# Friedel–Crafts Acylations of Aromatic Hydrocarbons. Part XI.[1,2] The Acetylation and Benzoylation of 2,6-Dimethylnaphthalene

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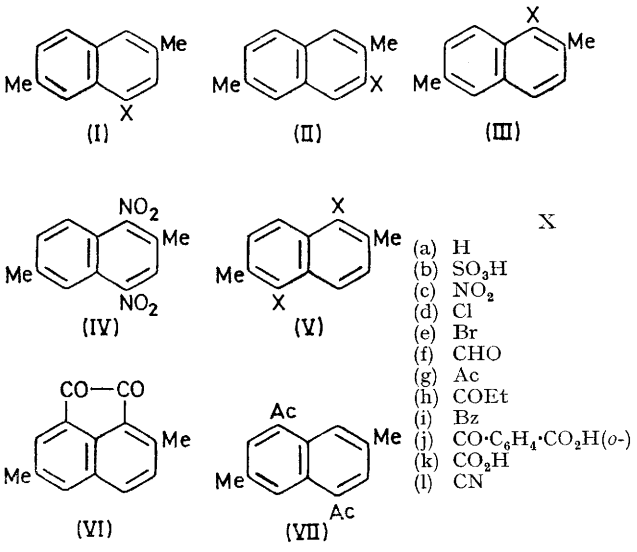
The Friedel–Crafts acetylation or benzoylation of 2,6-dimethylnaphthalene gives mainly 1-acetyl-3,7-dimethylnaphthalene or 1-benzoyl-2,6-dimethylnaphthalene, respectively. Smaller amounts of the other isomers are also formed. Diacetylation affords mixtures of 1,5-diacetyl-2,6-dimethylnaphthalene and 1,5-diacetyl-3,7-dimethylnaphthalene. Competitive acetylation of 2,6-dimethylnaphthalene and naphthalene in chloroform solution gives the following positional reactivities: 1-naphthyl 1·00, 2-naphthyl 0·31, 2,6-dimethyl-1-naphthyl 4·1, 3,7-dimethyl-1-naphthyl 8·1, 3,7-dimethyl-2-naphthyl 0·045; the values for the corresponding benzoylation are 1·00, 0·40, 260, 116, and 12, respectively.



THE aromatic substitution of 2,6- (or *amphi*-)dimethylnaphthalene (Ia) has been actively studied. Sulphonation has been reported to give 3,7-dimethylnaphthalene-1-sulphonic acid (Ib) below 40 °C,[3] or 2,6-dimethylnaphthalene-3-sulphonic acid (IIb) at about 140 °C.[3–5] Nitration, on the other hand, gave mainly 2,6-dimethyl-1-nitronaphthalene (IIIc).[4,6] Dinitration afforded either 2,6-dimethyl-1,4-dinitronaphthalene (IV), or 2,6-dimethyl-1,5-dinitronaphthalene (Vc).[6] More recently the formation of the isomers (IIIc) (81·6%), (Ic) (16·5%),




X
(a) H
(b) $SO_3H$
(c) $NO_2$
(d) Cl
(e) Br
(f) CHO
(g) Ac
(h) COEt
(i) Bz
(j) $CO{\cdot}C_6H_4{\cdot}CO_2H(o\text{-})$
(k) $CO_2H$
(l) CN

and (IIc) (1·9%) upon nitration were reported.[7] Chlorination of 2,6-dimethylnaphthalene afforded 1-chloro- (IIId) and 1,5-dichloro-2,6-dimethylnaphthalene (Vd).[8] A mixture of 1-bromo- (IIIe) and 1,5-dibromo-2,6-dimethylnaphthalene (Ve),[4] or a mixture of monobromo-derivatives (IIIe) (96·1%) and (Ie) (3·9%)[9] were reported for brominations.

Hydrocarbon (Ia) was reported to undergo the Gattermann aldehyde reaction to give 1-formyl-2,6-dimethylnaphthalene (IIIf).[10] Friedel–Crafts acylations of 2,6-dimethylnaphthalene (Ia) have been investigated by various workers. Clar, Wallenstein, and Avenarius[11] obtained an acetyl derivative, m.p. 70—71°, by the action of acetic anhydride and aluminium chloride on hydrocarbon (Ia) in carbon disulphide suspension, and labelled it the 1-isomer (IIIg) without proof. The same compound was obtained, and the same orientation assumed, by Dziewonski, Stec, and Zagala[12] by the use of nitrobenzene as solvent. A similar procedure was also assumed to give 1-propionyl-2,6-dimethylnaphthalene (IIIh).[12] Cook[13] prepared 1-benzoyl-2,6-dimethylnaphthalene (IIIi) by a Friedel–Crafts benzoylation in carbon disulphide suspension, and this has been confirmed by other workers.[14] Proof of structure was obtained by an Elbs cyclisation of the ketone to 3-methylbenz[*a*]anthracene.[13] *m*- and *p*-Toluoyl chlorides[13] react analogously [orientation as in (III)], as do 1- and 2-naphthoyl chlorides.[15,16] 1,5-Dibenzoyl-2,6-dimethylnaphthalene (Vi) could be obtained by a Friedel–Crafts benzoylation using an excess of reagents.[11] Elbs cyclisation of the diketone (Vi) led to the formation of dibenzo[*b*,*k*]chrysene, providing proof of orientation. A similar diacylation was shown to take place with 2-naphthoyl chloride.[16] With phthalic anhydride and aluminium chloride in tetrachloroethane solution a mixture of *o*-(2,6-dimethyl-1-naphthoyl)- (IIIj) and *o*-(3,7-dimethyl-1-naphthoyl)-benzoic acids (Ij) were obtained.[17] By the action of oxalyl chloride and aluminium chloride the hydrocarbon (Ia) was shown to yield 3,7-dimethylacenaphthenequinone (VI) and 2,6-dimethylnaphthalene-1-carboxylic acid (IIIk) (see below).[18]

[1] Part X, P. H. Gore, C. K. Thadani, S. Thorburn, and M. Yusuf, *J. Chem. Soc.* (*C*), 1971, 2329.
[2] Preliminary communication, P. H. Gore and M. Yusuf, *Chem. Comm.*, 1969, 1487.
[3] R. Weissgerber and O. Kruber, *Ber.*, 1919, **52**, 346.
[4] V. Vesely and F. Stursa, *Collection Czech. Chem. Comm.*, 1932, **4**, 21.
[5] O. Kruber and A. Marx, *Ber.*, 1939, **72**, 1970.
[6] F. Mayer and E. Alken, *Ber.*, 1922, **55**, 2278.
[7] A. Davies and K. D. Warren, *J. Chem. Soc.* (*B*), 1969, 873.
[8] J. C. Richer and N. Baskevitch, *Canad. J. Chem.*, 1968, **46**, 2975.
[9] J. B. Kim, C. Chen, J. K. Krieger, K. R. Judd, C. C. Simpson, and E. Berliner, *J. Amer. Chem. Soc.*, 1970, **92**, 910.
[10] L. E. Hinkel, E. E. Ayling, and J. H. Beynon, *J. Chem. Soc.*, 1936, 339.
[11] E. Clar, H. Wallenstein, and R. Avenarius, *Ber.*, 1929, **62**, 950.
[12] K. Dziewonski, K. Stec, and P. Zagala, *Bull. Acad. polon. Sci.*, 1938, 324.
[13] J. W. Cook, *J. Chem. Soc.*, 1932, 456.
[14] R. Scholl, J. Donat, and S. Hass, *Ber.*, 1935, **68**, 2034.
[15] J. W. Cook, *J. Chem. Soc.*, 1931, 489.
[16] L. F. Fieser and E. M. Dietz, *Ber.*, 1929, **62**, 1827.
[17] L. F. Fieser and M. Fieser, *J. Amer. Chem. Soc.*, 1933, **55**, 3342.
[18] R. Lesser and G. Gad, *Ber.*, 1927, **60**, 242.

The work here reported describes our detailed study of the Friedel–Crafts acetylation and benzoylation of 2,6-dimethylnaphthalene (Ia), catalysed by aluminium chloride.

*Syntheses.*—The ketones (IIg) and (IIIg) were obtained by independent syntheses. Bromination of the hydrocarbon (Ia) in chloroform–carbon tetrachloride gave a liquid bromo-derivative. Previously [4] 1-bromo-2,6-dimethylnaphthalene (IIIe) had been obtained as a solid, m.p. 34°. We could show indirectly that our material contained *ca.* 10% of the isomer 1-bromo-3,7-dimethylnaphthalene (Ie), since conversion *via* the cyano-derivatives to the acetyl-derivatives, by standard procedures,[19] gave a mixture of ketones (IIIg) and (Ig). 1-Acetyl-2,6-dimethylnaphthalene (IIIg) is a liquid, which could be obtained pure by preparative gas chromatography. The ketone, m.p. 70—71°, previously reported [11,12] as (IIIg) was shown [2] by i.r. and n.m.r. spectroscopy (see below) to be 1-acetyl-3,7-dimethylnaphthalene (Ig).

3,7-Dimethylnaphthalene-2-sulphonic acid [4] (IIb) was converted by fusion of its sodium salt with potassium cyanide into the nitrile (III). Addition of methylmagnesium iodide, and hydrolysis of the intermediate ketimine afforded 2-acetyl-3,7-dimethylnaphthalene (IIg), m.p. 104°. 2-Benzoyl-3,7-dimethylnaphthalene (IIi), m.p. 121°, was obtained analogously.

1-Acetyl-3,7-dimethylnaphthalene (Ig) with boiling hypochlorite gave 3,7-dimethylnaphthalene-1-carboxylic acid (Ik), m.p. 204—206°, which, *via* the acid chloride, and a Friedel–Crafts acylation using an excess of benzene, gave 1-benzoyl-3,7-dimethylnaphthalene (Ii), m.p. 83°.

Carbonation of the Grignard reagent from the bromo-compound (IIIe) afforded authentic 2,6-dimethylnaphthalene-1-carboxylic acid (IIIk), m.p. 173°. The acid, m.p. 204°, obtained [18] by the action of oxalyl chloride on the hydrocarbon (Ia) (see above) was therefore (Ik) and not (IIIk), as claimed.[18,20]

*Friedel–Crafts Acetylations.*—The results of the acetylation experiments on 2,6-dimethylnaphthalene (Ia) are summarised in Tables 1 and 2. The isomer proportions were determined by quantitative g.l.c. analysis, after initial purification of the reaction products by passage through alumina. Table 1 shows that the three monoacetyl derivatives (IIIg), (IIg), and (Ig) were formed in every reaction. The preferred point of attack in every case is at the 4-position of the hydrocarbon (Ia), *i.e.* at the α-naphthyl position which is not flanked by a methyl substituent, and which is therefore sterically more accessible. The nature of the solvent does not materially influence the orientation of substitution, as it does in related polycyclic systems.[19,21,22] The 1-position in (Ia) is, however, substituted to a larger extent in the solvents chloroform, ethylene dichloride, and carbon disulphide, which are regarded as 'normal' solvents in Friedel–Crafts acetylations.[23a] Nitrobenzene generally favours substitution at a β-naphthyl position, which in the present system is flanked by a methyl group. The results (Table 1)

TABLE 1

Monoacetylation of 2,6-dimethylnaphthalene

| Solvent | Addition procedure | Conditions | Overall yield (%) | Isomer proportions (%) (IIIg) | (IIg) | (Ig) |
|---|---|---|---|---|---|---|
| $CHCl_3$ | Perrier | 21°; 24 hr. | 91 | 33 | 0·4 | 66 |
| $C_2H_4Cl_2$ | Perrier | 22°; 24 hr. | 94 | 19 | 0·3 | 80 |
| $C_2H_4Cl_2$ | Rousset | 25°; 23 hr. | 87 | 38 | 1·7 | 60 |
| $CS_2$ | Perrier | 22°; 23 hr. | 94 | 31 | 2·6 | 66 |
| $C_6H_5NO_2$ | Perrier | 21°; 21 hr. | 32 | 11·6 | 4·8 | 84 |
| $C_6H_5NO_2$ | Bouveault * | 20°; 24 hr. | 80 | 3·2 | 1·2 | 96 |

* Method as in Ref. 12.

TABLE 2

Diacetylation of 2,6-dimethylnaphthalene in ethylene dichloride solution at 85 °C using the Perrier procedure

| Time (hr.) | Overall yield (%) | Ratio of diketones/ monoketones | Proportions of ketonic products (%) (Vg) | (VII) | Other diketones * |
|---|---|---|---|---|---|
| 3 | 90 | 1·5 | 36 | 59 | 5 |
| 24 | 91 | 12·6 | 15 | 76 | 9 |

* G.l.c. peaks at R.R.V. 1·59, 1·84, and 2·71 (see Experimental).

indicate steric hindrance to attack by the bulky acetylation reagent [24] of both the 1- and the 3-positions of the substrate (Ia). The preferred attack, therefore, at the 4-position of (Ia), giving ketone (Ig), appears to suggest an anomalous *meta*-orientation of the substituent methyl group. The 1-positions of 2-methylnaphthalene,[25] or 2,3-dimethylnaphthalene,[19] similarly possess low reactivities towards acetylation reagents.

Using the Rousset addition procedure [23b,26] in ethylene dichloride solution a higher yield of the hindered ketone (IIIg) could be obtained at the expense of isomer (Ig), probably due [19] to the presence of free aluminium chloride during the reaction.

A repetition of the Friedel–Crafts acetylation reaction carried out by Dziewonski *et al.*[12] showed that their product had, in fact,[2] structure (Ig), and not (IIIg) as had been claimed. The orientation of 12 derived compounds [12] must similarly be amended.

[19] P. H. Gore, C. K. Thadani, and S. Thorburn, *J. Chem. Soc.* (*C*), 1968, 2502.
[20] 'Elsevier's Encyclopaedia of Organic Chemistry,' ed. F. Radt, Elsevier, New York, 1950, vol. 12B, p. 144.
[21] (*a*) R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc.* (*C*), 1966, 181, 518; (*b*) P. H. Gore and C. K. Thadani, *J. Chem. Soc.* (*C*), 1966, 1729; 1967, 1498.
[22] P. H. Gore and C. K. Thadani, *J. Chem. Soc.* (*C*), 1967, 2619, and references therein.
[23] (*a*) P. H. Gore, in 'Friedel–Crafts and Related Reactions, ed. G. A. Olah, Interscience, New York, 1964, vol. III, part 1, p. 64; (*b*) p. 3.
[24] H. C. Brown, G. Marino, and L. M. Stock, *J. Amer. Chem. Soc.*, 1959, **81**, 3310.
[25] P. R. Wells and P. G. E. Alcorn, *Austral. J. Chem.*, 1963, **16**, 1109; P. H. Gore, A. S. Siddiquei, and S. Thorburn, unpublished.
[26] M. L. Rousset, *Bull. Soc. Chim. belges*, 1896, [3] **15**, 633; A. Claus and P. Feist, *Ber.*, 1886, **19**, 3180; H. Müller and H. von Pechmann, *Ber.*, 1889, **20**, 2261.

Diacetylation (Table 2) of the hydrocarbon (Ia), using two molar equivalents of reagents in boiling ethylene dichloride solution, gave good overall yields of at least five products. 1,5-Diacetyl-2,6-dimethylnaphthalene (Vg) and 1,5-diacetyl-3,7-dimethylnaphthalene (VII) could be separated by fractional crystallisation; small amounts of three isomeric diketones were also formed but not characterised. The structures

TABLE 3

Benzoylation of 2,6-dimethylnaphthalene at 20° for 1 hr. using the Perrier procedure

| Solvent | Overall yield (%) | Isomer Proportions (%) (IIIi) | (IIi) | (Ii) |
|---|---|---|---|---|
| $CHCl_3$ | 81 | 66 | 2·8 | 32 |
| $C_2H_4Cl_2$ | 92 | 66 | 2·7 | 31 |
| $CS_2$ | 93 | 63 | 2·5 | 34 |
| $C_6H_5NO_2$ | 88 | 83 | 2·5 | 15 |

TABLE 4

Relative reactivities of nuclear positions in competitive acylations of 2,6-dimethylnaphthalene and naphthalene in chloroform solution at 0°

| Naphthyl position | Relative reactivities Acetylation | Benzoylation |
|---|---|---|
| 1- | 1·00 | 1·00 |
| 2- | 0·31 | 0·40 |
| 2,6-dimethyl-1- | 4·1 | 260 |
| 3,7-dimethyl-2- | 0·045 | 12·3 |
| 3,7-dimethyl-1- | 8·1 | 116 |

of the ketones (Vg) and (VII) follow from their i.r. and n.m.r. spectra. Comparison of the results of the diacetylation experiments conducted for 3 hr. and 24 hr., respectively, shows that about half of ketone (Vg) initially formed undergoes conversion to ketone (VII), under essentially homogeneous conditions. This migration of hindered acetyl groups to unhindered positions is a further example of reversibility occurring in Friedel–Crafts acylation reactions.[22]

*Friedel–Crafts Benzoylations.*—The benzoylations of the hydrocarbon substrate (Ia) (Table 3), carried out under Perrier acylation conditions, gave good overall yields of the monoketones (IIIi), (IIi), and (Ii). Formation of the normal 1-ketone (IIIi) predominated, confirming the reports of earlier workers (see above). However, substantial amounts of isomer (Ii) were formed in most cases. As with the acetylation reaction formation of the β-isomer (IIi) was minimal. The normal product is generally formed in Friedel–Crafts benzoylation reactions of polycyclic aromatic hydrocarbons.[1,19,27,28] This contrasts with the anomalous acetylations of these substrates,[19,21b,22] in which the larger steric requirements of the acetylation reagents [24] have been implicated.

*Competitive Acylation Results.*—The reactivities of 2,6-dimethylnaphthalene (Ia) and of naphthalene were compared by competitive acetylation and benzoylation reactions conducted in chloroform solution. The molar ratios of ketones formed (acylnaphthalenes : acyl-2,6-dimethylnaphthalenes) were 1 : 5·42 for acetylations, and 1 : 137 for benzoylations. A comparison of positional reactivities (Table 4) shows for acetylations a four-fold reactivity enhancement at the 1-position of hydrocarbon (Ia), relative to the 1-position in naphthalene. This compares with the smaller enhancement (relative reactivity *ca.* 1·6) for the 1-position in the related 2,3-dimethylnaphthalene.[19] The reactivity of the 4-position of the substrate (Ia) is increased *ca.* eight-fold relative to the corresponding position of naphthalene. In contrast, the 3-position of the hydrocarbon (Ia) shows reduced reactivity, being *ca.* 1/7th that of the 2-position of naphthalene. It is clear that the methyl group superimposes a steric retarding influence on the electronic activation of both its *ortho*-positions, towards the acetylation reagent.

In contrast, the 1-position of 2,6-dimethylnaphthalene (Ia) exhibits a very high relative reactivity in the benzoylation reaction. The least reactive position of hydrocarbon (Ia) is still *ca.* 30 times as reactive as the corresponding 2-naphthyl position. The benzoylation reagent is both more selective and less reactive than the corresponding acetylation reagent. Also, there appears

TABLE 5

$^1$H N.m.r. spectra of derivatives of 2,6-dimethylnaphthalene

| Derivative | Chemical shifts, τ 1-*H* | 3-*H* | 4-*H* | 5-*H* | 7-*H* | 8-*H* | Aryl *H* | $COCH_3$ | 2-$CH_3$ | 6-$CH_3$ | Coupling constants (Hz) $J_{3,4}$ | $J_{7,8}$ | $J_{1,3}$ | $J_{5,7}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Ia) * | 2·54 | 2·85 | 2·45 | 2·54 | 2·85 | 2·45 | | | 7·60 | 7·60 | 8·0 | 8·0 | 1·8 | 1·8 |
| (IIIe) | | 2·76 | 1·87 | 2·54 | 2·70 | 2·49 | | | 7·47 | 7·57 | 8·6 | 8·7 | | 1·7 |
| (IIIl) | | 2·59 | 2·00 | 2·46 | 2·75 | 2·33 | | | 7·33 | 7·52 | 8·0 | 8·4 | | |
| (IIIg) | | 2·59 | 2·49 | 2·54 | 2·83 | 2·88 | | 7·53 | 7·56 | 7·67 | 8·6 | 8·3 | | 1·7 |
| (IIIi) | | | | | | | 1·9—2·8 | | 7·50 | 7·61 | | | | |
| (IIl) | 2·36 | | 1·92 | 2·41 | 2·58 | 2·29 | | | 7·35 | 7·48 | | 8·0 | | |
| (IIg) | 2·40 | | 1·89 | 2·40 | 2·65 | 2·37 | | 7·33 | 7·37 | 7·50 | | 8·4 | | 1·5 |
| (IIi) | | | | | | | 2·1—2·8 | | 7·52 | 7·59 | | | | |
| (Ig) | 1·59 | 2·47 | | 2·47 | 2·84 | 2·52 | | 7·44 | 7·53 | 7·58 | | 8·5 | | 1·6 |
| (Ii) | | | | | | | 2·0—2·8 | | 7·50 | 7·57 | | | | |
| (Ve) | | 2·59 | 1·80 | | 2·59 | 1·80 | | | 7·39 | 7·39 | 8·4 | 8·4 | | |
| (Vg) | | 2·77 | 2·50 | | 2·77 | 2·50 | | 7·44 | 7·62 | 7·62 | 9·0 | 9·0 | | |
| (VII) | 1·44 | 2·28 | | 1·44 | 2·28 | | | 7·30 | 7·48 | 7·48 | | | 1·5 | 1·5 |

* Reported 2(6)-$CH_3$ signals at τ 7·54 (Foch Fu-Hsie Yew, R. J. Kurland, and B. J. Mair, *Analyt. Chem.*, 1964, **36**, 843).

[27] F. R. Jensen, *J. Amer. Chem. Soc.*, 1957, **79**, 1226.
[28] P. H. Gore and J. A. Hoskins, *J. Chem. Soc.*, 1964, 5666.

to be no evidence of any steric interference to the benzoylations. The selectivity of substitution into 2,6-dimethylnaphthalene (Ia) is seen to increase in the sequence: detritiation (as derived from the kinetic data for 2-methylnaphthalene [29]), bromination,[9] nitration,[7] and Friedel–Crafts benzoylation.

$^1$H *N.m.r. Spectra.*—Details of the $^1$H n.m.r. spectra of the hydrocarbon (Ia) and 12 of its derivatives are given in Table 5. The naphthalenic protons could generally be satisfactorily resolved, except for derivatives (Ii), (IIi), and (IIIi), with which there is superposition of phenyl protons. The spectra provide confirmation of the structures proposed.

Two C$H_3$ resonances were observed in all the monosubstituted compounds. These signals are separated by a substantial amount by a substituent (1- or 3-) which is *ortho*- to one of the methyl groups (mean $\Delta\tau = 0{\cdot}12$ p.p.m.); for derivatives of (I) the methyl resonances were much closer together (mean $\Delta\tau = 0{\cdot}06$ p.p.m.). α,β-Coupling constants showed a mean value ($J$ 8·4 Hz) very close to that reported for parent naphthalene ($J_{1,2}$ 8·3 Hz).[30]

*I.r. Spectra.*—The C=O bands of the acyl derivatives of (Ia) are given in Table 6. The characteristic frequencies of hindered and unhindered acetyl-groups enable one to assign structures to the diacetyl derivatives (Vg) and (VII) with certainty.

TABLE 6

Carbonyl bands of ketones, in chloroform solution

| Ketone | $\nu_{max.}$ (cm.$^{-1}$) | Ketone | $\nu_{max.}$ (cm.$^{-1}$) |
|---|---|---|---|
| (IIIg) | 1689 | (IIi) | 1660 |
| (IIg) | 1669 | (Ii) | 1660 |
| (Ig) | 1664 | (Vg) | 1689 |
| (IIIi) | 1656 | (VII) | 1667 |

## EXPERIMENTAL

I.r. spectra were measured as KBr discs, or in chloroform solution, on a Unicam SP 200 or a Grubb–Parsons model GS3 spectrophotometer. The n.m.r. spectra were obtained at 60 or 100 MHz for solutions in deuteriochloroform, using tetramethylsilane as internal standard.

*Gas Chromatography.*—Analyses were performed using stainless-steel tubes 2 m. × 2·2 mm. (i. diam.) packed with (A) Bentone 34 (3·5%) and Carbowax 20M (1·5%) on Celite (60—80 mesh; treated with hexamethyldisilazane), or (B) SE 30 (10%) on Celite (100—120 mesh). Nitrogen was used as carried gas (i) at 176°, (ii) at 242°, or (iii) at 182°, together with a Philips instrument, model PV 4000, fitted with a flame-ionisation detector. Peak areas were measured by triangulation, or by direct weighing. Mass response towards the different compounds were determined, and corrections applied as appropriate. Relative retention data were: (a) using conditions (A)(i)- benzophenone 1·00, 1-acetyl-2,6-dimethylnaphthalene 1·92, 2-acetyl-3,7-dimethylnaphthalene 3·00, 1-acetyl-3,7-dimethylnaphthalene 4·09; (b) using conditions (B)(ii)- 1-acetylnaphthalene 1·00, 1,5-diacetyl-2,6-dimethylnaphthalene 1·93, 1,5-diacetyl-3,7-dimethylnaphthalene 2·27; (c) using conditions (B)(ii)- 1-benzoylnaphthalene 1·00, 2-benzoyl-3,7-dimethylnaphthalene 1·25, 1-benzoyl-2,6-dimethylnaphthalene 1·41, and 1-benzoyl-3,7-dimethylnaphthalene 1·53.

2,6-*Dimethylnaphthalene*-1-*carbonitrile* (IIIl).—A mixture of 1-bromo-2,6-dimethylnaphthalene (4·0 g.) b.p. 134—136°/1·8 mm.,[4] cuprous cyanide (2·0 g.), and dry pyridine (5 ml.) was heated under reflux at 190° (bath) for 6 hr. The thick, dark liquid thus obtained solidified on cooling. The solid was broken up, and extracted with chloroform. The extracts were washed with dilute ammonia solution, 3N-hydrochloric acid, and water, and then dried and evaporated to give a pale yellow solid (2·9 g., 94%), m.p. 83—88°. Pure 2,6-*dimethylnaphthalene*-1-*carbonitrile* had m.p. 88—89° (Found: C, 86·1; H, 5·7; N, 8·2. $C_{13}H_{11}N$ requires C, 86·2; H, 6·1; N, 7·7%), $\nu_{max.}$ ($CHCl_3$) 2205 cm.$^{-1}$ (C≡N).

1-*Acetyl*-2,6-*dimethylnaphthalene* (IIIg).—A solution of 2,6-dimethylnaphthalene-1-carbonitrile (7·2 g.) in dry benzene (200 ml.) was rapidly added to methylmagnesium iodide, prepared from magnesium (9·7 g.) and methyl iodide (57·0 g.) in ether (150 ml.); the mixture was boiled for 24 hr. To the cooled solution 3N-sulphuric acid (120 ml.) was added with stirring; most of the organic solvent was distilled off and the acidic layer was then boiled under reflux for 12 hr. After being cooled the solution was extracted with chloroform and the extract was washed with water and dried. Evaporation then gave a dark liquid of crude ketone, giving a pale yellow liquid (2·1 g., 27%) on distillation (b.p. 136—138°/1·5 mm.); g.l.c. showed the presence of *ca.* 5% of the ketone (Ig) (see below). Preparative g.l.c. gave pure 1-*acetyl*-2,6-*dimethylnaphthalene* (Found: C, 84·3; H, 7·4. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

2,6-*Dimethylnaphthalene*-1-*carboxylic Acid* (IIIk).—2,6-Dimethyl-1-naphthylmagnesium bromide, prepared from 1-bromo-2,6-dimethylnaphthalene (4·7 g.) and magnesium (0·5 g.) in dry benzene (50 ml.), was added to an excess of solid carbon dioxide under dry ether. The mixture was allowed to attain room temperature when 3N-hydrochloric acid was added to it with stirring. The organic layer was separated and extracted with 5% sodium hydroxide solution. The combined alkaline extracts on acidification with hydrochloric acid gave 2,6-*dimethylnaphthalene*-1-*carboxylic acid*, m.p. 172—173° (benzene) (Found: C, 77·7; H, 6·2. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%), $\nu_{max.}$ ($CHCl_3$) 1656 cm.$^{-1}$ (C=O).

1-*Benzoyl*-2,6-*dimethylnaphthalene* (IIIi).—This ketone was obtained by the method of Cook,[13] as crystals (yield 94%), m.p. 84° (lit.,[13] 84°) (Found: C, 87·7; H, 6·2. Calc. for $C_{19}H_{16}O$: C, 87·7; H, 6·2%).

2,6-*Dimethylnaphthalene*-3-*sulphonic Acid* (IIb).—A modified literature [3,4] method was used. 2,6-Dimethylnapthalene (10 g.) was heated with concentrated sulphuric acid (98%, 10 g.) at 135—140° for 3 hr. The mixture was then poured onto crushed ice to give a grey slurry. Attempts to recrystallise the sulphonic acid from 20% sulphuric acid [4] failed. The crude acid was converted into the sodium salt by an excess of 20% sodium hydroxide; the precipitate was collected, dried, and extracted with

[29] C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1112.

[30] D. C. F. Garbutt, K. G. R. Pachler, and J. R. Parrish, *J. Chem. Soc.*, 1965, 2324.

benzene in a soxhlet apparatus: crude sodium 2,6-dimethylnaphthalene-3-sulphonate (11 g., 67%), m.p. >350° was obtained.

3,7-*Dimethylnaphthalene*-2-*carbonitrile* (IIl).—Sodium 2,6-dimethylnaphthalene-3-sulphonate (10 g.) was intimately mixed with powdered potassium cyanide (5 g.), and the mixture was gently heated over a direct flame until vapours were no longer evolved. The condensate was taken up in benzene and the extract was washed with 3N-hydrochloric acid and water; it was then dried and evaporated to give a greenish yellow solid (1·7 g.). This was chromatographed on alumina from benzene, to give 3,7-*dimethylnaphthalene*-2-*carbonitrile* (0·5 g., 7%), m.p. 154—155° (Found: C, 86·1; H, 6·35; N, 7·7. $C_{13}H_{11}N$ requires C, 86·2; H, 6·1; N, 7·7%), $\nu_{max.}$ ($CHCl_3$) 2216 cm.$^{-1}$ (C≡N).

2-*Acetyl*-3,7-*dimethylnaphthalene* (IIg).—A solution of 3,7-dimethylnaphthalene-2-carbonitrile (0·4 g.) in dry benzene was added with stirring to excess of methylmagnesium iodide, prepared from iodomethane (6·5 ml.) and magnesium (1·3 g.), in ether. More benzene (100 ml.) was added to the mixture which was then boiled for 18 hr.; it was then cooled and 3N-sulphuric acid (100 ml.) was added to it. Most of the solvent was distilled off, and the acid layer was boiled under reflux for 12 hr. The cooled mixture was extracted with chloroform and the extracts were washed with water, dried, and evaporated to give a brown solid (0·15 g.). Chromatography on alumina afforded 2-*acetyl*-3,7-*dimethylnaphthalene*, m.p. 102—104° (Found: C, 84·3; H, 7·4. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

2-*Benzoyl*-3,7-*dimethylnaphthalene* (IIi).—This compound was prepared analogously to the ketone (IIg); 2-*benzoyl*-3,7-*dimethylnaphthalene* had m.p. 120—121° (alcohol) (Found: C, 87·7; H, 6·2. $C_{19}H_{16}O$ requires C, 87·7; H, 6·2%).

3,7-*Dimethylnaphthalene*-1-*carboxylic Acid* (Ik).—A mixture of 1-acetyl-3,7-dimethylnaphthalene (2·0 g.), sodium hydroxide (1·0 g.), and sodium hypochlorite (2% available chlorine; 100 ml.) was boiled under reflux for 4·5 hr. At the end of each hour more hypochlorite solution (30 ml.) was added. The mixture was then cooled and acidified with 3N-hydrochloric acid; the precipitated product was taken up in chloroform. The combined chloroform extract was then extracted with 3N-sodium hydroxide and this extract was strongly acidified. The resulting precipitate was collected, washed with water, and oven-dried. 3,7-*Dimethylnaphthalene*-1-*carboxylic acid* (1·0 g., 50%) had m.p. 204—206° (lit.,[18] m.p. for supposed '2,6-dimethylnaphthalene-1-carboxylic acid': 204°), $\nu_{max.}$ (KBr) 1660 cm.$^{-1}$ (C=O).

1-*Benzoyl*-3,7-*dimethylnaphthalene* (Ii).—3,7-Dimethylnaphthalene-1-carboxylic acid (0·35 g.) and thionyl chloride (3·5 ml.) were set aside for 17 hr. at room temperature. Excess of thionyl chloride was then removed, and the acid chloride was taken up in dry benzene (10 ml.); anhydrous aluminium chloride (0·24 g.) added in portions to the mixture which was then gently boiled for 4 hr. The product, isolated in the usual way, was 1-*benzoyl*-3,7-*dimethylnaphthalene* (0·40 g., 88%), m.p. 82—83° (Found: C, 87·5; H, 6·3. $C_{19}H_{16}O$ requires C, 87·7; H, 6·2%).

1,5-*Dibromo*-2,6-*dimethylnaphthalene* (Ve).—This compound was obtained by bromination of hydrocarbon (Ia) in chloroform–carbon tetrachloride at 25°, similar to the preparation of (IIIe). Needles of 1,5-dibromo-2,6-dimethylnaphthalene (yield 95%) had m.p. 158—159° (lit.,[4] 160—161°) (Found: C, 45·9; H, 3·2; Br, 50·8. Calc. for $C_{12}H_{10}Br_2$: C, 45·9; H, 3·2; Br, 50·9%).

*Friedel–Crafts Acylations*.—The experimental procedures adopted are those described elsewhere.[19] The conditions used for the acetylations are recorded in Tables 1 and 2, and for benzoylations in Table 3. For the diacetylation reactions 2 molar equivalents of acetyl chloride and of aluminium chloride were used. The acylations were usually conducted on 0·03M-scale.

1-*Acetyl*-3,7-*dimethylnaphthalene* (Ig).—The method used was that recommended by Dziewonski *et al.*[12] for the supposed '1-acetyl-2,6-dimethylnaphthalene'. Purification was effected by passage through a short column of alumina, from benzene and then recrystallisation (alcohol) to give 1-acetyl-3,7-dimethylnaphthalene, m.p. 70—71·5° (lit.,[12] m.p. 70—71°).

1,5-*Diacetyl*-2,6-*dimethylnaphthalene* (Vg) *and* 1,5-*Diacetyl*-3,7-*dimethylnaphthalene* (VII).—The ketonic product from the Friedel–Crafts diacetylation carried out for 3 hr. was chromatographed on alumina, and developed with benzene, to give two main fractions. The first fraction afforded 1,5-*diacetyl*-3,7-*dimethylnaphthalene*, m.p. 167—168° (alcohol) (Found: C, 79·8; H, 6·6. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). The second fraction afforded 1,5-*diacetyl*-2,6-*dimethylnaphthalene*, m.p. 177—178° (Found: C, 80·25; H, 6·7%).

*Competitive Acylations of* 2,6-*Dimethylnaphthalene and Naphthalene*.—These were carried out on 0·03 or 0·05 molar scale, by Perrier addition in chloroform solution, at 0°, by the method detailed earlier.[22] Analyses were carried out using conditions (B)(iii) for acetylations, or conditions (B)(ii) for benzoylations.

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