Chlorine as an Activating Group in an Electrophilic Substitution. The Friedel–Crafts Acetylation of 1-Chloronaphthalene

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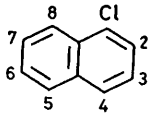
In the Friedel–Crafts acetylation of 1-chloronaphthalene all the seven monoketone isomers are formed, with 1-acetyl-4-chloronaphthalene usually predominating. In nitrobenzene solution the 2-, 6-, and 7-isomers are obtained in substantial amounts (10—30%). From competitive acetylations at 20 °C, and each reactant at 0.062 5 mol dm^{-3}, relative reactivities of naphthyl positions could be determined: in chloroform, 1- 1.00, 2- 0.45, 1-chloro-2- 0.23, 1-chloro-3- 0.16, 1-chloro-4- 5.1, 1-chloro-5- 0.28, 1-chloro-6- 0.31, 1-chloro-7- 0.28, and 1-chloro-8- 0.039; or, in nitromethane, 1.00, 4.1, 4.5, 0.011, 13, 0.76, 1.5, 1.5, and 0.65, respectively. This provides an example of activation towards electrophilic substitution by a chloro-substituent.

FRIEDEL–CRAFTS acetylations of 1-chloronaphthalene (1) have been reported several times.[1-3] The main product was described as 1-acetyl-4-chloronaphthalene, but its structure was not established unequivocally. Attack at the 5-, 7-, and 8-positions of the substrate (1) was also



(1)

reported,[3] the evidence being of the slenderest. A product of chlorine rearrangement, *viz.* 2-acetyl-6-chloronaphthalene, was, however, proven [1] for one experiment. Preferred *para*- (4-) substitution of the substrate (1) has also been reported for nitration,[4] sulphonation,[5] and halogenations.[6] The only quantitative results available are those for protodetritiations in trifluoroacetic acid at 70 °C, the most reactive (4-) position being deactivated by a factor of *ca.* 4 by the *para*-chloro substituent.[7]

The Friedel–Crafts acetylation of 1-chloronaphthalene (1) has now been investigated over a range of experimental conditions (Table 1). For chloroalkanes and carbon disulphide as solvents, excellent yields of ketones were obtained, with the 4-isomer predominating (75—84%). Five of the other isomers were formed in irregular small amounts and 1-acetyl-8-chloronaphthalene was obtained in traces (0.4—0.8%).

In nitro-solvents isomer proportions are significantly different. In nitromethane solution there is substantial formation of 2-acetyl-1-chloronaphthalene, at the expense of the main (4-) isomer. In contrast, in nitrobenzene solution there was found substantial formation of all the β-naphthyl isomers, *viz.* in addition to the 2-isomer (10—20%), the 6- and 7-isomers (15—30%) become important. With increasing temperature an increase in the proportions of these latter isomers was observed, and a decrease of the former.

The reactivities of the substituent positions of the substrate (1) have been measured against those of naphthalene, by the method of competitive substitutions, for solutions in chloroform and in nitromethane at 20 °C, as a function of reaction time. The results (Table 2) for the relative proportions of ketones formed were time-(*i.e.* concentration-) dependent. For chloroform solution the ratios of 1- to 2-acetylnaphthalenes were also time-dependent, but for nitromethane solution the ratios of both 1- to 2-acetylnaphthalenes and 4- to 2-acetyl-1-chloronaphthalenes were independent of time. Values extrapolated to zero reaction time allow us to make comparisons of the two substrates, 1-chloronaphthalene and naphthalene, at the initial concentration, of 0.062 5 mol dm^{-3} (for all reactants). The relative reactivities of individual positions thus obtained are collected in Table 3.

In chloroform solution six of the seven nuclear positions of 1-chloronaphthalene are less reactive than the corresponding positions of naphthalene, *i.e.* the chloro-substituent is generally deactivating. However, the 4-position of 1-chloronaphthalene is *activated* by a factor of *ca.* 5 with respect to the naphthalene 1-position. This result is unexpected, since for the Friedel–Crafts acetylation of chlorobenzene in 1,2-dichloroethane

TABLE 1

Friedel–Crafts acetylations of 1-chloronaphthalene by the Perrier procedure [a]

Solvent	Temp. (°C) [b]	Yield [c] (%)	Isomers (%) 2-	3-	4-	5-	6-	7-	8-
$CHCl_3$	20 [d]	97	3.6	2.4	79.8	4.4	4.8	4.4	0.56
CH_2Cl_2	20	95	2.8	2.5	83.3	3.8	3.7	3.5	0.40
$C_2H_4Cl_2$	20	95	2.4	2.9	81.1	3.7	8.1	1.3	0.63
CS_2	20	87	3.8	4.5	83.6	3.8	2.0	1.5	0.73
$MeNO_2$	20	95	22	0.040	62.3	2.7	5.4	5.3	2.3
$PhNO_2$	4	39	20.3	0.76	32.5	9.5	21.3	15.5	0.053
$PhNO_2$	20	46	12.9	1.0	36.9	6.0	25.0	18.2	0.042
$PnNO_2$	50	43	10.3	0.72	29.6	6.8	30.4	22.1	0.043

[a] The Perrier procedure involves final addition of substrate to the pre-formed complex of acyl chloride and aluminium chloride in the solvent. [b] Duration 6 h. [c] Percentage (w/w) includes any unreacted substrate (normally < 10% of the mixture). [d] When alternative addition procedures were used (Bouveault: final addition of the acyl component; Rousset: final addition of a mixture of substrate and acyl component; Elbs: final addition of the catalyst), very similar isomer proportions were obtained: 2- 3.2—3.8% 3- 2.3—3.7%, 4- 75.4—80.2%, 5- 3.5—3.7%, 6- 4.8—7.6%, 7- 4.4—6.9%, 8- 0.43—0.52%.

TABLE 2

Isomer ratios [a] obtained in competitive acetylations of 1-chloronaphthalene and naphthalene at 20 °C, for initial concentration 0.062 5 mol dm^{-3}, as functions of time

	$CHCl_3$ solution		$MeNO_2$ solution		
Time (min)	(1- + 2-AcN)/ 4-AcClN [b]	1-AcN/ 2-AcN [b]	(1- + 2-AcN)/ (2- + 4-AcClN) [b]	2-AcN/ 1-AcN [b]	4-AcClN/ 2-AcClN [b]
0	1.128 [c]	2.23 [c,d]	1.167 [c]	4.14 [e,f,g]	2.85 [e,h]
7			1.167	4.13	2.84
10	1.099	3.77	0.878	4.45	2 83
15	1.034	6.09			
30			0.915	3.44	2.94
45			1.233	3.93	2.83
60	0.978	7.68	1.369	4.66	2.83
120	0.908				
180	0.863				
240	0.855				
300	0.790				

[a] Molar ratios, after correction for detector mass-response. [b] Abbreviations: Ac = acetyl, N = naphthalene, ClN = 1-chloronaphthalene. [c] Extrapolated value. [d] Previously determined value 2.23 (ref. 9). [e] Mean of 17 determinations. [f] Standard deviation 0.47. [g] Previously determined value 4.10 (ref. 9). [h] Standard deviation 0.082.

TABLE 3

Relative reactivities of naphthyl positions, for acetylations at 20 °C at a concentration of 0.062 5 mol dm^{-3}

Naphthyl position	Relative reactivity			
	$CHCl_3$		$MeNO_2$	
1-	1.00		1.00	
2-	0.45	1.00	4.10	1.00
1-Chloro-2-	0.23	0.52	4.54	1.11
1-Chloro-3-	0.155	0.34	0.011	0.0027
1-Chloro-4-	5.14		13.0	
1-Chloro-5-	0.28		0.76	
1-Chloro-6-	0.31	0.69	1.52	0.37
1-Chloro-7-	0.28	0.63	1.49	0.36
1-Chloro-8-	0.039		0.65	

solution a partial rate factor was measured ($p_f = 0.125$) which indicates deactivation.[8]

In nitromethane solution the 4-position of the substrate (1) is again the most reactive position, the chloro-substituent causing activation by a factor of *ca.* 13. For the corresponding reaction of 1-methylnaphthalene a *ca.* 140-fold activation results,[9] indicating that of the two activating groups, a *para*-methyl group is the more effective by a factor of *ca.* 11 in nitromethane solution. The corresponding ratio in chloroform solution is *ca.* 12 : 1.

A similar comparison of the effects of a *p*-methyl-[10] and a *p*-chloro-substituent [8] for benzene in 1,2-dichloroethane solution at 25 °C, gives $f_p^{Me}/f_p^{Cl} = ca.\ 6\,000$. It is thus evident that there is a significant difference between the two aryl systems. Normally, *i.e.* for a benzene system, a chloro-substituent is said to affect the aromatic ring by a combination of $-I$ and $+M$ mechanisms; and, since overall deactivation results, $I > M$.[11] For the present system, where activation by chlorine has been observed, the chloro-substituent must be of the $I < M$ type, which requires that chlorine, by a conjugative mechanism, should be able to donate electrons much more effectively to the α-naphthyl *para*-position, than it is to a phenyl *para*-position. The reasons must be sought in the higher conjugating powers of an α-naphthyl position over a phenyl position,[12] and also in the electron demand of the electrophilic acetylating species.

The reactivity of the *peri*- (8-) position of 1-chloronaphthalene (1) is quite low in both solvents. This observation contrasts with results from nitrations, for which substantial formation (*ca.* 40%) of 1-chloro-8-nitronaphthalene has been reported.[13] *peri*-Acetylation is here subject to serious hindrance (*cf.* ref. 7). In acetylations of 1-methylnaphthalene [9] the corresponding *peri*-isomer, 1-acetyl-8-methylnaphthalene, was not formed at all.

EXPERIMENTAL

M.p.s are given in °C. Unless otherwise stated i.r. spectra were measured for KBr discs. ^{1}H N.m.r. spectra were obtained at 60 MHz for solutions in deuteriochloroform; signals were singlets, unless otherwise specified (c = complex).

1-Chloronaphthalene.—1-Chloronaphthalene was prepared from 1-naphthylamine by treatment of its diazonium salt solution with copper(I) chloride, in the usual way. It formed a pale yellow liquid, b.p. 81—83° at 0.7 mmHg, n_D^{19} 1.635 0 (lit.,[14] b.p. 259.3°, n_D^{20} 1.633 2), isomeric purity (by g.l.c.) >99.9%.

Friedel–Crafts Acetylations.—(1) *General.* The acetylations (Table 1) were carried out using equimolar quantities of 1-chloronaphthalene, acetyl chloride, and aluminium chloride, in the chosen solvent. The reactions were normally carried out using 1 g of substrate, and final concentrations of each reactant 0.25 mol dm^{-3}, at 20 ± 1 °C for 6 h. The mixtures of ketones were isolated in the usual way, and were then analysed by g.l.c. [glass column, 1.5 m long × 6.4 mm int. diam., filled with Bentone 34 (3.5%) and Carbowax 20M (1.5%) on 60—80 mesh Celite, used at 200 °C, with N_2 as carrier gas].

(2) *Competitive acetylations of 1-chloronaphthalene and naphthalene in chloroform or nitromethane.* A solution of 1-chloronaphthalene (0.813 g, 5.00 mmol) and naphthalene (0.640 g, 5.00 mmol) in the solvent (60 ml) was added rapidly (15 s) to a stirred mixture of aluminium chloride (0.667 g, 5.00 mmol) and acetyl chloride (0.392 g, 5.00 mmol) in the solvent (20 ml) at 20 ± 1 °C. Stirring was continued at 20 °C for a given time, and the mixture then added to ice and 10N-HCl, and worked up in the usual way. The residue obtained on careful evaporation was then analysed by g.l.c.

(3) *3-Acetyl-1-chloronaphthalene and 1-acetyl-4-chloronaphthalene.* (Modification of the procedure of Bassilios *et al.*[3]) A solution of 1-chloronaphthalene (16.3 g) in chloroform was added to a stirred solution of acetyl chloride (8.5 g) and aluminium chloride (16.0 g) in chloroform (total volume 100 ml). The mixture was kept at 40 °C for 30 min. The precipitate which formed was filtered off. Addition to a mixture of 10N-HCl and ice gave 1-acetyl-4-chloronaphthalene (19 g, 93%), m.p. 38° (light petroleum) (lit.,[3] 37—38°); $\nu_{max.}$ (film) 1 682 (C=O) and 772 cm^{-1} (C–Cl); τ 1.26 (m, 8-H), 1.72 (m, 5-H), 2.2—2.6 (c, 6-H, 7-H), 2.25 (d, 2-H), 2.51 (d, 3-H), and 7.34 (CH_3) ($J_{2,3}$ 8.1 Hz).

The filtrate from the above reaction was separately

treated with 10N-HCl and ice, to give an oily mixture, from which was obtained by preparative g.l.c. (glass column, 0.25 m long × 9.5 mm int. diam., filled with 20% OV 17 on 30—60 mesh Diatomite ' C ', at 180 °C, with N_2 as carrier gas) 3-*acetyl*-1-*chloronaphthalene* (126 mg, 0.6%), m.p. 65—66° (light petroleum) (Found: C, 70.2; H, 4.3; Cl, 16.9. $C_{12}H_9ClO$ requires C, 70.4; H, 4.4; Cl, 17.3%); $\nu_{max.}$ 1 678 (C=O) and 710 cm^{-1} (C–Cl); τ 1.4—2.6 (c, 5-, 6-, 7-, and 8-H), 1.43br (4-H), 2.03br (2-H), and 7.23 (CH_3).

2-*Acetyl*-1-*chloronaphthalene*.—A solution of methylmagnesium iodide [from magnesium (0.107 g) and iodomethane (0.62 g) in dry ether (40 ml)] was added dropwise to a solution of 1-chloro-2-naphthoyl chloride [15] (1.0 g) in dry ether (40 ml), and the mixture gently boiled for 3 h, then cooled, and treated with dilute sulphuric acid. The organic layer was separated, washed with 2.5N-NaOH then water, dried, and evaporated to give a crude ketone (0.54 g). Pure 2-*acetyl*-1-*chloronaphthalene* was obtained after column chromatography (alumina; benzene) and crystallisation (light petroleum), as white crystals, m.p. 76° (Found: C, 70.4; H, 4.7; Cl, 17.0. $C_{12}H_9ClO$ requires C, 70.4; H, 4.4; Cl, 17.3%); $\nu_{max.}$ 1 675 (C=O) and 796 cm^{-1} (C–Cl); τ 1.0—2.6 (c, arom. H) and 7.19 (CH_3).

5-*Chloronaphthalene*-1-*carbonitrile*.—1-Aminonaphthalene-5-carbonitrile [16] (4.0 g) was converted in the usual way, *via* a Sandmeyer reaction, into 5-*chloronaphthalene*-1-*carbonitrile* (2.6 g, 66%), as pale yellow crystals (ethanol), m.p. 148—148.5° (Found: C, 70.4; H, 3.3; Cl, 18.7; N, 7.4. $C_{11}H_6ClN$ requires C, 70.4; H, 3.2; Cl, 18.4; N, 7.5%); $\nu_{max.}$ 2 240 (C≡N) and 798 cm^{-1} (C–Cl); τ 1.57 (m, 8-H), 1.91 (m, 4-H), and 2.1—2.6 (c, arom. H) ($J_{7.8}$ 8.4 Hz).

The following compounds were prepared analogously: 5-*chloronaphthalene*-2-*carbonitrile* (69%), white needles (light petroleum), m.p. 142° (Found: C, 70.5; H, 3.4; Cl, 18.8; N, 7.4. $C_{11}H_6ClN$ requires C, 70.4; H, 3.2; Cl, 18.4; N, 7.5%); $\nu_{max.}$ 2 240 (C≡N) and 756 cm^{-1} (C–Cl); τ 1.62 (d, 4-H), 1.75 (d, 1-H), and 2.1—2.8 (c, arom. H) ($J_{1.3}$ 1.8, $J_{3.4}$ 8.6 Hz); 8-*chloronaphthalene*-2-*carbonitrile* (43%), pale yellow crystals (methanol), m.p. 112—113° (Found: C, 70.5; H, 3.3; Cl, 18.8; N, 7.3. $C_{11}H_6ClN$ requires C, 70.4; H, 3.2; Cl, 18.4; N, 7.5%); $\nu_{max.}$ 2 250 (C≡N) and 756 cm^{-1} (C–Cl); τ 1.35br (1-H), 2.06 (d, 4-H), 2.44 (d, 3-H), and 2.2—2.6 (c, arom. H) ($J_{3.4}$ 7.6, $J_{1.3}$ 1.2 Hz); 8-*chloronaphthalene*-1-*carbonitrile* (51%), white crystals (methanol), m.p. 145° (Found: C, 70.3; H, 3.3; Cl, 18.6; N, 7.2. $C_{11}H_6ClN$ requires C, 70.4; H, 3.2; Cl, 18.4; N, 7.5%); $\nu_{max.}$ 2 230 (C≡N) and 775 cm^{-1} (C–Cl); τ 1.49 (m, 4-H), 1.83 (m, 5-H), 2.03 (m, 2-H), and 2.2—2.6 (c, arom. H) ($J_{3.4}$ 8.8, $J_{2.3}$ 7.1 Hz).

1-*Acetyl*-5-*chloronaphthalene*.—A solution of 5-chloronaphthalene-1-carbonitrile (0.50 g) in dry ether (100 ml) was added rapidly, with stirring, to an excess of methylmagnesium iodide [from magnesium (0.64 g) and iodomethane (7.4) in ether (100 ml)]. The mixture was gently boiled for 18 h, then cooled, and a saturated solution of ammonium chloride added. The organic layer was separated and washed with water, and most of the solvent was distilled off. To the residue 3N-H_2SO_4 (100 ml) was added, and the mixture was boiled for 18 h. The combined chloroform extracts gave, on evaporation, a brown semi-solid (0.52 g). Column chromatography (alumina; benzene) and recrystallisation (alcohol) gave 1-*acetyl*-5-*chloronaphthalene* as white crystals, m.p. 54—54.5° (Found: C, 70.5; H, 4.7; Cl, 17.2. $C_{12}H_9ClO$ requires C, 70.4; H, 4.4; Cl, 17.3%); $\nu_{max.}$ 1 678 (C=O) and 758 cm^{-1} (C–Cl); τ 1.51 (m, 8-H), 2.11 (dd, 4-H), 2.2—2.8 (c, arom. H), and 7.25 (CH_3) ($J_{2.4}$ 1.2, $J_{3,4}$ 7.5 Hz).

The following compounds were prepared analogously: 6-*acetyl*-1-*chloronaphthalene* (crude yield 90%), pale yellow crystals (light petroleum), m.p. *ca.* 4°, or oily liquid (Found: C, 70.5; H, 4.7; Cl, 17.2%); $\nu_{max.}$ (film) 1 681 (C=O) and 740 cm^{-1} (C–Cl); τ 1.59 (d, 5-H), 1.6—2.7 (c, arom. H), and 7.27 (CH_3) ($J_{5.7}$ 1.8 Hz); 7-*acetyl*-1-*chloronaphthalene* (crude yield 93%), white crystals (light petroleum), m.p. 37—37.5° (Found: C, 70.6; H, 4.8; Cl, 17.3. $C_{12}H_9ClO$ requires C, 70.4; H, 4.4; Cl, 17.3%); $\nu_{max.}$ 1 680 (C=O) and 750 cm^{-1} (C–Cl); τ 1.06 (d, 8-H), 1.82 (dd, 6-H), 2.06 (d, 5-H), 2.20 (m, 4-H), 2.30 (m, 2-H), 2.48 (m, 3-H), and 7.30 (CH_3) ($J_{6.8}$ 1.8, $J_{5.6}$ 8.7, $J_{2,3}$ 7.2 Hz).

1-*Acetyl*-8-*chloronaphthalene*.—(1) Prepared as above (crude yield 96%), 1-*acetyl*-8-*chloronaphthalene* formed pale yellow crystals (light petroleum), m.p. 59—60° (Found: C, 70.6; H, 4.7; Cl, 17.0. $C_{12}H_9ClO$ requires C, 70.4; H, 4.4; Cl, 17.3%); $\nu_{max.}$ 1 692 (C=O) and 671 cm^{-1} (C–Cl); τ 1.68 (dd, 4-H), 2.36 (m, 5-H), 2.5—2.8 (c, arom. H), and 7.32 (CH_3) ($J_{2.4}$ 1.8, $J_{3.4}$ 7.8 Hz).

(2) A solution of 8-chloro-1-naphthoyl chloride [from 8-chloro-1-naphthoic acid [17] (2.0 g) and thionyl chloride (15 ml)] in dry ether (75 ml) was added to a suspension of dimethylcadmium [from anhydrous cadmium chloride (1.65 g), magnesium (0.44 g), and iodomethane (2.6 g)] in dry ether. The mixture was set aside for 72 h, then dilute sulphuric acid was added and the organic layer was separated, washed with 2.5N-NaOH then water, dried, and evaporated, to give a brown liquid (0.46 g, 24%). Pure 1-acetyl-8-chloronaphthalene (50 mg), m.p. 59—60°, was obtained after preparative t.l.c. (silica, 9 : 1 v/v chloroform–ethyl acetate) and crystallisation (Found: C, 70.8; H, 4.5; Cl, 17.4%); it was identical (mixed m.p., i.r. spectrum) with the ketone described under (1).

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