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The Phenolysis of Tetrahydrolinalyl and 2-Octyl Systems. The Rates, Steric Courses, and Product Distributions

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As tertiary and secondary systems with optical activity, tetrahydrolinalyl (methylethylisohexylcarbinyl) chloride or *p*-nitrobenzoate and 2-octyl *p*-toluenesulfonate have been selected, and their titrimetric and polarimetric rate constants (k_t and k_p) for S_N1 phenolyses have been measured in the presence of triethylamine (or sodium phenoxide) in 50 wt% phenol-benzene. At higher amine (or phenoxide) concentrations, the k_t and k_p coincide with each other for tetrahydrolinalyl chloride (at 25.0°C) or *p*-nitrobenzoate (at 100.0°C), and also for 2-octyl tosylate (at 75.0°C), exhibiting the typical features of the S_N1 solvolysis rate constant. In the absence of the amine (or sodium phenoxide), the k_t diminishes to show a gap between the k_p and the k_t, indicating the occurrence of an ion-pair return in the phenolysis for both systems. Under the same reaction conditions as those of the rate measurement, tetrahydrolinalyl chloride and *p*-nitrobenzoate yield the phenyl ether, with a predominant racemization accompanied by some net inversion of the configuration, whereas 2-octyl tosylate gives 2-octyl phenyl ether, *o*-, and *p*-2-octylphenols, with a net inversion of the configuration accompanied by a slight racemization. These steric results indicate that phenol can be considered as a typical solvolytic solvent. The product distributions have been assessed for the reactions of 2-octyl chloride (200°C) and of tetrahydrolinalyl chloride (25.0°C) with the molecule of phenol under the S_N1 phenolysis conditions, by extrapolating the product composition curves to a zero concentration of the phenoxide. For both systems, the phenol molecule is predominantly *O*-alkylated (74 and 99% respectively), accompanied by minor amounts of *C*-alkylation. In contrast to the phenol reaction, the phenoxide ion undergoes more *C*-alkylation (42 and 50% respectively).

Our previous studies of the phenolytic reactivity with regard to optically-active substrates have concentrated upon the optically-active 1-phenylethyl system;[1] the phenolysis of this system proceeded to yield 1-phenylethyl phenyl ether with a partially-retained configuration. This is not a standard result for the steric course of the solvolysis, since the solvolyses of such simple *sec*- and *tert*-alkyl (or aralkyl) systems have generally been reported to give a product with a partially-inverted onfiguration.[2] Therefore, we considered it of interest to examine whether the solvolysis of simple optically-active systems other than the 1-phenylethyl system would proceed with a retention of the configuration in the phenolic solvent or not; we selected the 2-octyl and the tetrahydrolinalyl (methylethylisohexylcarbinyl) systems, which are readily available and which also have been reported to give partially-inverted products in common solvolytic solvents[3] other than phenol.

Our results show that, in contrast to the 1-phenylethyl system, the phenolysis for both systems proceeds with a net inversion of the configuration—a standard result expected of the typical S_N1 solvolysis of a simple optically-active system. We will also report on the distributions of the phenolysis products in both systems.

Results and Discussion

The S_N1 *Characteristics of the Phenolyses of 2-Octyl and Tetrahydrolinalyl Systems.* The titrimetric and polarimetric rate constants (k_t and k_p) in a 50 wt% phenol-benzene solvent were measured in the presence of variable concentrations of triethylamine (or sodium phenoxide) on 2-octyl chloride at 175.0 and 200.0°C or on the *p*-toluenesulfonate at 75.0°C, and on tetrahydrolinalyl (methylethylisohexylcarbinyl) chloride at 25.0°C or on the *p*-nitrobenzoate at 100.0°C. Satisfactory first-order kinetic behavior, expected of a typical S_N1 reaction, was observed for each of the k_t's and k_p's; the results are tabulated in Table 1.

The effects of the triethylamine (or sodium phenoxide) concentrations upon the k_t and the k_p values in the phenolyses of 2-octyl tosylate and tetrahydrolinalyl *p*-nitrobenzoate are illustrated in Figs. 1 and 2 respectively. It is immediately obvious that the k_t's for the tetrahydrolinalyl *p*-nitrobenzoate (or chloride) are almost independent of the amine (or the phenoxide) concentrations; this is a typical kinetic feature of the S_N1 solvolysis (see also Table 1).

From Figs. 1 and 2 it is also evident that, at a zero concentration of the base, there exists a gap between the k_p and k_t values (*i.e.*, $k_p > k_t$) in the case of 2-octyl tosylate, and most probably in the case of tetrahydrolinalyl *p*-nitrobenzoate as well; these results indicate that the S_N1 phenolyses for these systems proceed with some "ion-pair" return.

The gap between the k_p and k_t values has already been observed in the phenolysis of 1-phenylethyl chloride.[4] However, in marked contrast to the 1-phenylethyl system, in which the gap actually widens as the

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[1] K. Okamoto, T. Kinoshita, and H. Shingu, This Bulletin, **43**, 1545 (1970), and the references cited therein.

[2] A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956); for the inversive solvolysis of the *tert*-alkyl system, see L. H. Sommer and F. A. Carey, *J. Org. Chem.*, **32**, 800, 2473 (1967).

[3] For the 2-octyl system, see a) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Amer. Chem. Soc.*, **87**, 3682 (1965); b) A. Streitwieser, Jr. and T. D. Walsh, *ibid.*, **87**, 3686 (1965); c) H. Weiner and R. A. Sneen, *ibid.*, **87**, 287 (1965); d) H. Weiner and R. A. Sneen, *ibid.*, **87**, 292 (1965). For tetrahydrolinalyl chloride, see e) E. D. Hughes, C. K. Ingold, R. J. L. Martin, and D. F. Meigh, *Nature*, **166**, 679 (1950).

[4] K. Okamoto, K. Takeuchi, and H. Shingu, This Bulletin, **35**, 525, (1962).

Table 1. The rate constants for the phenolysis of 2-octyl and tetrahydrolinalyl (THL) systems in 50 wt% phenol-benzene solvent

	Temp °C	RX M	Et_3N (PhONa) M	$10^4 \times k_t$ sec^{-1}	$10^4 \times k_p$ sec^{-1}
2-Oct Cl	175 (±1)	0.0921	0.0930	0.713	—
	200 (±1)	0.0872	0.0968	3.12	—
		0.0490	0.0495	3.85	—
		0.0496	0.0996	4.55	—
2-Oct OTs	75.0 (±0.1)	0.100	0.000	1.69	2.00
		0.100	0.102	1.83	2.08
		0.103	0.301	1.93	2.17
		0.102	0.498	2.35	2.33
		0.101	0.703	2.51	2.55
THL Cl	25.0 (±0.1)	0.100	0.000	6.13	—
		0.010	0.012	16.5	—
		0.023	0.025	16.5	—
		0.049	0.051	16.6	—
		0.100	0.102	16.5	16.3
		0.100	0.201	16.7	—
		0.100	0.303	17.1	—
THL OPNB[b]	100.0 (±0.1)	0.101	0.0000	9.43	—
		0.0500	0.0509[a]	9.73	—
		0.0998	0.103[a]	9.93	—
		0.103	0.148[a]	10.1_5	—
		0.102	0.000	—	10.3
		0.0495	0.0503[a]	—	10.1
		0.0989	0.0993[a]	—	9.6^2
		0.102	0.146[a]	—	9.8_5

a) Sodium phenoxide was used instead of triethylamine. b) THL=Tetrahydrolinalyl; OPNB=*p*-Nitrobenzoate.

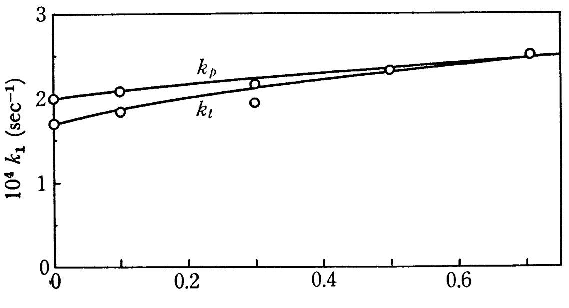

Fig. 1. Effect of the added triethylamine upon the first-order rate constants for the phenolysis of 2-octyl tosylate in 50 wt% phenol–benzene solvent at 75.0°C.

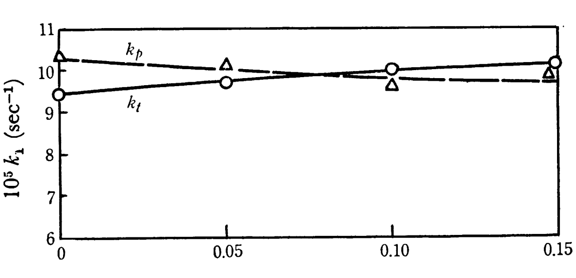

Fig. 2. Effect of the added sodium phenoxide upon the first-order rate constants for the phenolysis of tetrahydrolinalyl *p*-nitrobenzoate in 50 wt% phenol–benzene solvent at 100.0°C.

concentration of the base increases, in the 2-octyl and tetrahydrolinalyl systems the gap virtually disappears with an increase in the amine concentrations (see Figs. 1 and 2). The coincidence in the k_p and k_t values (within the limits of experimental error) suggests that the consumption rate ($k_2[PhOH]+k_2'[PhO^-]$ in Eq. (1)) of the ion-pair intermediate becomes far greater than the return rate (k_{-1} in Eq. (1)) at higher amine or phenoxide concentrations, and that the return phenomena virtually disappear as the amine or the phenoxide concentration increases.

These kinetic features can be expressed by the following reaction scheme, which contains a single ion-pair intermediate; the observed rate constant can be expressed by Eq. (1):

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [R^+\cdots X^-] \xrightarrow{k_2[PhOH]+k_2'[PhO^\ominus]} \text{Phenolysis products}$$

$$k_{obs.} = \frac{k_1(k_2[PhOH]+k_2'[PhO^\ominus])}{k_{-1}+k_2[PhOH]+k_2'[PhO^\ominus]} \quad (1)$$

For the acetolysis of 2-octyl tosylate, a similar reaction scheme with a single ion-pair intermediate has already been proposed by Streitwieser *et al.*[3a,b] Thus, providing that the above scheme applies to these phenolyses, from the data illustrated in Figs. 1 and 2 and from Eq. (1) the k_{-1}/k_2 ratio can be estimated to be 0.925(M) for the phenolysis of 2-octyl tosylate at 75.0°C and 0.467(M) for that of the tetrahydrolinalyl system at 100.0°C.

The Steric Courses of the Phenolyses of 2-Octyl Tosylate and of Tetrahydrolinalyl Chloride and p-*Nitrobenzoate.*

The phenolyses of optically-active 2-octyl tosylate were carried out at 75.0°C in 50 wt% phenol–benzene for one and for ten half-lives. By the chromatography on silica gel, from the reaction mixtures we isolated the

TABLE 2. THE PHENOLYSIS PRODUCTS AND THEIR OPTICAL ACTIVITIES IN THE PHENOLYSES OF OPTICALLY ACTIVE 2-OCTYL TOSYLATE OR TETRAHYDROLINALYL CHLORIDE AND *p*-NITROBENZOATE[a)]

		2-Octyl tosylate		THL Cl	THL OPNB
RX,	M	0.100	0.100	0.100	0.0989
	$[\alpha]_D$	+6.97°[b)]	+6.13°[b)]	+0.50°[b)]	−0.925°
		(±0.02°)	(±0.02°)	(±0.02°)	(±0.011°)
Et_3N,	M	0.0999	0.101	0.103	0.0993
Time,	hr	1.00[c)]	24.0	1.5	24
Temp,	°C	75.0	75.0	25.0	100
ROPh	α_D[b)]	−24.60°	−20.11°	+0.20°	+1.27°
		(±0.04°)	(±0.03°)	(±0.02°)	(±0.01°)
	α%[d)]	91.0 Inv.	84.7 Inv.	Inv. + predominant Rac.[e)]	16.2 Inv.
	Yield %	14.6	27.9	13.6	12.5
o-RC_6H_4OH	$[\alpha]_D$	−3.80°	−2.17°		
		(±0.28°)	(±0.15°)		
	α%	101 Inv.	65.7 Inv.	—	—
	Yield %	3.64	9.30		
p-RC_6H_4OH	$[\alpha]_D$	—5.83°	—4.69°		
		(±0.44°)	(0.05°)		
	α%	108 Inv.	98.2 Inv.	—	—
	Yield %	1.89	6.11		

a) The maximum rotations for the relevant optically active compounds in this Table are shown in Table 3.
b) The rotations for a neat sample at 21—25°C in a 1-dm tube. c) See text; ethy 2-octyl ether, which was obtained by the SN2 ethanolysis of the unchanged ROTs, possessed $[\alpha]_D$ −14.9°, and α% 91.2 (with respect to ROTs). d) A net steric course. e) See text; the calculated α% on the basis of the optical purity of tetrahydrolinalool, from which the starting chloride was prepared, amounts to 3.62%; the α%, calculated on the basis of the maximum rotation[11)] for tetrahydrolinalyl chloride, amounts to 3.21%.

elimination product in a 50—60% yield; this product was composed of 1-, *cis*-2-, and *trans*-2-octenes. From the subsequent eluents, the substitution products (2-octyl phenyl ether, *o*-, and *p*-2-octylphenols) were separated in a 40—60% yield. The configuration of each product was predominantly inverted, and the degree of racemization was quite small. The details of the results are tabulated in Table 2.

The inversion with some racemization is a standard result for the steric course of the solvolysis of a simple secondary alkyl system;[2)] similar stereochemical outcomes for the 2-octyl systems have been observed in acetic acid[3a,b)] and aqueous dioxane[3c,d)] solvents.

The phenolysis of tetrahydrolinalyl chloride, when conducted at 25.0°C in the 50 wt% phenol–benzene solvent for 10 half-lives, yielded a 86.2% yield of decenes (a mixture of 4 isomers), a 13.6% yield of tetrahydrolinalyl phenyl ether, and small amounts of *o*- and *p*-tetrahydrolinalylphenols (0.15 and 0.017% yields respectively); the configuration of the phenyl ether was inverted, with some racemization. Since we have no information about the extent of racemization during the retentive conversion of tetrahydrolinalool to tetrahydrolinalyl chloride, we can not estimate the optical purity of the starting chloride thus prepared nor, consequently, the exact degree of racemization for the phenyl ether in the course of the phenolysis. However, if we assume that the retentive chloride formation by thionyl chloride proceeds with a low degree of the racemization, as is observed in the case of optically-active 1-phenylethyl alcohol,[5)] we may expect that the tetrahydrolinalyl chloride phenolysis proceeds with a predominant racemization, with some net inversion.

Tetrahydrolinalyl *p*-nitrobenzoate, $[\alpha]_D^{21.0}$ −0.925°, was prepared from tetrahydrolinalool, $\alpha_D^{23.5}$ −0.43°, and *p*-nitrobenzoyl chloride in pyridine. The phenolysis of the *p*-nitrobenzoate was carried out at 100.0°C in the 50 wt% phenol–benzene solvent for 10 half-lives; it yielded a 85% yield of decenes (a mixture of 4 isomers), a 12.5% yield of tetrahydrolinalyl phenyl ether, and a small amount of *C*-alkylated phenols (less than a 0.5% yield). From the values of the maximum rotations of the *p*-nitrobenzoate and the phenyl ether (see Table 3), it was estimated that the phenolysis proceeded with a 83.8% racemization, accompanied by a net 16.2% inversion.

An inversion of the configuration with some racemization has been typically observed in the solvolyses of simple *tert*-alkyl systems, *e.g.*, in the solvolyses of tetrahydrolinalyl chloride in 80% aqueous acetone and methanol solvents,[3e)] in the methanolysis of methylethylisobutylcarbinyl hydrogen phthalate,[6)] and in solvolyses of methylethylphenylcarbinyl chloride,[7)]

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5) See the experimental part of our previous report: K. Okamoto, M. Hayashi, K. Komatsu, and H. Shingu, This Bulletin, **40**, 624 (1967).

6) W. von E. Doering and H. H. Zeiss, *J. Amer. Chem. Soc.*, **75**, 4733 (1953).

7) L. H. Sommer and A. F. Carey, *J. Org. Chem.*, **32**, 2473 (1967).

Table 3. The maximum rotations and the absolute configurations for the phenolysis products and relevant substrates

	$[\alpha]_D$ or α_D 22—25°	References
(*R*)-2-octyl phenyl ether	−38.7° (neat, 1 dm)	This work
(*R*)-*o*-2-octylphenol	−4.56° (in benzene)	This work
(*R*)-*p*-2-octylphenol	−6.57° (in benzene)	This work
(*R*)-tetrahydrolinalyl phenyl ether	+7.84° (neat, 1 dm)	This work
(*R*)-tetrahydrolinalyl *p*-nitrobenzoate	+1.67° (in benzene)	This work
(*R*)-2-octanol	+10.3° (neat, 1 dm)	Kornblum[a]
(*R*)-2-octyl *p*-toluenesulfonate	−9.96° (neat, 1 dm)	Streitwieser[b]
(*R*)-2-methyloctanoic acid	−16.4° (in *n*-heptane)	Ref. 11
(*S*)-tetrahydrolinalool	−0.76° (neat, 1 dm)	Ref. 12
(*R*)-tetrahydrolinalyl chloride	−0.63° (neat, 1 dm)	Ref. 12

a) Cited by N. Kornblum, L. Fishbein, and R. A. Smiley (*J. Amer. Chem. Soc.*, **77**, 6261 (1955)).
b) Calcd from the data reported by A. Streitwieser, Jr. *et al.* (Ref. 3a).

p-nitrobenzoate,[8] and hydrogen phthalate[8] in acetic acid,[8] methanol,[7,8] ethanol,[7] 80% aqueous ethanol,[7] and 75% aqueous dioxane.[7]

In conclusion, these steric results for both systems indicate that the phenolic solvent can be considered as a typical solvolytic solvent.

The Absolute Configurations and the Maximum Rotations for 2-Octyl Phenyl Ether, Tetrahydrolinalyl Phenyl Ether, and o- *and* p-*2-Octylphenols.* Optically-active compounds of the titled phenolysis products, the absolute configurations and maximum rotations of which are not yet known, were prepared from, or derived to, a known, optically-active compound by following the reaction schemes described below. The configurations and the rotations thus established are tabulated in Table 3, along with those of the relevant optically-active compounds. Using the values shown in Table 3, the net steric courses and extents of inversion (α%) in the course of the phenolyses have been estimated; they are tabulated in Table 2.

(*S*)-(+)-2-Octyl *p*-toluenesulfonate was treated with sodium phenoxide in dimethylformamide at 75.0°C for 20 hr. Since the reaction proceeds by means of the S_N2 mechanism, the (−)-2-octyl phenyl ether thus obtained was determined to possess the (*R*)-configuration.[9] The maximum rotation (Table 3) was calculated from the known rotation[3a] of 2-octyl tosylate:

$$(S)\text{-}(+)\text{-2-Oct-OTs} \xrightarrow[\text{in DMF}]{\text{NaOPh}} (R)\text{-}(-)\text{-2-Oct-OPh}$$

Optically-active *o*- and *p*-2-octylphenols, obtained by the acidic rearrangement of optically-active 2-octyl phenyl ether, were subjected to permanganate oxidation[10] in acetone. From the specific rotations of the optically-active 2-methyloctanoic acid[11] thus obtained, the maximum rotations of (*R*)-(−)-*o*-2-octylphenol and (*R*)-(−)-*p*-2-octylphenol were estimated (Table 3):

$$(R)\text{-}(-)\text{-}o\text{-2-Oct-}C_6H_4OH \xrightarrow[\text{in acetone}]{\text{KMnO}_4} (R)\text{-}(-)\text{-2-Me-Octanoic Acid}$$

$$(R)\text{-}(-)\text{-}p\text{-2-Oct-}C_6H_4OH \xrightarrow[\text{in acetone}]{\text{KMnO}_4} (R)\text{-}(-)\text{-2-Me-Octanoic Acid}$$

(*S*)-(−)-Methylethylisohexylcarbinol (Tetrahydrolinalool, THL-OH), with a somewhat lower rotation, was converted to potassium tetrahydrolinalate in benzene; then the potassium salt was treated with an excess of bromobenzene. The maximum rotation of the (*S*)-(−)-tetrahydrolinalyl phenyl ether thus obtained was calculated on the basis of the maximum rotation of tetrahydrolinalool[12] (Table 3):

$$(S)\text{-}(-)\text{-THL-OH} \xrightarrow[\text{in benzene}]{K}$$

$$(S)\text{-THL-OK} \xrightarrow{\text{PhBr}} (S)\text{-}(-)\text{-THL-OPh}$$

The Product Distribution for the Phenolyses of 2-Octyl and Tetrahydrolinalyl Chlorides. The composition of the phenolysis product after ten half-lives was determined by gas chromatography, using diphenyl ether as the internal standard. Each phenolysis was conducted with a sodium phenoxide/substrate ratio higher than 10 in order to keep the base concentration approximately invariant during the phenolysis.

In Table 4 the effect of the sodium pheoxide concentration upon the product composition is presented for the phenolyses of 2-octyl and tetrahydrolinalyl chlorides in the 50 wt% phenol–benzene solvent at 200.0 and 25.0°C respectively; it is also illustrated in Figs. 3 and 4.

The product composition for the tetrahydrolinalyl system is approximately invariant, despite the wide variation in the concentration of the phenoxide ion. In contrast to this system, in the 2-octyl system the olefin % decreases with an increase in the phenoxide concentration.

Since, in the reaction media, there exist two species of nucleophiles, *viz.*, the phenol molecule and the

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[8] L. H. Sommer and A. F. Carey, *J. Org. Chem.*, **32**, 800 (1967).

[9] The configuration of 2-octyl phenyl ether relative to the tosylate was assigned by J. Kenyon, H. Phillips, and V. P. Pittman, *J. Chem. Soc.*, **1935**, 1072.

[10] H. Hart and H. S. Eleuterio, *J. Amer. Chem. Soc.*, **76**, 516 (1954).

[11] A. Rothen and P. A. Levene, *J. Chem. Phys.*, **7**, 975 (1939).

[12] P. E. Verkade, K. S. De Vries, and B. M. Wepster, *Rec. Trav. Chim. Pays-Bas*, **83**, 367 (1964).

TABLE 4. EFFECT OF THE ADDED SODIUM PHENOXIDE UPON THE PRODUCT DISTRIBUTION FOR THE PHENOLYSES OF 2-OCTYL AND TETRAHYDROLINALYL CHLORIDES IN 50 wt% PHENOL–BENZENE SOLVENT

RX M × 10^4	NaOPh M	Product distribution %			
		Olefin	ROPh	o-RC_6H_4OH	p-RC_6H_4OH
		2-Octyl chloride, at 200°C			
8.8	0.0075	72.8[a]	19.2	4.94	3.06
8.4	0.0150	66.4	23.4	6.44	3.76
9.1	0.0300	63.4	24.8	7.50	4.32
9.5	0.0500	57.5	27.7	9.46	5.35
9.5	0.100	53.2	30.1	10.1	6.58
9.6	0.150	40.0	37.0	14.0	8.98
		Tetrahydrolinalyl chloride, at 25.0°C			
9.0	0.0075	84.0[b]	16.0	0.0250	0.00500
9.1	0.0150	86.0	14.0	0.0408	0.00506
9.2	0.0300	85.7	14.3	0.0429	0.00760
9.8	0.0500	86.0	13.9	0.0655	0.0127
10.1	0.100	85.6	14.3	0.136	0.0173
10.0	0.150	86.4	13.4	0.175	0.0162

a) A mixture of 3 isomers. b) A mixture of 4 isomers.

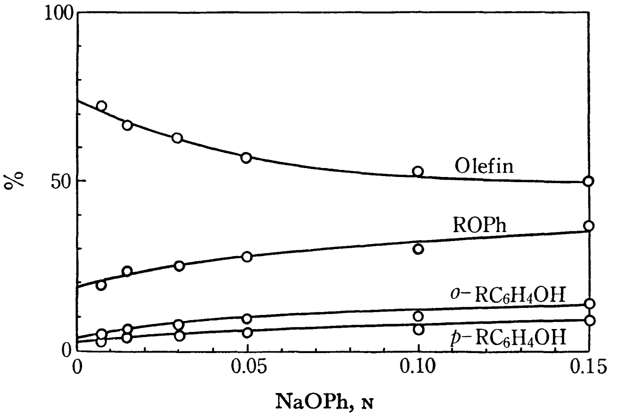


Fig. 3. Effect of the added sodium phenoxide upon the product distribution for the phenolysis of 2-octyl chloride in 50 wt% phenol–benzene solvent at 200.0°C.

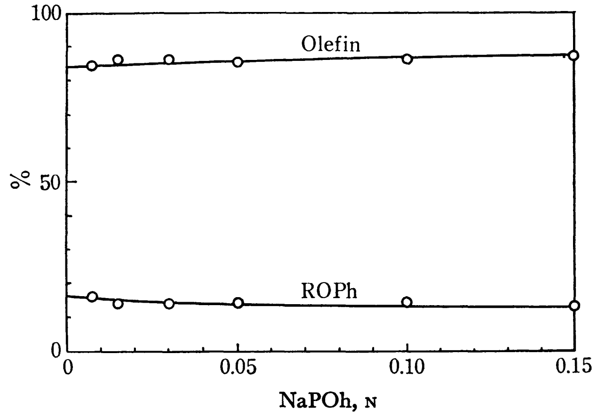


Fig. 4. Effect of the added sodium phenoxide upon the product distirbution for the phenolysis of tetrahydrolinalyl chloride in 50 wt% phenol–benzene solvent at 25.0°C.

TABLE 5. PRODUCT DISTRIBUTION FOR THE REACTIONS OF PHENOL MOLECULE AND PHENOXIDE ION

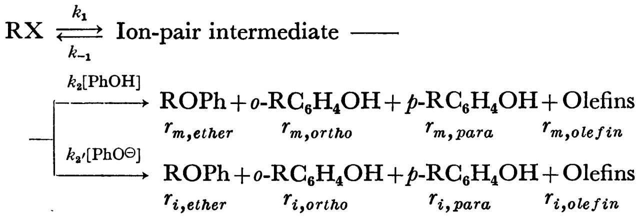
Substrate	Temp °C	Product distribution %			
		ROPh	o-RC_6H_4OH	p-RC_6H_4OH	Olefin
		The reaction of phenol molecule			
2-Octyl Cl	200.0	19.3	4.2	2.85	73.65
		(73.2)[b]	(16.0)	(10.8)	—
1-Adamantyl Cl[a]	100.0	91.5	8.0	0.5	—
THL Cl	25.0	15.9	0.017	0.003	84.1
		(99.874)	(0.107)	(0.019)	—
		The reaction of phenoxide ion			
2-Octyl Cl	200.0	52.5	27.1	9.98	12.4
		(58.6)	(30.3)	(11.1)	—
1-Adamantyl Cl[a]	100.0	70.0	23.0	9.0	—
THL Cl	25.0	10.6	8.3	2.1	82.4
		(50.5)	(39.5)	(10.0)	—
		The values for k_2'/k_2			
2-Octyl Cl	200.0	35.0	26.6	41.5	33.9
1-Adamantyl Cl[a]	100.0	128	134	56	—
THL Cl	25.0	63.4	7810	4990	100

a) K. Okamoto, K. Matsubara, and T. Kinoshita, This Bulletin, **45**, 1191 (1972).
b) Distribution % for the substitution products.

phenoxide ion, it is of interest to assess the product distribution for each species.

We can, first, estimate the product distribution for the reaction of the phenol molecule with the ion-pair intermediate by extrapolating the composition lines in Figs. 3 and 4 to a zero concentration of the phenoxide ion. The results are tabulated in Table 5, along with the distribution % for the phenolysis of 1-adamantyl chloride, which has previously been estimated by the same procedure.[13]

Secondly, providing that the phenol molecule and the phenoxide ion competitively attack the ion-pair intermediate at the product-formation step, and that the concentrations of the phenol molecule and the phenoxide ion are actually invariant during the reaction, we can assess the product distribution ($r_{i,x}$, *vide infra*) for the phenoxide-ion reaction, by using Eq. (2), which expresses the relationships between the observed product composition (*viz.*, $r_{obs.,\ olefin}$, $r_{obs.,\ ether}$, $r_{obs.,\ ortho}$, and $r_{obs.,\ para}$) and the estimated product distributions for the phenol reaction (*viz.*, $r_{m,\ olefin}$, $r_{m,\ ether}$, $r_{m,\ ortho}$, and $r_{m,\ para}$) or for the phenoxide reaction (*viz.*, $r_{i,\ olefin}$, $r_{i,\ ether}$, $r_{i,\ ortho}$, and $r_{i,\ para}$). The details for the derivation of Eq. (2) have been reported previously.[13]



$$\mathrm{RX} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{Ion-pair intermediate} \text{ —— } \begin{cases} \xrightarrow{k_2[\mathrm{PhOH}]} \underset{r_{m,ether}}{\mathrm{ROPh}} + \underset{r_{m,ortho}}{o\text{-}\mathrm{RC_6H_4OH}} + \underset{r_{m,para}}{p\text{-}\mathrm{RC_6H_4OH}} + \underset{r_{m,olefin}}{\text{Olefins}} \\ \xrightarrow{k_{2'}[\mathrm{PhO^{\ominus}}]} \underset{r_{i,ether}}{\mathrm{ROPh}} + \underset{r_{i,ortho}}{o\text{-}\mathrm{RC_6H_4OH}} + \underset{r_{i,para}}{p\text{-}\mathrm{RC_6H_4OH}} + \underset{r_{i,olefin}}{\text{Olefins}} \end{cases}$$

$$\frac{(r_{obs,x}-r_{m,x})}{([\mathrm{PhO^{\ominus}}]/[\mathrm{PhOH}])} = -\left(\frac{k_{2'}}{k_2}\right)r_{obs,x} + \left(\frac{k_{2'}}{k_2}\right)r_{i,x} \qquad (2)$$

In Eq. (2), x denotes olifin, ether, *ortho*, or *para*. Since we have already established the values for $r_{obs.,\ x}$, $r_{m,x}$, and ($[\mathrm{PhO^{\ominus}}]/[\mathrm{PhOH}]$), we can estimate the values for $r_{i,x}$ and $k_{2'}/k_2$ by a graphical method.[13] In Table 5 the results of the estimation of $r_{i,x}$ for 2-octyl chloride and tetrahydrolinalyl chloride are presented, along with the previously-reported values for 1-adamantyl chloride.[13]

From Table 5 it is immediately obvious that, for each substrate, the proportion of *O*-alkylation (the phenyl ether formation) is greater in the case of the phenol reaction than in the case of the phenoxide reaction. This indicates that the ambident phenol molecule reacts more selectively with the ion-pair intermediate than does the ambident phenoxide ion, which reacts more rapidly and, therefore, less selectively. The rapidness of the phenoxide reactions is reflected in the $k_{2'}/k_2$ rate ratio (27—7800), shown in Table 5.

It is also evident from Table 5 that the proportions of *O*-alkylation in the phenol-molecule reaction diminish in this sequence: tetrahydrolinalyl>1-adamantyl>2-octyl chlorides. It has been established in the case of 1-phenylethyl chloride[14] that the proportion of *O*-alkylation in the phenol-molecule reaction is virtually independent of the reaction temperature. If this is the case also in the phenolyses of these chlorides, the above-mentioned sequence of the proportions for *O*-alkylation on the phenol molecule will be independent of the temperature. Consequently, the sequence may indicate that the stabilization of the ion-pair intermediate in the tetrahydrolinalyl system contributes substantially to the enhanced tendency to undergo *O*-alkylation; this seems to be relevant, with the observation that the S_N1-like reaction of methyl iodide with silver nitrite predominantly yields the *O*-alkylation product, unlike the S_N2 reaction with sodium nitrite.[15]

For the phenoxide reaction there appears to be no simple correlation between the stability of the ion-pair intermediate and the structural sequence (*viz.*, 1-Ad>2-Oct>THL) for the *O*-alkylation proportions on the phenoxide ion; this sequence remains to be accounted for.

As has been mentioned above, the three substrates, 2-octyl, 1-adamantyl, and tetrahydrolinalyl chlorides, all undergo phenolysis to yield predominantly inversive, completely retentive, and substantially racemic phenyl ethers; it seems difficult to find a correlation between these steric outcomes and the sequence of the proportions of *O*-alkylation.

Rearrangement of the Phenyl Ether in the Medium of the Phenolysis. Since it is well known that the *sec*- and *tert*-alkyl phenyl ethers readily undergo a rearrangement to give *o*- and *p*-alkylphenols in the presence of an acidic catalyst,[16] the possibility of a rearrangement for 2-octyl phenyl ether and tetrahydrolinalyl phenyl ether even in the slightly acidic solvent phenol can not be eliminated. However, we detected no *o*- or *p*-alkylated phenols in the reaction mixtures when these phenyl ethers were subjected to a rearrangement in 50 wt% phenol–benzene for more than ten half-lives of the phenolysis at, respectively, 200 and 25°C. Consequently, all of the *o*- and *p*-alkylated phenols found in these phenolysis products are not produced as a result of the rearrangement of the phenyl ether, but are directly produced from the ion-pair intermediate in each phenolysis.

Experimental[17]

Materials. 2-Octyl chloride[18] and optically-active 2-octyl *p*-toluenesulfonate[19] were prepared in the usual

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[13] K. Okamoto, K. Matsubara, and T. Kinoshita, This Bulletin, **45**, 1191 (1972).

[14] The *O*-alkylation %: 80—82% (25, 50, and 75°C) (K. Okamoto and Y. Ito, unpublished results).

[15] N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, **77**, 6269 (1955).

[16] For a summary, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed., Cornell University Press, Ithaca and London (1969), pp. 904—906.

[17] A Hitachi Model 023-6003 gas-chromatographic instrument, with a flame ionization detector, a Shimadzu Model IR-27 spectrophotometer, and a Japan Electronic Optics 60 MHz instrument were used for the analytical work. Microanalyses were performed by the Elemental Analysis Center, Kyoto University. For the measurement of the optical rotations, a JASCO DIP-SL polarimeter was used.

[18] P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **59**, 473 (1924).

[19] A. Streitwieser, Jr. and A. C. Waiss, Jr., *J. Org. Chem.*, **27**, 290 (1962).

manners. The resolution of 2-octanol was perfomed according to the method of Kenyon.[20] Optically-active tetrahydrolinalyl *p*-nitrobenzoate (mp 39.5—40.1°C (cor.)) (see Tables 2 and 3) was prepared from tetrahydrolinalool[12] and *p*-nitrobenzoyl chloride in pyridine (*vide infra*) Optically-active tetrahydrolinalyl chloride[21] was prepared from tetrahydrolinalool.[12] Sodium phenoxide was prepared by refluxing a toluene solution of phenol with sodium metal. The other organic reagents employed were of an analytical reagent grade and were fractionated just prior to use. Titration with a Karl Fischer reagent indicated the water content of phenol to be less than 10^{-2} M.

Product Isolation. *The Phenolysis of 2-Octyl Tosylate (75°C)*: To 146 m*l* of a 1:1 (by wt.) mixture of phenol and benzene containing triethylamine (2.20 m*l*; 0.101 M), there was added optically-active 2-octyl *p*-toluenesulfonate (4.290 g, 0.01510 mol; $\alpha_D^{22.6}$ $+5.195\pm0.015°$, 1 dm, neat). The reaction mixture was kept at 75.0 ± 0.1°C for 24 hr (about 10 half-lives). The mixture was then diluted with 300 m*l* of ether, and washed successively with 10% aqueous sodium hydroxide (100 m*l*×5) and 10% aqueous sodium chloride (100 m*l*×5) to make it neutral to pH indicator paper. The ethereal solution, dried with magnesium sulfate, was concentrated by distillation; a part (3.74 wt%) of the residual liquid was examined by gas chromatography. The remainder was evapolated, and then separated by column chromatography on silica gel (60 g). The column was eluted successively with *n*-hexane, *n*-hexane–benzene (1:1 by vol.), benzene, benzene–ether (97:3 by vol.), and ether. The fractions eluted with *n*-hexane–benzene gave 2-octyl phenyl ether (681 mg; bp 130—135°C/4.0 mmHg; 21.9% yield; the same infrared spectrum as in an authentic sample; $\alpha_D^{21.0}$ $-10.05\pm0.02°$, 0.5 dm, neat). The fractions eluted with benzene gave *o*-2-octylphenol (99.8 mg; bp 138—145°C/4.0 mmHg; 3.21% yield; the same infrared spectrum as in an authentic sample; $[\alpha]_D^{21.4}$ $-2.17\pm0.15°$ (*c* 12.9, benzene)). The fractions eluted with benzene–ether gave *p*-2-octylphenol (64.7 mg; bp 140—145°C/4.0 mmHg; 2.17% yield; the same infrared spectrum as in an authentic sample; $[\alpha]_D^{22.0}$ $+4.69\pm0.05°$ (*c* 72.3, benzene)).

The Phenolysis of Tetrahydrolinalyl Chloride (25°C). A 1:1 (by wt.) mixture (94.5 m*l*) of phenol and benzene, containing triethylamine (1.48 m*l*; 0.1030 M), was prepared and kept at 25.0 ± 0.1°C for 1 hr. To the phenolic solvent, optically-active tetrahydrolinalyl chloride (2.000 m*l*, 1.703 g; 0.00965 mol; bp 55.0—59.5°C/4.0 mmHg; $\alpha_D^{25.3}$ $+0.50\pm0.02°$, 1 dm, neat) was then added. The reaction mixture was maintained for 1.5 hr (about 11 half-lives). After the working-up described above, an oily material (0.3668 g) was chromatographed on alumina (30 g). The fractions eluted with *n*-hexane gave tetrahydrolinalyl phenyl ether (0.1693 g; bp 145—150°C/4.0 mmHg; 7.51% yield; $\alpha_D^{22.3}$ $+0.20\pm0.02°$, 1 dm, neat; IR (CCl_4) 2950, 1590, 1490, 1460, 1220, 1140, and 700 cm^{-1}; NMR (CCl_4) δ 2.85 (m, 5H) and 8.85 (m, 21H)).

Found: C, 81.96; H, 11.40%. Calcd for $C_{16}H_{26}O$: C, 82.00; H, 11.18%.

The Phenolysis of Tetrahydrolinalyl p*-Nitrobenzoate (100°C).* Optically-active tetrahydrolinalyl *p*-nitrobenzoate (3.0345 g; 0.00989 mol; mp 39.5—40.1°C (corr.); $[\alpha]_D^{16.0}$ $-0.925\pm0.011°$ (*c* 26.5, benzene)) was dissolved in 97 m*l* of a 1:1 (by wt.) mixture of phenol and benzene, containing sodium phenoxide (0.0993 M). After 24 hr (about 10 half-lives) at 100.0 ± 0.1°C, the solution was treated in the usual way. A residual liquid (1.1055 g) was separated by thin-layer chromatography on silica gel to give tetrahydrolinalyl phenyl ether (0.2905 g; bp 145—150°C/4.0 mmHg; 12.5% yield; $\alpha_D^{16.5}$ $+0.635\pm0.005°$, 0.5 dm, neat).

Kinetic Measurements. *Titrimetric Rate Constant (k_t).* The previous procedure was followed.[22] For the runs of the tetrahydrolinalyl chloride phenolysis at 25°C, 1.000 m*l* aliquots were removed at intervals from 20 m*l* of the reaction mixture placed in a glass-stoppered flask. For the phenolyses of 2-octyl chloride, 2-octyl tosylate, and tetrahydrolinalyl *p*-nitrobenzoate at 200, 75, and 100°C respectively, the usual sealed-ampoule (1.000 m*l*) technique was employed. The diminution of the base concentrations was followed by titration with standard perchloric acid (0.05 N) in acetic acid, using crystal violet as the indicator. For the phenolysis of tetrahydrolinalyl chloride, carried out in the absence of a base, a 1 m*l* glass-stoppered flask was used. In this case, the free space was filled with liberated HCl in the course of the phenolysis. Therefore, after a specified length of time, the flask, filled with a 1 m*l* reaction mixture, was immersed and opened in a large quantity of cold acetic acid used as a stop-solvent. The increase in the HCl concentration was followed by titration with standard sodium acetate in acetic acid. All the rate data were treated graphically, plotting log $a/(a\text{-}x)$ against the time. In each case the reaction was followed to at least 70% completion; a smooth linear relationship was obtained. Infinity titers were determined after at least ten half-lives. The rate data are shown in Figs. 1 and 2 and in Table 1.

Polarimetric Rate Constant (k_p). For the phenolysis of 2-octyl tosylate, the usual sealed-ampoule (5 m*l*) technique was employed. Each ampoule, after having been kept at the reaction temperature for a specified time, was cooled and the reaction mixture was immediately transfered into a 2 dm polarimeter tube. The optical rotation was measured at room temperature. For the phenolysis of tetrahydrolinalyl *p*-nitrobenzoate, the observation of the optical rotation of a reaction mixture was impossible because of the low optical rotation of the reaction mixture. Therefore, the measurement was carried out by the use of another method as follows. After a specified reaction time, to 100 m*l* of the reaction mixture we added a large quantity of cold ether. The cold ethereal solution was promptly washed with cold 10% aqueous NaOH and then with cold 10% aqueous NaCl, and dried (Na_2SO_4); most of the solvent was subsequently removed by rotary-evaporation. To the residual liquid, benzene was added to make a 2.00 m*l* solution. The specific rotation of the benzene solution was determined. Thus, the rotations for two specified reaction times were treated graphically and a smooth first-order linear relationship was obtained. The data for the k_p's are shown in Figs. 1 and 2 and Table 1.

Product-distribution Analysis by Gas Chromatography. To several mg of 2-octyl chloride (or tetrahydrolinalyl chloride) with diphenyl ether (an internal standard), placed in a 12 m*l* ampoule, there was added 10 m*l* of a phenol–benzene (1:1 by wt.) solvent containing a specified amount of sodium phenoxide (or triethylamine). The sealed ampoule was kept at the reaction temperature for 10 half-lives. The reaction mixture was then diluted with 20 m*l* of ether, washed with 10% aqueous Na_2CO_3 and 10% aqueous NaCl, dried with $MgSO_4$, and distilled to leave 6—8 m*l* of the residual liquid, which was then analysed by glc using a 2 m×3 mm column with Apiezon Grease on Neopak 1A at 200°C.

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[20] "Organic Synthesis," Coll. Vol. I, (1967), p. 418.

[21] P. G. Stevens and N. L. McNiven, *J. Amer. Chem. Soc.*, **61**, 1295 (1939).

[22] K. Okamoto, H. Yamada, I. Nitta, and H. Shingu, This Bulletin, **39**, 299 (1966).

Rearrangement of the Phenyl Ethers. The usual sealed-ampoule technique was employed. To several mg of 2-octyl phenyl ether (or tetrahydrolinalyl phenyl ether), which contained diphenyl ether as an internal standard and which was placed in a 2 m*l* ampoule, we added 1 m*l* of a phenol–benzene (1:1 by wt.) mixture. The ampoule was kept at the same temperature as that of the chloride phenolysis for the 10 half-lives. The analysis was performed by glc using a 2 m×3 mm Apiezon Grease column at 200°C.

Syntheses of Optically-active Authentic Samples (cf. Table 3). (R)-(−)-2-Octyl Phenyl Ether. (*R*)-(−)-2-Octyl phenyl ether was prepared from (*S*)-(+)-2-octyl tosylate and sodium phenoxide under S_N2 reaction conditions. The reaction in DMF was determined to be a 2nd-order reaction, with k_2 3.58×10^{-3} ($\mathrm{sec}^{-1}\ \mathrm{M}^{-1}$) at 75.0°C. (*S*)-(+)-2-octyl tosylate (2.8467 g, 0.01001 mol; $\alpha_D^{22.6}$ $+5.195\pm0.015°$, 1 dm, neat), prepared from (*S*)-(+)-2-octanol $\alpha_D^{23.1}$ $+7.27\pm0.02°$, 1 dm, neat), was dissolved in 97.0 m*l* of DMF containing sodium phenoxide (2.44 g, 0.0210 mol). After 20 hr at 75°C, the mixture was treated as has been described above; the residual liquid was separated by column chromatography on basic alumina to give 2-octyl phenyl ether (1.461 g; bp 130—135°C/4.0 mmHg; 71.0% yield; $\alpha_D^{21.5}$ $-22.95\pm0.01°$, 1 dm, neat)

(S)-(−)-Tetrahydrolinalyl Phenyl Ether. A mixture of (*S*)-(−)-tetrahydrolinalool (3.160 g; 0.0200 mol; bp 54.0—59.5°C/5.0 mmHg; $\alpha_D^{23.5}$ $-0.43\pm0.02°$, 1 dm, neat) and potassium metal (0.78 g; 0.020 mol) in dry benzene (50 m*l*) was refluxed for 8 hr; the mixture then became homogeneous. To the mixture, bromobenzene (15.98 g; 0.200 mol) was added. The reaction mixture was then refluxed for an additional 14 hr. After the addition of ether (200m*l*), the mixture washed with 10% aqueous NaCl (100 m*l*×4) and dried with $MgSO_4$. The ethereal solutions was concentrated; the residual liquid was chromatographed on alumina. The fractions eluted with *n*-hexane and with benzene gave tetrahydrolinalyl phenyl ether (0.544 g, 0.00232 mol; bp 140—145°C/4.0 mmHg; 11.6% yield; $\alpha_D^{24.2}$ $-5.53\pm0.03°$, 1 dm, neat). The fractions eluted with ether and with ethanol gave unchanged tetrahydrolinalool (2.37 g; 75.0% recovery; $\alpha_D^{20.8}$ m$0.42\pm0.02°$, 1 dm, neat).

(S)-(−)-Tetrahydrolinalyl p-*Nitrobenzoate.* The usual method for the preparation of optically-active 1-phenylethyl *p*-nitrobenzoate[23] was modified for the preparation of tetrahydrolinalyl *p*-nitrobenzoate. A mixture of (*S*)-(−)-tetrahydrolinalool (4.07 g; 0.0257 mol; bp 54.0—59.5°C/5.0 mmHg; $\alpha_D^{23.5}$ $-0.43\pm0.02°$, 1 dm, neat) and *p*-nitrobenzoyl chloride (4.88 g; 0.0263 mol) in pyridine (12 m*l*) was stirred at 30.0—31.6°C for 5 hr in order to make it homogeneous. The mixture was then treated in the usual way to give (*S*)-(−)-tetrahydrolinalyl *p*-nitrobenzoate (6.55 g; 83.0% yield; mp 39.5—40.1°C (corr.); $[\alpha]_D^{21.0}$ $-0.925\pm0.011°$ (*c* 26.5, benzene); IR (CCl_4) 3000, 1790, 1380, 1340, 1230, 1150, 1080, and 700 cm^{-1}; NMR (CCl_4) δ 1.3 (m, 21H) and 8.2 (d, 4H)).

Found: C, 66.43; H, 8.33%. Calcd for $C_{17}H_{25}NO_4$: C, 66.42; H, 8.20%.

Oxidation of 2-Octylphenols. Optically-active (−)-*o*- and (+)-*p*-2-octylphenols were prepared by the rearrangement (in the presence of *p*-toluenesulfonic acid, 100°C, 21 hr) of (*R*)-(−)-2-octyl phenyl ether ($\alpha_D^{20.5}$ $-23.78\pm0.01°$, 1 dm, neat) in phenol–benzene (1:1 by wt.). The optically-active *o*- and *p*-2-octylphenols thus were oxidized to 2-methyloctanoic acid according to the procedure of Hart and Eleuterrio.[24] To a solution of *o*-2-octylphenol (1.94 g; 0.00943 mol; $[\alpha]_D^{24.1}$ $-0.31\pm0.09°$ (*c* 56.5, benzene)) in acetone (200 m*l*), we added potassium permanganate (10.3 g, 0.0652 mol) in distilled water (750 m*l*) at 10—15°C. The mixture was then stirred for 2 hr and acidified with 6 N sulfuric acid, and the manganese dioxane thus precipitated was dissolved by the addition of sodium bisulfite. The mixture was extracted with 10% aqueous $NaHCO_3$ (100 m*l*×4), and the extracts were acidified with 6 N H_2SO_4 (100 m*l*) and then extracted with benzene (100 m*l*×4). The benzene solution was dried with $MgSO_4$. After the solvent had been removed by rotary-evaporation, the residual oil was distilled *in vacuo* to give 2-methyloctanoic acid (0.339 g, 22.8% yield; bp 98.4—111.5°C/2.0 mmHg; $[\alpha]_D^{16.8}$ $-1.12\pm0.07°$ (*c* 28.5, *n*-heptane)). Since this conversion proceeds with the maintenance of the configuration of the assymmetric carbon atom, the configurations of 2-methyloctanoic acid and *o*-2-octylphenol should be identical. Thus, the specific rotation of optically-pure (*R*)-(−)-*o*-2-octylphenol may be estimated to be −4.56° (in benzene) on the basis of the value for optically-pure (*R*)-2-methyloctanoic acid, −16.4° (in *n*-heptane).[11] In the same manner, from (+)-*p*-2-octylphenol (2.64 g, 0.0128 mol; $[\alpha]_D^{24.1}$ $+1.70\pm0.26°$ (*c* 26.5, benzene)) (+)-2-methyloctanoic acid (0.0477 g, 2.3% yield; bp 106.0—111.2°C/0.8 mmHg; $[\alpha]_D^{24.6}$ $+4.25\pm0.19°$ (*c* 10.3, *n*-heptane)) was obtained. The specific rotation of optically-pure (*S*)-*p*-2-octylphenol can, therefore, be estimated to be +6.57° (in benzene).

The authors wish to express their thanks to Mr. Osamu Makino for his technical assistance.

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[23] H. L. Goering and J. P. Blanchard, *J. Amer. Chem. Soc.*, **76**, 5405 (1954).

[24] H. Hart and H. F. Eleuterio, *ibid.*, **76**, 516 (1954).