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Number and Structure of Solvolysis Intermediates. IV.[1] The Phenolysis of 1-(*p*-Tolyl)ethyl *p*-Nitrobenzoate: The Mechanism via a Single Stable Ion-Pair Intermediate with High Selectivity for Nucleophiles

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Optically active 1-(*p*-tolyl)ethyl *p*-nitrobenzoate (ROPNB) has been subjected to solvolysis in phenol where the solvolysis was previously found to proceed via a single stable ion-pair intermediate (Int-1) with high selectivity for nucleophiles, i.e., to exhibit the kinetic features expressed by the "B" pattern for the k_p–k_t profile. On the basis of the absolute configurations and the maximum rotations for the substrate and all of the products which have been chemically established, the stereochemical courses have been disclosed to be partial retention for ROPh formation ("retentive phenolysis") and partial inversion for *o*- and *p*-RC_6H_4OH formation with predominant racemization in the solvolysis. These stereochemical outcomes indicate that the key intermediate (Int-1) which provides all of the products should have the structure of a carbocation ion pair shielded at the rear side by a phenol molecule (*the rear-side shielded ion-pair intermediate*) similarly to the key intermediates which are known for some other phenolysis systems. Consequently, the rear-side shielded ion-pair intermediate plays a key role regarding product formation in all retentive phenolysis systems.

The S_N1 phenolysis which often produces retained products ("retentive solvolysis") without a configuration-holding group[2)] proceeds by various types of reaction mechanisms[3)] similarly to solvolysis in other solvolysis media.[3,4)] In view of the number of the solvolysis intermediate stages,[3)] almost all types of solvolysis mechanisms can be systematically determined, except for that via the dissociated (free) carbocation intermediate[5)] in S_N1 phenolyses and classified into two classes, i.e., one class via multiple (substantially two) ion-pair intermediate stages (A type) and the other via single ion-pair intermediate stage.[3)] The latter can be divided into two families: one via a single intermediate having selectivity (B type) and the other via a single intermediate having no selectivity for nucleophiles (the solvent molecule and an added nucleophile). The latter family is further sorted into two groups via a single intermediate with and without a life that is long enough to racemize by itself (C and D types, respectively).[3)] Such a classification has been practically made possible by the use of the pattern analysis of the k_p–k_t profiles by salt effects, which was partly proposed by Winstein and his co-workers[6)] and established by us,[3)] on the basis of the stability(reactivity)–selectivity relationship[7)] for the stability of solvolysis intermediates with the special salt effect.[6,8,9)] The mechanism of S_N1 solvolysis and the structure of the intermediates should be, in general, discussed after a confirmation of the number of solvolysis intermediate stages via which the solvolysis proceeds, though such discussions have been few, even now.[3)]

The structure of the key intermediates for product formation in the phenolysis was disclosed to be *a rear-side shielded ion pair* both for Int-2 of the 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl system[2)] and for Int-1 of 1-phenylethyl systems[1b,10)] as the representative examples for the A and C types, respectively. However, the structure of the key intermediate has not been completely elucidated for each system in the B type to which several systems have been found to belong, i.e., the phenolyses of 1-(*p*-tolyl)ethyl,[3)] 2,2-dimethyl-1-phenylpropyl,[3)] and 1,5-dimethyl-1-ethylhexyl *p*-nitrobenzoates,[3,11)] 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl trifluoroacetate,[3,10)] 1-methylheptyl tosylate,[3,12)] and 1,5-dimethyl-1-ethylhexyl chloride,[4,12)] the acetolyses of 2-(*p*-methoxyphenyl)propyl and 2-(*p*-methoxyphenyl)-1-methylethyl tosylates,[3,8)] and the trifluoroacetolysis of 1-methylpropyl tosylate.[3,13)] Among these systems, the phenolysis of the 1-(*p*-tolyl)ethyl system was selected as a target for a case study, since the mechanism and the intermediate structure have been clarified for the phenolysis systems which belong to the A and C types, respectively (vide supra);[1b—3,10)] the 1-(*p*-tolyl)ethyl system is the simplest aralkyl one similar to the other systems, for which the mechanisms were thoroughly examined.

In this paper, we wish to report on the reaction mechanism and the structure of the ion-pair intermediate on the basis of the stereochemical courses for the formation of all of the products in the solvolysis of 1-(*p*-tolyl)ethyl *p*-nitrobenzoate (ROPNB) in phenol.

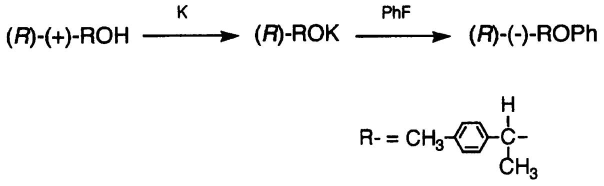
Results and Discussion

Absolute Configurations and Maximum Rotations for Compounds Relevant to the Phenolysis. Since the absolute configurations and maximum rotations have not been known for the substrate and the solvolysis products of the 1-(*p*-tolyl)ethyl system (RX), those have been established by relating them chemically to either 1-(*p*-tolyl)ethanol (ROH)[14)] (vide infra) or 3-(*p*-tolyl)butanoic acid (RCH_2COOH)[15)] with the known absolute configuration and the maximum rotation in the following ways. The absolute configurations and the maximum rotations of compounds relevant to the solvolysis are summarized in Table 1.

1-(*p*-Tolyl)ethanol (ROH). Optically active (+)-ROH was synthesized by a known asymmetric reduction.[14] The absolute configuration had been reported for ROH as (*R*)-(+).[14] The optical purity of (+)-ROH was determined by the ^{1}H NMR method (300 MHz/in CCl_4) using the corresponding diastereomeric 2-methoxy-2-phenyl-3,3,3-trifluoropropanoic acid esters.[16] From the specific rotation ($[\alpha]^{26}_{D}$ +20.50±0.03° (ethanol)) and the optical purity (39.6%), which was estimated from the relative peak-area ratio of the methoxyl protons for the diastereomers, the maximum specific rotation of ROH has been determined to be +51.8±0.1° (ethanol) (see Table 1 and Experimental section).

1-(*p*-Tolyl)ethyl *p*-Nitrobenzoate (ROPNB). Optically active (−)-ROPNB ($[\alpha]^{23}_{D}$ −8.27±0.05° (benzene)) was prepared by the reaction of (*R*)-(+)-ROH ($[\alpha[^{26}_{D}$ +20.50° (ethanol)) with *p*-nitrobenzoyl chloride in pyridine at 0 °C.[3a] The absolute configuration of ROPNB was established to be (*R*)-(−) since the configuration of ROH should be retained under the reaction conditions. The maximum specific rotation of ROPNB was estimated to be −28.5±0.2° (benzene) from the optical purity of the ROH ($[\alpha]^{27}_{D}$ +13.5° (ethanol)) which was directly produced by the $LiAlH_4$-reduction of the ROPNB and the racemization of ROH under the conditions of the reaction and work-up procedures (see Experimental section).

1-(*p*-Tolyl)ethyl Phenyl Ether (ROPh). A chemical method which was known for other systems[2] was employed. After (*R*)-(+)-ROH ($[\alpha]^{26}_{D}$ +20.50° (ethanol)) was changed to the potassium (*R*)-alcoholate, the alcoholate was treated with PhF to produce (*R*)-(−)-ROPh ($[\alpha]^{22}_{D}$ −7.87±0.08° (benzene)) (Scheme 1). The absolute configuration of ROPh was established to be (*R*)-(−), because the reaction center was different from the chiral center. Its maximum specific rotation was calculated as being −28.7±0.3° (benzene), on the basis of the optical purity of ROH ($[\alpha]^{21}_{D}$ +14.19° (ethanol)) which was recovered along with the produced ROPh under the synthetic reaction conditions.



Scheme 1.

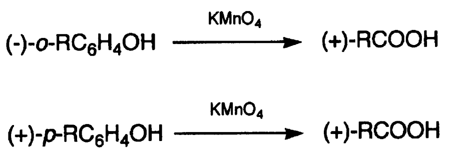
Table 1. Maximum Specific Rotations of 1-(*p*-Tolyl)ethyl Derivatives (RX) with *R*-Configuration

RX	Maximum specific rotation $[\alpha]_{D.max}$(°)[a]	
ROH	+51.8	(±0.1)[b]
ROPNB	−21.5	(±0.1)
ROPh	−28.7	(±0.3)
o-RC_6H_4OH	+84	(±2)
p-RC_6H_4OH	−72	(±18)
RCOOH	−397	(±2)[c]
RCH_2OH	+56.9	(±1.5)
RCH_2Cl	−(≥)25.7	(±1.3)[d]
RCH_2COOH	−65[e]	

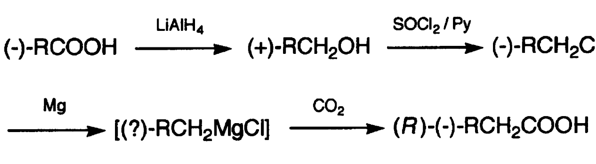
a) In benzene, unless otherwise noted. b) In ethanol. c) In acetone. d) In CCl_4: Owing to the possibility of racemization of the chloride under the synthetic reaction conditions, this is the lowest value as the absolute one. e) For the absolute configuration, Ref. 15a; for the maximum specific rotation, Ref. 15b.

***o*- and *p*-[1-(*p*-Tolyl)ethyl]phenols (*o*- and *p*-RC_6H_4OH)).** Both optically active (−)-*o*- and (+)-*p*-RC_6H_4OH ($[\alpha]^{27}_{D}$ −0.615±0.013° (benzene) and $[\alpha]^{27}_{D}$ +0.252±0.013° (benzene), respectively), which had been obtained in the phenolysis of (*R*)-(−)-ROPNB, were subjected to permanganate oxidation[11,12,17] to be converted into (+)-RCOOH (Scheme 2), according to a method originally employed by Hart and Eleuterio[17] (see Experimental section). Although the reaction mechanism has not been completely clarified, the absolute configuration of *o*- and *p*-RC_6H_4OH must be retained under the reaction conditions.

Since the absolute configuration and the maximum rotation were unknown for RCOOH, they have been determined by relating (−)-RCOOH chemically with (*R*)-(−)-RCH_2COOH, which has the known absolute configuration[15a] and maximum specific rotation ($[\alpha]_D$ 65° (benzene))[15b] (Scheme 3). (−)-RCOOH ($[\alpha]^{24}_{D}$−23.2° (acetone)) was prepared by optical resolution of the racemate which had been separately synthesized. Since the absolute configuration and the optical purity could be recognized to be retained during these chemical conversions, the absolute configuration of RCOOH has been established as being (*R*)-(−), and its maximum specific rotation has been proved to be 397±2° (acetone), on the basis of the optical purity of



Scheme 2.



Scheme 3.

(−)-RCH_2COOH ($[\alpha]_D^{25}$ −3.80° (benzene)) which was obtained as the product and had the known absolute configuration and maximum rotation (vide supra).[15)]

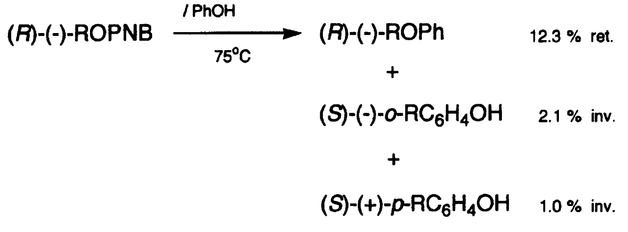
According to the retentive conversion of (−)-*o*- and (+)-*p*-RC_6H_4OH to (*S*)-(+)-RCOOH (vide supra: Scheme 2), the absolute configurations of *o*- and *p*-RC_6H_4OH have been confirmed to be (*R*)-(+) and (*R*)-(−), respectively. The maximum specific rotations have been estimated as being +84(±2)° and −72(±18)° (benzene) for the *o*- and *p*-isomers, respectively, on the basis of the optical purity of the produced RCOOH (Table 1).

The relationship between the absolute configuration and the sign of the optical rotation is same for the *o*- and *p*-aralkylphenols as those reported for (1-phenylethyl)-phenols[18)] and [1-(*p*-methoxyphenyl)-2,2-dimethylpropyl]phenols.[2)] The maximum specific rotations for the aralkylphenols are somewhat larger than those (+27.9° and −10.3°) for the (1-phenylethyl)phenols[18)] and are comparable with those (+64.5° and −60.4°) for [1-(*p*-methoxyphenyl)-2,2-dimethylpropyl]phenols.[2)]

Stereochemical Courses for the Solvolysis of ROPNB in PhOH. Optically active (*R*)-(−)-ROPNB was solvolyzed in phenol in the presence of NaOPh (0.188 M) (1 M=1 mol dm^{-3}) at 75.0±0.1°C for 22 h (15 times $t_{1/2}$) under identical conditions with those in a previous kinetic study.[3a)] The solvolysis products isolated by MPLC (medium-pressure liquid chromatography: silica gel) were ROPh, *o*-RC_6H_4OH, *p*-RC_6H_4OH, and *p*-methylstyrene similarly to those found in the previous work.[3a)] The net stereochemical course was deduced for the formation of each product by comparing the absolute configuration and the optical purity of the product with those of the substrate, which were established as mentioned above. The stereochemical outcomes are summarized in Scheme 4 and Table 2 along with those for the other 1-phenylethyl systems.[10,18)]

The phenolysis of ROPNB produced ROPh with 12.3% retained configuration ("retentive phenolysis") and slightly (2.0% and 1.0%) inverted *o*- and *p*-PC_6H_4OH, with predominant recemization, in the same way as the phenolyses of 1-phenylethyl *p*-nitrobenzoate[10)] and chloride[1b,18)] (Table 2).

The extent (%) of configurational retention for ROPh formation increases in the order Me<MeO[10)] <H[10)] <NO_2[10)] in the phenolyses of the *p*-substituted 1-phenylethyl *p*-nitrobenzoates (Table 2). This order corresponds inversely to that for the stability of the solvolysis intermediate,[3a,10)] except for the system with a *p*-MeO substituent, which was conducted under much milder conditions, i.e., in a phenol–benzene mixture solvent at 25 °C.[10)] The analogous tendency could be observed for the stereochemical courses for aralkylphenols in the phenolyses of the *p*-Me and unsubstituted systems. Although the nucleophilic attack would be more selective as the intermediate becomes more stable, the actual tendency is inverse, as mentioned above. Such an observation indicates that racemization of the products might be mainly governed by the racemization of the solvolysis intermediate, itself, not by a cancellation of the front- and rear-side attack to the intermediate.



Scheme 4.

The solvolysis intermediate itself may be more recemizable as the intermediate becomes more stable and has a longer life because the selectivity for a nucleophilic attack (from the front side or the rear side) may be dependent on the stability of the solvolysis intermediate.

Reaction Pathway and Intermediate Structure. Concerning the mechanism of S_N1 solvolysis and the structure of the solvolysis intermediates, phenol solvent has an advantage of providing more pieces of information than do other solvolysis solvents owing to its ambident characteristics. For the solvolysis mechanism of ROPNB in phenol, the experimental facts had been previously confirmed:

(1) The Key Intermediate Stage: The k_p−k_t pattern of B type[3a)] indicates that the added phenoxide attacks nucleophilically the first ion-pair intermediate (Int-1), not the second one (Int-2), to produce all of the products and to result in neither an ion-pair return nor racemization of the intermediate, itself, at a higher NaOPh concentration than 0.05 M.[3a)]

(2) Nucleophile and Product Distribution: The variation in the product distribution with the NaOPh concentration demonstrates that the nucleophilic attack at Int-1 by a solvent phenol molecule provides only ROPh, whereas that by the added phenoxide brings about *o*- and *p*-RC_6H_4OH, and *p*-methylstyrene together with ROPh.[3a)] The composition of products from NaOPh is shown by the constant one (ROPh : *o*-RC_6H_4OH : *p*-RC_6H_4OH : *p*-$MeC_6H_4CH{=}CH_2$ = 80 : 8 : 7 : 5 (%)) at a higher salt concentration than about 0.05 M.[3a)]

Accordingly, all of the partially retained ROPh and slightly inverted *o*-RC_6H_4OH in the presence of 0.188 M NaOPh are formed by a nucleophilic attack at Int-1 by the added NaOPh.

The stereochemical results in this work have provided useful information about the structure of the key intermediate for the product formation, as follows.

For the retentive ROPh formation in the solvolysis system, solvent-separated ion-pair model (a),[4,6)] four-center ion-pair model (b),[18,19)] and rear-side shielded

Table 2. Stereochemical Courses for the Products of the Solvolyses of 1-(*p*-Substituted Phenyl)ethyl *p*-Nitrobenzoates (ROPNB) in the Presence of NaOPh in Phenol[a)]

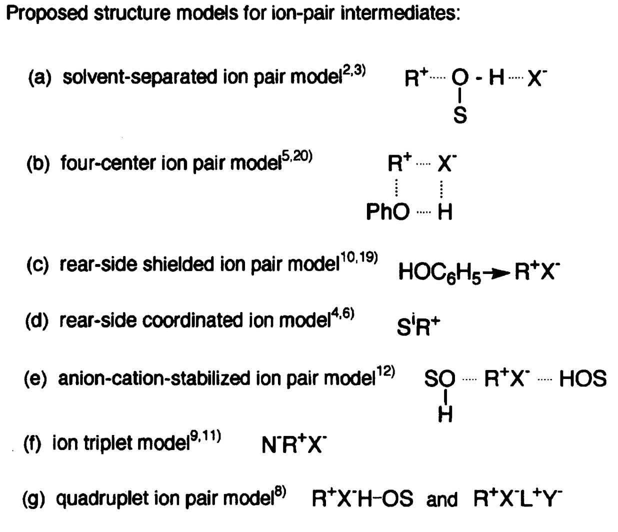
p-Substituent	Solvent	Temp.	Net stereochemical course, %[b)]			k_p–k_t
		°C	ROPh	*o*-RC_6H_4OH	*p*-RC_6H_4OH	pattern[c)]
MeO[d)]	PhOH–benzene (1 : 1 by wt.)	25	15.0 ret.	—	—	A
Me	PhOH	75	12.3 ret.	2.1 inv.	1.0 inv.	B
H[d)]	PhOH	125	34.5 ret.	9.35 inv.	11.6 inv.	C
H[e)]	PhOH–benzene (1 : 1 by wt.)	40	23.7 ret.	38.1 inv.	41.2 inv.	C
NO_2[d)]	PhOH	125	90.0 ret.	—	—	D

a) $[ROPNB]_0$=0.1 M, $[NaOPh]_0$=0.101—0.188 M, unless otherwise noted. b) Calculated from the optical purity of the product on the basis of that of the starting ROH, from which ROPNB was synthesized. c) See the text for each profile. d) Cited from Ref. 10. e) 1-Phenylethyl chloride in the presence of Et_3N (0.41 M); cited from Ref. 12.

ion-pair model (c)[2,20)] could provide reasonable explanations as a key intermediate (Scheme 5). Although they were all proposed for Int-2, not for Int-1, models (b) and (c) are also applicable to Int-1. However, model (a) could be inapplicable to Int-1, because it should be generated only via a contact ion pair as the precursor Int-1.[4,6)]

Although model (b) might also be able to offer an explanation for the formation of the inverted RC_6H_4OH, the inversion % of RC_6H_4OH should be higher than the retention % of ROPh, because the front-side attack should predominantly produce ROPh whereas a rear-side attack also should bring about ROPh as the main product, along with RC_6H_4OH. However, the produced *o*- and *p*-RC_6H_4OH are, in fact, more racemized than ROPh (Table 2), indicating that the rear-side attack would be virtually occupied by the C-alkylation.

These experimental features can be expressed by the following reaction scheme (Scheme 6), which contains a single stage of an ion-pair intermediate.[3a)] In view of the selective C-alkylation in the rear-side attack of phenoxide at Int-1, the Int-1 should have an ion-pair structure shielded by a phenol molecule at the rear side (the model (c)). For model (c), a predominant front-side attack of NaOPh would bring about retained ROPh (the main product; (ii) in Scheme 6)) via a four-center or six-center transition state[21)] and *o*- and *p*-RC_6H_4OH (the minor products; (iii) in Scheme 6)), while its rear-side attack would occur at the hydrogen atom of the HO group of a shielding phenol molecule to cause an induced nucleophilic attack of the *o*- and *p*-carbon atoms of the phenyl ring towards R^+; thus, the inverted aralkylphenols (*o*- and *p*-) are formed ((i) in Scheme 6). Also, a higher extent of racemization for RC_6H_4OH than that for ROPh would correspond to the coexistence of a minor retentive pathway along with the main inversive one in the RC_6H_4OH formation.

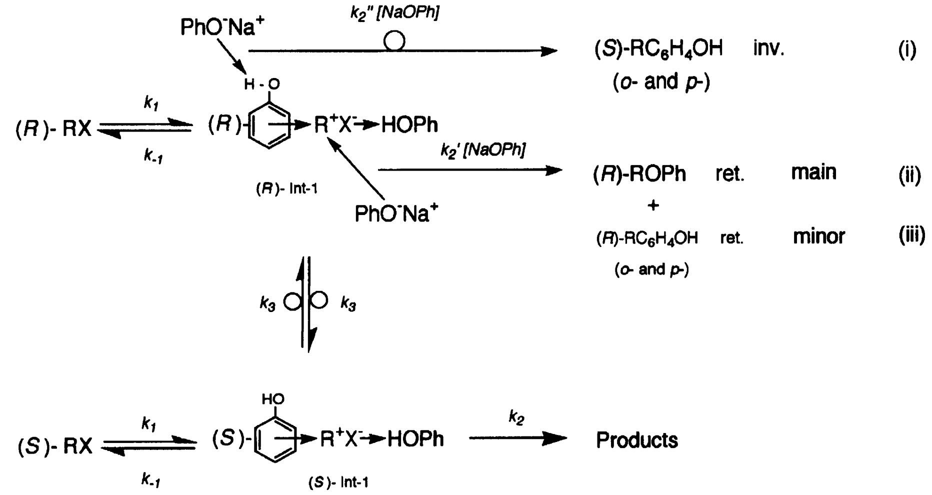


Scheme 5.

The total expressions for k_p and k_t, which can be derived by applying of the stationary-state treatment to Scheme 6,[3a)] have been confirmed to be compatible with all of the features of stereochemical results in this phenolysis system.

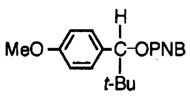
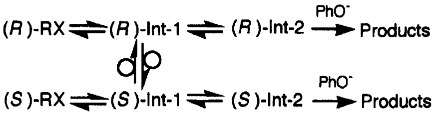
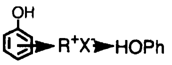
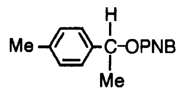
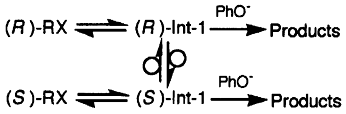
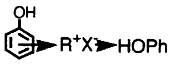
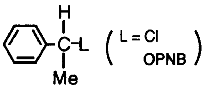
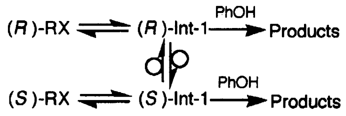
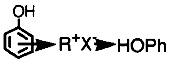
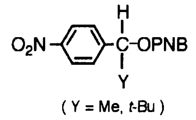
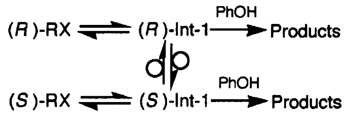
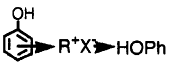
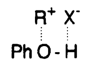
The rear-side shielded ion-pair model can be regarded as being an analogue of the anion-cation stabilized ion-pair model (e),[22)] the rear-side co-ordinated ion model (d),[23)] and the ion-triplet model (f)[24)] for Int-2, not for Int-1. The nucleophilic solvation for Int-2, not for Int-1, was discussed by Doering and Zeiss,[25)] by Schleyer and his co-workers,[26)] and by Richard and Jencks.[27)] Winstein's group also discussed the possibility of ion-pair intermediates solvated at the rear side in their more recent solvolysis scheme,[28)] although their traditional formulation[4a)] did not express this possibility. Chemical evidence was also found for nucleophilic solvation in the ion-pair intermediate by acetone[23a)] and dibutyl ether.[29)] In addition, stereochemical evidence was provided for nucleophilic rear-side solvation of hindered phenols[20a)] and nitriles.[20b,20c)]

Structure of the Key Intermediates in the Retentive S_N1 Phenolysis. The Int-1 in this system, therefore, has an analogous ion-pair structure to those for such a product-forming ion-pair intermediate as Int-1 in the phenolyses of 1-phenylethyl chloride[18)] and *p*-



Scheme 6.

Table 3. Structure of the Key Intermediates for Product Formation in the Retentive S_N1 Phenolyses

Substrate	k_p–k_t pattern[a)]	Reaction pathway[b)]	Structure of intermediates Int-1	Structure of intermediates Int-2	Ref.
	A		R^+X^-►HOPh		c)
	B				This work
	C				d)
	D		 or  ?		e)

a) See the text and Ref. 3. b) In the presence of such a salt as NaOPh. c) Ref. 2 d) Refs. 1b and 10. e) Refs. 10 and 12.

nitrobenzoate,[11)] and also Int-2 in the phenolysis of 2,2-dimethyl-1-(*p*-methoxyphenyl)propyl *p*-nitrobenzoate[2)] (Table 3).

In the three types (A, B, and C types of the k_p–k_t profile) of retentive S_N1 phenolysis systems which have been examined, all of the key intermediates for product formation have the structure of a rear-side shielded ion pair in spite of the difference in the stage of the solvolysis intermediate, i.e., Int-1 or Int-2. In the remaining D type of retentive phenolysis, which proceeds via a single ion-pair intermediate with neither selectivity for a nucleophile nor a long life, as to racemize by itself, the key intermediate for the formation of the highly retained (ca. 90%) ROPh[10)] might also be a rear-side shielded ion pair (c) similarly to those in the other systems mentioned above. However, the possibility of a four-center ion-pair intermediate (b) could not be ruled out, because the intermediate is much more reactive than the other ones.

In conclusion, the features of the stereochemical outcomes for the phenolysis of ROPNB indicate that the key intermediate Int-1 with high selectivity for the nucleophiles should be a rear-side shielded ion-pair intermediate in common with the other types of retentive phenolysis.

Experimental

^{1}H and ^{13}C NMR spectra were taken with Nicolet model

Table 4. Physical Constants and Spectral Data for 2-(p-Tolyl)propanoic Acid (R′COOH) and Its Derivatives

R′X	Mp (°C) (bp (°C/mmHg))	ν (cm^{-1})$^{b)}$	NMR (δ)$^{a)}$ –CH$_3$	$>$CH$_2$	$>$CH–	Ar	–OH
R′COOH	(140—150/5.0)	3600—2600 (OH) 1710 (C=O)	1.43(d, 3H) 2.27(s, 3H)		3.60(q, 1H)	6.98(s, 4H)	10.87(broad, 1H)
R′CH$_2$OH	(130—140/5.0)	3600 3450 (OH)	1.05(d, 3H) 2.10(s, 3H)	3.37(d, 2H)	2.55(q, 1H)	6.81(s, 4H)	3.22(broad, 1H)
R′CH$_2$Cl	(110—112/4.0)		1.45(d, 3H) 2.33(s, 3H)	2.98(d, 2H)	4.07(q, 1H)	6.98(s, 4H)	
R′CH$_2$COOH	84.3—86.0	3600—2400 (OH) 1700 (C=O)	1.23(d, 3H) 2.09(s, 3H)	2.50(d, 2H)	3.17(q, 1H)	7.00(s, 4H)	11.68(broad, 1H)

a) KBr disk. b) In CCl$_4$/90 MHz.

Table 5. ^{13}C NMR Spectral Data for 2-(p-Tolyl)propanoic Acid (R′COOH) and Its Devivatives$^{a)}$

R′X	–CH$_3$	$>$CH$_2$	$>$CH–	Ar		$>$C=O
R′COOH	17.9(q) 20.8(q)		44.9(d)	127.3(d) 129.2(d)	136.7(s) 136.8(s)	181.2(s)
R′CH$_2$OH	17.5(q) 20.7(q)	68.1(t)	41.6(d)	127.0(d) 128.9(d)	135.5(s) 140.7(s)	
R′CH$_2$Cl	21.0(q) 24.5(q)	46.2(t)	58.6(d)	126.0(d) 129.2(d)	134.8(s) 136.2(s)	
R′CH$_2$COOH	20.9(q) 21.9(q)	42.7(t)	35.7(d)	126.5(d) 129.2(d)	135.9(s) 142.4(s)	179.0(s)

a) δ: in CDCl$_3$, 23 MHz.

NP-300 NB, JEOL model GSX-270, and JEOL model JNM FX-90Q Fourier-transform instruments (300, 270, and 90 MHz, respectively, for ^{1}H) with an ^{1}H and ^{13}C dual probe. IR spectra were recorded with a Hitachi model 215 spectrophotometer. Optical rotations were measured with a JASCO model DIP-SL polarimeter. GLPC was performed with Hitachi model 163 instrument. MPLC was carried out with a Chemco chromatograph system comprising an 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. Solvolysis products were identified by a comparison of their IR, ^{13}C and ^{1}H NMR spectra, and chromatographic data with those of authentic samples.[3a)]

The physical properties, as well as IR, ^{1}H and ^{13}C NMR spectral data are summarized in Tables 4 and 5.

Materials. Sodium phenoxide was prepared by a previous method.[3a,10)] The preparation of racemic 1-(p-tolyl)ethanol was accomplished in the usual manner.[3a)] Racemic 1-(p-tolyl)ethyl chloride was obtained by a known chlorination method using SOCl$_2$.[2,11)] Racemic 1-(p-tolyl)ethyl p-nitrobenzoate was synthesized in a previously reported manner.[3a)] All of the other organic reagents were of an analytical grade, dried, and fractionated prior to use.

Optically Active 1-(p-Tolyl)ethanol (ROH). Optically active (R)-(+)-ROH ($[\alpha]_D^{26}$ +20.50±0.03° (c 10.9, ethanol)) was synthesized by a known asymmetric reduction of p-tolyl methyl ketone using LiAlH$_4$–quinine.[3a,14)] A mixture of the (R)-(+)-ROH (111 mg, 0.815 mmol) and (R)-(−)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride (204 mg, 0.808 mmol), which had been prepared from the corresponding (R)-(+)-acid,[16)] was stirred at ambient temperature for 18 h to provide a chiral ester (266 mg, 93.4 % yield). The optical purity of the chiral ester was determined by the ^{1}H NMR (300 MHz/in CCl$_4$): Diastereomeric chemical shift differences were observed for the methoxyl, the methyl, and the methine protons in 0.08, 0.07, and 0.05 ppm, respectively, and the optical purity was estimated to be 39.6% from the relative peak-area ratio (69.8/30.2) of the methoxyl protons for the diastereomers. From the specific rotation and the optical purity, the maximum specific rotation of ROH was determined to be +51.8±0.1° (ethanol) (Table 1).

Optically Active 1-(p-Tolyl)ethyl p-Nitrobenzoate. According to a previous method,[3a)] (R)-(+)-ROH ($[\alpha]_D^{26}$ +20.50±0.03° (ethanol)) was converted into (R)-(−)-ROPNB ($[\alpha]_D^{26}$ −8.27±0.05° (c 3.78, benzene), mp 69.8—70.5°C, 58.6% yield), a part of which was successively reduced to (R)-(+)-ROH ($[\alpha]_D^{27}$ +13.5±0.3° (c 0.333, ethanol), 41.9% yield) by the use of LiAlH$_4$ in ether at ambient temperature for 1.8 h. (R)-(+)-ROH ($[\alpha]_D^{23}$ +16.15±0.26° (c 1.17, ethanol)) was quantitatively recovered by similar workup procedures from an ether solution of (R)-(+)-ROH ($[\alpha]_D^{24}$ +17.90±0.04° (ethanol)) which had been kept under similar reaction conditions in the absence of LiAlH$_4$. These stereochemical results indicate that the reduction of the (R)-(−)-ROPNB should have directly produced (R)-(+)-ROH with $[\alpha]_D^{25}$ +15.0±0.3° (ethanol). On the basis of the optical purity (29.0±0.6%) of the (R)-(+)-ROH, the maximum specific rotation of ROPNB was determined to be −28.5±0.2° (benzene).

1-(*p*-Tolyl)ethyl Phenyl Ether. The previously-reported procedures[2] for the other system were applied. (*R*)-(+)-ROH (1.005 g, 0.00734 mol, $[\alpha]_D^{26}$ +20.50° (ethanol)) was refluxed with potassium (0.275 g, 0.00703 mol) in 1, 2-dimethoxyethane (30 ml) for 3 h to produce potassium (*R*)-alkoxide, which was subsequently refluxed with excess fluorobenzene (5.12 g, 0.0532 mol) for 13.5 h to give rise to a colorless oil, (*R*)-(−)-ROPh (0.587 g, 37.6% yield, $[\alpha]_D^{22}$ −7.87±0.08° (*c* 2.07, benzene)). At the same time, (*R*)-(+)-ROH (0.525 g, 52.2% yield, $[\alpha]_D^{21}$ +14.19±0.27° (*c* 0.74, ethanol)) was obtained by separating with MPLC (SiO_2) from ROPh. On the basis of the optical purity (27.4±0.5%) of the ROH, the maximum specific rotation was calculated for ROPh as −28.7±0.3° (ethanol).

Oxidation of *o*- and *p*-[1-(*p*-Tolyl)ethyl]phenols. Optically active (−)-*o*-RC_6H_4OH ($[\alpha]_D^{27}$ −0.615±0.013° (*c* 7.97, benzene)) and (+)-*p*-RC_6H_4OH ($[\alpha]_D^{27}$ +0.252±0.013° (*c* 7.95, benzene)) were prepared by the phenolyses of (*R*)-(−)-ROPNB in the presence of 0.188 M NaOPh (vide infra). According to the reported method,[11,12,17] the (−)-*o*-RC_6H_4OH (0.467 g, 0.00220 mol) was subsequently oxidized to (+)-RCOOH (0.116 g, 32.1% yield, $[\alpha]_D^{25}$ +2.9±0.1° (*c* 1.93, acetone)) as a colorless oil by stirring with a 2% aqueous $KMnO_4$ solution (140 ml) and acetone (45 ml) at room temperature for 26 h. In a similar manner, (+)-RCOOH (0.0500 g, 15.6% yield, $[\alpha]_D^{25}$ +1.4±0.3° (*c* 0.783, acetone)) was obtained from the (+)-*p*-RC_6H_4OH (0.413 g, 0.00195 mol, $[\alpha]_D^{27}$ +0.252±0.013° (*c* 7.95, benzene)).

2-(*p*-Tolyl)propanoic Acid. A solution of racemic RCl (18.0 g, 0.116 mol) in ether (60 ml) was added dropwise to magnesium (3.11 g, 0.128 mol) in ether (45 ml) under stirring and cooling with ice for 2 h. Then, a large excess amount of powdered dry ice was admitted into the mixture. After the usual work-up, RCOOH (6.94 g, 38.6% yield) was obtained as a yellow oil. The optical resolution of RCOOH (6.94 g, 0.0423 mol) was accomplished by the use of brucine (18.2 g, 0.0423 mol) in dry acetone (39 ml) to afford (−)-RCOOH (2.55 g, 73.4% yield, $[\alpha]_D^{24}$ −23.15±0.08° (*c* 1.30, acetone)) and (+)-RCOOH (3.48 g, 50.0% yield, $[\alpha]_D^{24}$ +18.36±0.02° (*c* 8.58, acetone)) from the diastereomeric precipitate and the supernatant, respectively.

Optically Active 2-(*p*-Tolyl)1-propanol. A solution of (−)-RCOOH (2.41 g, 0.0147 mol, $[\alpha]_D^{24}$ −23.15±0.08° (acetone)) in ether (40 ml) was added dropwise to a mixture of $LiAlH_4$ (0.783 g, 0.0205 mol) and ether (120 ml) for 10 min under stirring, cooling with ice, and a nitrogen atmosphere. After refluxing the mixture for 1 h and performing the usual work-up, (+)-RCH_2OH (2.07 g, 93.8% yield $[\alpha]_D^{26}$ +3.30±0.09° (*c* 1.06, benzene), bp 130—140 °C/5 mmHg) was isolated as a colorless oil (1 mmHg=133.322 Pa).

Optically Active 2-(*p*-Tolyl)propyl Chloride. A CCl_4 (10 ml) solution of (+)-RCH_2OH (1.95 g, 0.0130 mol, $[\alpha]_D^{26}$ +3.30±0.09° (benzene)) was added dropwise to a thionyl chloride (10 ml)–pyridine (5 ml) solution for 17 min under stirring and cooling with ice. After refluxing the solution overnight, the solution was worked up in usual manner to provide a colorless oil, (−)-RCH_2Cl (2.55 g, 73.4% yield, $[\alpha]_D^{25}$ −1.49±0.07° (*c* 1.34, CCl_4), bp 110—112 °C/4 mmHg).

Optically Active 3-(*p*-Tolyl)butanoic Acid. A mixture of (−)-RCH_2Cl (1.52 g, 0.00898 mol, $[\alpha]_D^{25}$ −1.49±0.07° (CCl_4)) and magnesium (0.288 g, 0.0118 mol) in ether (9 ml) containing small pieces of iodine was refluxed under stirring for 1.5 h. After cooling with ice, a large excess amount of powdered dry ice was added to the reaction mixture. By the usual work-up, (−)-RCH_2COOH (0.947 g, 59.2% yield, $[\alpha]_D^{25}$ −3.80±0.03° (*c* 2.87, benzene), mp 84.3—86.0 °C) was isolated as colorless crystals.

Its absolute configuration is known to be (*R*)-(−),[15a] and its optical purity has been estimated to be 5.85±0.05%, on the basis of the maximum rotation ($[\alpha]_D$ 65° (benzene)).[15b]

Isolation of Solvolysis Products. The previous procedures[2,3a] were followed. (*R*)-(−)-ROPNB (7.13 g, 0.0250 mol; $[\alpha]_D^{25}$ −6.70±0.03° (*c* 3.01, benzene), which had been synthesized from (*R*)-(+)-ROH, $[\alpha]_D^{22}$ +17.91±0.01° (benzene)), was solvolyzed in a phenol solution (200 ml) containing 0.188 M NaOPh at 75.0±0.1°C for 22 h (15 times $t_{1/2}$[3a]). After the usual work-up mentioned previously,[3a] the products were separated by MPLC (silica gel) to afford (*R*)-(−)-ROPh (3.47 g, 65.4% yield; $[\alpha]_D^{27}$ −1.23±0.01° (*c* 12.6, benzene); bp 150—152 °C/4 mmHg), and (*S*)-(−)-*o*-RC_6H_4OH (0.551 g, 10.4% yield; $[\alpha]_D^{27}$ −0.615±0.013° (*c* 7.97, benzene); bp 173—175 °C/4 mmHg) and (*S*)-(+)-*p*-RC_6H_4OH (0.365 g, 6.88% yield; $[\alpha]_D^{26}$ +0.252±0.013° (*c* 7.95, benzene), bp 185—195 °C/4 mmHg).

The stereochemical outcomes are summarized in Table 2 along with the previously reported ones for the other 1-arylethyl systems.[10,18]

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