Phenolysis and Competing Methanolysis of Optically Active 1-Phenylethyl Chloride in Sterically Hindered 2,6-Dialkylphenol Solvents

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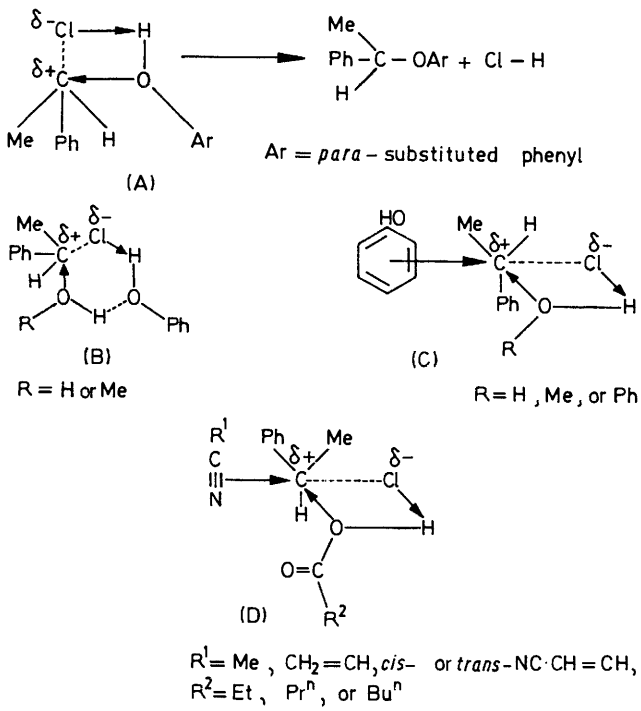
Phenolysis of optically active 1-phenylethyl chloride was carried out in 2,6-dimethyl- (I), 2,6-di-isopropyl- (II), 2,6-di-t-butyl- (III), or 2,6-di-t-butyl-4-methyl-phenol (IV) as solvent at 125°. Rates of S_N1 phenolysis decreased in the sequence (I) > (II) > (III) > (IV) (relative rates 511 : 6·46 : 1·00 : 0·038). In solvents (I) and (II) the corresponding aryl ethers and *p*-1-phenylethylphenols were obtained; in solvents (III) and (IV) no aryl ether was obtained, whereas 4-(1-phenylethyl)-2,6-di-t-butylcyclohexadienone and its 4-methyl derivative were isolated. The aryl ethers showed net retention of configuration, whereas all *C*-alkylated products in solvents (I)—(IV) underwent net inversion. Phenolyses in solvents (I)—(IV) containing 0·5—5% methanol gave methyl 1-phenylethyl ether with net retention, whereas methanolysis in methanol–benzene afforded the methyl ether with net inversion. The results can be accounted for by shielding of the ion-pair S_N1 intermediate from the rear by solvent phenol.

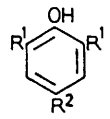
ONE of the few cases in which S_N1 reactions proceed with net retention of configuration in the absence of a neighbouring group is solvolysis of 1-phenylethyl chloride in *para*-substituted phenols giving the corresponding aryl ethers with 20—50% net retention.[1] To account for this retention, we have suggested that phenolysis involves a four-centre intermediate (A).[1b,2,3,†]



Furthermore, competitive solvolyses of 1-phenylethyl chloride in phenol–water (or –methanol) yield 1-phenylethyl alcohol [4] (or methyl ether [5]) and phenyl 1-phenylethyl ether, both with net retention (6—19%).[4,5] For this competing retentive hydrolysis (or methanolysis) we have proposed the cyclic intermediate (B).[4,5] However, we could not exclude the possibility that phenol shields the back-side of the ion-pair intermediate thus assisting front-side attack by water (or methanol) and even by phenol [intermediate (C)].[4,5]

Similar back-side shielding by alkyl cyanides or nitromethane has been suggested for retentive hydrolysis, butyrolysis, propionolysis, and valerolysis of optically active 1-phenylethyl chloride in aqueous acrylonitrile [6] and in carboxylic acid–nitrile and –nitromethane mixtures [intermediate (D)].[7]

In order to obtain data on possible shielding effects in S_N1 phenolysis we have carried out the phenolysis of



(I) $R^1 = Me$, $R^2 = H$
(II) $R^1 = Pr^i$, $R^2 = H$
(III) $R^1 = Bu^t$, $R^2 = H$
(IV) $R^1 = Bu^t$, $R^2 = Me$

optically active 1-phenylethyl chloride at 125° in pure 2,6-dimethyl- (I), 2,6-di-isopropyl- (II), 2,6-di-t-butyl- (III), and 2,6-di-t-butyl-4-methylphenol (IV) or containing a small amount of methanol.

When methanol was added to the hindered phenol solvents methanolysis was favoured over phenolysis because of steric hindrance by the 2- and 6-alkyl groups.[‡]

† Raber *et al.*[2] have recently proposed the intermediate $R^+ \cdots O{-}H \cdots X^- \cdots HOS$, instead of the four-centre structure (A). Results so far obtained do not allow a choice between the two formulations.

‡ It is known [8] that methanol is a slightly more effective catalyst than phenol in the acetolysis of t-butyl bromide.

[1] (*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.

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

[3] Solvolyses of 1-phenylethyl chloride in common solvolytic solvents yield net inversion: see (*a*) E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1937, 1201; (*b*) J. Steigman and L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 2536; (*c*) K. Okamoto, N. Uchida, S. Saito, and H. Shingu, *Bull. Chem. Soc. Japan*, 1966, **39**, 307; P. B. D. de la Mare, D. M. Hall, and E. Mauger, *Rec. Trav. chim.*, 1968, **87**, 1394; (*d*) V. J. Shiner, jun., S. R. Hartshorn, and P. C. Vogel, *J. Org. Chem.*, 1973, **38**, 3604.

[4] (*a*) K. Okamoto, M. Hayashi, and H. Shingu, *Bull. Chem. Soc. Japan*, 1966, **39**, 408; (*b*) K. Okamoto, M. Hayashi, K. Komatsu, and H. Shingu, *ibid.*, 1967, **40**, 624.

[5] K. Okamoto, K. Komatsu, and H. Shingu, *Bull. Chem. Soc. Japan*, 1967, **40**, 1677.

[6] K. Okamoto, K. Komatsu, and H. Shingu, *Bull. Chem. Soc. Japan*, 1966, **39**, 2785.

[7] K. Okamoto, I. Nitta, M. Dohi, and H. Shingu, *Bull. Chem. Soc. Japan*, 1971, **44**, 3220.

[8] K. Okamoto and H. Shingu, *Bull. Chem. Soc. Japan*, 1961, **34**, 1131.

If this is the case, retentive methanolysis *via* the cyclic intermediate (B) would be suppressed, whereas back-side shielding [intermediate (C)] would still be operative in spite of the steric hindrance of the alkyl groups which would have little effect on the shielding ability of the phenol molecule.

This paper reports that competing methanolysis of optically active 1-phenylethyl chloride is retentive in the hindered solvents (I)—(IV) and affords methyl 1-phenylethyl ether. We propose a mechanistic interpretation of these results in terms of back-side shielding [intermediate (C)].

RESULTS AND DISCUSSION

Rate and Product Distribution in Phenolysis of 1-Phenylethyl Chloride in Some Hindered Phenols as Solvent.—The phenolysis of 1-phenylethyl chloride was carried out in 2,6-dialkylphenols as solvents at 125° for 10 half-lives and the products were isolated by vacuum distillation and t.l.c. The product distributions are summarized in Table 1, along with the relevant data for phenolysis in phenol–benzene (1 : 1 w/w).

TABLE 1

Product distribution for phenolysis of 1-phenylethyl chloride (RCl) in hindered phenol solvents

					Product yield (%)			
Solvent	[RCl]/ M	[Et_3N]/ M	T/°C	t/h	Ether	Phenol	Di-enone	Total substitution
(IV)	0·100	0·120	125	594	0·00	0·00	4·14	4·14
(III)	0·100	0·120	125	141	0·00	0·00	0·98	0·98
(II)	0·102	0·124	125	40	22·8	5·15	0·74	28·7
(I)	0·101	0·120	125	3	45·9	6·17	0·00	52·1
Phenol [a]	0·175	0·408	40	3	62·5	13·3 (14·8) [b]	0·00	90·6

[a] From ref. 1*b*; solvent phenol–benzene (1 : 1 w/w). [b] Yield of 2-(1-phenylethyl)phenol.

In 2,6-dimethyl- and 2,6-di-isopropyl-phenol (I) and (II) 1-phenylethyl chloride gives the respective 1-phenylethyl ether in the presence of triethylamine which is added to neutralize liberated hydrogen chloride. However, in 2,6-di-t-butyl- and 2,6-di-t-butyl-4-methylphenol (III) and (IV) no 1-phenylethyl ether was obtained but small amounts of 4-alkylated cyclohexadienones were identified as the substitution product. This can be attributed to the size of the 2- and 6-t-butyl groups of (III) and (IV). Total substitution product yields diminish with increase in the size of the alkyl group, whereas the yields of the elimination product, styrene, increase.

Rate measurements were carried out by a titrimetric method; the first-order rate constants for phenolysis of 1-phenylethyl chloride in the hindered phenols (I)—(IV) are summarized in Table 2. All phenolyses obeyed good first-order kinetics in the presence of triethylamine, indicating that they are all S_N1 reactions.

TABLE 2

Phenolysis rates of 1-phenylethyl chloride (RCl) in hindered phenol solvents

Solvent	[RCl]/ M	[Et_3N]/ M	T/°C	k_1/s^{-1}	Relative rate (125°)
(IV)	0·100	0·120	125·0	$1·89 \times 10^{-7}$	0·0382
(III)	0·0997	0·119	125·0	$4·95 \times 10^{-6}$	1·00
(II)	0·102	0·124	125·0	$3·20 \times 10^{-5}$	6·46
(I)	0·101	0·120	125·0	$2·53 \times 10^{-3}$	511
Phenol [a]	0·075	0·107	25·0	$2·80 \times 10^{-4}$	790,000 [b]

[a] Solvent phenol–benzene (1 : 1 w/w); from ref. 1*b*. [b] Extrapolated by the Grunwald–Winstein treatment, assuming that the *m* value for 1-phenylethyl chloride in phenol–benzene is 1·00.

The rate of phenolysis decreases in the order PhOH > (I) > (II) > (III) > (IV) with increase in the size of the 2- and 6-alkyl groups and this indicates that steric hindrance of the hydroxy-group lowers the the ionizing power of the phenols.

The rate in 2,6-di-t-butyl-4-methylphenol (IV) is less than that in 2,6-di-t-butylphenol (III). Since the effect of the *para*-methyl group of (IV) on the rate cannot stem from steric origins, it can be ascribed to an electronic effect on the hydroxy-group. Thus, though phenols (III) and (IV) cannot yield the *O*-alkylated product, their hydroxy-groups still have ionizing power.

TABLE 3

Net steric effect for the phenolysis products of optically active 1-phenylethyl chloride (RCl) in hindered phenol solvents

						Net steric effect [b] and optical rotation [a]		
Solvent	[RCl]/ M	Optical rotation of RCl/° [a]	[Et_3N]/ M	T/°C	t/h	Ether	Phenol	Dienone
(IV)	0·100	+24·45	0·120	125	594			⩽20·0% inv. +3·46°
(III)	0·100	+24·45	0·120	125	141			⩽13·6% inv. −0·277°
(II)	0·102	+13·0	0·124	125	40	⩽14·8% ret. +1·12°	⩽14·6% inv. +1·17°	
(I)	0·101	−16·5	0·124	125	3	37·5% ret. −2·87°	20·0% inv. −0·227°	
Phenol [c]	0·175		0·408	40	3	31·0% ret.	41·2% inv. (38·1% inv.) [d]	

[a] α_D (1 dm, neat) for RCl; $[\alpha]_D$ (in benzene) for products. [b] Since the values for the maximum rotation of the derivatives of (II)—(IV) may be lower than the intrinsic values (see Table 4), the net steric effect (%) calculated for (II)—(IV) is the highest value. [c] Solvent phenol–benzene (1 : 1 w/w); from ref. 1*b*. [d] For 2-(1-phenylethyl)phenol.

Steric Course of Phenolysis of 1-*Phenylethyl Chloride in Hindered Phenols.*—Phenolysis of optically active 1-phenylethyl chloride was carried out in the hindered phenols (I)—(IV) at 125°, and from the optical rotations of the isolated products the net steric course of the reactions was deduced. The results are summarized in Table 3. The maximum rotations for the relevant 1-phenylethyl derivatives are in Table 4. Optically active 1-phenyl ethyl ethers, 4-(1-phenylethyl)-phenols, and cyclohexadienones, derived from phenols (II) and (III), were prepared from optically active 1-phenylethyl chloride and the potassium salt of phenols (II) and (III) under S_N2 conditions, during which nucleophilic substitution proceeds with inversion of configuration, although the possibility of racemization of 1-phenylethyl chloride has not been examined. In solvents (I) and (II)

TABLE 4

Maximum rotation (°) of (*R*)-1-phenylethyl derivatives of some phenols

R^1	R^2	Ether	Phenol	Dienone	Ref.
Bu^t	Me			$\leqslant -88{\cdot}5$ [a]	*b*
Bu^t	H		$\geqslant +14{\cdot}8$ [a]	$\geqslant +10{\cdot}45$ [a]	This work
Pr^i	H	$\geqslant +73{\cdot}1$ [a]	$\leqslant -77{\cdot}3$ [a]	$\leqslant -58{\cdot}7°$ [a]	This work
Me	H	+57·9	−8·6		*c*
H	H	−46·6	−10·26° (p-RC_6H_4OH) +27·85° (o-RC_6H_4OH)		*d*

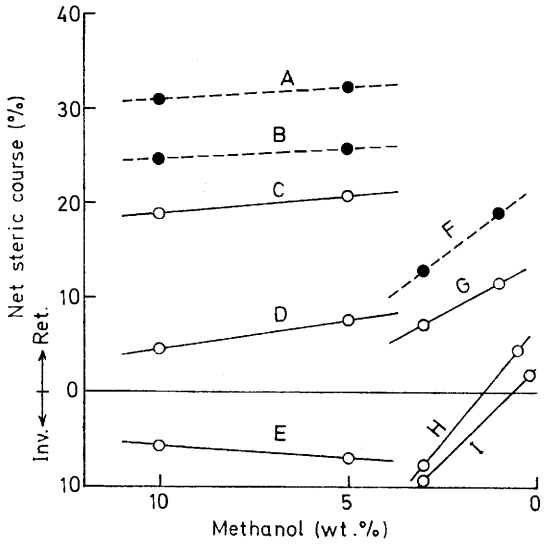
[a] Since the possibility of racemization of 1-phenylethyl chloride under S_N2 conditions has not been examined, these are the lowest values. [b] Ref. 16*b*. [c] Ref. 12; the value for the ether was recalculated from the literature value (51°) on the basis of a new value (125°) for the maximum rotation of 1-phenylethyl chloride (see H. M. R. Hoffmann and E. D. Hughes, *J. Chem. Soc.*, 1964, 1244). [d] Ref. 1*b*.

and PhOH, 1-phenylethyl ethers of net retained configuration were obtained, whereas all *C*-alkylated products, *i.e.* 4-(1-phenylethyl)-phenols and -cyclohexadienones, obtained in solvents (I)—(IV), showed net inversion. Since the hindered phenols are very weak acids,[9] the concentration of the phenolate anion is low in spite of the presence of triethylamine. Therefore, the inverted *C*-alkylated products probably stem from the respective phenol molecule which shields the ion-pair intermediate from the rear.

Steric Course of Competitive Phenolysis and Methanolysis in Hindered Phenols containing a Small Amount of Methanol.—Solvolyses of optically active 1-phenylethyl chloride were carried out in solvents (I)—(IV) containing 0·5—10% (w/w) of methanol, and the corresponding phenyl and methyl ethers were isolated by t.l.c. The net steric course of the reactions was determined from the changes in optical rotation. The results are summarized in Table 5 (see also Experimental section) and also illustrated in the Figure.

* Solvolysis of 1-(*p*-nitrophenyl)ethyl and 2,2-dimethyl-1-phenylpropyl *p*-nitrobenzoates in phenol gives phenyl ethers with net 90 and 93% retention, respectively, at 125°.

It is evident from the Figure that all the hindered phenols change the steric course of methanolysis of 1-phenylethyl chloride from net inversion to net retention upon increasing the concentration of the phenol. Optically active 1-phenylethyl chloride usually undergoes net inversion when solvolysed in methanol–benzene (Figure and Table 5) and other common solvents.[3] In these mixed solvents the chloride would be expected to favour association with methanol rather than a hindered phenol.



Effect of concentration of methanol on the steric course of formation of phenyl ethers (●) and methyl ethers (○) in competitive phenolysis and methanolysis of 1-phenylethyl chloride (0·1M) in solvents (I)—(IV), phenol, and benzene, containing a small amount of methanol and 0·1N-Et_3N at 125°: A, D, PhOH–MeOH; B, C, (I)–MeOH; E, PhH–MeOH; F, G, (II)–MeOH; H, (III)–MeOH; I, (IV)–MeOH

If this is the case,[8] the cyclic intermediate (B), which requires association of phenol with the chloride, is not plausible in the presence of methanol. Thus, it is probable that this unusual retentive methanolysis proceeds by back-side shielding [intermediate (C)]. The fact that among the phenols (III) and (IV) have less capacity to change the steric course of methanolyis from inversion to retention (see Figure) may be ascribed to steric hindrance to back-side shielding by the bulky substituents.

Although ionization by hydrogen bonding and subsequent four-centre attack [intermediate (A)] are necessary conditions for retentive phenolysis,[1,2] back-side shielding of the ion-pair intermediate, forming a π-complex between a phenol molecule and the 1-phenylethyl cation,[10] can control the steric course of the phenolysis to some extent[1] (sometimes substantially *) to give retained

[9] (*a*) L. A. Cohen and W. M. Jones, *J. Amer. Chem. Soc.*, 1963, **85**, 3397; (*b*) A. Fisher, G. J. Leary, R. D. Topsom, and J. Vaughan, *J. Chem. Soc.* (*B*), 1966, 782.

[10] For the recent study of the interaction between a carbonium ion and phenol see C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, 1973, **95**, 2701.

phenyl ethers, and to afford partially inverted *C*-alkylated products.

EXPERIMENTAL

I.r. spectra were taken with a Hitachi model 215 spectrophotometer and n.m.r. spectra with a Hitachi model R24 60 MHz instrument, 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. Products were identified by comparison of their i.r. and n.m.r. spectra and g.l.c. retention times with those of authentic samples.

Materials.—The resolution of 1-phenylethanol was performed by the Pope–Peachey method.[11] Optically active and racemic 1-phenylethyl chlorides were prepared by reaction of 1-phenylethanol with thionyl chloride as previously described.[1a] Other organic reagents were of analytical grade and were fractionated prior to use. Karl Fischer titration indicated the water content of hindered phenols to be $<10^{-3}$M.

Rate Measurements.—The previously reported procedure [1b] was followed and the usual sealed ampoule (1·000 ml) technique was employed. The diminution of base concentration was followed by titration with standard perchloric acid (0·05M) in acetic acid, using Crystal Violet as indicator. In each case, the reaction was followed to at least 70% conversion; smooth first-order linear relationships were obtained. The rate data are shown in Table 2.

Product Isolation.—(*a*) The reaction mixture was kept at 125° for at least 10 half-lives. It was then cooled at *ca.* 50° and after the addition of benzene was washed successively with aqueous 10% NaOH and aqueous 10% NaCl. The benzene solution was dried ($MgSO_4$) and concentrated and the residue was separated by preparative t.l.c. (silica gel).

(*b*) After being maintained at 125° for at least 10 half-lives, the reaction mixture was immediately concentrated by distillation *in vacuo*. Ether was added to the residual oil and the solution was washed with 10% aqueous NaCl, dried ($MgSO_4$), and concentrated. The residue was separated by t.l.c. (silica gel)

Phenolysis of 1-*Phenylethyl Chloride in* 2,6-*Xylenol* (I).—A solution of optically active 1-phenylethyl chloride (15·2 mmol), b.p. 55·0—55·3° at 4 mmHg, $\alpha_D^{19.7}$ −16·5 ± 0·05° (1 dm, neat), in 2,6-xylenol (I) (150 ml) containing triethylamine (0·124M) was kept at 125° for 3 h. After work-up as above (*a*) 1-phenylethyl 2,6-xylenyl ether (1·602 g), m.p. 31·4—32·8° (lit.,[12] 31—32°), $\alpha_D^{32.0}$ −2·87° (1 dm, neat), and 2,6-dimethyl-4-(1-phenylethyl)phenol (0·212 g), b.p. 175—180° at 2 mmHg (lit.,[13] 110—117° at 0·01 mmHg), $[\alpha]_D^{22.8}$ −0·227° (*c* 25·9%, benzene), were obtained.

Phenolysis of 1-*Phenylethyl Chloride in* 2,6-*Di-isopropylphenol* (II).—A solution of 1-phenylethyl chloride (19·8 mmol) in phenol (II) (195 ml) containing triethylamine (0·124M) was maintained at 125° for 40 h. After work-up (*b*) t.l.c. (silica gel) of the residual oil gave 1-phenylethyl 2,6-di-isopropylphenyl ether (1·271 g), b.p. 155—165° at 6 mmHg, $[\alpha]_D^{20.6}$ +1·12° (*c* 5·88%, benzene), and 2,6-di-isopropyl-4-(1-phenylethyl)phenol (0·2880 g), b.p. 150—160° at 4 mmHg (lit.,[14] 158—163° at 1 mmHg), $[\alpha]_D^{23.0}$ +1·17° (*c* 0·34%, benzene). 2,6-Di-isopropyl-4-(1-phenylethyl)-cyclohexa-2,5-dienone (0·1922 g), b.p. 150—160° at 4 mmHg, was obtained as a by-product.

Phenolysis of 1-*Phenylethyl Chloride in* 2,6-*Di-t-butylphenol* (III).—A solution of 1-phenylethyl chloride (21·3 mmol), $\alpha_D^{25.6}$ +24·45° (1 dm, neat), in phenol (III) (210 ml) containing triethylamine (0·120M) was kept at 125° for 141 h and work-up (*b*) gave 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbiphenyl (0·678 g), m.p. 184·8—185·6° (lit.,[15] 184—185°), $\nu_{max.}$ (CCl_4) 3630, 2980, 2940, 2890, 1600, 1450, 1370, 1240, 1190, and 600 cm^{-1}, and 2,6-di-t-butyl-4-(1-phenylethyl)-cyclohexa-2,5-dienone (0·0645 g), b.p. 125—135° at 1·5 mmHg, $[\alpha]_D^{24.6}$ −0·277° (*c* 0·723%, benzene).

Phenolysis of 1-*Phenylethyl Chloride in* 4-*Methyl*-2,6-*di-t-butylphenol* (IV).—A solution of 1-phenylethyl chloride (19·8 mmol) in phenol (IV) (195 ml) containing triethylamine (0·120M) was maintained at 125° for 594 h. After work-up (*b*) 4-methyl-4-(1-phenylethyl)-2,6-di-t-butylcyclohexa-2,5-dienone (0·267 g), b.p. 195—205° at 3 mmHg (lit.,[16] 118° at 0·2 mmHg), $[\alpha]_D^{36.0}$ +3·46° (*c* 0·320%, benzene), was obtained.

Competitive Phenolysis and Methanolysis of 1-*Phenylethyl Chloride in* 2,6-*Di-isopropylphenol* (II)–*Methanol.*—A solution of 1-phenylethyl chloride (15·2 mmol) in phenol (II)–methanol [99 : 1 (w/w); 150 ml] containing triethylamine (0·117M) was kept at 125° for 32 h. Work-up (*b*) gave methyl 1-phenylethylether (0·590 g), b.p. 36—50° at 4 mmHg (lit.,[5] 40—50° at 1 mmHg), $[\alpha]_D^{20.5}$ +1·86° (*c* 14·7%, 2,6-di-isopropylphenol), 2,6-di-isopropylphenyl 1-phenylethyl ether (0·803 g), b.p. 150—155° at 6 mmHg, $[\alpha]_D^{24.8}$ +1·88° (*c* 9·33%, benzene), 2,6-di-isopropyl-4-(1-phenylethyl)phenol (0·125 g), b.p. 145—150° at 2 mmHg, $[\alpha]_D^{18.0}$ +0·457° (*c* 4·17%, benzene), and 2,6-di-isopropyl-4-(1-phenylethyl)-cyclohexa-2,5-dienone (0·0832 g), b.p. 160—170° at 2 mmHg.

Methanolysis of 1-*Phenylethyl Chloride in Methanol–Benzene.*—A solution of 1-phenylethyl chloride (9·10 mmol) in methanol–benzene [1 : 9 (w/w); 90 ml] containing triethylamine (0·121M) was kept at 125° for 92 h. Work-up gave methyl 1-phenylethyl ether (0·861 g). Results of competitive phenolysis and methanolysis are summarized in Table 5.

Synthesis of 2,6-*Di-isopropylphenyl* 1-*Phenylethyl Ether.*—A mixture of potassium strips (0·600 g), 2,6-di-isopropylphenol (2·70 g), and *NN*-dimethylformamide (15·0 ml) was refluxed for 1·5 h until the metal disappeared. To the mixture, 1-phenylethyl chloride (3·00 ml), $\alpha_D^{22.2}$ +16·36° (1 dm, neat), was added and reflux was continued for an additional 3·5 h. Work-up gave 2,6-*di-isopropylphenyl* 1-*phenylethyl ether* (2·07 g), b.p. 150—155° at 2 mmHg, $[\alpha]_D^{19.3}$ −9·73° (*c* 11·4%, benzene), $\nu_{max.}$ (CCl_4) 2980, 2940, 2880, 1460, 1440, 1180, 1060, and 695 cm^{-1}; τ (CCl_4) 2·75 (5H, s), 3·05 (3H, s), 5·20 (1H, q), 6·80 (2H, m), 8·40 (3H, d), and 8·90 (12H, m) (Found: C, 85·15; H, 9·2. $C_{20}H_{26}O$ requires C, 85·05; H, 9·3%).

Synthesis of 2,6-*Di-isopropyl*-4-(1-*phenylethyl*)-*phenol and* -*cyclohexa*-2,5-*dienone.*—The alkylphenol and the dienone were synthesized according to the method of Kornblum and

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[14] W. B. Whalley and C. T. Holdrege, *J. Org. Chem.*, 1958, **23**, 512.
[15] T. H. Coffield, A. H. Filbey, G. G. Ecke, and A. J. Kolka, *J. Amer. Chem. Soc.*, 1957, **79**, 5019.
[16] (*a*) N. Kornblum and R. Seltzer, *J. Amer. Chem. Soc.*, 1961, **83**, 3668; (*b*) K. Okamoto, I. Nitta, and H. Shingu, *Bull. Chem. Soc. Japan*, 1970, **43**, 1768.

Seltzer [16a] and the modified method of Okamoto *et al.*[16b] From a mixture of potassium t-butoxide (4·00 g), tetraethylene glycol dimethyl ether (TGDM) (14·0 ml), t-butyl alcohol (12·0 ml), and 2,6-di-isopropylphenol (4·00 g), most of the t-butyl alcohol was distilled off. The remainder was added dropwise to 1-phenylethyl chloride (1·44 g), $\alpha_D^{26.5}$ +10·55° (1 dm, neat), in TGDM (10·0 ml) and the mixture was stirred at 125° for 0·5 h and maintained at 125° for an additional 5·5 h. To the mixture ether (30 ml) was added and the ethereal solution was washed with 10% aqueous NaCl and concentrated. Column chromatography (silica gel) of the residual oil gave 2,6-*di-isopropyl*-4-(1-*phenylethyl*)*phenol* (0·5372 g), b.p. 165—170° at 4 mmHg, $[\alpha]_D^{25.1}$ +6·52° (*c* 5·53%, benzene), $\nu_{max.}$ (CCl_4) 3640, 2970, 2940, 2880, 1600, 1470, 1450, 1390, 1290, 1200, 1160, and 600 cm^{-1}, τ (CCl_4) 2·70 (5H, s), 3·00 (2H, s), 4·85 (1H, s), 6·15 (1H, q), 6·75 (2H, m), 8·20 (3H, d), and 8·80 (12H, m) (Found: C, 85·1; H, 9·35. $C_{20}H_{26}O$ requires C, 85·05; H, 9·3%). 2,6-*Di-isopropyl*-4-(1-*phenylethyl*)*cyclohexa*-2,5-*dienone* (0·1196 g), b.p. 195—200° at 4 mmHg, $[\alpha]_D^{27.4}$ +4·95° (*c* 1·436%, benzene), $\nu_{max.}$ (CCl_4) 3030, 2970, 2940, 2880, 1660, 1600, 1470, 1390, 1200, 1150, and 600 cm^{-1}, τ (CCl_4) 2·80 (5H, s), 3·45 (1H, d), 3·70 (1H, d), 7·16 (1H, m), 7·45 (1H, dd), 8·10 (2H, m), 8·80 (12H, d), and 9·05 (3H, d) (Found: C, 85·0; H, 9·35. $C_{20}H_{26}O$ requires C, 85·05; H, 9·3%), was also obtained.

Synthesis of 4-(1-*Phenylethyl*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone*.—The alkylphenol was synthesized in a manner similar to 2,6-di-isopropylphenol. From 1-phenylethyl chloride (2·70 ml), $\alpha_D^{25.6}$ +24·45° (1 dm, neat), 4-(1-*phenylethyl*)-2,6-*di-t-butylcyclohexa*-2,5-*dienone* (0·533 g), b.p. 180—188° at 2 mmHg; $[\alpha]_D^{24.4}$ −2·04° (*c* 5·54%, benzene), $\nu_{max.}$ (CCl_4) 2970, 2940, 1680, 1600, 1365, 1180, 1080, and 600 cm^{-1}; τ (CCl_4) 2·90 (5H, s), 3·50 (1H, d), 3·75 (1H, d), 7·20 (1H, m), 7·40 (1H, dd), 8·75 (9H, s), 8·85 (9H, s), and 8·95 (3H, d) (Found: C, 85·1; H, 9·75. $C_{22}H_{30}O$ requires C, 84·8; H, 9·85%), and 4-(1-*phenylethyl*)-2,6-*di-t-butylphenol* (1·152 g), b.p. 160—180° at 3 mmHg, $[\alpha]_D^{24.4}$ −2·89 (*c* 9·26%, benzene), $\nu_{max.}$ (CCl_4) 3630, 2970, 1605, 1460, 1370, and 600 cm^{-1}, τ (CCl_4) 2·85 (5H, s), 3·10 (2H, s), 5·15 (1H, s), 6·05 (1H, q), 8·40 (3H, d), and 8·60 (18H, s) (Found: C, 85·05; H, 9·9. $C_{22}H_{30}O$ requires C, 84·8; H, 9·85%), were obtained.

TABLE 5

Net steric course for solvolytic products in competitive phenolysis and methanolysis of 1-phenylethyl chloride in hindered phenol solvents containing a small amount of methanol in the presence of triethylamine (0·1M) at 125°

Solvent (w %)	RCl α_D (°) [a]	Reaction time (h)	Net steric course, (% yield), {$[\alpha]_D$ (°)} [b]	
			Phenyl ether	Methyl ether
(IV) 99·85–methanol 0·15	+22·8	576	(0)	1·99% ret., (0·375), {+0·436}
(IV) 97·0–methanol 3·0	+16·7	400	(0)	9·36% inv., (9·53), {−1·50}
(III) 99·95–methanol 0·5	−40·0	75·3	(0)	4·38% ret., (2·51), {−1·68}
(III) 97·0–methanol 3·0	+16·4	65·0	(0)	7·44% inv., (12·7), {−1·16}
(II) 99·0–methanol 1·0	+16·4	32·0	⩽19·6% [c] ret., (18·7), {+1·88}	11·8% ret., (28·5), {+1·86}
(II) 97·0–methanol 3·0	+16·4	32·0	⩽13·1% [c] ret., (2·52), {+1·25}	7·19% ret., (30·3), {+1·13}
(I) 95·0–methanol 5·0	+13·0	19·0	26·0% ret., (7·28), {+1·55}	21·1% ret., (69·3), {+2·61}
(I) 90·0–methanol 10·0	+16·6	19·0	25·2% ret., (1·91), {+1·94}	19·2% ret., (63·4), {+3·06}
Phenol 95·0–methanol [d] 5·0		0·3	32·5% ret., (66·8)	7·77% ret., (4·2)
Phenol 90·0–methanol 10·0		0·4	31·0% ret., (55·5)	4·78% ret., (8·5)
Benzene 95·0–methanol 5·0	+18·1	116		6·78% inv., (67·8), {−1·18}
Benzene 90·0–methanol 10·0	+18·1	92		5·81% inv., (69·7), {−1·01}

[a] Neat, 1 dm. [b] In benzene. For maximum rotation of the methyl ether see ref. 5. [c] See footnote *b* in Table 3. [d] Ref. 5.

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