J. Chem. Soc. (B), 1970

The Reactivity of the Halogenonaphthols towards Nucleophiles. Part II.¹ The Kinetics and Mechanisms of the Reactions of 1-Halogeno-2-naphthols with Anilines

By M. Bosco, L. Forlani, and P. E. Todesco,* Istituto di Chimica Organica, Università, Via Amendola, 173, 70126 Bari, Italy

1-Halogeno-2-naphthols react with the X-substituted anilines yielding normal substitution products. The abnormal ' activating power of the OH-group in position 2 is related to the presence of tautomeric keto-enolic equilibrium wherein the hydrogen atom migrates from the hydroxylic oxygen atom to position 1, which carbon atom becomes tetrahedral. The reactive species is the keto-form which is an α -halogeno-oxo-derivative.

The second-order kinetic constants found experimentally decrease with increase of initial concentration of the reactant amine. This is consistent with the presence of both a first-order and a second-order process. The effects of structural changes in the nucleophile and in the leaving group indicate that the second-order process is similar to an $S_{N}2$ process while the first-order process has an $S_{N}1$ mechanism.

1-HALOGENO-2-NAPHTHOLS react with certain nucleophilic reagents more readily than the corresponding 1-halogenonaphthalenes.² Such reactivity seemed of interest since the halogeno-aromatic derivatives are generally activated to nucleophilic substitution by the -M effect of strong electron-withdrawing groups placed in a position conjugated with the carbon atom carrying the halogen.³ The hydroxyl group, on the other hand, executes a strong +M effect ³ so we would expect it to be strongly deactivating. To resolve this apparent anomaly, we have studied the reactions between halogenonaphthols and nucleophiles.

We have reported preliminary results from studies of reactions of 1-bromo-2-naphthols with amines in the absence of solvent ⁴ and of the reactions of 1-halogeno-2naphthols (Halogen = Br, Cl) with benzenethiolate.¹ In the first case normal products of substitution are obtained while in the second reductive dehalogenation is observed. We report herewith a study of the reactions between 1-halogeno-2-naphthol (halogen = Cl, Br) and substituted anilines in ethylene glycol as solvent.

RESULTS

1-Bromo-2-naphthol react with X-substituted anilines $(X = H, o-Me, -m-Me, p-Me, p-OMe, p . Cl, m . Cl, p . NO_2,$ and 2,6-Me₂) at 100 °C in ethylene glycol yielding almost quantitatively the expected 1-anilino-2-naphthols, according to the stoicheiometric equation (1) and in agreement with the results reported by Wahl and Lantz.²

$$\frac{2\text{Ph-NH}_2 + \text{Hal-C}_{10}\text{H}_6 - \text{OH} - }{\text{Ph-NH-C}_{10}\text{H}_6 - \text{OH} + \text{Ph-NH}_3^+ + \text{Hal}^- (1)}$$

Under the same experimental conditions the halogenonaphtholate ion (obtained by addition of 1 equiv. of Na to the ethylene glycol solution) does not react with aniline and

¹ Part I, M. Bosco, L. Forlani, and P. E. Todesco, Gazzetta,

¹ Part I, M. Bosco, L. Forlani, and P. E. 10desco, Gazzeua, 1967, **97**, 1594. ² M. A. Wahl and R. Lantz, Compt. rend., 1922, **175**, 171; Bull. Soc. chim. France, 1923, **33**, 93; M. Ringeissen, Compt. rend., 1934, **198**, 2180; Bull. Soc. chim. France, 1936, 333. ³ C. K. Ingold, 'Structure and Mechanism in Organic Chemis-try,' Cornell Univ. Press, Ithaca, N.Y., 1953; J. F. Bunnett, Ann. Rev. Phys. Chem., 1963, **14**, 271; J. F. Bunnett and R. E. Zahler, Chem. Rev., 1951, **49**, 273; S. D. Ross, in S. G. Cohen, A. Streitweiser, jun., and R. W. Taft, Prog. Phys. Org. Chem., 1963, **1**, 31; E. Buncel, A. R. Norris, and K. E. Russell, Quart. Fev., 1968, **22**, 123. Rev., 1968, 22, 123.

the 1-halogeno-2-naphthol can be recovered virtually quantitatively after a time much longer than that necessary for complete reaction with the undissociated halogenonaphthol.

Consistently halogenonaphthols react neither with an excess of sodium glycolate nor with an excess of sodium methoxide in methanol even after long reaction times in sealed ampoules at 100 °C, the starting materials being recovered unchanged. In both cases the u.v. spectra reveal that the halogenonaphthols are present in solution as halogenonaphtholate ions, the equilibria (2) determined by

$$R-O^{-} + Hal-C_{10}H_{6}-OH \implies ROH + Hal-C_{10}H_{6}O^{-} \quad (2)$$

the acidities of the alcohols and naphthols, lying almost entirely to the right. (For example, pK_a of methanol is 15.5; pK_a of 2-naphthol is 9.63. The introduction of an o-bromo-group in the series of phenols decreases the value by 1.58 units of pK_a . All data are measured in water.³ Since in water phenols and alcohols have different pK_a values, it seems reasonable that also in alcoholic solvents the difference is of the same order.)

Similar equilibria (3) are set up with amines; in the case RNH. + Hal-C H-OH ----

$$\operatorname{RNH}_{2} + \operatorname{Hal-C}_{10}\operatorname{H}_{6} - \operatorname{OH} = \operatorname{RNH}_{3}^{+} + \operatorname{Hal-C}_{10}\operatorname{H}_{6}\operatorname{O}^{-} (3)$$

of the reaction with a strongly basic amine such as piperidine the u.v. spectra of a mixture of piperidine and 1-halogeno-2-naphthol at 25 °C (at this temperature the substitution does not take place) have revealed the presence of a significant amount of naphtholate ion which is greatly reduced by adding piperidinium perchlorate. In the case of reaction with anilines the u.v. spectra at 25 °C have only small modifications. The results with piperidine will be reported elsewhere.

To avoid the complications arising from variation of the concentrations of the reactant species [due to equilibrium (3)] we have studied the reaction of 1-bromo-2-naphthol with substituted anilines in ethylene glycol at 100 °C using a large excess of nucleophile in the form of the perchlorates. The kinetic results, summarized in Table 1, show that the reactions are of the first order with respect to the halogenonaphthol (see results with p-toluidine labelled with a, b, and c), whereas the order in amine is less than unity as shown by the decrease in the values of k'' with increasing concentrations of amine.

⁴ M. Foá, A. Ricci, P. E. Todesco, and P. Vivarelli, Boll. Sci. Fac. Chim. ind. Bologna, 1965, 23, 233.
⁵ A. Albert and E. P. Serjeant, 'Ionisation Constants of Acid

and Bases,' Methuen and Co., London, 1962.

By plotting k' as a function of initial concentration of amine we obtain linear correlations between k' and aniline

TABLE 1

Rates of reaction of 1-bromo-2-naphthol (BN) with Xsubstituted anilines in ethylene glycol at 100 °C in the presence of 0.6M-X-anilinium perchlorate; [BN]_{initial} = 0.1M; [X-aniline] are the initial stoicheiometric concentrations (M) of X-substituted aniline; k' is the first-order rate coefficient in sec.⁻¹; k'' is the secondorder rate coefficient = k'/[X-aniline]

Aniline									
10 ² [Aniline] 10 ⁵ k' 10 ⁵ k''	$9.0 \\ 0.30 \\ 3.21$	$14 \\ 0.45 \\ 3.21$	$33 \\ 1.01 \\ 3.06$	$42 \\ 1 \cdot 28 \\ 3 \cdot 05$	$48 \\ 1.47 \\ 3.06$	$53 \\ 1 \cdot 60 \\ 3 \cdot 02$	$73 \\ 2 \cdot 19 \\ 3 \cdot 00$		
10²[⊅-Toluidine] 10⁵k′ 10⁵k‴	$2.0 \\ 0.13 \\ 6.50$	p^{-10} $4 \cdot 0$ $0 \cdot 25$ $6 \cdot 25$	6·0 0·3' 6·1'	10 7 0- 7 6-)# 60 00	10 ^b 0·60 6·00	$12 \\ 0.71 \\ 5.92$		
10²[p-Toluidine] 10⁵k′ 10⁵k″	$24 \\ 1 \cdot 40 \\ 5 \cdot 83$	$29 \\ 1 \cdot 69 \\ 5 \cdot 82$	$43 \\ 2 \cdot 5 \\ 5 \cdot 8$	$5 \\ 0 \\ 3 \\ 1 \\ 5 \\ 0$	i8 30 69	$67 \\ 3.80 \\ 5.67$	131 ° 7·30 5·57		
• [BN]1	nitial = ¢ [H	0·5м. ЗN] _{initiał}	b [B] = 0.0	N]initial 1 M.	= 0.0	25м.			
10²[p-Anisidine] 10⁵k′ 10⁵k″	$3.6 \\ 0.37 \\ 10.3$	р-Аг 7·5 0·71 9·47	isidine 22 2·0 9·4	2 7 2· 1 9·	7 53 37	40 3·70 9·25			
10 ² [m-Toluidine] 10 ⁵ k' 10 ⁵ k''	9·0 0·38 4·14	m-To 22 0·91 4·14	oluidine 39 1•6 4•1	8 0 3· 0 3·	1 23 99	84 3·38 4·02	108 4·26 3·94		
		p-Chlo	roanili	ne					
10²[p-Chloroanili 10⁵k′ 10⁵k″	ne]	15 0·25 1·67	44 0.66 1.50	70 1·0 1·4	2 6	$82 \\ 1 \cdot 19 \\ 1 \cdot 45$	$140 \\ 1.98 \\ 1.41$		
		m-Chlo	roanili	ne					
10 ² [<i>m</i> -Chloroanili 10 ⁵ k' 10 ⁵ k''	ne]	32 0·28 0·87	$70 \\ 0.58 \\ 0.83$	80 0·6 0·8	6 2	103 0·82 0·80	140 1·08 0·77		
		p-Niti	roanilir	ne					
10²[⊅-Nitroaniline 10⁵k′ 10⁵k″	e]	14 0·018 0·129	48 0∙028 0∙058	79 3 0·0 3 0·0	34 43	93 0∙036 0∙039			
o-Toluidine									
10 ² [o-Toluidine] 10 ⁵ k' 10 ⁵ k''	11 0·18 1·63	20 ∝ 0·31 1·55	$58 \\ 0.87 \\ 1.50$	63 0·95 1·50	100 ¢ 1·47 1·47	$100 \circ 1.45 1.45 1.45$	$145 \\ 2.08 \\ 1.43$		
^a [BN] _{initial} = 0.01 M. ^b [BN] _{initial} = 0.25 M. ^c [BN] _{initial} = 0.025 M.									
2.6-Dimethylaniline									
10 ² [2,6-Dimethyl 10 ⁵ k' 10 ⁵ k''	aniline]] 0.0	10 059 590	$26 \\ 0.125 \\ 0.480$	$12 \\ 0.5 \\ 0.4$	0 10 25	180 0·736 0·410		

concentration, in all cases of the form (4). Table 2 gives

$$k' = \frac{\text{Rate}}{[\text{Halogenonaphthol}]} = k_0' + k_2[\text{amine}] \quad (4)$$

the values of k_0' and k_2 for all the substituted anilines.

The kinetic data obtained with 1-chloro-2-naphthol

⁶ Data from this laboratory.

⁷ G. W. Wheland, 'Advanced Organic Chemistry,' J. Wiley and Sons, N.Y., 1960, sect. 14.8. measured at 150 °C because of the lower reactivity of the chloro-derivative are in Table 3.

DISCUSSION

The activation produced by the -OH group in the 1-halogeno-2-naphthols is clearly shown by our data. The reactivity of 1-bromo-2-naphthol with aniline as measured by the second-order rate coefficient (Table 2) is similar to that found for the case of the nitro-activated derivative. For example, the rate constant for the reaction between 1-bromo-4-nitronaphthalene and aniline in ethylene glycol at 100 °C in the presence of 0.6M-aniline perchlorate is $2\cdot5 \times 10^{-6}$ l. mole⁻¹ sec.^{-1.6}

Under the same experimental conditions the unactivated 1-bromonaphthalene is virtually unreactive towards aniline.

The activation produced by the -OH group is clearly not due to normal electronic effects. Consistently, the OMe group which has the same electronic effect³ behaves as a non-activating group in this kind of reaction, 1-bromo-2-methoxynaphthalene being completely unreactive under our experimental conditions.

On the other hand, the observed activating power of the -OH group is not due to the dissociation of 1halogeno-2-naphthol into the naphtholate ion, since when this dissociation takes place substitution does not occur.

The most probable explanation in agreement with the experimental data is that the reactive species arises from keto-enol tautomerism of the type (5). The



compound (II) must be considered as an α -halogeno-oxo- $\alpha'\beta'$ -unsaturated derivative. We have no direct evidence of the presence of (II) but, on the other hand, it is known that the tautomeric equilibrium in the case of phenols and naphthols is almost completely shifted towards the enol form.⁷

Christen and Zollinger,⁸ by n.m.r. spectroscopy, have demonstrated that compound (III) is an intermediate in the halogenation of the sodium salt of G-acid (III). It



seems reasonable therefore to consider (II) as the reactive form of the halogenonaphthols.

The concentration of (II) is related to the initial concentration of halogenonaphthols by the equilibrium constant $K_{\rm T} = [({\rm II})/[({\rm I})]$. Consequently all the kinetic constants reported in the Tables which contain the

⁸ M. Christen and H. Zollinger, Helv. Chim. Acta, 1962, 45, 2057.

concentrations of (II) are related to the true constants by the equation (6).

$$k_0' = (k_0')_{\text{True}} K_{\text{T}}; \ k_2 = (k_2)_{\text{True}} K_{\text{T}}$$
 (6)

When one considers a particular halogenonaphthol the comparison of k_0' and k_2 values is essentially a comparison between the 'true' kinetic constants and the determination of the values of $K_{\rm T}$ is not necessary for the interpretation of the results.

steric effects which are clearly demonstrated from the ratios in Table 4. The steric effects are actually larger than indicated by the ratios in Table 4, because the electronic effect of the methyl group acts in an opposite sense (see k_{p} -toluidine : $k_{aniline}$).

The observed 'element effect ' is relevant, the sequence $Cl \ll Br$ being found for both k_0 ' and k_2 values. [The comparison of rates for 1-chloro- and 1-bromo-2-naphthol is not fully justified since the values of k_T are

TABLE 2

Values of k_0' and k_2 (see text) of reactions of 1-bromo-2-naphthol with X-substituted anilines (k_0' in sec.⁻¹; k_2 in l. mole⁻¹ sec.⁻¹)

		<i>n</i> ₂	010 300.)		
$\mathbf{X} =$	p-OMe	p-Me	<i>m</i> -Me	o-Me	Н
105ko'	0.04 ± 0.01	0.05 ± 0.02	0.05 ± 0.02	0.04 ± 0.01	0.04 ± 0.01
$10^{5}k_{2}$	$9{\cdot}19\pm0{\cdot}03$	5.57 ± 0.02	3.93 ± 0.03	1.42 ± 0.01	2.96 ± 0.01
r	0.9999	0.9999	0.9998	0.9998	0.9999
x	<i>ф</i> -С1	477-C1	A-NO.	2.6-Me.	
105k.	0.05 + 0.01	0.06 + 0.02	0.016 + 0.001	0.02 + 0.01	
$10^{5}k_{2}$	1.38 ± 0.01	0.74 ± 0.02	0.023 ± 0.002	0.40 ± 0.01	
γ ⁻	0.9999	0.9993	0.9909	0.9998	

r are the correlation coefficients of equation (4).

On the basis of the experimental results, the formation of the normal product proceeds by two different pathways, the first depending only on the substrate and the second on the substrate and the reacting amines. In fact, k'_0 values are practically independent of the nature

TABLE 3

Rates of reaction of 1-chloro-2-naphthol with aniline in the presence of 0.6M-anilinium perchlorate at 150 °C in ethylene glycol. Concentration of 1-chloro-2-naphthol is 0.1M

10³[Anil	line]	271.3	473.1	773.9	998.6	1241
105k'	2	0.19	0.32	0.50	0.65	0.81
10 ⁵ k''		0.71	0.68	0.64	0.62	0.65
	$10^{5}k_{0}' =$	= 0.02 +	- 0.01;	$10^5 k_2 = 0$	63 + 0.02.	

and of the concentration of the amine; the observed variations being within experimental error. (The comparison of k_0' and k_2 values for different amines is in principle not fully justified since the reactions are carried out in the presence of different anilinium perchlorates. However, in a polar solvent the variations of the salt effect can probably be neglected, as secondary factors are probably responsible for the minor variation observed.)

In contrast, the values of k_2 show a dependence on both the concentration and the nature of the reacting aniline and electronic and steric effects are clearly distinguished.

In fact the values of k_2 for the *meta*- and *para*-substituted anilines correlate well (r = 0.9997) with the normal Hammett σ values; ⁹ for the *p*-NO₂ group the σ^- value is employed, as normally required in the case of anilines.¹⁰ The ρ coefficient is negative and of significant value ($\rho = -1.67 \pm 0.02$) indicating that the amine acts as a nucleophile and that bond-formation participates in the transition state.

A similar conclusion can be drawn by considering

different. However, the differences are probably not very great since the electronic effects of chlorine and bromine are much the same (see for example the relative σ_{para} values) and the carbon-halogen bond is not involved in the tautomeric equilibria. For this reason the very large differences in rates observed by changing the halogen probably refer to differences in the rates of the substitution processes.] This indicates that in both

TABLE 4 Values of $k_2(X \cdot Ph \cdot NH_2)$: $k_2(PhNH_2)$ $X = p \cdot Me$ o-Me 2,6-Me₂ Ratio = 1.88 0.48 0.14

reaction pathways bond-breaking is involved in the ratedetermining step.

The existence of two different reaction pathways, as indicated by the kinetic data, implies that the halogenooxo-derivative (II) behaves as a typical borderline



substrate, giving simultaneously a unimolecular substitution process $(S_N 1)$ which is not dependent on the amine and a bimolecular process $(S_N 2)$ which is (Scheme 1)

⁹ L. P. Hammett, *Chem. Rev.*, 1935, 17, 125; 'Physical Organic Chemistry,' McGraw-Hill Co., New York and London, 1940, ch. 7.

¹⁰ H. H. Jaffé, Chem. Rev., 1953, 53, 191.

The hypothesis that the α -halogeno-oxo-derivative undergoes an $S_{\rm N}1$ process (*i.e.*, formation of a carbonium ion near the carbonyl group) cannot be accepted without some reluctance. However, the presence of the condensed benzo-ring in the keto-form (II) may change the situation since in (II) C(1) is a typical benzylic carbon atom and $S_{\rm N}1$ processes occur readily in benzyl halides. A stabilization of a positive charge in the α -position with respect to a carbonyl group (synartetic ion) has been suggested by C. K. Ingold (personal communication).

 $S_{\rm N}$ and $S_{\rm N}$ processes usually compete when the two reaction pathways are of comparable difficulty. It is often possible, in particular cases, to eliminate the first or second component by structural variations.¹¹ In the present case a direct attack of the nucleophile on C(1)showed not to be particularly easy since C(1) atom is a cyclic secondary carbon atom, partly eclipsed by the π -electronic envelopment extended from carbonyl group to the benzo-condensed ring through the 3,4-ethylenic system. Consequently the $S_N 1$ process can take place concurrently and, in particular, when the reacting amine is highly sterically 'hindered' or when its nucleophilic power is low (*i.e.*, for the p-nitroaniline) the percentage of the S_N1 with respect to the S_N2 process increases markedly. In the case of 2,6-dimethylaniline small amounts (15% of yield) of the isomer (IV) were found



(m.p. = 186—188°))Found: C, 82·7; H, 6·5; N, 5·3°/o. Calc. for C₁₈H₁₄NO: C, 82·12; H, 6·45; N, 5·33°/o; $\nu_{max.}$ (NH) 3450 cm.⁻¹, ν (OH) 3610 cm.⁻¹; τ (CCl₄) 3·05 (2H, H₁ and H₄), τ (Me₂CO) 3·06 (H₄), 3·20 (H₁). The presence of this isomer, probably arising from the mesomeric structure of the intermediate cation [the normal substitution product, 1-(2',6'-dimethylphenyl)imino-2naphthol does not isomerise under the reaction conditions] strongly support the S_N1-like mechanism. Similar results have been obtained in the case of pnitroaniline which presents a high S_N1 : S_N2 ratio.



The bimolecular process which we have interpreted as a direct $S_N 2$ attack on C(1) could also arise, in principle, from attack of the nucleophile on the carbonyl group followed by an internal $S_N 2$ process as shown in Scheme 2. However, we have recently found ¹² that 1halogeno-4-naphthols (VI) react with aniline at rates comparable with those found with the 1,2-isomers, and give in the first stage normal substitution products which



then rapidly undergo oxidation-addition reactions (Scheme 3).



If the bimolecular substitution process proceeded as in Scheme 2 one would predict a very slow rate for the 1,4-derivatives since, for these compounds, the internal $S_N 2$ process is unfavoured. Since the rates of formation of substitution products [(VIII) in this case] are comparable with those observed for the 1,2-derivatives, Scheme 2 is eliminated.

All our data ^{1,6,12} show that the 1-halogeno-2-naphthols react with nucleophiles in ways depending on the nature of the nucleophile. All the experimental data can be interpreted in accord with the H.S.A.B.¹³ concepts as summarized in Scheme 4.



The hard reagents (alkoxides) attack the harder centre (H); reagents of intermediate softness (amines) attack both the hydrogen and the carbon [C(1)], soft reagents (PhS⁻) attack the halogen which is the softer centre.

In conclusion, the reactivity observed in the case of

¹¹ G. Kohnstam, A. Queen, and B. Shillaker, *Proc. Chem. Soc.*, 1959, 157; Y. Pocker, *J. Chem. Soc.*, 1959, 3939, 3944; P. Casapieri, E. R. Swart, *J. Chem. Soc.*, 1961, 4342; 1963, 1254; A. Fava, A. Iliceto, and A. Ceccon, *Tetrahedron Letters*, 1963, 685; A. Ceccon, I. Papa, and A. Fava, *J. Amer. Chem. Soc.*, 1966, **88**, 4643.

¹² V. Caló and P. E. Todesco, Chem. Comm., 1968, 571.

¹³ R. G. Pearson, J. Amer. Chem. Soc., 1963, **85**, 3533; 1967, **89**, 1827.

J. Chem. Soc. (B), 1970

1-halogeno-2-naphthol is not a halogeno-aromatic reactivity but is typical of halogeno-aliphatic derivatives, the keto-form (II) being responsible for all the phenomena observed.

EXPERIMENTAL

Materials.--Ethylene glycol was distilled under vacuum with a Vigreux column. The middle fraction was dried (Na₂SO₄) and distilled under vacuum (b.p. 115—116°/25 mm.¹⁴ 1-Bromo-2-naphthol, m.p. $84^\circ; {}^{15}$ 1-chloro-2naphthol, m.p. 70°; ¹⁶ 1-bromonaphthalene, b.p. 139°/16 mm.; ¹⁷ 1-bromo-2-methoxynaphthalene, m.p. 81-82; ¹⁸ anilines were allowed to react under conditions similar to those used for the kinetic experiments. When the reaction was complete (as indicated by titration of free halide-ion) the solution was poured on ice-water. The crude material was purified chromatographically on silica gel with benzeneethyl ether (10:1) as eluant.

In all cases the expected substitution product was obtained in high yields (80-90%). The characteristics of previously unknown products are given in Table 5.

Kinetics .-- The kinetic measurements were made titrimetrically by following the appearance of halide ion by the Volhard method.³ The organic substrate was extracted with carbon tetrachloride or chloroform before titration.⁴

TABLE	5
-------	----------

1-(X-Ph-NH)-2-naphthols

	M.p. (°C)	Solvent for crystallisation	Found				Required			
			c	Н	N	CI	C	Н	N	cì
<i>m</i> -Toluidine	104 - 105	Light petroleum	81.8	$5 \cdot 9$	5.3		81.91	6.06	5.61	
<i>p</i> -Chloroaniline	170 - 171	Light petroleum	71.7	4.5	$4 \cdot 9$	$13 \cdot 2$	71.24	4 · 4 8	5.19	13.14
<i>m</i> -Chloroaniline	108 - 109	Light petroleum	71.5	4.4	5.3	12.9	71.24	4.48	5.19	13.14
2,6-Dimethyl aniline	130-131	Light petroleum	83.3	6.5	$5 \cdot 3$		$82 \cdot 12$	6.45	5.33	

and 1-bromo-4-nitro-naphthalene, m.p. 85° 18 were prepared and purified by conventional methods.15-19

The X-substituted anilines were commercial products (Fluka), purified by vacuum distillation over Zn dust; the middle fractions were collected and used for kinetic measurements.

Anilinium perchlorates were prepared by mixing a cold ether solution of aniline and aqueous perchloric acid (70%)in the ratio 1:0.9 respectively. The solid material was filtered off, washed with cold anhydrous ether, and crystallised from ethyl acetate. The last traces of the solvent were removed by gentle warming under vacuum.

Products .-- 1-Halogeno-2-naphthols and X-substituted

¹⁴ A. Weissberger, 'Technique of Organic Chemistry,' vol. 7,

Organic Solvents, Interscience Publ. Inc., N.Y., 1955. ¹⁶ H. Franzen and G. Stauble, *J. prakt. Chem.*, 1921, **103**, 367. ¹⁶ H. E. Armstrong and H. C. Rossiter, *Chem. News*, 1889, 59, 225.

The k' values in Tables 1—5 are experimental pseudo-firstorder constants, evaluated graphically for reactions carried out in the presence of a larger excess of nucleophile with respect to halogenonaphthol. The first-order plots were linear up to 90% reaction.

When the concentration of the nucleophile is of the same order of magnitude or less than the concentration of halogenonaphthol, the k' values are evaluated by dividing the initial rates by the concentration of halogenonaphthol. The accuracy of k' values is $\pm 3\%$.

The financial assistance of Consiglio Nazionale delle Ricerche, Rome, is gratefully acknowledged.

[0/201 Received, February 6th, 1970]

¹⁷ H. T. Clarke, M. R. Brethen, Org. Synth., Coll. Vol. I, p. 121.
¹⁸ W. A. Davis, J. Chem. Soc., 1900, 77, 38.
¹⁹ H. H. Hodgson and J. Walker, J. Chem. Soc., 1933, 1620.