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The Retentive Solvolysis. VII. Structural Effect of the Leaving Group on the Steric Course of the S_N1 Phenolysis of 1-Phenylethyl Systems[*1]

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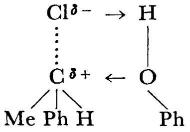
A series of optically active 1-phenylethyl systems with various leaving groups has been phenolyzed in the phenolic solvents. The 1-phenylethyl systems with a negative leaving group (*i.e.*, 1-phenylethyl chloride, bromide, 3,5-dinitrobenzoate, and tosylate) afforded 1-phenylethyl phenyl ether with a net retained configuration. In contrast, the 1-phenylethyl systems with a positively-charged leaving group (*i.e.*, the 1-phenylethyldiazonium ion, the diethyl-(1-phenylethyl)-oxonium ion, and the protonated 2,6-di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one) gave the 1-phenylethyl phenyl ether with a net inverted configuration. These results provide further support for the view that the retentive S_N1 phenolysis proceeds *via* a four-center transition state between the phenol molecule and the ion-pair intermediate. Besides the phenolic ether, the *o*- and *p*-(1-phenylethyl)-phenols with net inverted configurations were obtained from all optically active substrates except 1-phenylethyl 3,5-dinitrobenzoate and the 1-phenylethyldiazonium ion. The 3,5-dinitrobenzoate gave the completely racemic *o*-alkylated phenol, along with the inverted *p*-alkylated phenol, whereas the diazonium ion afforded the *o*-alkylated phenol with a net retained configuration, together with the inverted *p*-alkylated phenol. The stereochemical and mechanistic implications of the *C*-alkylation are also discussed on the basis of the results of the acidic rearrangement of the phenolic ether under the S_N1 phenolysis conditions.

Some years ago investigations in this laboratory showed that the S_N1 phenolysis of optically active 1-phenylethyl chloride occurs with a net retention (20—50%) of configuration to give 1-phenylethyl phenyl ether in the presence of aniline or triethylamine;[1)] in order to account for these results, we offered the explanation that the ether with the retained configuration was probably formed from an ion-pair and a phenol molecule *via* a four-centered transition state as follows:[1b,2)]



If this role of the phenol molecule were predominant in the retentive phenolysis of the chloride, we should observe the retention course in all 1-phenylethyl systems with a negative group such as the chlorine group. In contrast, for the case of the system with a positively-charged leaving group, the S_N1 phenolysis might proceed with a predominant inversion of configuration, as is typically observed in the other S_N1 solvolysis, since the positively-charged leaving group is conceivably unable to form such a specified transition state (*vide supura*) as the chlorine group does.

In order to ascertain these anticipations, we carried out the S_N1 phenolysis of several optically active 1-phenylethyl systems and examined the leaving-group influence. We chose 1-phenylethyl chloride, bromide, 3,5-dinitrobenzoate, and *p*-toluenesulfonate as the substrates with a negative leaving group; we also selected the 1-phenylethyldiazonium ion, the diethyl-(1-phenylethyl)-oxonium ion, and the protonated 2,6-di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexan-1-one as the systems with a positively-charged leaving group.

Results

Phenolysis of the 1-Phenylethyl System with a Negative Leaving Group. The results of the phenolysis of a familiar set of substrates with a negative leaving group are presented in Table 1, along with the respective first-order rate constants.

[*1] Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969; Preprints for the Meeting, III, p. 1645. For the previous papers of this series, see K. Okamoto *et al.*, Ref. 1a (Part I); Ref. 1b (Part II); Ref. 2 (Part III); Ref. 10 (Part IV); Ref. 13 (Part V); This Bulletin, **40**, 1677 (1967) (Part VI).

1) a) K. Okamoto, K. Takeuchi and H. Shingu, *ibid.*, **35**, 525 (1962); b) K. Okamoto, H. Yamada, I. Nitta and H. Shingu, *ibid.*, **39**, 299 (1966).

2) K. Okamoto, M. Hayashi and H. Shingu, *ibid.*, **39**, 408 (1966).

TABLE 1. THE FORMATION OF 1-PHENYLETHYL PHENYL ETHER IN THE PHENOLYSES OF THE 1-PHENYLETHYL SYSTEMS WITH A NEGATIVE LEAVING GROUP

Solvent	RX M rotation	Base M	Temp. °C	Time hr	ROPh Yield %	Net steric course α%[a]	k_1 min^{-1}
PhOH-CH_3CN (1 : 1 by wt.)	RCl 0.143 α_D^{31} +22.1° (1 dm)	Et_3N 0.424	40	97	58.1	11.0 ret. (10.9 ret.[d])	1.42×10^{-3}[d]
PhOH-CH_3CN (1 : 1 by wt.)	RBr 0.142 α_D^{23} −33.2° (1 dm)	Et_3N 0.419	40	19	55.7	16.3 ret.	6.68×10^{-3}
PhOH	RODNB[a] 0.0933 $[\alpha]_D^{26}$ −21.0° (*c* 5.3, benz.)	PhONa 0.0933	150	4.3	40.0	28.2 ret.	3.45×10^{-2}
PhOH-CH_3CN (1 : 1 by wt.)	ROTs[b] 0.0914	$CO(NH_2)_2$ 0.234	20—35	2.2	20.5	>2.0[c] ret.	rapid

a) Calculated taking into account lack of optical purity of the starting substrate; the rotations of the optically pure materials are taken to be 125° (H. M. R. Hoffmann and E. D. Hughes, *J. Chem. Soc.*, **1964**, 1244) for R-(+)-1-phenylethyl chloride, 170° (H. M. R. Hoffmann and E. D. Hughes, *loc. cit.*) for R-(+)-1-phenylethyl bromide, 50.7° ($[\alpha]_D$, see Experimental section) for R-(+)-1-phenylethyl 3,5-dinitrobenzoate (RODNB), and 46.6° (Ref. 1b) for S-(+)-1-phenylethyl phenyl ether.

b) Prepared *in situ* from 1-phenylethyl chloride, α_D^{18} −57.1° (1 dm, neat), and silver *p*-toluenesulfonate (see text).

c) Calculated on the basis of the rotation of 1-phenylethyl chloride used for the preparation of the tosylate.

d) Cited from Ref. 1b.

Optically active 1-phenylethyl chloride and bromide were subjected to phenolysis in the presence of three molar equivalents of triethylamine in a 1 : 1 (by wt.) mixture of phenol and acetonitrile at 40.0°C. As anticipated, satisfactory first-order kinetic behavior was titrimetrically observed for each halide (Fig. 1) ; product analysis by chromatography showed that both halides gave 1-phenylethyl phenyl ether with a net retained configuration (Table 1), along with net inverted *o*- and *p*-(1-phenylethyl)-phenols (Table 3).

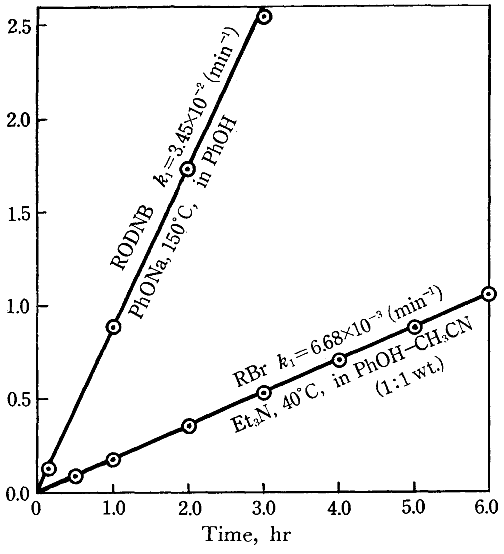


Fig. 1. The first-order plots for the phenolysis of the 1-phenylethyl system.

Optically active 1-phenylethyl 3,5-dinitrobenzoate was phenolized in the presence of one molar equivalent of sodium phenoxide in the phenol solvent. Because of the sluggishness of this phenolysis at the temperature (40°C) employed for the halides, the phenolysis was carried out at an elevated temperature (150°C). The decrease in the quantity of sodium phenoxide, followed titrimetrically, obeyed good first-order kinetics (Fig. 1). When chromatographed, the reaction mixture gave 1-phenylethyl phenyl ether with a 28% retained configuration (Table 1), along with completely racemized *o*-(1-phenylethyl)-phenol and 12% inverted *p*-(1-phenylethyl)-phenol (Table 3).

By modifying the method described by Hoffmann,[3] optically active 1-phenylethyl *p*-toluenesulfonate was prepared *in situ* from optically active S-(−)-1-phenylethyl chloride and silver *p*-toluenesulfonate in the acetonitrile solvent at 20°C. In order to determine the configuration of the tosylate thus formed, the concentrated solution of the tosylate was subjected to the reductive cleavage with sodium-naphthalene in tetrahydrofuran.[4] From the reaction mixture, R-(+)-1-phenylethyl alcohol was isolated by chromatography (see Experimental section). This indicates that the tosyl-

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[3] H. M. Hoffmann, *Chem. Ind.* (London), **1963**, 336.

[4] W. D. Closson, P. Wriede and S. Bank, *J. Amer. Chem. Soc.*, **88**, 1581 (1966).

ate was formed with a net inversion of configuration, since it has been confirmed, for the other tosylates, that, in this reductive fission, no alkyl-oxygen bond, but only a sulfur-oxygen bond, is cleaved.[4]

$$\text{S-(}-\text{)-RCl} \xrightarrow[\text{in CH}_3\text{CN}]{\text{AgOTs}} \text{R-(?)-RO-Ts} \xrightarrow[\text{in THF}]{\text{Na-Naph.}}$$
$$\text{R-(}+\text{)-RO-H}$$

When hydrolyzed, the tosylate gave S-(−)-1-phenylethyl alcohol, along with styrene (see Experimental section). This also indicates the inversive steric course for the formation of the tosylate, since, for the hydrolysis of the 1-phenylethyl system, a net inversion of configuration is typically observed.[5]

$$\text{S-(}-\text{)-RCl} \xrightarrow[\text{in CH}_3\text{CN}]{\substack{\text{AgOTs}\\ \Omega}} \text{R-(?)-ROTs} \xrightarrow{\substack{\text{H}_2\text{O}\\ \Omega}}$$
$$\text{S-(}-\text{)-ROH}$$

To the acetonitrile solution of R-1-phenylethyl *p*-toluenesulfonate so prepared, we added a phenol solvent which contained about two molar equivalents of urea as a weak base.[6] After a rapid phenolysis at 20–35°C, R-(−)-1-phenylethyl phenyl ether, with a retained configuration, was isolated by chromatography, along with S-(−)-*o*-(1-phenylethyl)-phenol and S-(+)-*p*-(1-phenylethyl)-phenol (Tables 1 and 3).

Thus, in the phenolysis of the 1-phenylethyl system with a negative leaving group in the presence of a base, a net retention for the formation of the phenolic ether is the standard result, rather than a net inversion, this being shown in the following scheme:

$$\text{R-RCl} \xrightarrow[\text{in PhOH-CH}_3\text{CN}]{\text{Et}_3\text{N, 40°C}} \text{R-ROPh}$$

$$\text{S-RBr} \xrightarrow[\text{in PhOH-CH}_3\text{CN}_3]{\text{Et}_3\text{N, 40°C}} \text{S-ROPh}$$

$$\text{S-RODNB} \xrightarrow[\text{in PhOH}]{\text{PhONa, 150°C}} \text{S-ROPh}$$

(ODNB = 3,5-dinitrobenzoate)

$$\text{R-ROTs} \xrightarrow[\text{in PhOH-CH}_3\text{CN}]{\text{CO(NH}_2)_2\text{, 20—35°C}} \text{R-ROPh}$$

The S_N1 Phenolysis of the 1-Phenylethyl System with a Positively-charged Leaving Group. The S_N1 phenolysis of this type can be classified as an S_N1 substitution of the missing-charge type.[7] As a representative S_N1 phenolysis of the missing-charge type, the phenolysis of the optically active 1-phenylethyldiazonium ion was conducted in a mixture of phenol and water. The diazonium was prepared *in situ* by adding concentrated hydrochloric acid to the mixture of optically active R-(+)-1-phenylethylamine and sodium nitrite in a 4 : 1 mixture of phenol and water at −8—+2°C. The diazotization and the succeeding nucleophilic reaction proceeded rapidly, with the evolution of nitrogen. From the reaction mixtures, a small amount of 1-phenylethyl phenyl ether with a net inverted configuration was isolated by chromatography (Table 2). In addition, *o*-(1-phenylethyl)-phenol with a net retained configuration and *p*-(1-phenylethyl)-phenol with a net inverted configuration were isolated (Table 3). In view of the poor yield (total 10.0%) of the substitution products and the 55% recovery of the starting amine, under these reaction conditions most of the nitrous acid was probably consumed by the phenol solvent to give the nitrosophenol. Besides the phenolic products, 1-phenylethyl alcohol with a 34.2% retained configuration was also isolated in a 5.30% yield. This retained alcohol seems to be formed from the diazonium hydroxide by a kind of S_Ni mechanism.[8]

As another example of the S_N1 phenolysis of a missing-charge type, we undertook the phenolysis of the diethyl-(1-phenylethyl)-oxonium ion. Optically active diethyl-(1-phenylethyl)-oxonium fluoroborate was prepared *in situ* in 1,2-dichloroethane from ethyl fluoroborate and S-(−)-1-phenylethyl ethyl ether.

$$\text{S-ROEt} + \text{EtBF}_4 \xrightarrow[\text{in ClCH}_2\text{CH}_2\text{Cl}]{} \text{S-R}\overset{+}{\text{O}}\text{Et}_2\text{BF}_4^-$$

The oxonium ion in 1,2-dichloroethane was subjected to phenolysis by addition of a mixture of phenol and 1,2-dichloroethane (*ca.* 10 : 1 by wt.) at 16—25°C. After the usual working-up, *o*- and *p*-(1-phenylethyl)-phenols with net inverted configurations were obtained (Tables 2 and 3); no phenolic ether was found in the products. This is most probably because of the rapid rearrangement of the *inverted* phenyl ether, initially formed, to the *inverted* *o*-(1-phenylethyl)-phenol, with a net retention of configuration, under the acidic reaction conditions. In fact, we confirmed that optically active 1-phenylethyl phenyl ether rapidly rearranges into *o*-(1-phenylethyl)-phenol, with a 35% retention of configuration, in the presence of hydrochloric acid in a 1 : 1 mixture of phenol and 1,2-dichloroethane (see Experimental section).

As has previously been reported,[9] the acidic cleavage of 2,6-di-*t*-butyl-4-methyl-4-(1-phenyl-

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5) For an excellent summary of the solvolysis of 1-phenylethyl systems, see P. B. D. de la Mare, D. M. Hall and E. Mauger, *Rec. Trav. Chim. Pays-Bas*, **87**, 1394 (1968).

6) For the use of urea as a base, see W. S. Trahanovsky, M. P. Doyle and P. D. Bartlett, *J. Org. Chem.*, **32**, 150 (1967).

7) E. D. Hughes and D. J. Wittingham, *J. Chem. Soc.*, **1960**, 806.

8) For the mechanism of the formation of the retained alcohol from the diazohydroxide *via* the diazonium hydroxide, see E. H. White and D. J. Woodcock, " Cleavage of the Carbon-Nitrogen Bond," in " The Chemistry of the Amino Group," ed. by S. Patai, Interscience Publishers, New York (1968), pp. 407—498.

9) K. Okamato, I. Nitta and H. Shingu, This Bulletin, submitted for publication; to be published in the next issue.

TABLE 2. THE FORMATION OF 1-PHENYLETHYL PHENYL ETHER IN THE PHENOLYSES OF THE 1-PHENYLETHYL SYSTEMS WITH A POSITIVELY-CHARGED LEAVING GROUP

Solvent	RX M	Temp. °C	Time hr	ROPh Yield %	Net steric course α% [a]	
PhOH-H_2O[b]	R-$RN_2^+Cl^-$[c] 1.80	−8—+2	2	0.152	8.36 inv.	This work[f]
PhOH-$ClCH_2CH_2Cl$ (1 : 1 by wt.)	S-R$\overset{+}{O}Et_2$[d] 0.144	16—25	0.33	—	— (inv.)	This work
PhOH	S-$RDBC^+$[e] 0.195 $[\alpha]^{19}_D$ +18.6°	75	1.5	12.2	13.5 inv.	Ref. 9

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a) See the footnote a of Table 1.

b) The composition of the mixture was changed from 79 : 21 to 66 : 34 during the reaction (see Experimental section).

c) Prepared from 1-phenylethylamine, α^{17}_D +14.0° (1 dm, neat); the rotation of the optically pure amine was taken to be 38.88° (1 dm, neat) (W. Leithe, *Monatsh. Chem.*, **51**, 385 (1929)).

d) Prepared from 1-phenylethyl ethyl ether, $\alpha^{21.5}_D$ −7.18° (1 dm, neat), and ethyl fluoroborate; the rotation of the optically pure ether was taken to be 94.8° (1 dm. neat) (K. Mislow, *J. Amer. Chem. Soc.*, **73**, 4043 (1951)).

e) The protonated 2,6-di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexan-1-one.

f) 1-Phenylethylamine (55.0%) was recovered; 1-phenylethyl alcohol (5.3% yield) with 34.2% retention of configuration was obtained besides the phenolic products, illustrated in Tables 2 and 3.

TABLE 3. THE FORMATION OF (1-PHENYLETHYL)-PHENOLS IN THE PHENOLYSES OF 1-PHENYLETHYL STSTEMS

Solvent	RX[a] M	Base M	Temp. °C	Time hr	*o*-RPhOH[a] Yield %	*o*-RPhOH[a] Net steric course, α%[d]	*p*-RPhOH[a] Yield %	*p*-RPhOH[a] Net steric course, α%[d]
PhOH-CH_3CN (1 : 1 by wt.)	RCl 0.143	Et_3N 0.424	40	97	17.0	41.2 inv.	12.6	48.5 inv.
PhOH-CH_3CN (1 : 1 by wt.)	RBr 0.142	Et_3N 0.419	40	19	16.2	53.6 inv.	11.1	50.6 inv.
PhOH	RODNB 0.0933	PhONa 0.0933	150	4.3	11.4	0.00 rac.	8.22	11.6 inv.
PhOH-CH_3CN (1 : 1 by wt.)	ROTs 0.0914	$CO(NH_2)_2$ 0.234	20—35	2.2	6.24	>8.67[c] inv.	12.3	>15.7[c] inv.
PhOH-H_2O[a]	$RN_2^+Cl^-$[e] 1.80	—	−8—+2	2	1.19	1.30[c] ret.	3.24	29.2[c] inv.
PhOH-$ClCH_2CH_2Cl$ (1 : 1 by wt.)	R$\overset{+}{O}Et_2BF_4^-$ 0.144	—	16—25	0.33	34.8	9.00[c] inv.	55.2	4.33[c] inv.
PhOH[b]	$RDBC^+$ 0.195	—	75	1.5	18.6	10.2 inv.	48.6	15.9 inv.

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a) See the footnotes in Tables 1 and 2.

b) Cited from Ref. 9.

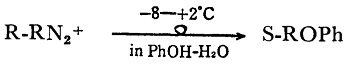
c) Calculated on the basis of the rotations of the starting 1-phenylethyl chloride, amine, and ethyl ether, respectively; see the footnotes in Table 2.

d) The rotations of optically pure samples were taken to be 27.85° (1 dm, neat) for R-(+)-*o*-(1-phenylethyl)-phenol and 10.26° ($[\alpha]_D$) for S-(+)-*p*-(1-phenylethyl)-phenol (see Ref. 13).

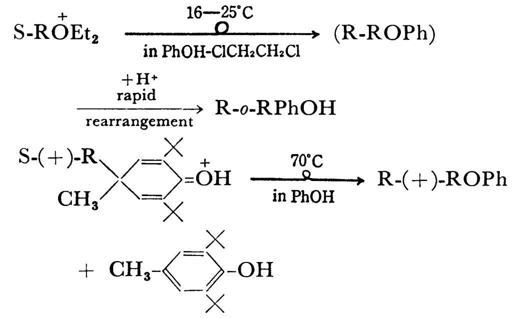
e) See the footnote f in Table 1.

ethyl)-cyclohexadien-1-one into a 1-phenylethyl compound and 2,6-di-*t*-butyl-4-methylphenol is also considered to be a typical S_N1 reaction of the missing-charge type for the protonated dienone; this optically active dienone in the phenol solvent gives 1-phenylethyl phenyl ether with a net inverted configuration, along with *o*- and *p*-(1-phenylethyl)-phenols with net inverted configurations (Tables 2 and 3).

Thus, contrary to the cases of the negative leaving groups, in the phenolysis of the 1-phenylethyl system with a positively-charged leaving group, a net inversion of configuration is standard for the formation of the phenolic ether, as is typically observed in the usual S_N1 reactions. This is illustrated in the following scheme :



$$\text{R-RN}_2^+ \xrightarrow[\text{in PhOH-H}_2\text{O}]{-8\text{—}+2^\circ\text{C}} \text{S-ROPh}$$



Discussion

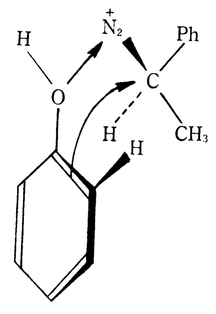
The Steric Course of the Formation of the Phenyl Ether. All the results presented above are consistent with the expected results as regards the steric courses of the formation of the phenolic ether; consequently, they lend support to the previous suggestion that the phenol molecule acts as a component of the four-center transition state which leads to the retentive phenolysis.

However, it has been established that, in the acrylonitrile solvent which does not solvate the negative leaving group but the positively-charged carbonium ion, 1-phenylethyl chloride is hydrolyzed to the unusual retentive course when it is conducted in the 97% aqueous acrylonitrile solvent.10) This most probably indicates that the specific solvation, or coordination,5) of acrylonitrile on the back-side of the cationic component of the ion-pair intermediate can cause the retentive hydrolysis. In other words, a sort of back-side shielding5,11) of the ion-pair intermediate may operate in the acrylonitrile solvent. Considering this factor, therefore, we can not exclude the possibility that the phenol molecule also acts as a back-side shielder just as the acrylonitrile molecule does, although its role may be minor in comparison with the concomitant front-side four-center attack of the phenol molecule.

The Steric Course of the Formation of the Alkylated Phenol. As illustrated in Table 3, in the phenol-acetonitrile solvent the formation of *o*- and *p*-(1-phenylethyl)-phenols proceeds with a predominant inversion of configuration; in the other phenolic solvents, inverted 1-phenylethylphenols are also obtained, irrespective of the charge-type of the leaving group (Table 3). These results can be explained as a consequence of the back-side attack of the phenoxide ion (or the phenol molecule) on the ion-pair intermediate.

As an exception to the general trend, 1-phenylethyl 3,5-dinitrobenzoate afforded a racemic *o*-(1-phenylethyl)-phenol in the phenolic solvent. Since, in view of the facile acidic rearrangement with retention of configuration in the phenol-acetonitrile solvent at 40°C (see Experimental section), the retentive rearrangement of 1-phenylethyl phenyl ether to *o*-(1-phenylethyl)-phenol would proceed rather rapidly, even in the absence of a strong acid, at such an elevated temperature as 150°C, the formation of the racemic *o*-(1-phenylethyl)-phenol may be explained as the result of the fortuitous compensation of retention and inversion, caused by the concurrence of the retentive rearrangement and the inversive direct alkylations.

As another exceptional case of especial interest, the 1-phenylethyldiazonium ion gave a *retained o*-(1-phenylethyl)-phenol in the aqueous phenol solvent. Under similar acidic conditions, the rearrangement of 1-phenylethyl phenyl ether to *o*-(1-phenylethyl)-phenol was found to be comparatively slow (see Experimental section); moreover, any rearrangement should give an *inverted o*-(1-phenylethyl)-phenol, since, in the case of the diazonium ion, the *inverted* phenyl ether is formed and its rearrangement proceeds with a retention of configuration (*vide supra*) (Table 2). Therefore, the formation of the *o*-(1-phenylethyl)-phenol is probably caused by the "direct" and *retentive C*-alkylation of the phenol molecule; this is illustrated in the following scheme:



Hart and his collaborators12) found that *o*-(1-phenylethyl)-phenol with a retained configuration is formed from 1-phenylethyl chloride in the phenol solvent in the absence of a base; they suggested that this is a direct and retentive alkylation with a four-center transition state. However, this result, at least partly, may stem from the rearrangement of the initially-formed phenyl ether with a retained configuration:

$$\text{R-RCl} + \text{PhOH} \xrightarrow[\text{in PhOH}]{} \text{(R-ROPh)} \xrightarrow[\text{rapid}]{\text{H}^+} \text{R-}o\text{-RPhOH}$$

$$\text{R-RCl} + \text{PhOH} \xrightarrow{\text{in the absence of a base}} \text{R-}o\text{-RPhOH (Hart } et\ al.^{12)}\text{)}$$

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10) K. Okamoto, K. Komatsu and H. Shingu, *ibid.*, **39**, 2785 (1966).

11) a) W. von E. Doering and H. H. Zeiss, *J. Amer. Chem. Soc.*, **75**, 4733 (1953); b) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 6233 (1957); c) A. Streitwieser, Jr., and S. Andreades, *ibid.*, **80**, 6553 (1958); d) H. Weiner and R. A. Sneen, *ibid.*, **87**, 287, 292 (1965); e) N. Kornblum and D. E. Hardies, *ibid.*, **88**, 1707 (1966).

12) H. Hart, W. L. Spliethoff and H. S. Eleuterio, *ibid.*, **76**, 4547 (1954).

In fact, we confirmed that when the phenolysis of 1-phenylethyl chloride was conducted in the absence of the amine, no phenolic ether was obtained, while the retained *o*-(1-phenylethyl)-phenol, along with the inverted *p*-(1-phenylethyl)-phenol, was obtained in a 1 : 1 mixture of phenol and acetonitrile, and that under the same reaction conditions the phenolic ether undergoes a rapid rearrangement to give *o*-(1-phenylethyl)-phenol with a 74% retention of the configuration (see Experimental section).

Experimental

Materials. The R-(+)-1-phenylethyl chloride was prepared by the reaction of R-(+)-1-phenylethyl alcohol with thionyl chloride in a manner previously described.[13] The S-(−)-1-phenylethyl bromide was prepared by the reaction of R-(+)-1-phenylethyl alcohol with phosphorous tribromide after the method described by Hoffmann and Hughes.[14] The S-(−)-1-phenylethyl 3,5-dinitrobenzoate ($[\alpha]_{\mathrm{D}}^{24}$ −23.7° (*c* 5.4, benzene), mp 101.5—103.4°C (corr.)) was synthesized by the reaction of S-(−)-1-phenylethyl alcohol, $\alpha_{\mathrm{D}}^{22}+20.64°$ (1 dm, neat), with 3,5-dinitrobenzoyl chloride according to the method of Buckles and Maurer.[15] On the basis of this result, the value for the maximum rotation of the 3,5-dinitrobenzoate was calculated to be 50.7° ($[\alpha]_{\mathrm{D}}$), using 44.2°[16] as the value for the maximum rotation of 1-phenylethyl alcohol. 1-Phenylethylamine was resolved according to the method of Theilacker and Winkler.[17] S-(−)-1-Phenylethyl ethyl ether, $\alpha_{\mathrm{D}}^{21.5}-7.18°$ (1 dm, neat), was prepared by the reaction of R-(+)-1-phenylethyl chloride, $\alpha_{\mathrm{D}}^{16}+22.3°$ (1 dm, neat), with potassium carbonate in ethanol after the method described by Kenyon and Phillips.[18] The silver *p*-toluenesulfonate was prepared from silver oxide and *p*-toluenesulfonic acid. All the other reagents employed were of an analytical reagent grade and were purified by fractional distillation.

The Isolation of the Reaction Products (General Procedure). A flask containing a reaction mixture was placed in a constant-temperature bath for at least ten half-lives. The reaction mixture was cooled at 0°C; then, after the addition of water (100 cc), the mixture was extracted with ether (4×100 cc). The combined extracts were washed successively with 10% aqueous sodium hydroxide (4×100 cc) and 10% aqueous sodium chloride (several 100-cc portions) until the washings became neutral to pH indicator paper. The ethereal solution, dried with anhydrous magnesium sulfate, was concentrated; the residual oil was chromatographed using an elution column packed with silica gel, 50-cc portions being taken out. The combined alkaline extracts were acidified with hydrochloric acid, and the resulting oil was extracted with ether; the dried ether extracts were concentrated and the residual oil was distilled *in vacuo* in order to recover some phenol. This residual oil was added to the sample (*vide supra*) for the chromatography.

The Phenolysis of Optically Active 1-Phenylethyl Chloride in the Phenol-Acetonitrile (1: 1 by Wt.) Solvent at 40°C. A mixture of phenol (42.8 g), acetonitrile (42.8 g), and triethylamine (6.09 cc; 0.424 M, as determined by titration) was prepared. To a 77.9-cc portion of the mixture, we added optically active 1-phenylethyl chloride (1.50 cc, 0.0113 mol; bp 56.0—58.0°C/4.0 mmHg; $\alpha_{\mathrm{D}}^{31.2}$ $+22.09\pm0.03°$, 1 dm, neat). The reaction mixture so prepared was kept at 40.0±0.1°C for 97 hr. After the working-up described above, an oily material (2.12 g) was chromatographed over silica gel (80 g; Nakarai, No. 11-A, 100—200 mesh). The column was eluted successively with *n*-hexane-benzene (1: 1 by vol.), benzene, benzene-ether (97: 3 by vol.), ether, and ethanol, 50-cc portions being taken out. Fractions 4—9, obtained using *n*-hexane - benzene (1: 1 by vol.), gave 1-phenylethyl phenyl ether (1.284 g; 58.1% yield; the infrared spectrum was the same as that of an authentic sample; $\alpha_{\mathrm{D}}^{27.5}-0.455\pm0.015°$, 0.5 dm, neat). Fractions 15—21, obtained using benzene, gave *o*-(1-phenylethyl)-phenol (0.376 g; bp 140—145°C/4.0 mmHg; 17.0% yield; the infrared spectrum was the same as that of an authentic sample: $\alpha_{\mathrm{D}}^{28.4}-1.015\pm0.015°$, 0.5 dm, neat). Fractions 26—31, obtained using benzene-ether (97: 3 by vol.), gave *p*-(1-phenylethyl)-phenol (0.278 g; bp 150—156°C/4.0 mmHg; 12.6% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_{\mathrm{D}}^{28.5}+0.12\pm0.02°$ (*c* 27.3, benzene)).

The Phenolysis of Optically Active 1-Phenylethyl Bromide in the Phenol-Acetonitrile (1: 1 by Wt.) Solvent at 40°C. A mixture of phenol (42.8 g), acetonitrile (42.8 g), and triethylamine (5.85-cc, 0.419 M) was prepared. To a 90.0-cc portion of the mixture, we added optically active 1-phenylethyl bromide (2.00 cc, 0.0145 mol; bp 48.0—53.8°C/0.7 mmHg; $\alpha_{\mathrm{D}}^{23.2}-33.15\pm0.04°$, 0.5 dm, neat). The reaction mixture so prepared was maintained at 40.0±0.1°C for 19 hr. After the working-up described above, an oily material (2.550 g) was chromatographed over silica gel (80 g). Fractions 7—15, obtained using *n*-hexane - benzene (1: 1 by vol.), gave 1-phenylethyl phenyl ether (1.448 g; 55.7% yield; the infrared spectrum was the same as that of an authentic sample; $\alpha_{\mathrm{D}}^{22.6}-1.475\pm0.045°$, 0.5 dm, neat). Fractions 19—29, obtained using benzene, gave *o*-(1-phenylethyl) phenol (0.420 g; bp 125—130°C/3.0 mmHg; 16.2% yield; the infrared spectrum was the same as that of an authentic sample; $\alpha_{\mathrm{D}}^{25.6}+2.90\pm0.05°$, 0.5 dm, neat). Fractions 35—45, obtained using benzene-ether (97: 3 by vol.), gave *p*-(1-phenylethyl)-phenol (0.288 g; bp 140—150°C/4.0 mmHg; 11.1% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_{\mathrm{D}}^{22.4}$ $-0.70\pm0.04°$ (*c* 69.4, benzene)).

The Phenolysis of Optically Active 1-Phenylethyl 3,5-Dinitrobenzoate in the Phenol Solvent at 150°C. To a mixture of phenol (40 cc) and sodium phenoxide (0.4490 g, 0.00386 mol; 0.0933 M), we added optically active 1-phenylethyl 3,5-dinitrobenzoate (1.0952 g, 0.00386 mol; mp 98.6—100.5°C (corr.); $[\alpha]_{\mathrm{D}}^{25.9}-21.0\pm0.28°$ (*c* 5.32, benzene)). The reaction

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[15] R. E. Buckles and J. E. Maurer, *J. Org. Chem.*, **18**, 1588 (1953).

[16] D. J. Cram, K. R. Kopecky, F. Hauck and A. Langemann, *J. Amer. Chem. Soc.*, **81**, 5754 (1959).

[17] W. Theilacker and H. G. Winkler, *Chem. Ber.*, **37**, 690 (1954).

[18] J. Kenyon and H. Phillips, *J. Chem. Soc.*, **1930**, 1676.

mixture was kept at 150.0±0.1°C for 4.3 hr. After the working-up described above, an oily material (0.5067 g) was chromatographed over silica gel (40 g). Fractions 2—4, obtained using *n*-hexane - benzene (1: 1 by vol.), gave 1-phenylethyl phenyl ehter (0.305 g; bp 140—141°C/4.0 mmHg; 40.0% yield; the infrared spectrum was the same as that of an authentic sample; $\alpha_D^{26.7} -3.045 \pm 0.025°$, 0.5 dm, heat). Fractions 8—11, obtained using benzene, gave *o*-(1-phenylethyl)-phenol (0.0872 g; bp 148—149°C/4.0 mmHg; 11.4% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{26.7}$ 0.00+0.06° (*c* 23.6, benzene)). Fractions 16—19, obtained using benzene-ether (97: 3 by vol.), gave *p*-(1-phenylethyl)-phenol (0.0627 g; bp 150—155°C/4.0 mmHg; 8.22% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{27.4} +0.554 \pm 0.262°$ (*c* 34.3, benzene)).

The Phenolysis of Optically Active 1-Phenylethyl *p*-Toluenesulfonate in the Phenol-Acetonitrile (1: 1 by Wt.) Solvent at from 20°C to 35°C. A solution (75 cc) of silver *p*-toluenesulfonate (4.221 g, 0.01508 mol in acetonitrile was prepared and kept at 20.0±0.1°C). When optically active 1-phenylethyl chloride (2.00 cc, 0.0148 mol; bp 45.0—46.1°C/1.0 mmHg; $\alpha_D^{18.2} -57.105 \pm 0.035°$, 1 dm, neat) was then added to the solution, the precipitates of silver chloride appeared immediately. To the mixture, there was added a solution (85 cc) of urea (2.140 g, 0.0356 mol) in a mixture of phenol and acetonitrile (5.5: 1.0 by wt.). The reaction mixture so prepared was maintained at from 20.0°C to 35.0°C for 2.17 hr. The mixture was then cooled at 0°C and poured onto a mixture of ether and water (1: 1 by vol.; 200 cc). The precipitates of silver chloride were separated by filtration. After the working-up described above, an oily material (1.7820 g) was chromatographed over silica gel (50 g). Fractions 7—10, obtained using *n*-hexane - benzene (1: 1 by vol.), gave 1-phenylethyl phenyl ether (0.6008 g; 20.5% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{19.6} -0.43 \pm 0.20°$ (*c* 42.1, benzene)). Fractions 14—17, obtained using benzene, gave *o*-(1-phenylethyl)-phenol (0.1831 g; bp 135—140°C/3.0 mmHg; 6.24% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{20.4} -1.0; \pm 0.85°$ (*c* 38.2, benzene)). Fractions 19—27, obtained using benzene and benzene-ether (97: 3 by vol.), gave *p*-(1-phenylethyl)-phenol (0.3604 g; bp 145—160°C/5.0 mmHg; 12.3% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{24.1} +0.733 \pm 0.221°$ (*c* 58.7, benzene)).

The Reductive Cleavage of Optically Active 1-Phenylethyl *p*-Toluenesulfonate with Sodium-Naphthalene. Into a solution of silver *p*-toluenesulfonate (12.40 g, 0.0444 mol) in acetonitrile (32 cc), we added optically active 1-phenylethyl chloride (2.00 cc, 0.0148 mol; bp 45.0—46.1°C/1.0 mmHg; $\alpha_D^{18.2} -57.105 \pm 0.035°$, 1 dm, neat). The flask was kept at 20.0±0.1°C for 3 hr. The reaction mixture was then cooled at 0°C, and burnt sodium chloride (5.50 g, 0.0942 mol) and ether (15 cc) were added successively. Precipitates of silver chloride (13.27 g) was separated by filtration. The filtrate was concentrated to about 20 cc by a rotary-evaporator at room temperature. To the concentrated solution, tetrahydrofuran (5 cc) was added. After the separation of the additional precipitates of silver chloride (2.08 g) by filtration, the filtrate was concentrated to about 10 cc. From the concentrated solution, 0.5 cc of an aliquot was pipetted, after which the solvent was removed by distillation *in vacuo* (at room temperature) to give white crystals, which rapidly became reddish violet when exposed to air. The crystals showed IR absorption (in CCl_4) at 3070, 2950, 1600, 1495, 1450, and 700 cm^{-1}. Following the method described by Closson *et al.*,[4)] a concentrated solution of 1-phenylethyl *p*-toluenesulfonate was added, drop by drop, into a tetrahydrofuran solution (150 cc) of sodium (1.23 g, 0.0535 mol) and naphthalene (7.00 g, 0.0547 mol) at −3.0°C under nitrogen; the color of the mixture was dark green. After the addition of the tosylate, there was immediately added, drop by drop, a mixture of tetrahydrofuran (15 cc) and distilled water (5 cc) at from 4.0°C to 7.0°C; the color become grey. After the addition of distilled water (10 cc), the reaction mixture was poured onto water (150 cc); sodium chloride (50 g) was then added, and the mixture was extracted with ether (four 50-cc portions). After the combined extracts had then been dried with anhydrous magnesium sulfate, the solution was concentrated to about 10 cc. The white crystals were separated by filtration; the crystals were washed with ethanol (two 5-cc portions); the filtrate was combined with washings and concentrated to about 10 cc. The second crop was filtered and washed with ethanol. The procedure was repeated seven times. The combined white crystals were characterized as naphthalene (5.78 g, 82.6% recov.; the infrared spectrum was the same as that of an authentic sample; mp 79.0—79.8°C). The residual material (2.30 g), concentrated from the final filtrate, was chromatographed over silica gel (50 g). Fractions 1—8, obtained using *n*-hexane, gave naphthalene (0.7795 g; the infrared spectrum was the same as that of an authentic sample; mp 79.5—80.0°C). Fractions 9—13, obtained using benzene, gave slightly yellow crystals (0.3091 g). Fractions 19—28, obtained using successively benzene, benzene-ether (1: 1 by vol.), and ether, gave 1-phenylethyl alcohol (0.6184 g; bp 75.0—80.0°C/4.0 mmHg; 11.3% yield; the infrared spectrum was the same as that of an authentic sample; $\alpha_D^{19.8} +0.248 \pm 0.107°$, 1 dm, neat).

The Hydrolysis of Optically Active 1-Phenylethyl *p*-Toluenesulfonate in the Aqueous Acetonitrile. A solution of silver *p*-toluenesulfonate (6.5226 g, 0.0234 mol) and optically active 1-phenylethyl chloride (2.00 cc, 0.0148 mol; bp 47.5—49.6°C/2.0 mmHg; $\alpha_D^{15.0} -56.42 \pm 0.04°$, 1 dm, neat) in acetonitrile (70.0 cc) was kept at 19.8±0.1°C for 23.7 hr. Precipitates of silver chloride were separated by filtration. The filtrate was treated with water (10 cc), dried with anhydrous magnesium sulfate, and concentrated by distillation. The distillation of the residual material (0.7700 g) under reduced pressure afforded 1-phenylethyl alcohol (0.5121 g; bp 66.5—67.0°C/2.5 mmHg; 28.2% yield; the infrared spectrum was the same as that of an authentic sample; $\alpha_D^{19.2} -0.31 \pm 0.10°$, 0.5 dm, neat), along with styrene (0.3070 g; 19.9% yield; the infrared spectrum was the same as that of an authentic sample).

The Phenolysis of Optically Active 1-Phenylethyldiazonium Salt in a Mixture of Phenol and Water (79: 21 to 66: 34 by Vol.) at from −8°C to +2°C. A mixture of phenol (44.20 g), distilled water (12.00 g), sodium nitrite (13.00 g, 0.1885 mol), and optically active 1-phenylethylamine (22.90 g, 0.1884 mol; bp 64.0—64.5°C/10.0 mmHg; $\alpha_D^{17.0} +13.96 \pm$

0.04°, 1 dm, neat) was prepared in a flask cooled in an ice-salt bath. To the mixture so prepared, we added concentrated hydrochloric acid (16.56 cc, 0.0113 mol), drop by drop, at from −8.0°C to +2.4°C. The reaction proceeded very fast, with the evolution of nitrogen. The volume of nitrogen was measured with a gas burette (708 cc). The reaction mixture was treated according to the above procedures; the unchanged amine was recovered from the acidic extracts. An oily material (7.5026 g) was chromatographed over silica gel (180 g). Fractions 10—13, obtained using *n*-hexane - benzene (1: 1 by vol.), gave an oily material (0.1961 g) containing 1-phenylethyl phenyl ether; this material was rechromatographed over basic alumina (15 g; Nakarai, Alumina Activated 200, *ca.* 200 mesh) to give 1-phenylethyl phenyl ether (0.0566 g; bp 141—146°C/4.0 mmHg; 0.152% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{18.8}+1.40\pm0.22°$ (*c* 40.7, racemic 1-phenylethyl alcohol)). Fractions 18—25, obtained using benzene, gave an oily material (0.7125 g) containing *o*-(1-phenylethyl)-phenol; this material was rechromatographed over basic alumina (30 g) to give *o*-(1-phenylethyl)-phenol (0.4428 g; bp 145—150°C/4.0 mmHg; 1.19% yield; the infrared spectrum was the same as that of an authentic sample; $\alpha_D^{22.8}+0.065\pm0.015°$, 0.5 dm, neat). Fractions 28—43, obtained using benzene and benzene-ether (97: 3 by vol.), gave *p*-(1-phenylethyl)-phenol (1.2094 g; bp 150—155°C/4.0 mmHg; 3.24% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{19.0}+1.07\pm0.09°$ (*c* 65.1, benzene)). Fractions 46—59, obtained using ether, gave 1-phenylethyl alcohol (1.2191 g; bp 90—95°C/10.0 mmHg; 5.30% yield; the infrared spectrum was the same as that of an authentic sample; $\alpha_D^{20.5}+2.69\pm0.02°$, 0.5 dm, neat). The combined acidic solution was made alkaline with 30% aqueous sodium hydroxide; the resulting oil was worked-up in the usual manner, and distilled under reduced pressure to give 1-phenylethylamine (12.60 g; bp 68.5—70.5°C/10.0 mmHg; 55.0% recov.; $\alpha_D^{20.7}+13.59\pm0.015°$, 1 dm, neat).

The Phenolysis of Optically Active Diethyl-(1-phenylethyl)-oxonium Fluoroborate in the Phenol-1,2-Dichloroethane (1: 1 by Wt.) Solvent at from 16°C to 25°C. Optically active diethyl-(1-phenylethyl)-oxonium fluoroborate was prepared by a modification of Meerwein's procedure;[19] all the operations were carried out under a nitrogen atmosphere. Silver fluoroborate (1.93 g, 0.00991 mol) was dissolved in 1,2-dichloroethane (20 cc); to the solution, ethyl iodide (1.54 g, 0.00991 mol) was then added. The yellow precipitate was filtered; to the filtrate, optically active 1-phenylethyl ethyl ether (1.49 g, 0.00991 mol; bp 71.0—73.2°C/10.0 mmHg; $\alpha_D^{21.5}-7.18\pm0.02°$,1 dm, neat) was then added. To the mixture so prepared, a mixture of phenol (28.5 g) and 1,2-dichloroethane (3.44 g) was added. The mixture was kept at room temperature (16.0°C to 24.5°C) with stirring. After the working-up described above, an oily material (1.5921 g) was chromatographed over silica gel (70 g). Fractions 1—3, obtained using *n*-hexane - benzene (1: 1 by vol.), gave polystyrene (0.0437 g; 4.24% yield; the infrared spectrum was the same as that of an authentic sample). Fractions 6—9, obtained using benzene, gave *o*-(1-phenylethyl)-phenol (0.6834 g; bp 145—150°C/4.0 mmHg; 34.8% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{17.5}+0.19\pm0.03°$ (*c* 58.0, benzene)). Fractions 11—19, obtained using benzene and benzene-ether (97: 3 by vol.), gave *p*-(1-phenylethyl)-phenol (1.0810 g; bp 150—153°C/4.0 mmHg; 55.2% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{17.9}-0.146\pm0.048°$ (*c* 41.0, benzene)).

The Phenolysis of Optically Active 1-Phenylethyl Chloride in the Absence of a Base in the Phenol-Acetonitrile (1: 1 by Wt.) Solvent. A mixture of phenol (41.8 g) and acetonitrile (41.8 g) was prepared. To 78.4 cc of the mixture, we then added optically active 1-phenylethyl chloride (2.00 cc, 0.0148 mol; bp 39.8—40.2°C/2.5 mmHg; $\alpha_D^{16.8}-53.32\pm0.02°$, 1 dm, neat). The reaction mixture so prepared was kept at 40.0±0.1°C for 73 hr. After the working-up described above, an oily material (3.1180 g) was chromatographed over silica gel (90 g). Fractions 7—14, obtained using benzene, gave *o*-(1-phenylethyl)-phenol (1.0032 g; bp 145—150°C/4.0 mmHg; 34.9% yield; the infrared spectrum was the same as that of an authentic sample; $\alpha_D^{21.6}-0.455\pm0.045°$, 0.5 dm, neat). Fractions 17—24, obtained using benzene-ether (97: 3 by vol.), gave *p*-(1-phenylethyl-)phenol (1.8583 g; bp 151—158°C /4.0 mmHg; 62.8% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{20.8}-0.532\pm0.223°$ (*c* 39.5, benzene)).

The Acidic Rearrangement of Optically Active 1-Phenylethyl Phenyl Ether in the Phenol-Acetonitrile (1: 1 by Wt.) Solvent at 40°C. Into 5 cc of a mixture containing phenol and acetonitrile (1: 1 ratio by wt.), anhydrous hydrogen chloride was bubbled for about 10 min. The acidic mixture was then diluted with the 1: 1 mixture of phenol and acetonitrile to make a solvent with the desired hydrogen chloride concentration. The exact normality (0.0234 N) was determined by titration with standard 0.05 N sodium acetate in acetic acid (crystal violet). A mixture of optically active 1-phenylethyl phenyl ether (0.8163 g, 0.00411 mol; bp 135—139°C/4.0 mmHg; $\alpha_D^{23.7}-6.41\pm0.02°$, 1 dm, neat) and the acidic solvent (41.7 cc) was maintained at 40.0±0.1°C for 5 hr. After the working-up described above, an oily material (1.2839 g) was chromatographed over basic alumina (40 g; Nakarai, Alumina Activated 200, *ca.* 200 mesh). Fractions 4—6, obtained using *n*-hexane - benzene (1: 1 by vol.), gave 2,3-diphenylbutane (0.0084 g; 1.94% yield). Fractions 8—11, obtained using *n*-hexane-benzene (1: 1 by vol.), gave *o*-(1-phenylethyl)-phenol (0.1908 g; bp 145—150°C/4.0 mmHg; 23.4% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{22.4}+2.85\pm0.32°$ (*c* 53.1, benzene)). Fractions 14—20, obtained using benzene, gave *p*-(1-phenylethyl)-phenol (0.6163 g; bp 155—158°C/5.0 mmHg; 75.8% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{22.3}+1.21\pm0.09°$ (*c* 73.6, benzene)).

The Acidic Rearrangement of Optically Active 1-Phenylethyl Phenyl Ether in the Phenol-1,2-Dichloroethane (1: 1 by Wt.) Solvent at 21°C. A mixture of phenol - 1,2-dichloroethane (1: 1 by wt.) containing the desired concentration of anhydrous hydrogen chloride (0.145 N, as determined by titration)

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[19] H. Meerwein, in Houben-Weyl, " Methoden der organischen Chemie," Georg Thieme Verlag, Stuttgart, (1965) Bd. VI/3, p. 338.

was prepared in a manner similar to that described above. To the acidic solvent (20.2 cc), optically active 1-phenylethyl phenyl ether (0.5871 g, 0.00298 mol; bp 140—145°C/4.0 mmHg; $\alpha_D^{19.2}-1.29\pm0.03°$, 0.5 dm, neat) was added. The reaction mixture so prepared was allowed to stand at room temperature (21.0°C) for 0.5 hr. After the working-up described above, an oily material (0.5782 g) was chromatographed over silica gel (20 g). Fractions 2—5, obtained using *n*-hexane - benzene (1: 1 by vol.) and benzene, gave *o*-(1-phenylethyl)-phenol (0.2854 g; bp 145—151°C/4.0 mmHg; 48.6% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{22.0}+0.54\pm0.06°$ (*c* 66.4, benzene)). Fractions 7—11, obtained using benzene and benzene - ether (97: 3 by vol.), gave *p*-(1-phenylethyl)-phenol (0.2069 g; bp 155—158°C/4.0 mmHg; 35.3% yield; the infrared spectrum was the same as that of an authentic sample; $[\alpha]_D^{22.0}-0.91\pm0.066°$ (*c* 45.2, benzene)).

The Acidic Rearrangement of Racemic 1-Phenylethyl Phenyl Ether in a Mixture of Phenol and Water (79: 21 to 66: 34 by Wt.) at from −6°C to +2°C. A mixture of phenol (37.6 g) and distilled water (10.0 g) was prepared. To 30 cc of the mixture, racemic 1-phenylethyl phenyl ether (0.9731 g; bp 140—145°C/4.0 mHg) was added. To the stirred mixture, concentrated hydrochloric acid (6.90 cc; Nakarai, reagent-grade quality, min. 35.5%) was added, drop by drop, over a 2-hr period at from −6.0°C to +2.0°C. After the working-up described above, an oily material (0.8975 g) was chromatographed over silica gel (30 g). Fractions 1—4, obtained using *n*-hexane - benzene (1: 1 by vol.), gave 1-phenylethyl phenyl ether (0.8751 g; 90.0% recov.; the infrared spectrum was the same as that of an authentic sample). Fractions 9—11, obtained using benzene, gave *o*-(1-phenylethyl)-phenol (0.0124 g; 0.0128% yield; the infrared spectrum was the same as that of an authentic sample). Fractions 14—17, obtained using benzene-ether (97: 3 by vol.), gave *p*-(1-phenylethyl)-phenol (0.0139 g; 0.0143% yield; the infrared spectrum was the same as that of an authentic sample).

Kinetic Measurements. The previous procedure[1] was followed; the usual sealed-ampoule (1.000 cc) technique was employed. The diminution of base concentrations was followed by titration with standard perchloric acid (0.05 N) in acetic acid, using crystal violet as the indicator. All the data were treated graphically by a plot of log $a/(a-x)$ against the time. In each case, the reaction was followed to at least 80% conversion; a smooth linear relationship was thus obtained. Infinity titers were determined after at least ten half-lives. The rate data are shown in Fig. 1 and Table 1.