S 20.   *The Acylation of Naphthalene by the Friedel–Crafts Reaction.*

By G. BADDELEY.

Naphthalene has been acetylated and benzoylated in both methylene and ethylene chlorides. Almost exclusive α-substitution has been obtained in the absence of added reagents capable of combining with the acid chloride–aluminium chloride addition compound. Considerable β-substitution, particularly at higher temperatures, has been obtained in the presence of nitrobenzene, nitromesitylene, and excess of acid chloride respectively. It is suggested that this effect is due to the greater steric resistance to attack in the α-position by the more bulky aluminium chloride complexes.

VARIATION in the site of substitution with experimental conditions is a striking feature of the chemistry of naphthalene which has so far not received an adequate explanation. The oldest and most familiar instance, that of sulphonation, is complicated by the reversibility of the reaction; but this difficulty does not apply to the process of acylation in the presence of aluminium chloride in which similar variations have been observed. The literature on the acetylation and benzoylation of naphthalene by the Friedel–Crafts method is summarised by Lock (*Monatsh.*, 1943, **74**, 77) and Thomas (" Anhydrous Aluminium Chloride in Organic Chemistry," Monograph Series No. 87, New York, 1941), and is somewhat conflicting. Unfortunately, most of the reaction mixtures were heterogeneous, and the relative extents of α- and β-substitution were seldom determined accurately.

G 2

Usually, the aluminium chloride has been added gradually to a mixture of acid chloride and hydrocarbon in carbon disulphide. Perrier (*Bull. Soc. chim.*, 1903, **31**, 859), also employing carbon disulphide as solvent, introduced the modification of first forming the acid chloride–aluminium chloride complex and subsequently adding the hydrocarbon. This procedure involves warming a mixture of the two chlorides, alone or in the presence of carbon disulphide, and though satisfactory with some acid chlorides, *e.g.*, benzoyl chloride (Fieser, " Experiments in Organic Chemistry," 2nd Edit., p. 192), is unsatisfactory for general application owing to the low solubility of the complexes in carbon disulphide. This difficulty has now been overcome by employing solvents in which homogeneous solutions are readily obtained at ordinary temperatures. The following solvents, with their dielectric constants at 20° in parentheses, are in the order of decreasing ability to provide homogeneous solutions when molecular proportions of aluminium chloride and acetyl chloride are brought together at 20°: ethylene chloride (10), methylene chloride (10), ethylidene chloride (10), ethylene bromide (6·3), ethyl bromide (9·4), acetylene tetrachloride (8·2), and chloroform (5·0). Carbon disulphide (2·6), carbon tetrachloride (2·2), tetrachloroethylene (2·4), and light petroleum (*ca.* 2) are very poor solvents. *p*-Methoxybenzoyl chloride clearly demonstrates the limitations of carbon disulphide as a solvent in which to form an acid chloride–aluminium chloride complex. The gradual addition of aluminium chloride to a solution of *p*-methoxybenzoyl chloride in carbon disulphide gives an insoluble complex which prevents ready contact between the two components. Raising the temperature does not overcome this low solubility, and is undesirable as demethylation ensues. No ready reaction occurs when naphthalene is added. On the other hand, *two* molecular proportions of aluminium chloride dissolve in a solution of *p*-methoxybenzoyl chloride in ethylene or methylene chloride. The clear solution of the complex *p*-MeO·C$_6$H$_4$·COCl–2AlCl$_3$ gives an immediate reaction with naphthalene and an excellent yield of α-*p*-methoxybenzoyl-naphthalene.

Table I summarises results which have now been obtained by the acetylation and benzoylation of naphthalene in ethylene and methylene chlorides at 35° by acid chloride–aluminium chloride complex (1 mol.) alone or in the presence of excess (1 mol.) of acid chloride or other selected agents (1 mol.). The acetic anhydride–aluminium chloride complex is also included as an acetylating agent.

TABLE I.

Expt. no.	Acylating agent (1 mol.).	Selected agent (1 mol.).	α- and β-Naphthyl ketones.		
			Yield, %.*	α, %.	β, %.
1	(CH$_3$·CO)$_2$O–2AlCl$_3$	None	60	97·5	2·5
2	CH$_3$·COCl–AlCl$_3$	,,	93	98·0	2·0
3	,,	CH$_3$·COCl	76	60	40
4	,,	CH$_3$·COCl–AlCl$_3$	93^a	97·5	2·5
5	,,	C$_6$H$_5$·COCl	70^b	40	60
6	,,	2 : 4 : 6-Me$_3$C$_6$H$_2$·NO$_2$	88	29	71
7	,,	C$_6$H$_5$·NO$_2$	82	40	60
8	,,	C$_6$H$_5$·NO$_2$–AlCl$_3$	87	97·5	2·5
9	,,	C$_6$H$_5$·NO$_2$ as solvent	82	34	66^c
10	C$_6$H$_5$·COCl–AlCl$_3$	None	86	96	4
11	,,	C$_6$H$_5$·COCl	60	60	40
12	,,	C$_6$H$_5$·COCl–AlCl$_3$	86^a	96	4
13	,,	C$_6$H$_5$·NO$_2$	80	70	30
14	,,	C$_6$H$_5$·NO$_2$–AlCl$_3$	85	96	4
15	,,	C$_6$H$_5$·NO$_2$ as solvent	75	68	32
16	,,	*m*-C$_6$H$_4$(NO$_2$)$_2$	80	90	10

* The yields are only approximate, and differences of less than 5% are not significant.
a The further acylation of the naphthyl ketone is a much slower reaction.
b Benzoylnaphthalene (10%) was also obtained.
c St. Pfau and Ofner (*Helv. Chim. Acta*, 1926, **9**, 669) found α : β : : 11 : 89.

Almost pure α-naphthyl ketones are obtained in ethylene and methylene chlorides in the absence of reagents which combine with the acid chloride–aluminium chloride complex. Considerable β-substitution, comparable with that in nitrobenzene as solvent, occurs when molecular proportions of nitrobenzene, nitromesitylene, and additional acid chloride respectively are present. But it is again almost excluded when additional aluminium chloride is added to engage these reagents. β-Substitution is not greatly increased by the presence of *m*-dinitrobenzene; this reagent, apparently, although sufficiently basic to combine with aluminium chloride (Walker and Spencer, *J.*, 1904, **85**, 1106), does not combine appreciably with the acid chloride–aluminium chloride complex. The present work clearly indicates that the gradual

addition of aluminium chloride to a mixture of acid chloride and naphthalene must result in considerable β-substitution especially during the first half of the addition.

The need for use of at least one molecular proportion of aluminium chloride in such Friedel–Crafts reactions arises from combination of the chloride with the resulting ketone :

$$R \cdot CCl{:}O{-}AlCl_3 + C_{10}H_8 = C_{10}H_7 \cdot CR{:}O{-}AlCl_3 + HCl$$
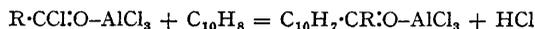
and it is recognised that similar combination with the acid chloride used is the condition for occurrence of the reactions. The influence of the various substances added in the above experiments must be attributed to the fact that in these cases the substituting agent is not the acid chloride–aluminium chloride complex itself but a larger complex with the added reagent. One effect of such extended complex formation is to reduce the electron demand and hence the activity for acylation purposes. This is illustrated in Table II which summarises results which have been obtained at 35° by the addition of benzene, naphthalene, and anisole respectively to a solution of acetyl chloride (1 mol.) and aluminium chloride (1 mol.) in nitrobenzene and in ethylene chloride alone or in the presence of selected agents (1 mol.). It is,

TABLE II.

Solvent.	Selected agent.	benzene.	Reaction with : naphthalene.	anisole.
Nitrobenzene	None	Nil[a]	Moderate	Fast
Ethylene chloride	,,	Fast	Fast	,,
,, ,,	m-$C_6H_4(NO_2)_2$	,,	,,	,,
,, ,,	$C_6H_5 \cdot NO_2$	Slow	Moderate	,,
,, ,,	$(C_6H_5)_2CO$	Nil	Nil	Slow
,, ,,	p-$MeO \cdot C_6H_4 \cdot COMe$	,,	,,	Nil

a Chopin (*Bull. Soc. chim.*, 1924, **35**, 610) observed that acetophenone can be prepared by the Friedel–Crafts method in nitrobenzene if undissolved aluminium chloride is also present. This is, no doubt, a surface reaction.

however, highly improbable that this effect promotes the β-substitution noticed in Table I, since the α-position in naphthalene is normally more reactive than the β-, and shows itself to be so in the sulphonation reaction. Another explanation must therefore be sought, and it is suggested that this is to be found in the greater steric resistance to attack in the α-position by the more bulky aluminium chloride complexes. In the β-position, of course, no such resistance is encountered.

Whereas Roux (*Ann. Chim.*, 1887, **12**, 289), Claus and Tersteegen (*J. pr. Chem.*, 1890, **42**, 517), and Caille (*Compt. rend.*, 1911, **153**, 393) obtained increased yields of β-ketone at higher temperatures, Lock (*loc. cit.*) observed no change of the α : β ratio with temperature. Although the data now obtained and listed in Table III confirm the results of the earlier workers, the combined yields of α- and β-naphthyl ketones are less at the higher temperatures, and the change in the α : β ratio may be due in part to a readier decomposition of the α-ketones. Table III shows the results when a solution of acid chloride (1 mol.) and aluminium chloride (1 mol.) in nitrobenzene was gradually added to a solution of naphthalene in nitrobenzene at the selected temperature.

TABLE III.

Acid chloride.	Temp.	Yield, %.	α- and β-Naphthyl ketones. α, %.	β, %.
$CH_3 \cdot COCl$	35°	82	34	66
,,	100	76	25	75
,,	120	70	19	81
$C_6H_5 \cdot COCl$	35	75	68	32
,,	150	54	38	62

EXPERIMENTAL.

α- and β-Naphthyl Methyl Ketones.—The former (m. p. 10·5°, Lock, *loc. cit.*) was identified by its picrate, m. p. 118° (Stobbe and Lenzner, *Annalen*, 1911, **380**, 95). The m. p.s of mixtures of the two ketones were as follows :

β, %	100	95	90	85	80	75	70	65	60	55	50	45	40
M. p.	55·0°	52·7°	50·4°	48·0°	45·5°	43·0°	40·4°	37·5°	34·4°	31·0°	27·5°	23·6°	19·5°

These data were applied to the analysis of the ketonic mixtures obtained in the reactions described below. The amount of the α-ketone was confirmed in each case by quantitative isolation of the picrate by the following method. The ketone (*ca.* 1 g.) was accurately weighed into a conical flask (100 c.c.)

together with picric acid (1·2 mols.). Ethanol (50 c.c.), saturated with the picrate of the α-ketone at 18°, was added, and a homogeneous solution obtained by warming. After a day at 18° the picrate was isolated in a sintered glass funnel, washed with ethanol (10 c.c.) saturated with the picrate, dried, and weighed. Occasionally, depending on the amount of β-ketone present, the picrate had a low m. p. and was recrystallised from ethanol saturated with the picrate. The mixture was again left for a day at 18° before the picrate was isolated and weighed. Each analysis was duplicated using pure α-naphthyl methyl ketone. A similar procedure in which the picrate of phenyl β-naphthyl ketone was quantitatively isolated, purified, and weighed, was employed to confirm the composition of mixtures of phenyl α- and β-naphthyl ketones.

(1) Acetic anhydride (20·4 g.; 1 mol.) was gradually added to a well stirred mixture of aluminium chloride (56 g.; 2 mols.) in ethylene chloride (100 c.c.). After ½ hours' stirring, a solution of naphthalene (25·6 g.) in ethylene chloride (50 c.c.) was gradually added. The temperature was kept at 35° during the addition, but was subsequently raised to 50° to complete the reaction. After decomposition with dilute hydrochloric acid the product provided a fraction (20 g.; b. p. 163°/15 mm.; m. p. 9·0° and mixed m. p. 9·5° with pure α-naphthyl methyl ketone) which was almost pure α-naphthyl methyl ketone. Picrate analysis indicated 97·5% of α-ketone.

(2) A solution of acetyl chloride (8 g.; 1 mol.) and aluminium chloride (14 g.; 1 mol.) in ethylene chloride (30 c.c.) was gradually added to a solution of naphthalene (13 g.) in ethylene chloride (30 c.c.) at 35°. A ready reaction occurred, and a solid separated. The mixture was decomposed with dilute hydrochloric acid, and the product provided a fraction (16 g.; b. p. 163°/15 mm.; m. p. 9·0° and mixed m. p. 9·5° with pure α-naphthyl methyl ketone) which was almost pure α-naphthyl methyl ketone. Picrate analysis indicated 98% of α-ketone. A similar result was obtained when the solution of naphthalene was gradually added to the solution of acetyl and aluminium chlorides.

(3) Experiment (2) was repeated, using acetyl chloride (16 g.; 2 mols.), and the product provided a fraction (13 g.; b. p. 165°/15 mm.; m. p. 20·0°) which contained 40·5% of β-ketone (60·5% of α-ketone by picrate analysis).

(4) The above experiment was repeated with aluminium chloride (28 g.; 2 mols.). The product provided a fraction (16 g.) which was almost pure α-ketone, m. p. 9·0° and mixed m. p. 9·5°. Picrate analysis indicated 98·0% of α-ketone.

(5) A solution of benzoyl chloride (14 g.; 1 mol.), acetyl chloride (8 g.; 1 mol.), and aluminium chloride (14 g.; 1 mol.) in ethylene chloride (30 c.c.) was added to a solution of naphthalene (13 g.) in ethylene chloride (25 c.c.) at 35°. Naphthyl methyl ketones (12 g.; b. p. 165°/15 mm.; m. p. 34·0°) and phenyl naphthyl ketones (3 g.; b. p. 223°/15 mm.) were obtained. The mixture of methyl ketones contained 59·5% of β-ketone (40% of α-ketone by picrate analysis).

(6) A solution of nitromesitylene (20 g.; 1·2 mols.), acetyl chloride (10 g.; 1·2 mols.), and aluminium chloride (17 g.; 1·2 mols.) in ethylene chloride (25 c.c.) was added to a solution of naphthalene (13 g.) in ethylene chloride (25 c.c.) at 35°. The product provided a fraction (15 g.; m. p. 42·5°) which contained 74% of β-ketone (28·5% of α-ketone by picrate analysis).

(7) The nitromesitylene in the above experiment was replaced by nitrobenzene (15 g.; 1·2 mols.), and the product provided a fraction (14 g.; m. p. 34·0°) which contained 59·5% of β-ketone (41% of α-ketone by picrate analysis).

(8) The previous experiment was repeated with aluminium chloride (34 g.; 2·4 mols.), and almost pure α-ketone (14·8 g.) was obtained. Picrate analysis indicated 97·5% of α-ketone.

(9) Experiment (2) was repeated with nitrobenzene as solvent. The ketone (14 g.; m. p. 38·0°) contained 66% of β-ketone (35% of α-ketone by picrate analysis). At 100° the reaction provided ketone (13 g.; m. p. 43·0°) containing 75% of β-ketone (26% of α-ketone by picrate analysis). The reaction was also carried out at 120°; the resulting ketone (12 g.; m. p. 46·0°) contained 81% of β-ketone (22% of α-ketone by picrate analysis).

α- *and* β-*Benzoylnaphthalene.*—These, m. p. 75·5° and 82·0° respectively (Mollarits and Merz, *Ber.*, 1873, **6**, 541), gave picrates, m. p. 75° (Found : N, 9·2. Calc. for $C_{23}H_{15}O_8N_3$: N, 9·1%), and 115° (Rousset, *Bull. Soc. chim.*, 1896, **15**, 71) respectively. The m. p.s of mixtures of the two ketones were as follows :

β, %	100	95	90	85	80	75	70	65	60
M. p.	82·0°	78·1°	74·1°	70·2°	66·3°	62·4°	58·4°	54·5°	51·0°
α, %	100	95	90	85	80	75	70	65	60
M. p.	75·5°	72·8°	70·1°	67·5°	65·0°	62·4°	59·8°	57·3°	55·0°

These data were applied, in the manner described in Experiment 11, to the analysis of the ketonic mixtures obtained in the following reactions.

(10) A solution of naphthalene (128 g.) in ethylene chloride (200 c.c.) was added to a solution of aluminium chloride (140 g.; 1 mol.) and benzoyl chloride (141 g.; 1 mol.) in ethylene chloride (200 c.c.) at 35°. The product provided a fraction (200 g.; b. p. 225°/15 mm.; m. p. 73·0° and mixed m. p. 74·5° with the pure α-benzoylnaphthalene) which contained 96% of α-ketone. The result was the same when the order of mixing was reversed.

(11) A solution of naphthalene (13 g.) in ethylene chloride (25 c.c.) was added to a solution of aluminium chloride (14 g.; 1 mol.) and benzoyl chloride (30 g.; 2 mols.) in ethylene chloride (30 c.c.) at 35°. The final product provided a fraction (14 g.) which melted at 55°. This m. p., which was raised by small additions of α-ketone and depressed by small additions of β-ketone, indicated 60% of α-ketone. The product (2·35 g.; m. p. 55·0°) and pure α-ketone (0·22 g.) gave a mixture (m. p. 56·5°) compatible with 63·4% of α-ketone; the subsequent addition of pure β-ketone (1·50 g.) gave a mixture (m. p. 51·0° and raised by small additions of β-ketone) compatible with 60% of β-ketone. Thus the initial ketone mixture contained 60% of α- and 40% of β-benzoylnaphthalene.

(12) The above experiment was repeated with aluminium chloride (28 g.; 2 mols.). The product provided a fraction (20 g.) which contained 96% of α-ketone.

(13) A solution of naphthalene (13 g.) in ethylene chloride (25 c.c.) was added to a solution of aluminium chloride (14 g.; 1 mol.), benzoyl chloride (14 g.; 1 mol.) and nitrobenzene (12·5 g.; 1 mol.) in ethylene chloride (30 c.c.) at 35°. The product provided a fraction (18·5 g.) which contained 70% of α- and 30% of β-ketone.

(14) When aluminium chloride (28 g.; 2 mols.) was employed in the foregoing experiment, the product provided a fraction (19·5 g.) which contained 96% of α-ketone.

(15) Experiment (13) was repeated using nitrobenzene as solvent. The reaction was s ow and the product provided a fraction (17·5 g.) which contained 68% of α- and 32% of β-ketone. At 150° the reaction provided a mixture (12·5 g.) of 38% of α- and 62% of β-ketone.

(16) When the nitrobenzene in experiment (13) was replaced by *m*-dinitrobenzene (17 g.; 1 mol.), the product provided a fraction (18·5 g.) which contained 90% α- and 10% of β-ketone.

p-*Methoxybenzoylnaphthalene.*—*p*-Methoxybenzoyl chloride (17 g.) in ethylene chloride (50 c.c.) was shaken in the cold with aluminium chloride (33 g.), and the clear solution decanted from undissolved aluminium chloride (3 g.). A ready reaction occurred on addition of naphthalene (13 g.) in ethylene chloride (50 c.c.). The mixture was decomposed with ice and dilute hydrochloric acid, and the ethylene chloride layer was separated, washed with dilute sodium hydroxide solution, and dried (K_2CO_3). Distillation provided a fraction, b. p. 274—275°/15 mm. (22 g.; 85%), which readily solidified and recrystallised from ethanol in colourless prisms, m. p. 101—101·5° (Found : C, 82·3; H, 5·4. Calc. for $C_{18}H_{14}O_2$: C, 82·45; H, 5·3%). This substance is identical (m. p. and mixed m. p.) with the product of the Friedel–Crafts reaction between α-naphthoyl chloride and anisole (Meister, Lucius and Brüning, B.P., 234,173, 1924) and is, therefore, α-*p*-methoxybenzoylnaphthalene.

COLLEGE OF TECHNOLOGY, MANCHESTER. [*Received, July* 6*th*, 1948.]