The Halogenation of Phenolic Ethers and Anilides. Part XVI. Kinetics of the Chlorination of Diphenylyl and Naphthyl Ethers.*

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Extensive investigations (Parts I—XIV, *J.*, 1928—1943) of the rates of nuclear chlorination of aromatic ethers have shown that substituents exert their effects on reaction rates mainly, if not entirely, through changes in the energy of activation, without markedly affecting the probability factor P of the modified Arrhenius equation, $k = PZe^{-E/RT}$. For the ethers p-RO·C_6H_4·X especially the results accord with the view that the substituents OR and X contribute additively to the value of E. A similar analysis of velocity coefficients has now been made for series of diphenylyl ethers and for some naphthyl ethers.

In the diphenylyl series the results, taken as a whole, conform closely with those found among the phenyl ethers, although the ratios of the velocity coefficients for the ethers RO·C_6H_4·C_6H_4·X show slight variations from the values found in the earlier series.

In the naphthyl series, on the other hand, some divergences were observed.

The quantitative study of the nuclear chlorination of aromatic ethers has been extended to include several series of ethers derived from 4-hydroxydiphenyl and from 1-naphthol. As in the simpler phenolic ethers, deactivating substituents, such as the halogens and the nitro-group, were introduced in order to bring the rates within the range of accurate measurement, and to confine substitution to a single nuclear position. In the diphenylyl series, most of the ethers carried a deactivating substituent in the second ring, and were mostly of the type RO·C_6H_4·C_6H_4·X. In the naphthol series, ethers of 2- and 4-nitro- and 2- and 4-chloro-1-naphthol have been studied.

Table 1. *Diphenylyl Ethers. Velocity coefficients for the chlorination of ethers of the types :* (*a*) RO·C_6H_4·C_6H_4X, (*b*) 4 : 3-RO·C_6H_3Cl·C_6H_4·NO_2-4, *and* (*c*) [4 : 3-RO·C_6H_3Cl·$]_2$ *in* 99% *acetic acid,* at 20°.

$[Cl_2] = 0·005$; [ether] $= 0·010$; [HCl] $= 0·025$.

	Type X	R = Me	Et	Pr^n	Pr^i	Bu^n
(*a*)	4-Nitro	8·27	15·66	16·97	32·9	—
	4-Fluoro	47·4	91·8	—	—	—
	4-Chloro	36·7	71·0	—	148	—
	4-Bromo	34·2	65·4	—	—	—
	H	76	144	163	293 *	162
	2-Nitro	22·3	43·1	47·9	93·1	—
(*b*)		0·019	0·0387	0·0415	0·0564	—
(*c*)		0·362	0·716	0·771	0·977	—

$[Cl_2] = 0·0025$; [ether] $= 0·005$; [HCl] $= 0·0125$.

	Ether	R = Me	CH_2Ph	p-NO_2·C_6H_4·CH_2·
(*a*)	X = 4-Nitro	7·91	5·35	—
	H	74·7	54·3	10·37

* This represents a very rapid reaction which is complete within a few minutes.

The velocity coefficients are recorded in Tables 1 and 3 and the velocity ratios in Tables 2 and 4. The method of determining the rates was the same as in previous investigations, and the values were calculated from the usual expression for a bimolecular reaction, the unit of time being the minute and of concentration mole $l.^{-1}$. The relative directive powers of alkoxy-groups are expressed in the usual form 100 k_X^{OR}/k_X^{OMe}.

Diphenylyl Ethers.—Table 2, where the relative directive effects of alkoxy-groups are summarised, shows that for several series of diphenylyl ethers the values of the relative directive effects of these groups agree closely with those found for the simpler ethers,

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* Part XV, *J.*, 1949, 1389.

$RO{\cdot}C_6H_4X$. The measure of this agreement is best seen from Table 6, which gives the mean values for the several series of diphenylyl and phenyl ethers.

TABLE 2. *Relative directive effects of the groups* OR *in compounds of the above types. Values of* $100k_X^{OR}/k_X^{OMe}$.

Type X	R = Me	Et	Pr^n	Pr^i	Bu^n	CH_2Ph	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$
(*a*) 4-Nitro	100	190	205	398	—	68	—
4-Fluoro	100	194	—	—	—	—	—
4-Chloro	100	193	—	402	—	—	—
4-Bromo	100	191	—	—	—	—	—
H	100	190	215	385	213	73	13·9
2-Nitro	100	194	215	417	—	—	—
(*b*)	100	204	218	297	—	—	—
(*c*)	100	198	213	270	—	—	—
Phenyl ethers (mean)	100	199	223	440	223	68	14·1

TABLE 3. *Naphthyl ethers. Velocity coefficients for the chlorination of ethers of the types* (a) 1 : 2-$RO{\cdot}C_{10}H_6{\cdot}X$ *and* (b) 1 : 4-$RO{\cdot}C_{10}H_6{\cdot}X$ *in* 99% *acetic acid, at* 20°.

$[Cl_2] = 0{\cdot}005$; [ether] $= 0{\cdot}010$; [HCl] $= 0{\cdot}025$.

Type X	R = Me	Et	Pr^n	CH_2Ph	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$
(*a*) NO_2	0·728	1·005	—	—	0·097
Cl	14·64	22·87	27·06	10·75	2·40
(*b*) NO_2	42·5	75·2	72·0	25·2	—

$[Cl_2] = 0{\cdot}001$; [ether] $= 0{\cdot}002$; [HCl] $= 0{\cdot}005$.

Type of ether	R = Me	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$
(*b*) NO_2	39·5	6·38
Cl	—	*ca.* 650

TABLE 4. *Relative directive effects of the groups* OR *in compounds of the above types. Values of* $100k_X^{OR}/k_X^{OMe}$.

Type X	R = Me	Et	Pr^n	CH_2Ph	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$
(*a*) NO_2	100	139	—	—	13·3
Cl	100	156	184	73	16·4
(*b*) NO_2	100	177	170	59	16·2

TABLE 5. *Phenyl ethers. Velocity coefficients for the chlorination of ethers of* o-*nitrophenol in* 99% *acetic acid, at* 20°.

$[Cl_2] = 0{\cdot}005$; [ether] $= 0{\cdot}05$; [HCl] $= 0{\cdot}025$.

R = Me	Et	Pr^n
0·0180	0·0362	0·0414

Relative directive effects of the groups OR *in ethers of* o-*nitrophenol. Values of* $100k_X^{OR}/k_X^{OMe}$.

	R = Me	Et	Pr^n
	100	203	230
Phenyl ethers (mean)	100	199	223

TABLE 6. *Mean relative directive powers of alkoxy-groups. Values of* $100k_X^{OR}/k_X^{OMe}$.

	R = Me	Et	Pr^n	Pr^i	Bu^n	$PhCH_2$	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$
Diphenylyl ethers	100	194	213	361 *	213	70	13·9
Phenyl ethers	100	199	223	440	223	68	14·1

* The value for the *iso*propoxy-group in the diphenylyl series must not be regarded as strictly comparable since it includes values for ethers which have a polar substituent adjacent to the *iso*-propoxy-group. It has been previously shown that this gives rise to anomalous results in the phenyl ethers.

In accordance with previous results, such agreement indicates that in the diphenylyl ethers the probability factor of the modified Arrhenius equation is essentially constant. This was confirmed by an analysis of the velocity coefficients for a number of diphenylyl ethers at 20° and 35°. In a plot of the energies of activation against the values of $3 \log_{10} k_{20}$ all the points fall on or near to the line of slope $-2{\cdot}303\boldsymbol{R}T$ given in Part XII

(*J.*, 1942, 418). Because many of the ethers are highly reactive, only a limited number could be investigated in this way, but among those examined the values of E and of $\log PZ$ respectively ranged from 13,170 cals. and 8·44 for 3-chloro-4-ethoxy-4′-nitrodiphenyl to 10,170 cals. and 8·52 for 4-methoxy-4′-nitrodiphenyl.

It is interesting to speculate to what extent a series of diphenylyl ethers, p-RO·C_6H_4·C_6H_4X, may be compared with the simpler phenyl ethers, p-RO·C_6H_4X, for, despite the obvious similarity in the directive powers of alkoxy-groups, there are small differences. If the bond uniting the two nuclei in the diphenylyl ethers is an invariable single bond, the group C_6H_4X may be regarded as a single substituent, in which case the relative effects of the alkoxy-groups would be expected to be the same as in the phenyl series. On the other hand, if, as is generally believed, this bond possesses some double-bond character interaction between the two benzene rings, with the consequent distribution of electronic charges over two instead of one nucleus, may occur to a degree varying with the polar character of the substituent (Le Fèvre and Le Fèvre, *J.*, 1936, 1130; Lennard-Jones and Turkevitch, *Proc. Roy. Soc.*, 1937, *A*, **158**, 297; Dhar, *Proc. Nat. Inst. Sci. India*, 1949, **15**, 11; *Chem. Abs.*, 1949, **43**, 4655). Such effect may account for the small differences in the diphenylyl and phenyl ethers, but differences of this order (cf. Table 6) may also be expected from the experimental errors.

Apart from their bearing on the effect which substituents exert on the energy of activation, and on the additive nature of these effects, our results afford a comparison between the deactivating effect of substituents in ethers of the two types p-RO·C_6H_4·C_6H_4X and p-RO·C_6H_4X. As expected, the deactivating influence of X is very much greater when it is situated in the nucleus undergoing chlorination. The magnitude of this difference is significant, for, whereas the rate of chlorination of anisole is of the order 1×10^3, and that of p-nitroanisole is $2·9 \times 10^{-3}$, the velocity coefficients for 4-methoxydiphenyl and 4-methoxy-4′-nitrodiphenyl are 76 and 8·3, respectively. The following velocity coefficients illustrate this effect in greater detail for three of the halogens and for the nitro-group.

Velocity coefficients at 20°.

Ether	X = H	F	Cl	Br	NO_2
p-MeO·C_6H_4X	—	2·35 *	1·23	1·26	0·0029
4-MeO·C_6H_4·C_6H_4X-4	76·0	47·4	36·7	34·2	8·3
4-MeO·C_6H_4·CO·C_6H_4X-4	1·26	1·07	0·87	0·85	0·385

* Calculated from the observed value for the benzyl ether, cf. *Trans. Faraday Soc.*, 1941, **37**, 739.

These results are as expected, but the magnitude of the effects is here brought out clearly for the first time. A nitro-group in a diphenylyl ether reduces the rate of chlorination of the parent ether 9-fold, whereas in the phenyl series, the reduction is of the order of 10^6.

The values for the diphenylyl ethers may also be compared with those for ethers based on benzophenone (cf. Part VIII) in which the carbonyl group interpolated between the two benzene rings imposes an electronic constraint and so suppresses further the effect of a polar substituent. So powerful a polar substituent as a nitro-group only reduces three-fold the rate of chlorination of 4-methoxybenzophenone.

Naphthyl Ethers.—An extensive study of naphthyl ethers has not been possible because of their high reactivity and the consequent difficulties in obtaining accurate measurements, and Table 3 shows the range of compounds examined to be restricted to ethers derived from 2- and 4-nitro-1-naphthol and from 2- and 4-chloro-1-naphthol.

Although limited in scope, the results (Table 4) show that, taken as a whole, the relative directive effects of OR groups in naphthalene compounds differ appreciably from the values found for phenyl and diphenylyl ethers. The influence of the various alkoxy-groups on the rates of chlorination remain in the order EtO > MeO > $PhCH_2$·O > p-NO_2·C_6H_4·CH_2·O, but their relative directive effects are less widely spaced. Moreover, these effects do appear here to be dependent on the nature of the second substituent.

These results are only a first study in the naphthalene series. A more comprehensive investigation is necessary before the results can be compared satisfactorily with those in the simpler aromatic ethers. They do, however, illustrate a number of points. First, they confirm the higher general reactivity of naphthalene compounds as compared with benzene compounds, as is borne out by the following rate constants :

	Substituent			
	4-NO_2	4-Cl	2-NO_2	2-Cl
Substituted 1-naphthyl methyl ethers	42·5	*ca.* 4×10^3	0·728	14·6
Substituted anisoles	0·0029	1·26	0·018	4·44

Secondly, they show that, whereas in the benzene series the *ortho*-substituted ether is more reactive than the corresponding *para*-substituted compound (cf. Table 5 and *J.*, 1935, 1831, 1835), in the naphthalene series the 2-substituted ether is far less reactive than its 4-substituted isomer (cf. Table 3).

EXPERIMENTAL

Purification of Acetic Acid.—Orton and Bradfield's method (*J.*, 1927, 983), whereby commercial acetic acid is distilled from " AnalaR " chromium trioxide and the calculated amount of pure acetic anhydride, unexpectedly failed with some post-war materials to give a satisfactory medium, and it was eventually found that the " purified " acetic acid contained a small amount of hydrochloric acid, which, by reacting with the dichloramine-T used in the velocity measurements, liberated enough free chlorine to start the reaction prematurely. The " purified " acetic acid was therefore re-distilled from solid silver acetate. In addition the method used earlier for determining the rate constants was modified by reducing the length of time the aromatic ether and the dichloramine-*T* were together in solution before the reaction was started. Any risk that the reaction might be started by a trace of hydrochloric acid was thereby removed.

Determination of Rate Constants.—The following procedure was adopted. The aromatic ether was dissolved in acetic acid (80—85 ml.) in a 100-ml. standard flask, and water $(1 - x)$ ml., where x ml. is the amount of water in 100 ml. of the acid plus the water added in the constant-boiling hydrochloric acid, was added. The flask was then maintained at 20° for 30 min. After the requisite amount of dichloramine-T solution at 20° had been added, acetic acid, also at 20°, was added to bring the total volume to within y ml. of the graduation mark ; y ml. of constant-boiling hydrochloric acid (being the calculated amount) were quickly added and the flask was shaken thoroughly and replaced in the thermostat. A stop-watch was started simultaneously with the first shake of the flask, and 10 ml. portions were withdrawn at intervals for estimation of the free chlorine. With these precautions, constant and reproducible results were always obtained.

To ensure the purity of the ethers, solid ethers were crystallised at least three times, usually from methanol, ethanol, or acetic acid, and liquid ethers were fractionally distilled until a constant value was obtained for the velocity coefficient, which was found to be a more reliable criterion of purity than the usual physical constants. The following random selection of examples illustrates the constancy of the mean values in individual experiments : (*a*) 4′-nitro-4-*iso*propoxydiphenyl had $k = 32·9$ after two crystallisations from methyl alcohol and one from acetic acid, and $k = 33·0$ and 32·9 after two further crystallisations from methyl alcohol; (*b*) 2-chloro-1-naphthyl ethyl ether, a liquid, had $k = 22·9$ and 23·1 after three fractional distillations, and $k = 22·5$ and 23·0 after two later distillations.

Unless otherwise stated, the ethers were prepared by standard methods from the phenol and the appropriate alkyl, aryl, or substituted aryl bromide or iodide. Methyl ethers were usually prepared by the action of methyl sulphate on an aqueous solution of the sodium phenoxide.

(a) *Diphenylyl ethers.* 4-Hydroxy-4′- and -2′-nitrodiphenyls were prepared by Brynmor Jones and Chapman's method (*J.*, 1952, 1829). From 4-hydroxy-4′-nitrodiphenyl the following 4′-nitro-4-diphenylyl ethers were prepared: methyl, m. p. 110°; *ethyl,* yellow prisms (from methyl alcohol), m. p. 107—108° (Found : C, 69·3; H, 5·5. $C_{14}H_{13}O_3N$ requires C, 69·1; H, 5·4%); n-*propyl* and iso*propyl*, pale yellow plates (from methyl alcohol), m. p. 74—75° (Found : C, 69·5; H, 6·1. $C_{15}H_{15}O_3N$ requires C, 70·0; H, 5·9%) and m. p. 77—78° (Found : C, 70·1; H, 5·8%), respectively; *benzyl,* yellow plates (from glacial acetic acid), m. p. 171—172° (Found: C, 74·7; H, 4·8. $C_{19}H_{15}O_3N$ requires C, 74·7; H, 4·9%); 2 : 4-*dinitrophenyl,* a microcrystalline powder (from a large volume of alcohol), m. p. 168° (Found : C, 56·4; H, 2·8. $C_{18}H_{11}O_7N_3$ requires C, 56·7; H, 2·9%).

From 4-hydroxy-2′-nitrodiphenyl the following 2′-nitro-4-diphenylyl ethers were obtained : *methyl, ethyl,* and iso*propyl*, yellow slender prisms (from methyl alcohol), m. p. 61—62° (Found :

C, 68·2; H, 4·8. $C_{13}H_{11}O_3N$ requires C, 68·1; H, 4·8%), m. p. 54—55° (Found: C, 69·1; H, 5·3. $C_{14}H_{13}O_3N$ requires C, 69·1; H, 5·4%), and m. p. 43—44° (Found: C, 70·8; H, 5·9. $C_{15}H_{15}O_3N$ requires C, 70·0; H, 5·9%), respectively; n-*propyl* ether, a yellow liquid, b. p. 180°/5 mm. (Found: C, 70·7; H, 6·2%).

4-Chloro-4′-hydroxydiphenyl was prepared by chlorinating 4-diphenylyl acetate in carbon tetrachloride containing a trace of iodine as catalyst, and hydrolysing the resulting chlorodiphenylyl acetates with alcoholic hydrogen chloride (cf. Savoy, *Proc. Louisiana Acad. Sci.*, 1947, **10**, 205; *Chem. Abs.*, 1948, **42**, 1919). After four crystallisations from aqueous acetic acid 4-chloro-4′-hydroxydiphenyl was obtained as a crystalline solid, m. p. 147—148°, and from this three 4′-chloro-4-diphenylyl ethers were prepared: *methyl*, m. p. 105° (Found: C, 71·0; H, 5·3. $C_{13}H_{11}OCl$ requires C, 71·4; H, 5·1%); *ethyl*, m. p. 123° (Found: C, 72·4; H, 5·3. $C_{14}H_{13}OCl$ requires C, 72·3; H, 5·6%); both crystallised from aqueous ethanol in clusters of plates, while the *isopropyl ether* separated from the same solvent as plates, m. p. 127—128° (Found: C, 73·2; H, 6·2. $C_{15}H_{15}OCl$ requires C, 73·0; H, 6·1%).

4-Bromo-4′-hydroxydiphenyl was obtained as follows: 4-nitrodiphenyl (Bell, Kenyon, and Robinson, *J.*, 1926, 1242) was brominated by Le Fèvre and Turner's method (*J.*, 1926, 2045) and the 4′-nitro-compound reduced by stannous chloride and concentrated hydrochloric acid (Bell and Robinson, *J.*, 1927, 1127). Diazotisation of the 4-amino-compound, followed by decomposition of the diazonium salt with dilute sulphuric acid, gave the 4-bromo-4′-hydroxydiphenyl as a solid, m. p. 165—167°, after crystallisation from alcohol (cf. Gray, Hartley, and Brynmor Jones, *J.*, 1952, 1959, for an improved synthesis of this compound). The *methyl* and *ethyl ethers* crystallised from aqueous acetic acid in silky plates, m. p. 145° (Found: C, 59·0; H, 4·4. $C_{13}H_{11}OBr$ requires C, 59·3; H, 4·2%) and m. p. 139° (Found: C, 60·4; H, 4·9. $C_{14}H_{13}OBr$ requires C, 60·7; H, 4·7%), respectively.

4-*Fluoro*-4′-*methoxydiphenyl*, which crystallised from ethyl alcohol as slender prisms, m. p. 90—91° (Found: C, 77·1; H, 5·6. $C_{13}H_{11}OF$ requires C, 77·2; H, 5·5%), was prepared as follows. 4-Methoxy-4′-nitrodiphenyl was reduced to the amino-compound by West's method (*J.*, 1925, **127**, 494). When the amino-compound had been diazotised, 4-methoxydiphenyl-4′-diazonium borofluoride was precipitated by the addition of an excess of sodium borofluoride solution to the cold diazonium solution. The carefully dried diazonium fluoroborate was then decomposed by heat to the methyl ether (cf. Balz and Schiemann, *Ber.*, 1927, **60**, 1186). 4-*Ethoxy*-4′-*fluorodiphenyl*, prepared similarly, crystallised from ethyl alcohol in small plates, m. p. 99° (Found: C, 77·8; H, 5·9. $C_{14}H_{13}OF$ requires C, 77·8; H, 6·1%).

From 4-hydroxydiphenyl seven diphenylyl ethers were prepared. The methyl, ethyl, *n*- and *iso*propyl, and *n*-butyl ethers had m. p.s 88—89°, 76°, 76°, 73°, and 75°, respectively (cf. Brewster and Puttman, *J. Amer. Chem. Soc.*, 1939, 3083). The *benzyl ether* crystallised from acetic acid in plates, m. p. 129° (Found: C, 87·6; H, 6·2. $C_{19}H_{16}O$ requires C, 87·7; H, 6·2%), and the p-*nitrobenzyl ether*, m. p. 164—165° (Found: C, 75·0; H, 4·8. $C_{19}H_{15}O_3N$ requires C, 74·8; H, 4·9%), separated from acetic acid–ethyl alcohol in pale yellow plates.

3-Chloro-4′-nitro-4-diphenylyl ethers were obtained by the chlorination of 4-alkoxy-4′-nitrodiphenyls in acetic acid, the chlorine being generated from the calculated amount of dichloramine-T with concentrated hydrochloric acid. The *methyl ether* crystallised from acetic acid and from acetic acid–ethyl alcohol as clusters of pale yellow prisms, m. p. 143—144° (Found: C, 59·0; H, 3·7. $C_{13}H_{10}O_3NCl$ requires C, 59·2; H, 3·8%). The *ethyl*, n-*propyl*, and iso-*propyl ethers*, obtained as yellow prisms from methyl alcohol, had m. p. 106—107° (Found: C, 60·4; H, 4·5. $C_{14}H_{12}O_3NCl$ requires C, 60·5; H, 4·4%), m. p. 64—65° (Found: C, 62·0; H, 4·6. $C_{15}H_{14}O_3NCl$ requires C, 61·8; H, 4·8%), and m. p. 68—69° (Found: C, 61·6; H, 4·9%), respectively.

3 : 3′-Dichloro-4 : 4′-dihydroxydiphenyl was prepared by the chlorination of 4 : 4′-dihydroxydiphenyl in acetic acid solution with dichloramine-T and hydrochloric acid. It crystallised from a large volume of water as small prisms, m. p. 128°. Its *dimethyl ether* crystallised from ethyl alcohol and from acetic acid in plates, m. p. 157—158° (Found: C, 59·0; H, 4·2. $C_{14}H_{12}O_2Cl_2$ requires C, 59·4; H, 4·3%). The *diethyl* and *diisopropyl ethers* separated from ethyl and methyl alcohols as plates, m. p. 116—117° (Found: C, 61·3; H, 5·1. $C_{16}H_{16}O_2Cl_2$ requires C, 61·7; H, 5·2%), and m. p. 80° (Found: C, 63·3; H, 6·0. $C_{18}H_{20}O_2Cl_2$ requires C, 63·7; H, 5·9%), respectively. The *di*-n-*propyl ether* was obtained from methyl alcohol as prisms, m. p. 65—66° (Found: C, 63·3; H, 5·9. $C_{18}H_{20}O_2Cl_2$ requires C, 63·7; H, 5·9%).

(b) *Naphthyl ethers.* 4-Nitro-1-naphthol, m. p. 164°, was obtained by the alkaline hydrolysis of 4-nitro-1-naphthylamine, prepared by Hodgson and Walker's method (*J.*, 1933, 1205). Its methyl ether, prepared by Hodgson and Smith's method (*J.*, 1935, 672), crystallised from alcohol in yellow-orange prisms, m. p. 82—83°. Woroshzoff (*Zeitsch. Farb. Ind.*, 1911, **10**, 169) gave m. p. 81°; Hodgson and Smith, 85°. The ethyl ether also separated from alcohol as yellow prisms, m. p. 115°, while the n-*propyl ether* crystallised from ethyl and methyl alcohols as yellowish-brown prisms, m. p. 66° (Found: C, 67·2; H, 5·7. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7%). The *benzyl* and p-*nitrobenzyl ethers* had m. p. 91—92° (Found: C, 72·9; H, 4·6. $C_{17}H_{13}O_3N$ requires C, 73·1; H, 4·7%), and m. p. 189° (Found: 63·3; H, 3·8. $C_{17}H_{12}O_5N_2$ requires C, 63·0; H, 3·7%), respectively.

2-Nitro-1-naphthol was obtained by Hodgson and Kilner's method (*J.*, 1924, 807); it crystallised from alcohol in slender orange-yellow prisms, m. p. 128°. The methyl ether was prepared by treating dry sodium 2-nitro-1-naphthoxide with methyl sulphate and xylene for 3 hr. at 145°. After unchanged sulphate had been hydrolysed with hot aqueous sodium hydroxide, the cooled mixture was extracted with ether and dried. Evaporation of the ether, followed by addition of a small amount of light petroleum (b. p. 60—80°) precipitated the methyl 2-nitro-1-naphthyl ether. Three crystallisations from light petroleum gave yellow prisms, m. p. 80—81° (Clemo, Cockburn, and Spence, *J.*, 1931, 1271, gave m. p. 80°). The *ethyl ether*, similarly prepared, was obtained by steam-distillation as a yellow liquid. After purification by fractional distillation, it crystallised from light petroleum (b. p. 40—60°) as fine yellow prisms, m. p. 25—26° (Found: C, 66·1; H, 5·2. $C_{12}H_{11}O_3N$ requires C, 66·3; H, 5·1%). Heermann (*J. pr. Chem.*, 1891, **44**, 240) reported this ether as yellow needles, m. p. 84°. Attempts to prepare ethyl 2-nitro-1-naphthyl ether by Heermann's method resulted in the isolation of the 4-nitro-isomer, m. p. 115°. The p-*nitrobenzyl* 2-*nitro*-1-*naphthyl ether* crystallised from aqueous acetic acid–methyl alcohol and from acetic acid as slender yellow prisms, m. p. 141—142° (Found: C, 63·1; H, 3·9. $C_{17}H_{12}O_5N_2$ requires C, 63·0; H, 3·7%).

4-Chloro-1-naphthol, prepared by treating a solution of α-naphthol in chloroform with sulphuryl chloride (Lesser and Gad, *Ber.*, 1923, **56**, 972), and purified by crystallisation from chloroform, had m. p. 120—121°. The *benzyl* and 2 : 4-*dinitrophenyl ethers* separated from aqueous acetic acid as prisms, m. p. 94° (Found: C, 75·5; H, 4·8. $C_{17}H_{11}OCl$ requires C, 76·0; H, 4·9%), and as yellow prisms, m. p. 130° (Found: C, 55·7; H, 2·5. $C_{16}H_9O_5N_2Cl$ requires C, 55·7; H, 2·6%), respectively. The p-*nitrobenzyl ether* crystallised from acetic acid and had m. p. 145° (Found: C, 64·9; H, 3·9. $C_{17}H_{12}O_3NCl$ requires C, 65·1; H, 3·9%).

4-Chloro-1-naphthyloxyacetic acid after several crystallisations from aqueous acetic acid melted at 167° (Haskelberg, *J. Org. Chem.*, 1947, **12**, 426, gave m. p. 169°). Steam-distillation of the mother-liquors obtained in the preparation of 4-chloro-1-naphthol gave 2-chloro-1-naphthol as an impure greyish-white solid (cf. Lesser and Gad, *loc. cit.*). Crystallisation from light petroleum (b. p. 40—60°) failed to purify it—the best specimen melted 2—3° lower than the pure product, and ethers prepared from such specimens gave unsatisfactory velocity coefficients. The 2-chloro-1-naphthol was eventually purified by conversion into its toluene-*p*-sulphonyl ester (pyridine being used as solvent), and this was readily purified by crystallisation from methyl alcohol and from acetic acid. Hydrolysis of the pure ester, m. p. 101°, gave a specimen of the 2-chloro-1-naphthol which, after one crystallisation from light petroleum (b. p. 40—60°), melted sharply at 64—65°. The *methyl ether* crystallised from methyl alcohol as prisms, m. p. 42—43° (Found: C, 68·7; H, 4·7. $C_{11}H_9OCl$ requires C, 68·6; H, 4·7%). The p-*nitrobenzyl ether* crystallised from ethyl alcohol in clusters of prisms, m. p. 101—102° (Found: C, 64·8; H, 4·1. $C_{17}H_{12}O_3NCl$ requires C, 65·1; H, 3·9%). The *ethyl* and n-*propyl ethers* were liquids, b. p. 130°/4 mm. (Found: C, 70·0; H, 5·7. $C_{12}H_{11}OCl$ requires C, 69·7; H, 5·4%) and b. p. 140°/3 mm. (Found: C, 71·1; H, 6·7. $C_{13}H_{13}OCl$ requires C, 70·7; H, 5·9%), respectively. The *benzyl ether* was obtained as a brownish liquid, which, after fractional distillation, crystallised from methyl alcohol in clusters of prisms, m. p. 49—50° (Found: C, 76·1; H, 5·1. $C_{17}H_{13}OCl$ requires C, 76·0; H, 4·9%).

(c) *Phenyl ethers.* *o*-Nitroanisole and *o*-nitrophenetole were obtained as yellow liquids, b. p. 142°/12 mm. and 148°/21 mm., respectively, from *o*-nitrophenol. *o*-Nitrophenyl *n*-propyl ether was prepared by an adaptation of Richardson's method (*J.*, 1926, 522) from *o*-chloronitrobenzene and *n*-propyl alcohol and had b. p. 157—158°/17 mm.

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