absence of the added hindered base.[1] In addition, in phenol–methanol, the total percentage yield of phenolic products decreased with an increase in the concentration of added perchlorate (Figure 2). These eliminate contribution of the phenoxide possibly induced from the hindered amine by Bu_4NClO_4.

Accordingly, the added nucleophile which attacks Int-2 should be the perchlorate itself, although perchlorate is generally considered to be very weak as either a nucleophile or a base. It is important to remember that the low basicity is based on its behaviour in more polar solvents. The relative basicities are strongly dependent on the solvent polarity.[43] Thus, examples of nucleophilic[44] or basic[44a] intervention by the perchlorate in the solvent such as benzene,[44a] ether,[44b,c] dichloromethane,[44b] ethyl acetate,[44b] and acetic acid,[44d] are well documented. The perchlorate perturbation on Int-2 should lead to formation of another intermediate (Int-2′) similarly to the pathway originally proposed by Winstein and his co-workers[3,45] (Scheme 6). The intermediate (Int-2′) may be an ion-pair, and it may be rapidly consumed by the solvent molecule to produce the final products.



Scheme 6.

* The N_{BS} value of solvent nucleophilicity was reported as +0.01 for methanol,[46] whereas it has been estimated as −2.51 for phenol by the use of the solvolysis rates of CH_3OTs in 80% aqueous ethanol[46] and in phenol[47] and the *Y* value of phenol (1.77).[48]

At the stage of nucleophilic attack at Int-2′, methanol, which is much more nucleophilic than phenol,* may act as the predominant nucleophile, but affording all the products, *i.e.*, ROMe, ROPh, and *o*- and *p*-RC_6H_4OH.

Structure of the second ion-pair intermediate. In Scheme 6, Int-1 signifies a contact ion-pair intermediate R^+X^- which can racemize itself. There is no evidence for the existence of dissociation of Int-2 into a free (dissociated) carbonium ion (see footnote on p. 1876). As for the structure of the second ion-pair (Int-2), which can give rise to a retained phenyl ether, a variety of models have been proposed (Scheme 7). On the basis of stereochemical outcomes of the solvolyses in pure phenol (Table 3) and in phenol–methanol (Table 4), we can make a choice among these structural models of the intermediate Int-2.

Proposed ion-pair structures:

(a) solvent-separated ion-pair model[2,3] $R^+ \cdots O(S)\text{–}H \cdots X^-$

(b) four-centre ion-pair model[5,20] $R^+ \cdots X^-$ with PhO and H bridging

(c) rear-side shielded ion-pair model[1h,10,19] $HOC_6H_5 \rightarrow R^+ \cdots X^-$

(d) rear-side co-ordinated ion model[4,6] S^iR^+

(e) anion–cation-stabilized ion-pair model[12] $S\,O \cdots R^+X^- \cdots HOS$ (H)

(f) ion-triplet model[9,11] $N^-R^+X^-$

(g) quadruplet ion-pair model[8] $R^+X^-H\text{–}OS$ and $R^+X^-L^+Y^-$

Scheme 7.

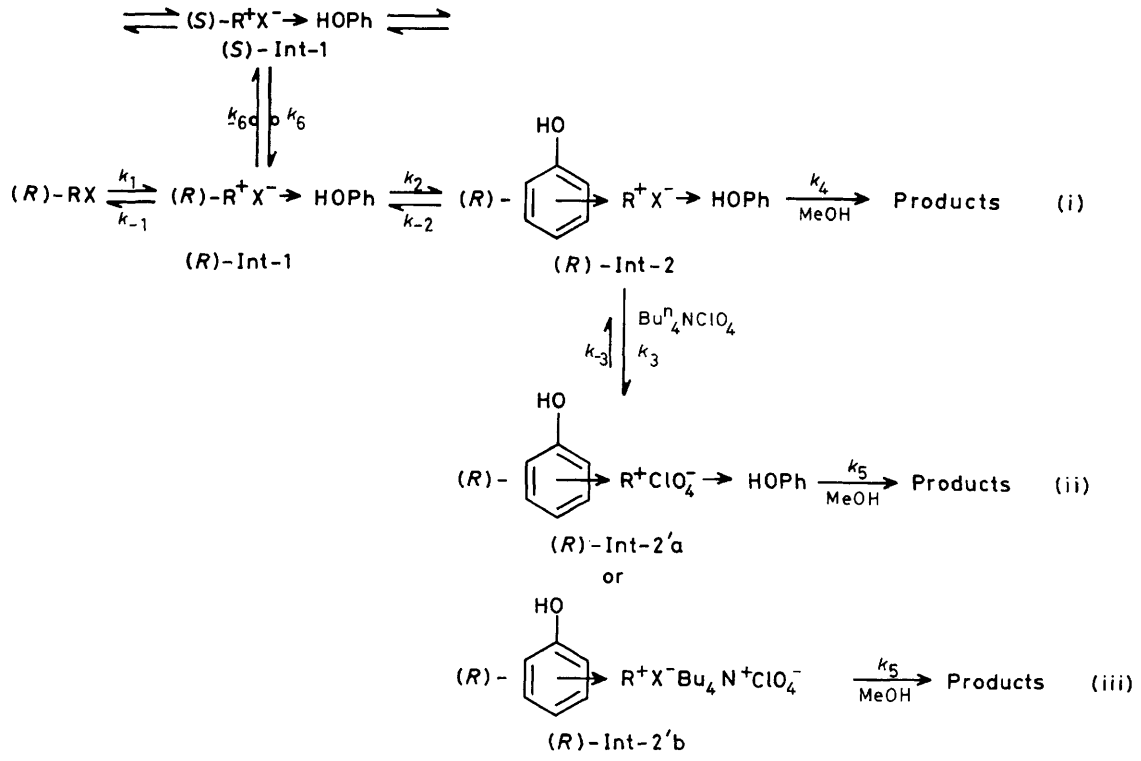
Although the methanol-separated ion-pair model (a)[2,3] seems to account for the formation of retained ROMe and inverted ROPh and RC_6H_4OH (Table 4), methanol can hardly enter a space between the carbocation and the leaving group thus excluding many phenol molecules which have much higher ionizing power.[48]

As one probable model for the structure of Int-2, the four-centre ion-pair model (b)[5,20] can elucidate the formation of retained ROMe (Table 4) *via* a six- or a four-centre association,[23] but it cannot explain the changeover of the stereochemical courses of ROPh and RC_6H_4OH formation from partial retention (in pure phenol; Table 3) to partial inversion (in phenol–methanol solvent; Table 4).

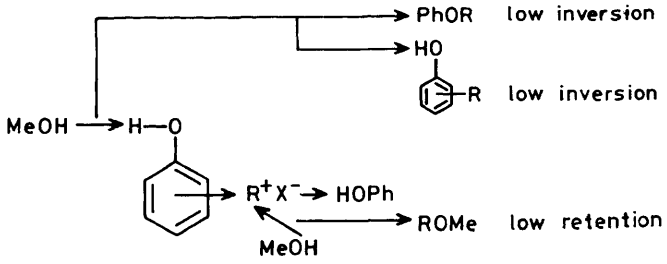
A quadruplet ion-pair model (g)[8] can give no reasonable explanation for the changeover of the stereochemical course.

The rear-side shielded ion-pair model (c)[1h,10] may be associated with another phenol molecule from the rear-side. Such model can be regarded as an analogue of the anion–cation-stablized ion-pair model (e) by Dannenberg and his co-workers,[12] the rear-side co-ordinated ion model (d) by de la Mare and his co-workers[6] and by Weiner and Sneen,[4] and the ion-triplet model (f) by Koskikallio[9] and Dvorko and his co-workers.[11] Nucleophilically solvated ion-pair intermediates have been discussed by Doering and Zeiss,[49] by Schleyer and his co-workers,[21d,50] and by Richard and Jencks.[51] In the more recent solvolysis scheme Winstein's group[52] has also discussed the possibility of ion-pair intermediates solvated at the rear-side, although their traditional formulation[2a] did not express this possibility. Chemical evidence for nucleophilic solvation in the ion-pair intermediate by acetone[4a] and dibutyl ether[53] has also been reported. In addition, stereochemical evidence has been presented for nucleophilic rear-side solvation of hindered phenols[10] and nitriles.[19]

All the predominant stereochemical results of competitive solvolysis (Table 4) and phenolysis (Table 3) can be reasonably



Scheme 8.



Scheme 9.

explained by the use of a rear-side shielded ion-pair intermediate model as follows.

First, in the phenolysis in pure phenol solvent containing NaOPh (Table 3), the phenoxide would react as a predominant nucleophile towards Int-2 at higher NaOPh concentrations. Although its rear-side attack on the hydrogen atom of shielding phenol might accelerate bond formation between R^+ and the shielding phenol molecule, predominant front-side attack would give rise to the phenolysis products with the retained configuration.

Secondly, in phenol–methanol containing $Bu^n_4NClO_4$, there are two possibilities for the behaviour of added $Bu^n_4NClO_4$ towards Int-2. An anionic exchange of Int-2 might occur directly with ClO_4^- to form Int-2'a (an ion-pair), in a way similar to the reaction pathway presented by Winstein and his co-workers[45] and it may be essentially identical with the anionic exchange mechanism of Hughes *et al.*[54] [Scheme 7 and (ii) in Scheme 8]. Alternatively, an ion-pair $Bu^n_4N^+ClO_4^-$ would exchange with a phenol molecule of Int-2 to give Int-2'b in the same way as Pocker's[55] and Topsom's[8] pathways [(ii) in Scheme 8]. Both exchange reactions should proceed retentively since the rear-side is shielded by a phenol molecule.

Corresponding to the two possibilities for behaviour of the perchlorate, two types of model have been depicted for the structure of Int-2', *i.e.* Int-2'a and Int-2'b in Scheme 8.

For either Int-2'a or Int-2'b in the presence of the perchlorate [(ii) or (iii) in Scheme 8] or Int-2 in the absence of the salt [(i) in Scheme 8], methanol, which is more nucleophilic than phenol, may attack both from the front-side and from the rear-side. Front-side attack produces the retained methyl ether probably *via* a four- or six-centre transition state,[23] whereas rear-side attack might occur at the hydrogen atom of the HO group of a shielding phenol molecule to cause induced nucleophilic attacks both on the hydroxylic oxygen atom and on the carbon atom of the phenyl ring towards R^+; thus inverted ROPh and RC_6H_4OH (*o*- and *p*-) are produced (Scheme 9; Table 4).

Obviously, these explanations can apply only to the predominant pathways leading to the final products with optical activity. In PhOH–MeOH, there is more racemization of ROMe than of ROPh (Table 4). This suggests that an inversive pathway for ROMe formation might coexist with the predominant, retentive one. Hence a rear-side 'open', not shielded, ion-pair as a four-centre ion-pair[5,20] or a solvent-separated ion-pair[2,3] might contribute in small amounts to ROMe formation. A similar indication can be obtained from the greater racemization for ROPh than for RC_6H_4OH in pure phenol (Table 3). In any event, the fact that all the products suffer significant racemization (Tables 3 and 4) indicates a relatively long life for Int-1, leading to its self-racemization as shown in Scheme 8.

According to the Scheme 8, the total rate expressions for k_p and k_t [equations (1) and (2)] can be derived by application of the stationary-state treatment. These are compatible with all the kinetic results (Table 1 and Figure 1).

$$k_p = \frac{k_1}{1 + \dfrac{k_{-1}}{\left\{k_2 \Big/ \left(1 + \dfrac{k_{-2}}{k_4 + k_3[Bu_4NClO_4]k_5/(k_5 + k_{-3})}\right)\right\} + 2k_6}} \quad (1)$$

Table 5. Physical constants, spectral data, and elemental compositions for 2,2-dimethyl-1-(*p*-methoxyphenyl)propanol (**1**) and its derivatives

		Spectral data[a]					Elemental composition			
			^{1}N.m.r. (δ)				Found		Required	
Compound	M.p. (°C)	$\nu_{max.}$ cm^{-1}	Ar	–CH–	Bu^t	Others	C (%)	H (%)	C (%)	H (%)
(**1**)	Oil	3 150—3 650 (OH)	6.87	4.11	0.83	2.51 (OH) 3.66 (MeO)				
(**2**)[b]	Oil	1 510, 1 610	6.98	4.60	1.00	3.72 (MeO)	68.0	8.2	67.8	8.05
(**3**)	Oil	2 240 (CN)	6.95	3.39	1.00	3.77 (MeO)				
(**4**)	98.6 –101.5	1 700 (CO_2H)[c] 2 830 (MeO)[c]	7.11[d]	3.35[d]	1.01[d]	3.76 (MeO)[d] 11.91 (OH)[d]	70.1	8.3	70.25	8.2
(**5**)	154.5 –158.3	1 690 (CO_2H)[c] 3 000—3 600 (OH)	7.02[e]	3.35[e]	0.99[e]		68.7	7.7	69.2	7.7
(**6**)	75.1 –76.5	1 690 (C=O)[c] 3 000—3 600[c] (OH)	6.83	3.44	0.94	2.02 (COMe)	75.5	8.9	75.7	8.8
(**7**)	119.4 –121.3	3 200 (OH)[c] 3 400 (OH)[c]	6.98[d]	2.33[d]	0.99[d]	1.09 (Me)[d] 1.80 (OH)[d] 4.45 (–CH–O)[d]	75.4	9.85	75.0	9.7
(**8**)	Oil	1 290 (P=O) 3 500—3 650 (OH)	7.13	2.00 –2.41	0.93	0.86 (Me) 1.29 (Me) 4.11 (CH_2)				
(**9**)	Oil	3 600 (OH)	7.20	2.17	0.94	0.94 (Me) 4.18—4.69 (–CH–O)				
(**10**)	Oil	1 710 (C=O)	7.18	3.45	0.95	1.98 (COMe)				
ROMe	Oil	1 100 (MeOR)[f] 1 250 (MeOAr)[f]	7.00[d]	3.71[d]	0.87[d]	3.17 (MeOR)[d] 3.80 (MeOAr)[d]	74.9	9.8	75.0	9.7

[a] In CCl_4, unless otherwise noted. [b] Found: Cl, 16.4. $C_{12}H_{17}COCl$ requires Cl, 16.7%. [c] KBr disk. [d] In $CDCl_3$. [e] In $CDCl_3$–$(CD_3)_2CO$. [f] In $CHCl_3$.

$$k_t = \frac{k_1}{1 + \frac{k_{-1}}{k_2}\left(1 + \frac{k_{-2}}{k_4 + k_3[Bu_4NClO_4]k_5/(k_5 + k_{-3})}\right)} \quad (2)$$

$k_{-3} = k_{-3}'[X]$ or $k_{-3}'[PhOH]$
(for Int-2′a or Int-2′b, respectively)
$k_4 = k_4' + k_4''[MeOH] + k_4'''[PhOH]$
$k_5 = k_5' + k_5''[MeOH] + k_5'''[PhOH]$

In the context of the role of $Bu^n_4NClO_4$ in the product-forming stage, further examination is in progress of the common ion effect by the use of an isotope-labelled anion common to the leaving group of the substrate.

Experimental

^{13}C and ^{1}H n.m.r. spectra were taken with a JEOL model JNM FX-100 25 MHz Fourier transform and a Hitachi R-24 60 MHz instruments, respectively. For the chiral n.m.r. shift experiments, a JNM FX-100 (100 MHz) spectrometer equipped with a ^{1}H probe was used. I.r. spectra were recorded with a Hitachi model 215 spectrophotometer. Optical rotations were measured with a JASCO model DIP-SL polarimeter. G.l.p.c. was performed with Hitachi model 163 and model 023-6003 instruments. M.p.l.c. was done with a chromatograph system composed of a FMI model RP-SY-2 pump and a Merck silica gel 60 column. M.p.s were measured on a Yamato model MP-21 apparatus. Microanalyses were performed by the Elemental Analytical Centre, Kyoto University. Solvolysis products were identified by comparison of their i.r., ^{13}C and ^{1}H n.m.r. spectra, and chromatographic data with those of authentic samples. The physical properties, i.r., and ^{1}H and ^{13}C n.m.r. spectral data are summarized in Tables 5 and 6.

Materials.—Sodium phenoxide was synthesized in the usual way.[25] Tetra-n-butylammonium perchlorate, an analytical reagent grade, was recrystallized from ethanol and dried *in vacuo*. 2,6-Di-t-butyl-4-methylpyridine was prepared by a known method.[56] 2,2-Dimethyl-1-(*p*-methoxyphenyl)propanol (**1**) was synthesized and resolved in the previously reported manner.[16] Optically active and racemic 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoates (ROPNB) were prepared by the usual method.[16] Cyanotrimethylsilane was prepared by the literature method.[57]

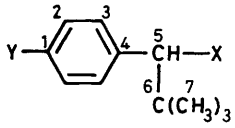
2,2-*Dimethyl*-1-(p-*methoxyphenyl*)*propyl chloride* (**2**). *Method A.* To a solution of thionyl chloride (2 ml) in CCl_4 (10 ml), (+)-(**1**) (0.479 g), $\{[\alpha]_D^{25}$ +15.22° (*c* 5.867 in benzene)}, was added dropwise at −59 to −53 °C and the mixture was stirred at −53 to −22 °C for 70 min to give (+)-(**2**) (0.495 g), $\{[\alpha]_D^{24}$ +8.59 ± 0.04° (*c* 3.39 in CCl_4)}.

Method B. A mixture of (−)-(**1**) (0.404 g), $\{[\alpha]_D^{24}$ −23.1° (*c* 2.02 in CCl_4)}, and pyridine (0.16 ml) was added dropwise to phosphorus trichloride (0.551 g) at −5 °C and the mixture was heated at 50 °C for 1.5 h, producing (+)-(**2**) (0.086 g), $\{[\alpha]_D^{25}$ + 1.29° (*c* 1.56 in CCl_4)}.

Method C. A solution of (+)-(**1**) (5.78 g), $\{[\alpha]_D^{27}$ +19.2° (*c* 4.64 in benzene)}, in pyridine (29 ml) was added dropwise to thionyl chloride (5.8 ml) at −5 °C. After stirring for 40 min, (+)-(**2**) (3.84 g), $\{[\alpha]_D^{26}$ +29.3° (*c* 1.64 in CCl_4)}, was obtained by the usual work-up.

1-*Cyano*-2,2-*dimethyl*-1-(p-*methoxyphenyl*)*propane* (**3**). *Method A.* To a solution of (+)-(**2**) (3.22 g), $\{[\alpha]_D^{23}$ +29.30 ± 0.09° (*c* 1.64 in CCl_4)}, and cyanotrimethylsilane (2.00 g) in CH_2Cl_2 (47 ml), there was slowly added $SnCl_4$ (0.974 g) dropwise at 0 °C. After stirring at 0 °C for 2 h, the mixture was

Table 6. ^{13}C N.m.r. data for 2,2-dimethyl-1-(*p*-methoxyphenyl)propanol (**1**) and its derivatives[a]



Compound	C–1	C–2(d)	C–3(d)	C–4(s)	C–5(d)	C–6(s)	C–7(q)	X	Y
(**1**) X = OH	158.5	112.7	128.5	134.4	81.7	35.5	25.7		55.0
Y = MeO	(s)								(q, MeO)
(**2**) X = Cl	158.9	112.8	129.6	131.7	74.2	37.2	26.8		55.1
Y = MeO	(s)								(q, MeO)
(**3**) X = CN	159.2	113.5	130.2	125.2	48.7	34.9	27.1	120.4	55.1
Y = MeO	(s)							(s, CN)	(q, MeO)
(**4**)[b] X = CO_2H	159.8	114.1	131.9	129.5	60.8	34.6	28.0	175.5	55.8
Y = MeO	(s)							(s, C = O)	(q, MeO)
(**5**)[b] X = CO_2H	157.0	115.5	131.9	128.6	60.8	34.6	28.0	175.4	
Y = OH	(s)							(s, C = O)	
(**6**) X = COMe	155.4	115.1	131.4	127.1	67.3	34.4	27.9	32.4	
Y = OH	(s)							(q, Me)	
OH								211.6	
|								(s, C = O)	
(**7**) X = CHMe	154.4	114.8	131.9	131.3	61.7	34.1	29.5	24.2	
Y = OH	(s)							(q, Me)	
								67.8	
OH								|	
|								(d, –CH–)	
(**8**) X = CHMe	136.5	118.8	132.3	130.3	61.5	34.2	29.3	24.2	16.0
Y = $(EtO)_2PO$	(s)							(q, Me)	(q, Me)
‖								67.2	64.4
O								|	
OH								(d, –CCH–)	(t, CH_2)
|									
(**9**) X = CHMe	130.9	126.0	127.3	139.7	62.3	34.0	29.4	24.1	
Y = H	(d)							(q, Me)	
								67.2	
								|	
								(d, –CH–)	
(**10**) X = COMe	130.2	126.9	127.9	135.9	67.9	34.3	27.9	32.4	
Y = H	(d)							(q, Me)	
								208.7	
								(s, C = O)	
ROMe X = OMe	158.8	112.8	129.3	131.6	91.6	35.6	26.2	57.1	55.0
Y = OMe	(s)							(q, MeO)	(q, MeO)

[a] δ; in $CDCl_3$ unless otherwise noted. [b] In CD_3CN.

worked up and subjected to m.p.l.c. Elution with hexane–ether (9:1) afforded (+)-(**3**) (2.55 g), $\{[\alpha]_D^{23}$ +0.037 ± 0.006° (*c* 16.2 in CCl_4)}.

Method B. A mixture of (+)-(**2**) (0.736 g), $\{[\alpha]_D^{29}$ +18.2° (*c* 1.05 in CCl_4)}, sodium cyanide (0.270 g), benzyltriethylammonium chloride (0.0792 g), and water (0.8 ml) was stirred at ambient temperature for 28 h. The crude product was separated by preparative t.l.c. [hexane–ether (4:1)/SiO_2] to give (+)-(**3**) (0.490 g), $\{[\alpha]_D^{24}$ +0.095 ± 0.034° (*c* 8.91 in CCl_4)}.

3,3-*Dimethyl*-2-(p-*methoxyphenyl*)*butanoic acid* (**4**). *Method A.* A hydrolysis of (+)-(**3**) (0.474 g), $\{[\alpha]_D^{24}$ +0.095° (*c* 8.91 CCl_4)}, was carried out in a 42% aqueous H_2SO_4 solution (5.4 ml) for 4 days under reflux and gave (+)-(**4**) (0.381 g), $\{[\alpha]_D^{27}$ + 0.37 ± 0.26° (*c* 3.82 in acetone)}.

Method B. As for the method for 3,3-dimethyl-2-phenylbutanoic acid,[58] racemic (**2**) (0.543 g) was converted into the Grignard reagent with magnesium (0.104 g) in tetrahydrofuran activated by addition of a few drops of 1,2-dichloroethane under nitrogen. The solution was then stirred for 1 day under CO_2 to produce (**4**) (0.313g) as crystals. Optical resolution of (**4**) by the use of optically active 1-phenylethylamine, $\{[\alpha]_D^{24}$ +37.6° (*c* 2.84 in benzene)}, in 70% ethanol gave optically active (**4**), $\{[\alpha]_D^{27}$ +33.0° (*c* 4.01 in acetone); $[\alpha]_D^{28}$ −8.44° (*c* 4.45 in acetone)}.

3,3-*Dimethyl*-2-(p-*hydroxyphenyl*)*butanoic acid* (**5**). A mixture of (−)-(**4**) (4.442 g), $\{[\alpha]_D^{28}$ −2.71° (*c* 4.00 in acetone)}, and 47% HBr[34] (9.24 ml) was stirred for 20 h under reflux to produce (−)-(**5**) (4.144 g), $\{[\alpha]_D^{30}$ −2.70 ± 0.01° (*c* 8.46 in acetone)}, as slightly brown crystals.

4,4-*Dimethyl*-3-(p-*hydroxyphenyl*)*pentan*-2-*one* (**6**). A mixture of (−)-(**5**) (4.14 g), $\{[\alpha]_D^{29}$ −2.70° (acetone)}, and methyllithium, which had been prepared from methyl iodide (22.8 g) and lithium (2.22 g) in ether (140 ml), was refluxed for 3 h to give (−)-(**6**) (2.835 g), $\{[\alpha]_D^{30}$ −13.26 ± 0.01° (*c* 4.07 in CCl_4)}, as crystals.

4,4-*Dimethyl*-3-(p-*hydroxyphenyl*)*pentan*-2-*ol* (**7**). (−)-(**6**) (0.709 g), $\{[\alpha]_D^{28}$ −11.22° (CCl_4)}, was reduced with lithium aluminium hydride (0.132 g) in dry ether (20 ml) under reflux for 70 min to produce (−)-(**7**) (0.687 g), $\{[\alpha]_D^{28}$ −0.798 ± 0.009° (*c* 11.3 in THF)}, as crystals.

4,4-*Dimethyl*-3-(p-*diethoxyphosphinoxyphenyl*)*pentan*-2-*ol* (**8**). According to the method of Kenner and Williams,[35] (−)-(**7**) (0.627 g), $\{[\alpha]_D^{28}$ −0.798° (THF)}, was treated with 50% NaH (0.481 g) in THF (4.4 ml) at room temperature. After 30 min, diethyl chlorophosphate (1.73 g) was added dropwise to the

mixture and it was stirred at room temperature for 17 h. Separation by m.p.l.c. afforded (−)-(**8**) (1.015 g), $\{[\alpha]_D^{27}$ −0.590 ± 0.011° (*c* 17.8 in CCl_4)}, as a slightly yellow oil.

4,4-*Dimethyl*-3-*phenylpentan*-2-*ol* (**9**). To a stirred solution of (−)-(**8**) (0.924 g), $\{[\alpha]_D^{27}$ −0.590° (CCl_4)}, in liquid NH_3 (*ca.* 20 ml) was added sodium metal (0.190 g) in small portions. The mixture was stirred under reflux for 1 h and separated by m.p.l.c. to give (−)-(**9**) (0.351 g), $\{[\alpha]_D^{27}$ −0.752 ± 0.031° (*c* 6.38 in CCl_4)}, as an oil.

4,4-*Dimethyl*-3-*phenylpentan*-2-*one* (**10**). The alcohol (−)-(**9**) (0.321 g), $\{[\alpha]_D^{27}$ −0.752° (CCl_4)}, was oxidized with the chromium trioxide–pyridine complex,[36] which had been prepared from chromium trioxide (1.08 g) and pyridine (1.69 ml) in CH_2Cl_2 (26 ml). After stirring at room temperature for 40 min, (−)-(**10**) (0.269 g), $\{[\alpha]_D^{28}$ −10.79 ± 0.04° (*c* 4.48 in CCl_4)}, was provided as an oil.

Oxidation of o- *and* p-[2,2-*Dimethyl*-1-(p-*methoxyphenyl*)-*propyl*]*phenol* (o- *and* p-RC_6H_4OH).—Optically active (−)-*o*- and (−)-*p*-RC_6H_4OH were prepared by the phenolyses of optically active ROPNB in the presence of NaOPh and subsequently oxidized to RCO_2H (**4**) by the use of 2% aqueous $KMnO_4$ solution (80 ml) in acetone (20 ml)[16,37,38] at room temperature for 15 h. From (−)-*o*-RC_6H_4OH (0.112 g), $\{[\alpha]_D^{24}$ −2.54 ± 0.08° (*c* 1.13 in benzene)}, and (−)-*p*-RC_6H_4OH (0.901 g), $\{[\alpha]_D^{23}$ −1.32 ± 0.07° (*c* 4.16 in benzene)}, (+)-(**4**) (0.023 g), $\{[\alpha]_D^{24}$ + 2.45 ± 0.11° (*c* 0.628 in acetone)}, and (−)-(**4**) (0.264 g), $\{[\alpha]_D^{23}$ −1.36 ± 0.19° (*c* 1.03 in acetone)}, were obtained, respectively.

2,2-*Dimethyl*-1-(p-*methoxyphenyl*)*propyl Methyl Ether* (ROMe).—The reaction of (−)-ROH (**1**) (2.01 g), $\{[\alpha]_D^{27}$ −25.58 ± 0.04° (*c* 4.856 in benzene)}, with Bu^nLi (1.4M; 37.4 ml)–TMEDA (6.76 g) in 1,2-dimethoxyethane (60 ml) at room temperature for 40 min gave rise to the lithium alkoxide, which was subsequently stirred with an excess of methyl iodide (17.3 g) at room temperature for 15 h to yield (−)-ROMe (1.01 g), $\{[\alpha]_D^{28}$ −64.56 ± 0.22° (*c* 1.8 in benzene)}. Simultaneously, the unchanged (−)-(**1**) (0.734 g), $\{[\alpha]_D^{28}$ −21.61 ± 0.07° (*c* 4.221 in benzene)}, was recovered.

2,2-*Dimethyl*-1-(p-*methoxyphenyl*)*propyl Phenyl Ether* (ROPh).—(+)-(**1**) (0.501 g), $\{[\alpha]_D^{26}$ +20.56 ± 0.04° (*c* 4.121 in benzene)}, was refluxed for 9 h with potassium (0.098 g) in 1,2-dimethoxyethane (15 ml) to produce the potassium alkoxide, which was subsequently refluxed for 15 h with an excess of fluorobenzene (1.00 g) to form (−)-ROPh (0.906 g), $\{[\alpha]_D^{20}$ − 20.60 ± 0.05° (*c* 3.581 in benzene)}.

N.m.r. Measurements for Determination of Optical Purity of ROH (**1**).—The previous ^1H n.m.r. chiral shift reagent method[16] was followed, using tris-[3-(trifluoromethylhydroxymethylene)(D-camphorato)]europium(III) [Eu(fmc)$_3$] as a new shift reagent. The ^1H n.m.r. spectrum was taken for a $CDCl_3$–CCl_4 (1:1 v/v) solution of (−)-(**1**) (0.15M), $\{[\alpha]_D^{21}$ −37.77 ± 0.09° (*c* 1.252 in CCl_4)}, and Eu(fmc)$_3$ (0.18M). The methine proton was observed as two peaks at δ 7.48 and 7.30 (δ 4.11 in the absence of the shift reagent) with a peak area ratio of 1.000:11.70. From this relative peak area ratio and the optical specific rotation obtained for the same sample of ROH, the maximum specific rotation was determined as 44.83 ± 0.11° (CCl_4).

Solvolysis Rate Measurements.—The usual aliquot technique[15] was employed for measurements of k_p and k_t. The rate data against the added salt concentration are shown in Table 1 and Figure 1.

Product Distribution Analysis.—Product distributions for the solvolyses were analysed by g.l.p.c. in a manner similar to those reported earlier.[48]

Isolation of Solvolysis Products.—The previous procedures[15] were followed. As a representative run, isolation of products in the solvolysis of ROPNB in PhOH–MeOH (97:3 w/w) in the presence of $Bu^n_4NClO_4$ (0.18M) at 75.0 ± 0.1 °C is described in the following. (+)-ROPNB (9.717 g), $\{[\alpha]_D^{26.5}$ +78.06° (*c* 1.34 in benzene)}, which had been prepared from (−)-(**1**), $\{[\alpha]_D^{27.1}$ −25.58° (benzene)}, was solvolysed in phenol–methanol (97:3 w/w) in the presence of $Bu^n_4NClO_4$ (0.180M) at 75.0 °C for 23 h. After the usual work-up, the products were separated by m.p.l.c. and preparative t.l.c. (silica gel) to afford (−)-ROPh (1.457 g), $\{[\alpha]_D^{27.3}$ −3.21 ± 0.04° (*c* 9.78 in benzene)}, (+)-*o*-RC_6H_4OH (0.039 g), $\{[\alpha]_D^{22.0}$ + 0.310 ± 0.155° (*c* 2.57 in benzene)}, (−)-*p*-RC_6H_4OH (0.289 g), $\{[\alpha]_D^{27.4}$ −0.150 ± 0.056° (*c* 3.15 in benzene)}, and (−)-ROMe (0.517 g), $\{[\alpha]_D^{32.0}$ −1.88 ± 0.04° (*c* 7.73 in benzene)].

All the stereochemical results are summarized in Table 4 for the solvolyses in the phenol–methanol solvent and in Table 3 for the phenolyses in pure phenol solvent.

Acknowledgements

We thank the Ministry of Education, Science, and Culture for a Grant-in-Aid for Scientific Research.

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Received 31*st December* 1987; *Paper* 7/2277