Retentive Solvolysis. Part XI.[1,†] Retentive Phenolyses of Optically Active Secondary and Tertiary Systems without a Group imposing Configurational Restriction

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The rate, product distribution, and stereochemical course for phenolyses of 17 compounds, including three *p*-substituted 1-phenylethyl systems, eight *m*- or *p*-substituted 2,2-dimethyl-1-phenylpropyl systems, 1-phenylpropyl, 2-methyl-1-phenylpropyl, *p*-chlorodiphenylmethyl, and 1-methyl-1-phenylpropyl *p*-nitrobenzoate, and 1-ethyl-1,5-dimethylhexyl chloride and trifluoroacetate have been investigated. The titrimetric rate constants for *p*-substituted 1-phenylethyl *p*-nitrobenzoates and for *m*- or *p*-substituted 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoates follow the Yukawa–Tsuno correlation in pure phenol as solvent. All phenyl ethers, major products of phenolyses, show net retention of configuration; in particular, the extent of retention was 97.4% for 2,2-dimethyl-1-(*p*-nitrophenyl)propyl phenyl ether and 90.0% for 2,2-dimethyl-1-phenylpropyl phenyl ether in the presence of triethylamine. *C*-Alkylated products are formed to a small extent and show net inversion in ten phenolyses examined; among these, *o*- and *p*-(2,2-dimethyl-1-phenylpropyl)phenol which are produced from the *p*-nitrobenzoate show almost completely inverted configuration. Variations in the polarimetric and titrimetric rates, in the product yield, and in the extent of retention have been examined for various concentrations of added base in the phenolyses of eight selected substrates. On the basis of these results, the mechanism and stereochemical course of the phenolyses are discussed by the use of a generalized scheme, previously proposed for the phenolyses of 1-phenylethyl systems. The maximum rotations and the absolute configurations of the compounds have been determined by chemical or n.m.r. shift reagent methods.

WE reported previously[1] that S_N1 phenolyses of optically active 1-phenylethyl *p*-nitrobenzoate (3a) and its *p*-methoxy- (1a) and *p*-nitro-derivatives (5a) proceed with predominant retention of configuration in phenolic solvents. From the results of a detailed study on variations in the extent of retention, in the yield of products, and in the titrimetric and polarimetric rate constants, for various concentrations of added sodium phenoxide, a generalized phenolysis scheme was proposed to explain the formation of a phenyl ether with retained configuration from a substrate without a group imposing configurational restrictions.[1] On the mechanism,[2] several models, such as four-centre,[3,4] cyclic,[5] back-side shielding,[6,7] and solvent-separated ion-pair[8-10] models, which can explain the formation of the product of retention, have been proposed as key intermediates in retentive solvolysis. In contrast to the variety of models, there are few examples[11,12] of retentive solvolysis,

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† Presented at the International Symposium on Nucleophilic Substitution, Pocono Manor, 1975.

[1] Part X, K. Okamoto, T. Kinoshita, Y. Takemura, and H. Yoneda, *J.C.S. Perkin II*, 1975, 1426.

[2] For a leading reference see P. B. D. de la Mare and B. E. Swedlund in 'The Chemistry of the Carbon–Halogen Bond,' ed. S. Patai, Interscience, London, 1973, vol. 1, ch. 7.

[3] (*a*) K. Okamoto, K. Takeuchi, and H. Shingu, *Bull. Chem. Soc. Japan*, 1962, **35**, 525; (*b*) K. Okamoto, H. Yamada, I. Nitta, and H. Shingu, *ibid.*, 1966, **39**, 299.

[4] K. Okamoto, T. Kinoshita, and H. Shingu, *Bull. Chem. Soc. Japan*, 1970, **43**, 1545.

[5] K. Okamoto, M. Hayashi, and H. Shingu, *Bull. Chem. Soc. Japan*, 1966, **39**, 408; K. Okamoto, M. Hayashi, K. Komatsu, and H. Shingu, *ibid.*, 1967, **40**, 624; K. Okamoto, K. Komatsu, and H. Shingu, *ibid.*, p. 1677.

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[7] P. B. D. de la Mare, D. M. Hall, and E. Mauger, *Rec. Trav. chim.*, 1968, **87**, 1394.

[8] D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1971, **93**, 4821.

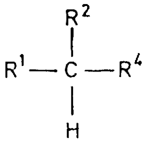
[9] J. M. Harris, J. F. Fagan, F. A. Walden, and D. C. Clark, *Tetrahedron Letters*, 1972, 3023; J. M. Harris, A. Becker, J. F. Fagan, and F. A. Walden, *J. Amer. Chem. Soc.*, 1974, **96**, 4484.

[10] H. L. Goering, R. G. Briody, and G. Sandrock, *J. Amer. Chem. Soc.*, 1970, **92**, 7401; H. L. Goering and H. Hopf, *ibid.*, 1971, **93**, 1224.

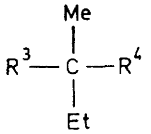
[11] Refs. 3–5 and 10.

[12] H. L. Goering, R. G. Briody, and J. F. Levy, *J. Amer. Chem. Soc.*, 1963, **85**, 3059; H. L. Goering and J. F. Levy, *ibid.*, 1964, **86**, 120; H. L. Goering and S. Chang, *Tetrahedron Letters*, 1965, 3607.

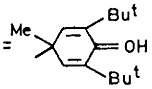
and this dearth seems to be a cause of the diversity of mechanisms. Therefore, we extended our previous work on (1a), (3a), and (5a) to other secondary arylcarbinyl systems (2a), (4a), and (6a)—(14a), and also to



(1) $R^1 = Me$, $R^2 = p\text{-}MeOC_6H_4$
(2) $R^1 = Me$, $R^2 = p\text{-}MeC_6H_4$
(3) $R^1 = Me$, $R^2 = Ph$
(4) $R^1 = Me$, $R^2 = m\text{-}ClC_6H_4$
(5) $R^1 = Me$, $R^2 = p\text{-}NO_2C_6H_4$
(6) $R^1 = Et$, $R^2 = Ph$
(7) $R^1 = Pr^i$, $R^2 = Ph$
(8) $R^1 = Bu^t$, $R^2 = p\text{-}MeOC_6H_4$
(9) $R^1 = Bu^t$, $R^2 = p\text{-}MeC_6H_4$
(10) $R^1 = Bu^t$, $R^2 = Ph$
(11) $R^1 = Bu^t$, $R^2 = m\text{-}ClC_6H_4$
(12) $R^1 = Bu^t$, $R^2 = p\text{-}ClC_6H_4$
(13) $R^1 = Bu^t$, $R^2 = p\text{-}NO_2C_6H_4$
(14) $R^1 = Ph$, $R^2 = p\text{-}ClC_6H_4$
(15) $R^1 = Me$, $R^2 = n\text{-}C_6H_{13}$



(16) $R^3 = Ph$
(17) $R^3 = i\text{-}C_6H_{13}$

a; $R^4 = OCOC_6H_4NO_2\text{-}p$
b; $R^4 = Cl$
c; $R^4 = Br$
d; $R^4 = OCOC_6H_3(NO_2)_2\text{-}3,5$
e; $R^4 = OTs$
f; $R^4 = \overset{+}{N_2}Cl^-$
g; $R^4 = \overset{+}{O}Et_2BF_4^-$
h; $R^4 =$ 

i; $R^4 = OCOCF_3$
j; $R^4 = OPh$
k; $R^4 = o\text{-}HOC_6H_4$
l; $R^4 = p\text{-}HOC_6H_4$
m; $R^4 = OH$
n; $R^4 = OCOCH_3$
o; $R^4 = COOH$

some tertiary carbinyl systems (16a) and (17a and i) intending to obtain new information which might contribute to mechanistic interpretation of retentive solvolysis of a substrate without a group which restricts configurational mobility.

RESULTS AND DISCUSSION

Effect of Added Base on Titrimetric Rate Constants.—Titrimetric measurements of the phenolysis rate were carried out in pure phenol (Y +1.77 *), in phenol–benzene (1 : 1 w/w; Y +0.425 [13]), and in phenol–toluene (1 : 1 w/w) as solvent. Satisfactory first-order kinetic behaviour, as expected for a typical S_N1 solvolysis, was observed for each of the 17 substrates over a wide range of initial concentration of added sodium phenoxide or triethylamine. The rate constants with 0.1M base are tabulated in Table 1, along with the data for relevant substrates.[1,4,14]

TABLE 1

Titrimetric phenolysis rates of some alkyl and aralkyl systems in the presence of sodium phenoxide or triethylamine

Compound [a]	Solvent	T/°C	$[NaOPh]_0$/N	k_t/s^{-1} [b]
(1a) [c]	PhOH	125.0	0.104	4.1×10^{-2}
	PhOH–benzene (1 : 1 w/w)	25.0	0.101	1.01×10^{-4}
(2a)	PhOH	125.0	0.104	1.78×10^{-3}
(3a) [c]	PhOH	125.0	0.103	1.85×10^{-4}
(3b)	PhOH–benzene (1 : 1 w/w)	50.0	0.107 [d]	1.60×10^{-3}
(3c) [e]	$PhOH–CH_3CN$ (1 : 1 w/w)	40.0	0.419 [d]	6.68×10^{-3}
(3d) [e]	PhOH	150.0	0.093 3	3.45×10^{-2}
(4a)	PhOH	125.0	0.103	4.62×10^{-5}
(5a) [c]	PhOH	125.0	0.102	7.95×10^{-6}
(6a)	PhOH	125.0	0.152	5.85×10^{-5}
(7a)	PhOH	125.0	0.105	2.22×10^{-5}
(8a)	PhOH	125.0	0.111	4.13×10^{-3}
(8i)	PhOH	75.0	0.212	1.23×10^{-1}
(9a)	PhOH	125.0	0.105	5.41×10^{-5}
(10a)	PhOH	125.0	0.104	1.50×10^{-6}
(10i)	PhOH	75.0	0.127	3.31×10^{-5}
(11a)	PhOH	125.0	0.104	4.62×10^{-7}
(12a)	PhOH	125.0	0.105	1.49×10^{-6}
(13a)	PhOH	125.0	0.117	2.31×10^{-8} [f]
(14a)	PhOH	125.0	0.104	3.21×10^{-3}
	PhOH–benzene (1 : 1 w/w)	100.0	0.100	1.90×10^{-4}
(16a)	PhOH	125.0	0.105	6.50×10^{-2}
	PhOH–benzene (1 : 1 w/w)	50.0	0.113 [d]	7.81×10^{-5}
(17a) [g]	PhOH	125.0	0.103	5.75×10^{-2}
(17b)	PhOH–toluene (1 : 1 w/w)	25.0	0.108 [d]	1.64×10^{-4}
	PhOH–benzene [g] (1 : 1 w/w)	25.0	0.102 [d]	1.65×10^{-3}
(17i)	PhOH–toluene (1 : 1 w/w)	50.0	0.105 [d]	3.54×10^{-4}

[a] $[Compound]_0 = 0.09$—0.10M. [b] Accurate to within ±1.0%. [c] Ref. 1. [d] In the presence of Et_3N instead of NaOPh. [e] Ref. 4. [f] Calculated on the basis of the rate of diminution of (13a) and the ratios of the solvolysis product (13j—l) to the carbonyl reaction product (13m) at 25.5—66.1% conversion (720 h). [g] Ref. 14.

Regarding seven *p*-nitrobenzoates selected as representatives, the titrimetric rate constants (k_t) decrease in the sequence (16a) > (17a) > (14a) > (3a) > (6a) > (7a) > (10a) (relative rates *ca.* 45 300 : 38 300 : 2 140 : 123 : 39.0 : 14.8 : 1.00 in phenol at 125°). Particularly, four alkylphenylmethyl *p*-nitrobenzoates [(3a), (6a), (7a), and (10a)] exhibit a reactivity parallel with that of the corresponding chlorides in aqueous ethanol; [15] there is a linear free energy relationship (correlation coefficient 0.999; standard deviation 0.051) between the phenolysis and the hydrolysis rates, reflecting similar transition states to each other.

When the effect of added base on the k_t was examined, the k_t values for the phenolyses of (8a and i), (10a), and (17b) exhibited a two-stage rise with increase in the concentrations of the added sodium phenoxide or triethylamine. This is attributed to a composite phenomenon of two salt effects, designated special [16]

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* Grunwald–Winstein Y value extrapolated from data in ref. 13.

[13] K. Okamoto, K. Matsubara, and T. Kinoshita, *Bull. Chem. Soc. Japan*, 1972, **45**, 1191.

[14] K. Okamoto and T. Kinoshita, *Bull. Chem. Soc. Japan*, 1972, **45**, 2802.

[15] G. Baddeley, J. Chadwick, and H. T. Taylor, *J. Chem. Soc.*, 1954, 2405.

[16] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2767.

and normal[17] by Fainberg and Winstein. As reported previously, similar observations have been made on the phenolyses of (1a),[1] (3b),[3a] (15e),[14] and (17a).[14] The quantities[16] which characterize the special salt effect, *i.e.* k_t°, $k_t^{\circ}{}_{,\mathrm{ext}}/k_t^{\circ}$, and $[\mathrm{NaOPh}]_{\frac{1}{2}}$, are tabulated in Table 2, along with the values for b[17] which designates a slope of linear increase in k_t and characterizes the normal salt effect. Table 2 also shows the b values for nine systems in which added base exerts only the normal salt effect. It is obvious that in the phenolyses, in which the special salt effect is observed, both phenoxide ion and phenol molecule react with the ion-pair intermediate to give the phenolysis products. Considering the constancy of product distribution for various concentrations of added phenoxide ion, it is most probable, in the phenolysis of the nine systems (Table 2) in which only the normal salt effect is observed, that only phenol can react with the ion-pair intermediate in spite of the presence of the phenoxide ion in the reaction medium.

TABLE 2

Effect of added base on the titrimetric rate constants (special and normal salt-effect)

Compound [a]	Solvent	T/°C	$k_t^0{}_{,\mathrm{ext}}$/s^{-1}	$k_t^0{}_{,\mathrm{ext}}/k^0{}_t$	$[\mathrm{NaOPh}]_{\frac{1}{2}}$/N	b
(1a) *	PhOH–benzene (1 : 1 w/w)	25.0	8.39×10^{-5}	1.40	0.02	2.20
(3b) [c]	PhOH–benzene (1 : 1 w/w)	25.0	3.17×10^{-4}	4.95	0.003 6 [d]	−0.40 [d]
(8a)	PhOH	125.0	4.45×10^{-3}	1.52	0.12	0.84
(8i)	PhOH	75.0	1.30×10^{-1}	2.09	0.10	0.16
(10a)	PhOH	125.0	1.42×10^{-6}	1.67	0.11	4.40
(15e) [e]	PhOH–benzene (1 : 1 w/w)	75.0	2.00×10^{-4}	1.18	0.30 [f]	0.40 [f]
(17a) [e]	PhOH–benzene (1 : 1 w/w)	100.0	1.03×10^{-3}	1.09	0.035	−0.30
(17b)	PhOH–toluene (1 : 1 w/w)	25.0	1.90×10^{-4}	1.52	0.02 [f]	−1.10 [f]
	PhOH–benzene (1 : 1 w/w)	25.0	1.65×10^{-4}	2.69	0.006 [f]	0.00 [f]
(3a) *	PhOH	125.0	1.71×10^{-4}	1.00		1.00
(5a) *	PhOH	125.0	6.48×10^{-6}	1.00		2.20
(6a)	PhOH	125.0	4.03×10^{-5}	1.00		3.00
(7a)	PhOH	125.0	2.05×10^{-5}	1.00		0.39
(10i)	PhOH	75.0	1.62×10^{-5}	1.00		9.40
(13a)	PhOH	125.0	1.75×10^{-8} [g]	1.00		2.70
(14a)	PhOH–benzene (1 : 1 w/w)	100.0	1.64×10^{-4}	1.00		2.40
(16a)	PhOH–benzene (1 : 1 w/w)	50.0	9.25×10^{-5}	1.00		−0.92 [e]
(17i)	PhOH–toluene (1 : 1 w/w)	50.0	3.42×10^{-4}	1.00		0.00 [e]

[a] $[\mathrm{RX}]_0$ = 0.05 or 0.10M. * Ref. 1. [c] Ref. 3*a*. [d] In the presence of added aniline instead of sodium phenoxide. [e] Ref. 14. [f] In the presence of triethylamine instead of sodium phenoxide. [g] See footnote *f* in Table 1.

Application of the Yukawa–Tsuno Equation.—Rate constants for hydrolysis (or ethanolysis[18]) of several aralkyl systems, such as the 1-phenylethyl compounds, (3b)[19] and (3n),[20] 2,2-dimethyl-1-phenylpropyl chloride (10b),[21] cumyl *p*-nitrobenzoate[18] and chloride,[22] *p*-chlorodiphenylmethyl chloride (14b),[23] and 2,2-dimethyl-1-(1,1-dimethylethyl)-1-phenylpropyl *p*-nitrobenzoate,[18] are reported to be well correlated by the Brown–Okamoto $\rho\sigma^+$ equation.[22] In contrast, the σ^+ plots of log k_t for the phenolyses of *m*- or *p*-substituted 1-phenylethyl and 2,2-dimethyl-1-phenylpropyl systems show definitely curved lines. However, linear plots are given by the use of the Yukawa–Tsuno equation,[24] $\log k/k_0 = \rho[\sigma^0 + r(\sigma^+ - \sigma^0)]$, with ρ −1.74 and r 1.86 (correlation coefficient −0.993; standard deviation 0.040) for (1a)—(5a) and with ρ −2.37 and r 1.99 (correlation coefficient −0.990; standard deviation 0.031) for (8a)—(13a). In view of the similar r values for both 1-phenylethyl and 2,2-dimethyl-1-phenylpropyl systems, it is not conceivable that σ-participation[25] by a methyl group of the neopentyl group causes a curved σ^+ plot for 2,2-dimethyl-1-phenylpropyl system. The different features of σ^+ and $\sigma^0 + r(\sigma^+ - \sigma^0)$ plots in the linear free energy relationships between hydrolysis of the chlorides [(1b)—(5b) and (8b)—(13b)] and phenolysis of the *p*-nitrobenzoates [(1a)—(5a) and (8a)—(13a)] may be attributed to the difference of the leaving groups or to the difference of the solvolysis solvents.§

Maximum Rotations and Absolute Configurations.—Since the rotations for the optically pure samples and the absolute configurations were not known previously for the phenolysis products, they were determined, prior to examination of the stereochemical course, by chemical method.

The previously reported S_N2 reaction method,[1] originally employed by Hoffmann and Hughes,[26] was applied to determine the maximum rotations for the phenyl ethers (6j)—(8j), (10j), (13j), and (14j), starting with the respective trifluoroacetates and sodium phenoxide. The optical rotation of (14j) decreased with the progress of the S_N2 reaction of (14i) with sodium phenoxide. The maximum rotation was thus calculated from

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§ Experiments to clarify this point are under way.

[17] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2763.

[18] H. Tanida and H. Matsumura, *J. Amer. Chem. Soc.*, 1973, **95**, 1576.

[19] V. J. Shiner, W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, 1968, **90**, 418; G. T. Bruce, A. R. Cooksey, and K. J. Morgan, *J.C.S. Perkin II*, 1975, 551.

[20] E. A. Hill, M. L. Gross, M. Stasiewicz, and M. Mannion, *J. Amer. Chem. Soc.*, 1969, **91**, 7381.

[21] A. Fisher, D. I. Stedman, and J. Vaughan, *J. Chem. Soc.*, 1963 751.

[22] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913.

[23] S. Nishida, *J. Org. Chem.*, 1967, **32**, 2692.

[24] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 965, 971.

[25] I. L. Reich, A. Diaz, and S Winstein, *J. Amer. Chem. Soc.*, 1969, **91**, 5635; S. H. Liggero, R. Sustmann, and P. v. R. Schleyer, *ibid.*, 1969, **91**, 4571; W. M. Schubert and W. L. Henson, *ibid.*, 1971, **93**, 6299; H. S. Mosher, *Tetrahedron*, 1974, **30**, 1733.

[26] H. M. R. Hoffmann and E. D. Hughes, *J. Chem. Soc.*, 1964, 1244.

the rotation at zero conversion which was estimated by graphical extrapolation of the data for various conversions (see Table 10, footnote *f*).

The optically active trifluoroacetates used in the S_N2 method were prepared with retention of configuration from the corresponding optically active alcohol (ROH).[1]

The phenyl ether (16j) was prepared from bromobenzene and the potassium salt of the optically active alcohol (16m) under conditions similar to the case of (17j).[14]

The maximum rotations for the alcohols (6m)—(9m) and (13m), were determined by a ^1H n.m.r. shift reagent method (see Table 12). The absolute configuration of (13m) was assigned on the basis of the results of nitration of the optically active acetate (10n) and subsequent hydrolysis, as in the case of (5m).[1]

The maximum rotations and the absolute configuration of alkylated phenols (6k), (6l), (10k), and (10l) were calculated from the maximum rotations of the carboxylic acids (6o)[27] and (10o),[27] which were obtained by the potassium permanganate oxidation[14] of the respective alkylated phenols,[14] according to the method originally employed by Hart and Eleuterio[28] (see Experimental section).

The maximum rotations of the *R*-configuration for 30 compounds (alcohols, *p*-nitrobenzoates, trifluoroacetates, phenyl ethers, and alkylated phenols) are tabulated in Table 3, together with maximum rotations reported for six *R*-systems.

Steric Course of Phenyl Ether Formation.—Products of phenolyses under conditions identical with those in the kinetic measurements were isolated by preparative t.l.c. The net steric course was deduced for phenyl ether formation by comparing the optical purity and the absolute configuration for the purified ether with those

TABLE 3

Maximum rotations (°) [a] of (*R*)-aralkyl and -alkyl derivatives

	$R^1R^2R^3CX$								
	R^1	R^2	R^3	ROH	$ROCOC_6H_4NO_2$-*p*	$ROCOCF_3$	ROPh	*o*-RC_6H_4OH	*p*-RC_6H_4OH
(6)	Et	Ph	H	+59.2 [b,c] +35.8	−56.6	+251	−16.6 −49.7 [b]	−18.9	−21.4
(7)	Pr^i	Ph	H	+27.3 [b,c] +67.6 [c,d]	−91.1	+150	−32.1		
(8) [e]	Bu^t	*p*-$MeOC_6H_4$	H	(+)27.0	(−)89.6	(+)110	(−)5.84		
(10)	Bu^t	Ph	H	+27.4 [c]	−223	+86.3	−25.5	−83.6	+82.5
(13)	Bu^t	*p*-$NO_2C_6H_4$	H	+34.8	−203	+111	−0.871		
(14) [e]	Ph	*p*-ClC_6H_4	H	(+)32.1 [f,g]	(+)27.3 [f,h]	(−)19.2	(+)19 [f]		
(16)	Et	Ph	Me	+17.6 [b,i]	−58.6 [f,j]	+20.5 [b]	+12.8		
(17)	Et	i-C_6H_{13}	Me	+0.76 [b,k]	+1.67 [l]	+5.14 [b]	+26.3 +7.48 [b,l]		

[a] $[\alpha]_D$ (*c* 0.5—35, benzene), unless otherwise noted. [b] α_D (neat, 1 dm). [c] For absolute configuration, see R. McLeod, E. J. Welch and H. S. Mosher, *J. Amer. Chem. Soc.*, 1960, **82**, 876. [d] $[\alpha]_D$ (*c* 7—10, ether). [e] The absolute configuration for the system is unknown. [f] $[\alpha]_D$ (*c* 1—20, chloroform). [g] Ref. 41. [h] H. L. Goering, R. G. Briody, and G. Sandrock, *J. Amer. Chem. Soc.*, 1970, **92**, 7401. [i] D. J. Cram and J. Allinger, *J. Amer. Chem. Soc.*, 1954, **76**, 4516. [j] Ref. 32. [k] P. E. Verkade, K. S. De Vries, and B. M. Wepster, *Rec. Trav. chim.*, 1964, **83**, 367. [l] Ref. 14.

TABLE 4

Retentive phenyl ether formation in phenolysis of some aralkyl and alkyl systems

Compound [a]	Solvent	*T*/°C	Added base	$[Base]_0$/N or M	Net steric course, retention (%)
(1a) [b]	PhOH–benzene (1 : 1 w/w)	25.0	NaOPh	0.108	16.6
(1i)	PhOH–benzene (1 : 1 w/w)	25.0	NaOPh	0.100	15.0
(3a) [b]	PhOH	125.0	NaOPh	0.113	34.5
(3b) [c]	PhOH–benzene (1 : 1 w/w)	50.0	NaOPh	0.109	29.7
(3c) [d]	PhOH–CH_3CN (1 : 1 w/w)	40.0	Et_3N	0.419	16.3
(3d) [d]	PhOH	150.0	NaOPh	0.093 3	28.2
(3e) [d]	PhOH–CH_3CN (1 : 1 w/w)	20—35	$CO(NH_2)_2$	0.234	>2.0 [e]
(5a) [b]	PhOH	125.0	NaOPh	0.097 1	90.0
(6a)	PhOH	125.0	NaOPh	0.110	38.2
(7a)	PhOH	125.0	NaOPh	0.110	38.9
(8a)	PhOH	125.0	NaOPh	0.125	15.5
(8i)	PhOH	75.0	NaOPh	0.110	5.79
(10a)	PhOH	125.0	NaOPh	0.114	82.4
	PhOH	125.0	Et_3N	0.162	90.9
(10i)	PhOH	75.0	NaOPh	0.127	40.7
(13a)	PhOH	125.0	NaOPh	0.117	93.8
	PhOH	125.0	Et_3N	0.101	97.4 (±3.0)
(14a)	PhOH–benzene (1 : 1 w/w)	100.0	NaOPh	0.101	55 [f]
(16a)	PhOH–benzene (1 : 1 w/w)	50.0	Et_3N	0.110	39.8
(17b)	PhOH–toluene (1 : 1 w/w)	25.0	Et_3N	0.115	>6.43 [e]
		75.0	Et_3N	0.109	(>12.8 [e] inv.)
(17i)	PhOH–toluene (1 : 1 w/w)	50.0	Et_3N	0.103	43.0

[a] $[RX]_0$ = 0.05 or 0.10M. [b] Ref. 1. [c] Ref. 29. [d] Ref. 4. [e] Calculated on the basis of the optical purity of the alcohol, from which the starting substrate was prepared. [f] See text.

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of the substrate; the values for maximum rotations of optically pure compounds (Table 3) were employed.

In Table 4, the results are summarized for 1-phenylethyl trifluoroacetate (1i), 1-phenylpropyl *p*-nitrobenzoate (6a), 2-methyl-1-phenylpropyl *p*-nitrobenzoate (7a), five 2,2-dimethyl-1-phenylpropyl systems, (8a and i), (10a and i), and (13a), *p*-chlorodiphenylmethyl *p*-nitrobenzoate (14a), 1-methyl-1-phenylpropyl *p*-nitrobenzoate (16a), and two 1-ethyl-1,5-dimethylhexyl systems (17b and i), together with those previously reported for seven 1-phenylethyl systems (1a),[1] (3a),[1] (3b),[29] (3c),[4] (3d),[4] (3e),[4] and (5a).[1]

All the substrates shown in Table 4 give rise to phenyl ethers with retention of configuration accompanied with some racemization. The extent of retention for the aralkyl systems increases in the sequence (3a) [1] $<$ (6a) $<$ (7a) $<$ (10a), whereas the rate of phenolysis decreases in the order (3a) [1] $>$ (6a) $>$ (7a) $>$ (10a) (Table 1); the same trend in the comparison of the extent of retention and the phenolysis rate has been observed for *p*-substituted 1-phenylethyl *p*-nitrobenzoates (1a),[1] (3a),[1] and (5a),[1] and for *p*-substituted 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoates (8a), (10a), and (13a).

Among the percentage retentions, those for (5a), (10a), and (13a) are strikingly high (90.0,[1] 82.4, and 93.8%, respectively). In addition, when the phenolysis was carried out in the presence of triethylamine instead of sodium phenoxide, the extent of retention for (10a) and (13a) increases to 90.0 and 97.4%, respectively. The latter value for (13a) is the highest known in the phenolyses of a substrate without a group restricting configurational mobility.

Goering and his collaborators [10,12] have also reported *retentive* hydrolysis of several esters without a group imposing configurational restriction. In these hydrolyses an oxygen-18 labelling technique must be used to discriminate between nucleophilic substitution on an alkyl carbon from that on a carbonyl carbon. In contrast to the hydrolysis, the phenolysis products, phenyl ether and *C*-alkylated phenols, are unequivocal in that they are produced by nucleophilic substitution on saturated carbon. In the case of phenolysis of (13a) a considerable amount of the corresponding alcohol (13m), a product of carbonyl reaction, was obtained besides the phenolysis products (*cf.* footnote *f* in Table 1).

Winstein and Morse [30] have reported that some α-phenyl-substituted neopentyl systems (10b, c, and e), are solvolysed in acetic acid or in 80% aqueous ethanol with inversion of configuration accompanying some racemization and that they afford a small amount of rearranged product. However, in phenolyses of *p*-substituted 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoates (8a), (10a), and (13a), no rearranged products were obtained, indicating little contribution by a possible σ-participation by a methyl group in the neopentyl groups of (8), (10), and (13).[25]

In phenolysis of *p*-chlorodiphenylmethyl *p*-nitrobenzoate (14a) the phenyl ether (14j) was obtained with predominant racemization accompanied by slight (1.9%) retention after 10 half-lives. However, it was found that the ether (14j) racemized under the phenolysis condition and even in a chloroform solution or in a neat state at room temperature. Therefore, the net steric course for the formation of (14j) was estimated to be 55% at 0% conversion by a graphical extrapolation from the data at 23—52% conversion.

Phenolyses of 1-ethyl-1,5-dimethylhexyl compounds (17b and i) gave rise to partially *retained* phenyl ether (17j) in phenol–toluene (1 : 1 w/w) solvent; this is a unique example among aliphatic compounds without a configuration-holding group. With an increase in reaction temperature, the net steric course of the phenyl ether (17j) formation from (17b) changed from retention to partial inversion at 75°. The analogous change in the steric course has been known about the retentive halogenation of alcohols with hydrogen halides or thionyl halides.[31,32]

Steric Course of C-*Alkylated Phenol Formation*.—Steric courses of *C*-alkylated phenol formation from 1-phenylpropyl and 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoates (6a) and (10a) were examined; both *ortho*- and *para*-alkylated phenols were produced with inversion of configuration. The results are listed in Table 5 together with those previously reported for phenolyses of 1-phenylethyl systems (3a—h) [1,4,6,29] and 1-methylheptyl tosylate (15e).[14]

C-Alkylated phenol formation in the phenolyses of 12 compounds of four systems [(3), (6), (10), and (15)] proceeds with net inversion of configuration, except the case of *ortho*-alkylation of 1-phenylethyldiazonium chloride (3f), in which case *C*-alkylation proceeds with predominant racemization accompanied by slight retention.[4]

Although phenoxide ion attacks a chiral ion-pair intermediate from the rear to produce the phenyl ether or *C*-alkylated phenol with inversion of configuration,[1,3] a phenol molecule can also give rise to *C*-alkylated phenols with inversion by the back-side shielding of the ion-pair.[6] Conceivably, either or both can contribute to *C*-alkylation with inversion.

In phenolysis of (10a) phenoxide ion does not contribute to any product formation, and, consequently, the phenyl ether (10j) with strikingly high retention (Table 4) and *C*-alkylated phenols (10k) and (10l) with almost complete inversion (Table 5) are derived from only a phenol molecule. In view of these, a back-side shielded ion-pair [1,6] seems to be a key intermediate for phenyl ether formation with retention of configuration in phenolysis of (10a).

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[30] S. Winstein and B. K. Morse, *J. Amer. Chem. Soc.*, 1952, **74**, 1133.

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O- and C-Alkylation in Phenolysis.—The product distribution, *i.e.*, the ratio of phenyl ether and *ortho*- and *para*-alkylated phenol, was examined for phenolyses of nine substrates with various concentrations (0.05—0.50M) of added sodium phenoxide (or triethylamine) under conditions identical with those employed in rate measurements. The results are summarized in Table 6, along with those reported previously for 11 compounds.

TABLE 5

C-Alkylated phenol formation with inversion of configuration in the phenolysis of some aralkyl and alkyl systems

Compound [a]	Solvent	T/°C	Added base	$[\text{Base}]_0$/N or M	Net steric course, inversion (%)	
					o-RC_6H_4OH	*p*-RC_6H_4OH
(3a) [b]	PhOH	125.0	NaOPh	0.113	9.35	11.6
(3b) [c]	PhOH–benzene (1 : 1 w/w)	50.0	NaOPh	0.109	14.4	31.2
(3b) [d]	2,6-Xylenol	125.0	Et_3N	0.124		20.0
(3b) [d]	2,6-$Pr^i{}_2C_6H_3OH$	125.0	Et_3N	0.124		$\leqslant$14.6
(3c) [e]	PhOH–CH_3CN (1 : 1 w/w)	40.0	Et_3N	0.419	53.6	50.6
(3d) [e]	PhOH	150.0	NaOPh	0.093 3	0.00	11.6
(3e) [e]	PhOH–CH_3CN (1 : 1 w/w)	20—35	$CO(NH_2)_2$	0.234	8.67 [f]	15.7 [f]
(3f) [e]	PhOH–H_2O [g]	−8 to +2			(1.30 [f] ret.)	29.2 [f]
(3g) [e]	PhOH–$ClCH_2CH_2Cl$ (1 : 1 w/w)	16—25			9.00 [f]	4.33 [f]
(3h) [e,h]	PhOH	75.0			10.2	15.9
(6a)	PhOH	125.0	NaOPh	0.110	8.3	9.8
(10a)	PhOH	125.0	NaOPh	0.114	99 (±11)	115 (±12)
(15e) [i]	PhOH–benzene (1 : 1 w/w)	75.0	Et_3N	0.101	101 (±7)	65.7 (±4.5)

[a] $[RX]_0$ = 0.1M. [b] Ref. 1. [c] Ref. 29. [d] Ref. 6. [e] Ref. 4. [f] Calculated on the basis of the optical purity of starting (3b), (3; $R^4 = NH_2$), and (3; R^4 = OEt), respectively. [g] The composition of the mixture changed from 79 : 21 to 66 : 34 (w/w) during the reaction. [h] Protonated 4-methyl-4-(1-phenylethyl)2,6-di-t-butylcyclohexadienone. [i] Ref. 14.

TABLE 6

Product distributions in the phenolysis of some aralkyl and alkyl systems in the presence of sodium phenoxide or triethylamine

Compound [a]	Solvent	T/°C	$[\text{NaOPh}]_0$/N	Yield (%)			
				Ether	*o*-RC_6H_4OH	*p*-RC_6H_4OH	Olefin
(1a) [b]	PhOH–benzene (1 : 1 w/w)	25.0	0.108	59.8	4.2	1.9	31.0
(3a) [b]	PhOH	125.0	0.113	63.5	8.8	7.0	20.0
(3b) [c]	PhOH–benzene (1 : 1 w/w)	50.0	0.109	56.3	9.8	10.3	
(3c) [d]	PhOH–CH_3CN (1 : 1 w/w)	40.0	0.419 [e]	55.7	16.2	11.1	
(3d) [d]	PhOH	150.0	0.093 3	40.0	11.4	8.2	
(3e) [d]	PhOH–CH_3CN (1 : 1 w/w)	20—35	0.234 [f]	20.5	6.2	12.3	
(3f) [d]	PhOH–H_2O	−8 to +2		0.15 [g]	1.2 [g]	3.2 [g]	
(3g) [d]	PhOH–$ClCH_2CH_2Cl$ (1 : 1 w/w)	16—25		0.0 [g]	34.8 [g]	55.2 [g]	
(3h) [h]	PhOH	75.0		12.2	18.6	48.6	
(5a) [b]	PhOH	125.0	0.101	8.8	0.4	3.2	55.0
(6a)	PhOH	125.0	0.110	44.9	6.5	2.8	
(7a)	PhOH	125.0	0.110	57.3	4.5	3.6	
(8a)	PhOH	125.0	0.125	53.4 [i]	15.7	31.3	
(10a)	PhOH	125.0	0.114	72.6	8.3	18.6	
(13a) [j]	PhOH	125.0	0.117	0.61	2.0	3.5	
(14a)	PhOH–benzene (1 : 1 w/w)	100.0	0.101	73.8	2.8	1.9	
(16a)	PhOH–benzene (1 : 1 w/w)	50.0	0.110 [e]	34.9	0.1	0.1	52.0 [k]
(17a) [l]	PhOH	125.0	0.103	13.5	0.1	0.02	84.0 [m]
(17b)	PhOH–toluene (1 : 1 w/w)	25.0	0.115 [e]	25.8	0.4	0.05	72.5 [m]
(17i)	PhOH–toluene (1 : 1 w/w)	50.0	0.103 [e]	13.2	0.1	0.1	

[a] $[RX]_0$ = 0.10M. [b] Ref. 1. [c] Ref. 29. [d] Ref. 4. [e] In the presence of Et_3N (M) instead of NaOPh. [f] In the presence of $CO(NH_2)_2$ (M) instead of NaOPh. [g] See footnote *f* in Table 5. [h] See footnote *g* in Table 5. [i] The phenyl ether has rearranged partly to the aralkylated phenols under the phenolysis conditions. [j] After 720 h, (13m) (60.0% yield; with 100% retention of configuration) and phenyl *p*-nitrobenzoate (49% yield) were obtained besides the phenolysis products: unchanged (13a) (29.0% recovery; 0.1% racemization) was recovered. [k] A mixture of three isomers (*ca.* 2 : 2 : 1) by g.l.c. [l] Ref. 14. [m] A mixture of four isomers by g.l.c.

There are two kinds of nucleophiles in the phenolysis media with added sodium phenoxide (or triethylamine), *i.e.*, phenol and phenoxide ion (or phenoxide ion-pair); the extrapolated value for product distribution at zero phenoxide concentration can be considered as the distribution for phenol alone.[13,29,33]

As previously reported,[34] a linear free energy relationship (stability–selectivity relationship; correlation coefficient 0.99 [34]) between phenolysis rate (k_t) of nine *p*-nitrobenzoates [(1a), (3a), (5a)—(7a), (10a), (14a), (16a), and (17a)] and the selectivity of *O*- and *C*-alkylation by phenol during attack on the phenolysis intermediate has been observed.

Ratio of Polarimetric and Titrimetric Rate Constants.—Polarimetric rate constants, k_p, for phenolyses of 1-phenylpropyl *p*-nitrobenzoate (6a), 2-methyl-1-phenylpropyl *p*-nitrobenzoate (7a), four 2,2-dimethyl-1-phenyl-

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TABLE 7

Ratios of polarimetric to titrimetric rate constants in the phenolysis of aralkyl and alkyl systems in the absence of added base

Compound [a]	Solvent	T/°C	$k_p°/s^{-1}$ [b]	$k_p° : k_t°$ ratio	Kinetic feature [c]
(1a) [d]	PhOH–benzene (1 : 1 w/w)	25.0	1.14×10^{-4}	1.90	A
(3b) [e]	PhOH–benzene (1 : 1 w/w)	25.0	3.48×10^{-4}	5.85	A
(8a)	PhOH	125.0	5.90×10^{-3}	2.01	A
(8i)	PhOH	75.0	1.30×10^{-1}	2.10	B
(10a)	PhOH	125.0	1.42×10^{-6}	1.67	B
(15e) [f]	PhOH–benzene (1 : 1 w/w)	75.0	2.00×10^{-4}	1.18	B
(17a) [f]	PhOH–benzene (1 : 1 w/w)	100.0	1.03×10^{-3}	1.09	B
(17b)	PhOH–toluene (1 : 1 w/w)	25.0	$(1.99 \pm 0.09) \times 10^{-4}$	1.59	B
(3a) [d]	PhOH	125.0	2.23×10^{-4}	1.30	C
(6a)	PhOH	125.0	5.32×10^{-5}	1.32	C
(7a)	PhOH	125.0	2.43×10^{-5}	1.19	C
(14a)	PhOH–benzene (1 : 1 w/w)	100.0	2.63×10^{-4}	1.60	C
(16a)	PhOH–benzene (1 : 1 w/w)	50.0	1.29×10^{-4}	1.39	C
(5a) [d]	PhOH	125.0	$(6.77 \pm 0.67) \times 10^{-6}$	1.04 ± 0.10	D
(10i)	PhOH	75.0	1.60×10^{-5}	0.988	D
(17i)	PhOH–toluene (1 : 1 w/w)	50.0	3.42×10^{-4}	1.00	D

[a] $[\text{Compound}]_0 = 0.100\text{M}$. [b] Accurate to within ±3%, unless otherwise noted. [c] See Figure 1. [d] Ref. 1. [e] Ref. 3a. [f] Ref. 14.

propyl systems (8a and i) and (10a and i), *p*-chlorodiphenylmethyl *p*-nitrobenzoate (14a), 1-methyl-1-phenylpropyl *p*-nitrobenzoate (16a), and 1-ethyl-1,5-dimethylhexyl chloride (17b) and trifluoroacetate (17i) were determined under conditions identical with those of the titrimetric rate measurements in the presence of various concentrations of base. The graphically extrapolated values ($k_p°$) for zero base concentration are summarized in Table 7 along with those previously reported for 1-phenylethyl systems,[1,3a] 1-ethyl-1,5-dimethylhexyl *p*-nitrobenzoate (17a),[14] and 1-methylheptyl tosylate (15e).[14] The values for the $k_p° : k_t°$ ratio are in the range of 1.0—2.1, except 5.85 for 1-phenylethyl chloride (3b).[3a]

The polarimetric rate constant is usually a better scale for the intrinsic ionization constant. Therefore, the stability–selectivity relationship[34] may be expressed with a line with better linearity when k_p values are used instead of k_t values, though this has not been carried out because of the scarcity of the k_p data.

Mechanism of Phenolysis.—Provided that there is no normal salt effect in the phenolysis, the features of dependence of k_p and k_t on base concentration can be classified into four patterns A—D (Figure 1).

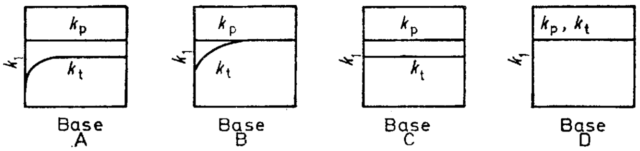


FIGURE 1 Four patterns of the dependence of k_p and k_t on the base concentration

The k_t lines in patterns A and B increase with increase in the concentration of added base. This means that the phenoxide ion, derived from the base added to phenolic solvent, reacts with the phenolysis intermediate. As discussed in the cases of (1a)[1] and (3b),[3a] pattern A indicates that there are two successive intermediates and that the phenoxide ion does not attack the first intermediate but the second. As it is pointed out on the phenolyses of (15e) and (17a),[14] in pattern B the phenoxide ion reacts with the first phenolysis intermediate.

The eight compounds which have been examined for dependence of k_p and k_t upon base concentration belong to pattern A or B (Table 7).

Reflecting the rise in k_t in the patterns A and B, a

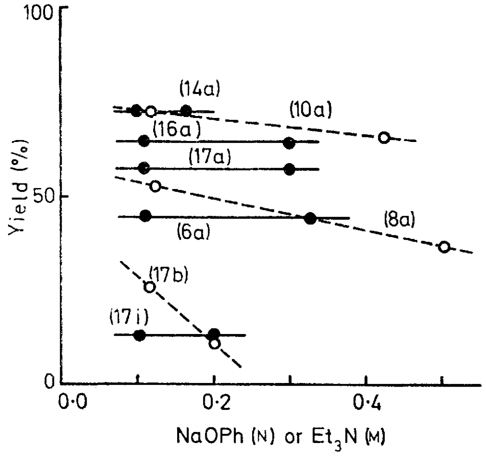


FIGURE 2 Effect of base concentration on the yield (%) of phenyl ether in phenolyses of several aralkyl and alkyl compounds

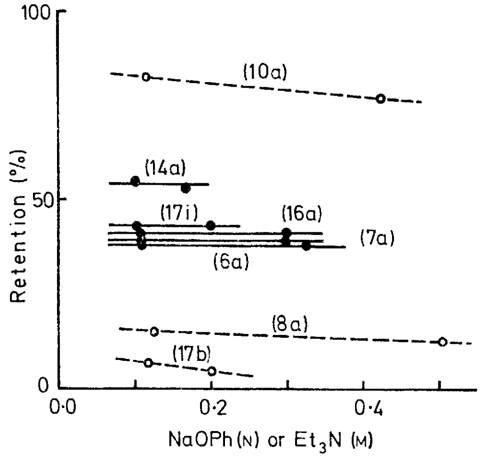
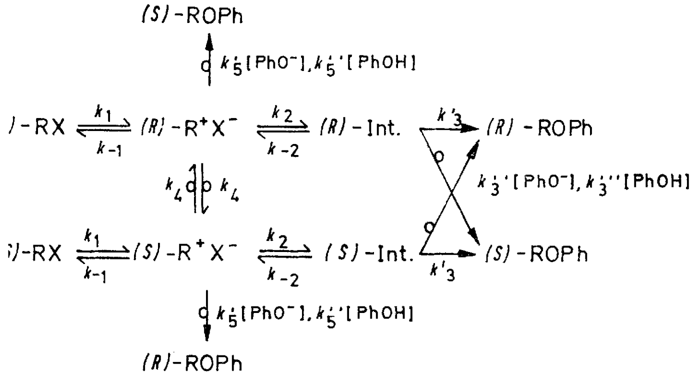


FIGURE 3 Effect of base concentration on the extent (%) of retention of configuration for phenyl ether formation in phenolyses of several aralkyl and alkyl compounds

decrease in the yield of the phenyl ether formation (Figure 2) and a decrease in the extent of retention of the phenyl ether (Figure 3) are observed with increase in base concentration in phenolyses of (8a), (10a), and (17b). The same trend in the yield and the extent of retention has been observed in the phenolysis of (1a).[1] From these features shown in Figures 2 and 3 it is indicated for phenolyses with patterns A and B that phenol predominantly gives the phenyl ether with retention of configuration, whereas the phenoxide ion produces less phenyl ether with inversion of configuration.

The eight compounds the kinetic features of which have been proved to belong to pattern C or D are also listed in Table 7. In addition, it is observed in the phenolyses of (6a), (7a), (14a), (16a), and (17i) (pattern C or D) that addition of sodium phenoxide (or triethylamine) gives rise to virtually no variation in the yield and extent of retention for phenyl ether formation (Figures 2 and 3). The same tendency in the yield and extent of retention has been observed in the phenolysis of (3a) and (5a).[1]



SCHEME

From the features of these phenolyses, which are classified as pattern C or D, no phenoxide ion but only phenol contributes to the formation of the phenyl ether in C and D.

Furthermore, it is also observed for the compounds which belong to pattern C (Table 7) that with progress of phenolysis the extent of retention for phenyl ether formation decreases and the racemization of recovered substrate increases. This is a consequence expected from the gap between k_t and k_p in pattern C.

It has been observed in the phenolysis of (5a) [1] that the recovered substrate did not show any racemization as a reflection of the pattern D. The same result is observed in the phenolysis of (13a). Although the polarimetric rate measurement has not been carried out for compound (13a), it is probable that (13a) follows pattern D.

Although complex generalized schemes, which take the retentive product into consideration, have been proposed by several investigators,[7,8,35] another generalized phenolysis mechanism (Scheme),[1] which we have proposed for 1-phenylethyl, 1-methylheptyl, and 1-ethyl-1,5-dimethylhexyl systems, can also explain all the results observed in the phenolyses treated in this study.

In the Scheme the second intermediate (Int.) is the key intermediate for retentive phenolysis; the retained phenyl ether is derived only from the second intermediate (Int.) which has a structure preferably depicted by a four-centre or back-side shielding model.[3,6]

According to the Scheme, the total rate expressions for k_p and k_t are given in equations (1) and (2).

$$k_p = \frac{k_1}{1 + \dfrac{k_{-1}}{2k_4 + k_5 + k_2k_3/(k_3 + k_{-2})}} \qquad (1)$$

$$k_t = \frac{k_1}{1 + \dfrac{k_{-1}}{k_5 + k_2k_3/(k_3 + k_{-2})}} \qquad (2)$$

$$k_3 = k_3' + k_3''[\mathrm{PhO^-}] + k_3'''[\mathrm{PhOH}]$$
$$k_5 = k_5'[\mathrm{PhO^-}] + k_5''[\mathrm{PhOH}]$$

In order to express the simplest reaction scheme for each substrate, the rate constants which can be neglected in the generalized scheme are tabulated in Table 8.

TABLE 8

Possible mechanisms for the phenolyses with patterns A—D

Kinetic feature pattern	Rate constants which can be neglected in the Scheme	Compound
A	k_5'	(1a), (3b), (8a)
B	k_3''	(8i), (10a), (17b)
B	k_3'' and k_3'	(15e), (17a)
C	k_5' and k_3''	(3a), (6a), (7a), (14a), (16a)
D	k_5', k_3'', and k_4	(5a), (10i), (13a), (17i)

EXPERIMENTAL

^{1}H N.m.r. spectra were taken with a Hitachi model R24 60 MHz instrument, i.r. spectra with a Hitachi model 215 spectrophotometer, and g.l.c. was performed with a Hitachi model 023-6003 instrument with an ionization detector. Optical rotations were measured with a JASCO DIP-SL polarimeter. Microanalyses were performed by the Elemental Analysis Centre, Kyoto University.

Materials.—The alcohols (2m),[36] (4m),[36] (6m),[37] (7m),[38] (10m),[39] (11m),[40] (12m),[40] (14m),[41] and (16m)[42] were prepared by known methods and resolved by the use of chloroform–acetone (1 : 3 v/v) as solvent. 2,2-Dimethyl-1-(*p*-methoxyphenyl)propan-1-ol (8m) [22,43] and (13m) were resolved,

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using strychnine. 2,2-*Dimethyl*-1-(p-*nitrophenyl*)*propan*-1-*ol* (13m), m.p. 83.0—84.0°, b.p. 160° at 12 mmHg, $\nu_{max.}$ (CCl_4) 3 640, 1 600, 1 510, and 1 340 cm^{-1}, τ (CCl_4) 1.75—2.60 (4 H, m, ArH), 5.60 (s, methine H), 7.70 (s, OH), and 9.10 (9 H, s, CH_3) (Found: C, 62.9; H, 7.0. $C_{11}H_{15}NO_3$ requires C, 63.1; H, 7.25%), was prepared together with 2,2-*dimethyl*-1-(o-*nitrophenyl*)*propan*-1-*ol*, b.p. 150—155° at 3 mmHg, $\nu_{max.}$ (CCl_4) 3 640, 1 600, 1 510, and 1 340 cm^{-1}, τ (CCl_4) 1.9—2.6 (4 H, m, ArH), 4.70 (s, methine H), 7.70 (s, OH), and 9.11 (9 H, s, CH_3) (Found: C, 63.3; H, 7.3. $C_{11}H_{15}NO_3$ requires C, 63.1; H, 7.25%), by nitration of (10m). The nitration of (*R*)-(+)-(10m), $[\alpha]_D^{28}$ +13.6° (benzene), gave (+)-(13m), 32.5% yield, $[\alpha]_D^{29}$ +16.1° (benzene), and its *o*-nitro-analogue, 21.0% yield, $[\alpha]_D^{29}$ −21.1° (benzene). 1-Ethyl-1,5-dimethylhexanol (17m) was prepared by hydrogenation of linalool (Shiono Kôryô).

TABLE 9

B.p.s, m.p.s, spectral data, and elemental compositions for *p*-nitrobenzoates and trifluoroacetates

Compound	B.p. (°C) [m.p. (°C)] [a]	Spectral data		Elemental composition (%)			
				Found		Required	
		$\nu_{max.}$/cm^{-1} [b]	Chemical shift (τ) [b]	C	H	C	H
(7a)	[82.1—83.0]	1 720	8.9 (d, 6 H)	68.3	5.9	68.2	5.7
(8a)	[84.2—85.0]	1 240, 1 720	6.4 (s, 3 H), 9.0 (s, 9 H)	66.5	6.2	66.5	6.2
(9a)	[127.5—128.4]	1 730	8.4 (s, 3 H), 9.0 (s, 9 H)	69.65	6.55	69.7	6.45
(10a)	[118.6—119.0]	1 730	4.3 (s, 1 H), 9.0 (s, 9 H)	68.9	6.3	69.0	6.1
(11a)	[142.7—143.4]	1 730	4.8 (s, 1 H), 9.0 (s, 9 H)	62.1	5.25	62.15	5.2
(12a)	[147.8—148.6]	1 730	4.4 (s, 1 H), 9.0 (s, 9 H)	62.1	5.3	62.15	5.2
(13a)	[133.4—134.3]	1 270, 1 340, 1 720	9.0 (s, 9 H)	60.5	5.3	60.3	5.1
(6i)	84—89 at 3 mmHg	1 780	2.7—3.3 (m, 5 H)	57.2	4.9	56.9	4.8
(7i)	96—108 at 4 mmHg	1 780	8.9 (d, 6 H)	58.7	5.4	58.5	5.3
(8i)	155—160 at 2 mmHg	1 250, 1 790	6.4 (s, 3 H)	58.0	6.0	57.9	5.9
(10i)	120—122 at 3 mmHg	1 780	4.4 (s, 1 H), 9.0 (s, 9 H)	59.8	6.0	60.0	5.8
(13i)	110—120 at 0.04 mmHg	1 280, 1 350, 1 780	9.0 (s, 9 H)	51.2	4.8	51.2	4.6
(14i)	85—91 at 4 mmHg	1 780	2.3—2.9 (m, 9 H)	57.2	3.3	57.3	3.2
(17i)	48—52 at 3 mmHg	1 780		56.9	8.4	56.7	8.3

[a] Uncorrected. [b] In CCl_4.

TABLE 10

Synthesis of optically active aralkyl phenyl ethers (ROPh) from the respective aralkyl alcohols (ROH)

Optical rotation of ROH(°) [a] (A)	Optical rotation of $ROCOCF_3$(°) [a] (B)	(B) : (A)	$[ROCOCF_3]_0$ /M	$[NaOPh]_0$ /N	*T*/°C	*t*/h	Optical rotation of ROPh(°) [a] (C)	Yield of ROPh (%) [b]	(C) : (B)
(6m) +13.97 [c]	(6i) +59.14	4.23 (4.24) [d]	0.103	0.205	25.0	18	(6j) +11.74 [c]	13.5	0.199 (0.198) [d]
(7m) −22.0 [e]	(7i) −48.8	2.22 (2.22) [d]	0.100	0.209	100.0	42	(7j) −10.26	34.0	0.210 (0.214) [d]
(8m) −6.54	(8i) −26.6	4.07 (4.06) [d]	0.100	0.204	50.0	41	(8j) −1.43	17.3	0.053 8 (0.053 3) [d]
(10m) +21.03	(10i) +66.3	3.15 (3.15) [d]	0.100	0.442	100.0	21	(10j) +19.7	4.25	0.297 (0.296) [d]
(13m) +13.6	(13i) +43.2	3.18 (3.18) [d]	0.100	0.120	125.0	22	(13j) +0.340	40.0	0.007 87 (0.007 85) [d]
(14m) +2.73	(14i) −1.63	0.597 (0.599) [d]	0.100	0.301	25.0	0.2	(14j) −1.03	1.3	0.632
			0.10	0.30	25.0	0			1.0 [f] (1.0) [d,f]

[a] $[\alpha]_D$ (*c* 1—35, benzene). [b] Based on $ROCOCF_3$. [c] α_D (neat, 1 dm). [d] The mean value of duplicate or triplicate measurements. [e] $[\alpha]_D$ (*c* 6.11, ether). [f] Extrapolated from the values 0.632, 0.396, 0.234, 0.049 6, and 0.011 6, for longer reaction times, 0.2, 0.5, 1.0, 2.0, and 25 h, respectively.

Aralkyl *p*-nitrobenzoates, (2a),[36] (4a),[36] (6a),[44] (14a),[45] and (16a),[32] were prepared by known methods. Other aralkyl *p*-nitrobenzoates (7a)—(13a) were prepared from the corresponding alcohols and *p*-nitrobenzoyl chloride;[1] the m.p.s, some spectral data, and elemental compositions are tabulated for seven new *p*-nitrobenzoates in Table 9.

Aralkyl trifluoroacetates (6i), (7i), (8i), (10i), (13i), and (14i), and 1-ethyl-1,5-dimethylhexyl trifluoroacetate (17i) were prepared from the respective alcohols and trifluoroacetic anhydride;[1] physical data are summarized for seven new trifluoroacetates in Table 9.

Optically active phenyl ethers (6j), (7j), (8j), (10j),

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[44] H. Kropf, J. Golbrich, and M. Ball, *Tetrahedron Letters*, 1969, 3427.

[45] H. L. Goering and J. F. Blanchard, *J. Amer. Chem. Soc.*, 1954, **76**, 5405.

(13j), and (14j), were synthesized by the S_N2 reaction of the trifluoroacetate with sodium phenoxide in DMF as solvent; the results are summarized in Table 10 and the physical data are tabulated in Table 11.

Optically active 1-methyl-1-phenylpropyl phenyl ether (16j), $[\alpha]_D^{20}$ −4.40° (benzene), was synthesized in 20.0% yield by the reaction of the potassium salt of (16m), $\alpha_D^{19.5}$ −6.06° (neat, 1 dm), with bromobenzene by a previously reported method.[33]

Optically active phenols (6k and l) and (10k and l) were prepared by phenolyses of (6a), $[\alpha]_D^{28}$ −21.2° (benzene), and (10a), $[\alpha]_D^{25}$ −103.0° (benzene), respectively, in the presence of toluene-*p*-sulphonic acid at 125° in a manner similar to that reported earlier.[4,14,29] The other alkylated phenols (7k and l), (8k and l), (14k and l), and (16k and l), were synthesized by a similar method. Their physical data are listed in Table 11.

TABLE 11

B.p.s, spectral data, and elemental compositions for phenolysis products

Compound	B.p. (°C) at *p*/mmHg	Spectral data		Elemental composition (%)			
				Found		Required	
		$\nu_{max.}$/cm^{-1} [a]	Chemical shift (τ) [a]	C	H	C	H
(6j)	140—145 at 1	1 240	2.8—3.4 (m, 10 H)	84.9	7.6	84.9	7.6
(6k)	160—175 at 3	3 620	5.15 (s, 1 H)	85.0	7.7	84.9	7.6
(6l)	185—190 at 3	3 350, 3 620	4.85 (s, 1 H)	85.0	7.7	84.9	7.6
(7j)	161—165 at 1	1 240	8.9 (d, 6 H)	84.8	8.0	84.9	8.0
(7k)	180—182 at 4	3 620	9.0 (d, 6 H), 5.39 (s, 1 H)	84.8	8.0	84.9	8.0
(7l)	198—200 at 4	3 350, 3 620	9.1 (d, 6 H), 4.76 (s, 1 H)	85.05	8.2	84.9	8.0
(8j)	170—180 at 3	1 240, 1 250	6.25 (s, 3 H), 9.00 (s, 9 H)	80.0	8.25	79.95	8.2
(8k)	200 at 2	1 250, 3 610	5.26 (s, 1 H)	80.2	8.4	79.95	8.2
(8l)	200 at 2	1 250, 3 400, 3 610	5.20 (s, 1 H)	80.15	8.2	79.95	8.2
(10j)	180—200 at 3	1 240	9.00 (s, 9 H)	84.95	8.35	84.95	8.4
(10k)	190—200 at 3	3 620	5.01 (s, 1 H), 9.00 (s, 9 H)	84.95	8.5	84.95	8.4
(10l)	190—200 at 3	3 400, 3 620	4.90 (s, 1 H), 9.00 (s, 9 H)	84.9	8.3	84.95	8.4
(13j)	170—180 at 0.01	1 240, 1 340, 1 520	9.00 (s, 9 H)	71.65	6.8	71.55	6.7
(13k)	200—230 at 0.01	1 340, 1 520, 3 620	4.40 (s, 1 H)	71.7	6.9	71.55	6.7
(13l)	220—250 at 0.01	1 340, 1 520, 3 400	4.31 (s, 1 H)	71.8	6.9	71.55	6.7
(14j)	218—225 at 5	1 220	2.4—3.0 (m, 14 H)	77.15	5.2	77.4	5.15
(14k)	209—220 at 3	3 650	5.10 (s, 1 H)	77.55	5.2	77.4	5.15
(14l)	223—226 at 3	3 400, 3 650	4.89 (s, 1 H)	77.55	5.2	77.4	5.15
(16j)	150—155 at 3	1 230	2.6—3.6 (m, 10 H)	85.05	8.15	84.9	8.0
(16k)	160—165 at 3	3 620	5.30 (s, 1 H)	84.85	8.15	84.9	8.0
(16l)	165—170 at 2	3 400, 3 620	4.90 (s, 1 H)	85.0	8.1	84.9	8.0

[a] In CCl_4.

TABLE 12

Determination of maximum rotations for arylalkyl-methanols by ^1H n.m.r. spectroscopy [a] with $Eu(facam)_3$ [b]

Compound	Optical rotation of ROH(°)	Proton	Shifts for enantioners (p.p.m.) [c]	Peak area ratio	Optical purity (%)	Maximum rotation °	
							Mean value [d]
(6m)	−16.4 [e]	α-H	1.06; 1.14	33.0 : 18.7	27.7	59.2 [e]	59.2 [e,f]
(7m)	+13.5 [e]	α-H	1.12; 1.22	6.30 : 18.3	48.8	27.7 [e]	27.3 [e]
	+33.0 [g]					67.6 [g]	67.6 [g,h]
(8m)	−6.19 [i]	α-H	0.72; 0.78	10.3 : 6.40	23.3	26.6 [i]	27.0 [i]
(10m)	+17.3 [i]	α-H	1.22; 1.30	4.00 : 17.9	63.5	27.2 [i]	27.4 [i,j]
(13m)	+13.6 [k]	*o*-H	1.28; 1.33	16.0 : 6.90	39.7	34.3 [k]	34.8 [k]

[a] Taken with a 60 MHz n.m.r. instrument. [b] Tris-[3-trifluoroacetyl-(+)-camphorato]europium(III) (0.1—0.2M) shift reagent: ROH molar ratios were in the range 0.5—0.9. Downfield shift from the original position for *S*- and *R*-enantiomers (see text). [d] For duplicate or triplicate measurements. [e] α_D (neat, 1 dm). [f] Literature value for the highest rotation: 29.2° (neat, 1 dm) (ref. 35). [g] $[\alpha]_D$ (*c* 4.1, ether). [h] Literature value for the highest rotation: 49° (*c* 4.3, ether) (footnote *c* in Table 3). [i] $[\alpha]_D$ (*c* 8—25, benzene). [j] Literature value for the highest rotation: 27.3° (*c* 9, benzene) (G. Vavon and B. Angelo, *Compt. rend.*, 1947, 1435). [k] $[\alpha]_D$ (*c* 12.5, chloroform).

Optically active *ortho*- and *para*-alkylated phenols (6k and l) and (10k and l) were oxidized to the respective carboxylic acids (6o) and (10o) [27] by potassium permanganate.[3b,14,28] From (6k) (0.900 g), $[\alpha]_D^{27}$ −0.306° (benzene), and (6l) (0.736 g), $[\alpha]_D^{29}$ +0.188° (benzene), (*R*)-(−)-(6o) (0.103 g), $[\alpha]_D^{31}$ −1.27 ± 0.06° (ethanol), and (*S*)-(+)-(6o) (0.130 g), $[\alpha]_D^{31}$ +0.690 ± 0.024° (ethanol), were obtained, respectively. From (10k) (0.384 g), $[\alpha]_D^{25}$ −1.86° (benzene), and (10l) (1.46 g), $[\alpha]_D^{25}$ −0.310° (benzene), were obtained (*R*)-(−)-(10o) (0.168 g), $[\alpha]_D^{17}$ −1.40 ± 0.021° (chloroform), and (*S*)-(+)-(10o) (0.350 g), $[\alpha]_D^{20}$ +0.236 ± 0.043° (chloroform), respectively.

The maximum rotations for the aralkylphenols were estimated on the basis of those for optically pure (*S*)-(6o), $[\alpha]_D$ +78.5° (ethanol),[27] and (*R*)-(10o), $[\alpha]_D$ −62.9° (chloroform).[27] The results are tabulated in Table 3.

Isolation of Phenolysis Products.—The previous procedure [1] was followed. As a representative run, isolation of the products in phenolysis of (10a) is described in the following. A solution (77 ml) of (*R*)-(−)-(10a) (2.41 g), $[\alpha]_D^{25}$ −103.0° (benzene), in phenol containing sodium phenoxide (0.114N) was kept at 125° for 599 h. After work-up, (*R*)-(−)-(10j) (1.342 g), $[\alpha]_D^{21}$ −9.73° (benzene), (*S*)-(+)-(10k) (0.153 g), $[\alpha]_D^{23}$ +38.3° (benzene), and (*S*)-(−)-(10l) (0.344 g), $[\alpha]_D^{20}$ −43.9° (benzene), were obtained.

The structure of phenolysis product was assigned on the basis of the spectral data and elemental compositions (Table 11).

Rate Measurements.—The usual aliquot or sealed ampoule technique [1] was employed for titrimetric and polarimetric rate measurements. The rate data are summarized in Tables 1, 2, and 7.

N.m.r. Measurements for Determination of Optical Purity.—The ^{1}H n.m.r. shift reagent method [1] was followed, using tris[trifluoroacetyl-(+)-camphorato]europium(III) as shift reagent. The results are summarized in Table 12.

We thank the Ministry of Education for a Grant-in-Aid for Scientific Research and Dr. T. Kunishige, Shiono Kôryô Co., Ltd., Osaka, for kindly donating to us optically active linalool.

[5/2038 *Received, 20th October*, 1975]