Friedel–Crafts Acylations of Aromatic Hydrocarbons. Part VII.† The Acetylation and Benzoylation of 2,3-Dimethylnaphthalene

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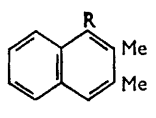
The Friedel–Crafts acetylation or benzoylation of 2,3-dimethylnaphthalene affords mixtures of 1-, 5-, and 6-monoacyl, and 1,5- and 1,6-diacyl derivatives. The proportions of these products depend on the reaction conditions. The main monobenzoylation product is 1-benzoyl-2,3-dimethylnaphthalene, but acetylation favours the formation of 1-acetyl-6,7-dimethylnaphthalene. This anomaly is explained in terms of the steric requirements of the acylation species. Competitive Perrier acetylation of 2,3-dimethylnaphthalene and naphthalene in chloroform solution gives the following relative reactivities of the nuclear positions: 1-naphthyl 1·00, 2-naphthyl 0·31, 2,3-dimethyl-1-naphthyl 1·59, 2,3-dimethyl-5-naphthyl 7·14, and 2,3-dimethyl-6-naphthyl 3·68. The corresponding values for benzoylation are 1·00, 0·04, 172, 38·2, and 7·7, respectively.

FRIEDEL–CRAFTS acylations of 2,3-dimethylnaphthalene (Ia) have been investigated by several workers. Fieser and Peters [1] obtained a 79% yield of 1-benzoyl-2,3-dimethylnaphthalene (Ib), m.p. 126°, by the action of benzoyl chloride and aluminium chloride in boiling carbon disulphide. The orientation was established by an Elbs condensation to give 4-methyl-1,2-benzanthracene.[1] With analogous conditions to those of the benzoylation reaction, Cook [2] obtained monoketones with 1- and 2-naphthoyl chlorides and, without proof, assigned structures (Ic) and (Id), respectively, to them. By the action of excess of benzoyl chloride and aluminium chloride on hydrocarbon (Ia) in tetrachloroethane at 55—60°, Clar [3] obtained a 66% yield of a dibenzoyl derivative, m.p. 182—183°. The structure originally proposed [3] was that of the 1,4-derivative (IIa). However, since this ketone could not be condensed to a benzopentaphene, the orientation was later [4] assumed to be 1,5- (IIIa). Phenylacetyl chloride and aluminium chloride were reported, again without proof, to acylate the 6-position,[5] and 2-thenoyl chloride the 1-position.[6] By the action of succinic anhydride in nitrobenzene solution, a 70% yield of β-(2,3-dimethyl-6-naphthoyl)-propionic acid (IVa) could be obtained (proof by degrad-

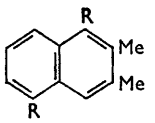


(I)

R
a; H
b; Bz
c; 1-CO·$C_{10}H_7$
d; 2-CO·$C_{10}H_7$
e; CO·C_6H_4·CO_2H(*o*-)
f; Ac
g; Br
h; CN
j; C(Me):NH
k; C(Ph):NH

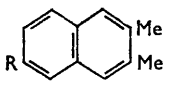
(II)

R
a; Bz
b; Ac
c; Br
d; CN
e; C(Me):NH
f; C(Ph):NH



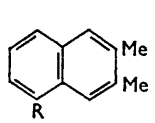
(III)

R
a; Bz
b; Ac
c; CO_2H



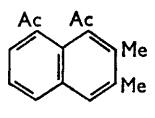
(IV)

R
a; CO[CH_2]$_2$$CO_2H$
b; CO·C_6H_4·CO_2H(*o*-)
c; CN
d; Ac
e; CO_2H
f; Bz

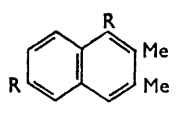


(V)

R
a; CO·C_6H_4·CO_2H(*o*-)
b; SO_3H
c; CN
d; C(Me):NH
e; Ac
f; CO_2H
g; Bz



(VI)



(VII)

R
a; Ac
b; Bz

† Parts I—VI of this Series are considered to be: I, P. H. Gore and J. A. Hoskins, *J. Chem. Soc.*, 1964, 5666; II, P. H. Gore and J. A. Hoskins, *J. Chem. Soc.*, 1965, 5744; III, P. H. Gore and C. K. Thadani, *J. Chem. Soc.* (*C*), 1966, 1729; IV, P. H. Gore and J. A. Hoskins, *Chem. Comm.*, 1966, 835; V, P. H. Gore and C. K. Thadani, *J. Chem. Soc.* (*C*), 1967, 1498; VI, R. B. Girdler, P. H. Gore, and C. K. Thadani, *J. Chem. Soc.* (*C*), 1967, 2619.

[1] L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 3742.
[2] J. W. Cook, *J. Chem. Soc.*, 1933, 1592.
[3] E. Clar, 'Aromatische Kohlenwasserstoffe,' Springerverlag, Berlin, 2nd edn., 1952; E. Clar, personal communication, November, 1964.
[4] E. Clar, personal communication, November, 1967.
[5] N. P. Buu-Hoï, N. Hoán, and P. Jacquignon, *J. Chem. Soc.*, 1951, 1381.
[6] N. P. Buu-Hoï and N. Hoán, *Rec. Trav. chim.*, 1949, **68**, 5.

ation).[7] With phthalic anhydride and aluminium chloride in tetrachloroethane at 0°, all three positions were substituted, to give the acids (Ie) (35%), (IVb) (7·3%), and (Va) (17%).[8]

A Friedel–Crafts acetylation of hydrocarbon (Ia) was not reported until 1963, when Anderson *et al.*[9] obtained, from reactions carried out in tetrachloroethane solution, a monoketone, m.p. 75—77°, and a diketone, m.p. 116—117°; their structures were reported (without evidence) as the 1- (If), and the 1,4-ketones (IIb), respectively.

We here report a detailed study of the acetylation and benzoylation of 2,3-dimethylnaphthalene (Ia), catalysed by aluminium chloride.

Syntheses.—The authentic ketones required were obtained by straightforward synthetic routes. Bromination of the hydrocarbon (Ia), by the method of Arnold and Liggett,[10] gave the 1-bromo-derivative (Ig) in 79% yield; the orientation follows from its n.m.r. spectrum (see below). With excess of bromine the 1,4-dibromo-derivative (IIc) could be obtained in quantitative yield. The bromo-compound (Ig) was converted in 50% yield into the nitrile (Ih), upon being heated with cuprous cyanide in dry pyridine (cf. ref. 11), a procedure successful with other polycyclic systems.[12,13] On treatment with a large excess of methylmagnesium iodide, the nitrile (Ih) afforded the ketimine (Ij), characterized as its hydrochloride. The ketimine (Ij) gave 1-acetyl-2,3-dimethylnaphthalene (If), m.p. 31—32°, in 60% yield after prolonged heating with 3N-sulphuric acid. 1-Benzoyl-2,3-dimethylnaphthalene (Ib), m.p. 125—126°, was similarly obtained, the hydrolysis of the ketimine (Ik) also being slow. *ortho*- or *peri*-Substitution has been reported [13,14] to give ketimines which are remarkably resistant to acid. The dibromo-compound (IIc) could similarly be converted, *via* the dinitrile (IId), into the diacetyl (IIb), m.p. 131—132°, and the dibenzoyl (IIa), m.p. 202—203°, derivatives. The overall yields were again low, due to the slow hydrolyses of the 1,4-ketimines [(IIe) and (IIf)]. The assignments of structure made to Anderson's [9] ketones were, therefore, wrong.

6,7-Dimethylnaphthalene-1-sulphonic acid [15] (Vb) was converted into the nitrile (Vc) by fusion with potassium cyanide. Addition of methylmagnesium iodide, and hydrolysis of the intermediate ketimine (Vd), readily afforded 1-acetyl-6,7-dimethylnaphthalene (Ve), m.p. 74—75°. The ketone (Ve) with boiling dilute hypochlorite gave 6,7-dimethylnaphthalene-1-carboxylic acid (Vf) which, *via* the acid chloride, and a Friedel–Crafts acylation using excess of benzene, gave the benzoyl derivative (Vg), m.p. 95—96°. The acetyl derivative (Ve) with more concentrated hypochlorite afforded 5,8-dichloro-6,7-dimethylnaphthalene-1-carboxylic acid (orientation by n.m.r.), which could be converted into the corresponding benzoyl derivative. 6,7-Dimethylnaphthalene-2-carbonitrile [8] (IVc) was converted into 2-acetyl-6,7-dimethylnaphthalene (IVd), m.p. 98—99° in an analogous manner to that described for its isomer (Vc). Hypochlorite treatment of the latter gave the 2-carboxylic acid (IVe), which was converted into the 2-benzoyl derivative (IVf), m.p. 117—118°, by way of a Friedel–Crafts acylation.

Friedel–Crafts Acetylations.—The results of the acetylation experiments on 2,3-dimethylnaphthalene (Ia) are given in Tables 1 and 2. The isomer proportions were determined by quantitative g.l.c. analysis, after prior purification of the crude reaction products by passage through alumina. Table 1 shows that the three monoketones (If), (Ve), and (IVd) are formed in each acylation.

TABLE 1

Monoacetylation of 2,3-dimethylnaphthalene

Solvent	Temp.	Time (hr.)	Total yield (%)	Products (%) (If)	(Ve)	(IVd)
CS_2 *	0—7°	1	98	21	40	39
	20	47				
$(CH_2Cl)_2$ * ...	20	3	,,	24	55	21
$CHCl_3$ *	25	5	,,	20	58	22
$PhNO_2$ * ...	20	24	,,	1·5	21	78
$(CHCl_2)_2$ † [a]	0	1	,,	41	21	38
	20	23				
CS_2 † [b]	0	1	94	29	40	31
	20	47				

* Perrier addition procedure. † Rousset addition procedure.

[a] Method of Anderson (personal communication), who reported a 54% yield of (Ve) (see text). [b] Method quoted in Anderson, *et al.* (ref. 9), using Price's general procedure (C. C. Price, *Org. Reactions*, 1946, **3**, 1); a yield of 62% of so-called (If), m.p. 75—77°, was reported.

The preferred point of attack is the 5- position in carbon disulphide, chloroform, or ethylene chloride, the 1-position in tetrachloroethane (using the Rousset [16] procedure), or the 6-position in nitrobenzene solution (using the Perrier [17] procedure). These acetylations can therefore be regarded as typical, in that the orientation of substitution, like that of other naphthalenes,[18,19a] is profoundly influenced by the solvent. In the Rousset

[7] R. D. Haworth and F. M. Bolam, *J. Chem. Soc.*, 1932, 2248; R. H. Martin and J. Senders, *Bull. Soc. chim. belges*, 1955, **64**, 221.

[8] L. F. Fieser and M. Fieser, *J. Amer. Chem. Soc.*, 1933, **55**, 3342.

[9] E. L. Anderson, J. E. Casey, jun., M. Emas, E. E. Force, E. M. Jensen, R. S. Matz, and D. E. Rivard, *J. Med. Chem.*, 1963, [6], **6**, 787.

[10] R. T. Arnold and R. W. Liggett, *J. Amer. Chem. Soc.*, 1942, **64**, 2875.

[11] H. Beyer and H. Fritsch, *Ber.*, 1941, **74**, 494.

[12] E. Mosettig and J. van der Kamp, *J. Amer. Chem. Soc.*, 1932, **54**, 3328; M. S. Newman, *J. Amer. Chem. Soc.*, 1937, **59**, 2472.

[13] W. E. Bachman and M. C. Kloetzel, *J. Org. Chem.*, 1938, **3**, 55.

[14] W. E. Bachman and L. H. Pence, *J. Amer. Chem. Soc.*, 1935, **57**, 1131.

[15] E. A. Coulson, *J. Chem. Soc.*, 1938, 1305.

[16] M. L. Rousset, *Bull. Soc. chim. belges*, 1896, [3], **15**, 633.

[17] G. Perrier, *Ber.*, 1900, **33**, 815; *Bull. Soc. chim. France*, 1904, [3], **31**, 859.

[18] R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc.* (*C*), 1966, 518.

[19] P. H. Gore, in ' Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, vol. III, part 1, (*a*) pp. 64 *et seq.*, (*b*) p. 247.

method, in which a mixture of substrate and acyl chloride is added to a suspension of aluminium chloride, the yield of the 1-isomer (If) is significantly greater [and the 6-isomer (IVd) less] than in the more usual Perrier method, when carried out in carbon disulphide suspension. When an excess of reagents is employed (Table 2),

TABLE 2

Mono- and di-acetylation of 2,3-dimethylnaphthalene

Solvent	Temp.	Time (hr.)	Total yield (%)	Products (%) (If)	(Ve)	(IVd)	Di-ketones [a]	Ratio of mono- to di-ketones
$(CH_2Cl)_2$ *	20°	24	98	Trace	74	Trace	25	2·9 : 1
$CHCl_3$ *	20	24	,,	,,	90	5	5	19 : 1
$PhNO_2$ *	20	24	93	,,	46	53	1	99 : 1
CS_2 † [b]	0—5	1·5	98	,,	60	37	2·5	39 : 1

* Perrier addition procedure. † Rousset addition procedure.

[a] Ratio of isomers (IIIb) : (VIIa) was *ca.* 4 : 1. [b] Method of Anderson, *et al.* (ref. 9).

the proportion of the 1-isomer (If) decreases, and that of the 5-isomer (Ve) increases. In fact, in chloroform solution an 80% yield of the latter ketone can be isolated in this way. The generally low reactivity of the 1-position of the hydrocarbon (Ia) in Friedel–Crafts acetylations finds a parallel in 2-methylnaphthalene,[19b] where the 1-isomer is obtained only in traces,[20] and points to a degree of steric hindrance (see below). The greater proportion of the 1-isomer obtained from the hydrocarbon (Ia) by the Rousset procedure, can be explained since contact with free aluminium chloride is involved in the initial stages of the reaction. On the surface of the free catalyst, acetyl cations can be formed at the expense of the usual reagent (the acetyl chloride–aluminium chloride addition complex), and, having lower steric requirements, can effectively substitute the 1-position, which the addition complex cannot easily do. A species close in structure to a free acetyl cation has been suggested before as the attacking reagent of hindered aromatic positions, in particular the 9-anthryl [21] and the 4-phenanthryl [22] positions.

A repetition of the acetylation experiment described by Anderson *et al.*[9] showed that their product had, in fact, been the 5-isomer (Ve), m.p. 73—74°; the orientation of a derived glyoxal [9] must also be amended.

Diacetylation (Table 2) of the hydrocarbon (Ia) was attempted by using an excess of reagents under mild conditions. A maximum yield (25%) of mixed diacetyl derivatives was obtained in ethylene chloride, whilst small amounts only were formed in chloroform, carbon disulphide, or nitrobenzene. The formation of diacetyl derivatives in only low yields agrees with the behaviour of otherwise reactive naphthalene systems, *viz.* 2-methoxynaphthalene,[23] or 2-methylnaphthalene,[24] and may be due, in part, to the precipitation of the monoketones as their aluminium chloride complexes early in the reaction. The three monoacetyl derivatives [(If), (Ve) and (IVd)] were separately treated in chloroform solution with aluminium chloride (2 mol.) and acetyl chloride (4 mol.), at room temperature for 18—24 hr. The 5- (Ve) and the 6- (IVd) isomer were substantially unchanged under these 'diacylation' conditions. Further acetylation of the 1-isomer (If), however, gave *ca.* 1% of mixed diketones, and traces of both the 5- and the 6-isomers, as well as of the parent hydrocarbon (Ia). Reversibility, therefore, is a factor in the acylation of this system, and comparable in magnitude with that experienced with 2-methoxynaphthalene.[23] It cannot account quantitatively for the normal formation in a Friedel–Crafts acetylation of the isomers (Ve) and (IVd) from the parent (Ia).

The diacetylation product, m.p. 116—117°, reported by Anderson *et al.*,[9] could not have been 1,4-diacetyl-2,3-dimethylnaphthalene (IIb) as claimed, since this ketone melts at 131—132° (see above). In our hands two diketones were formed, the main product (A) of m.p. 116—117°, and a small yield only of an isomer (B), m.p. 113—114°. Ketone (A) was monodeacylated to 1-acetyl-6,7-dimethylnaphthalene (Ve) upon being boiled with 10% sulphuric acid in glacial acetic acid (Cook's reagent,[25] which can displace acyl groups at hindered positions [26]). Ketone (A) could, therefore, be 1,5- (IIIb) or 1,8-diacetyl-2,3-dimethylnaphthalene (VI); the former orientation is preferred, since ketone (A) is stable in the presence of warm piperidine or activated alumina, reagents which convert [27] 1,8-diacetylnaphthalene into 3-methylphenalen-1-one. Ketone (B) could be isolated pure in traces only: we suggest that it is 1,6-diacetyl-2,3-dimethylnaphthalene (VIIa), which would appear the most likely orientation from the i.r. and n.m.r. spectra and theoretical considerations, and also by analogy with the 1,6-diacetyl derivatives obtained from 2-methoxynaphthalene [23] or 2-methylnaphthalene.[24]

Friedel–Crafts Benzoylations.—The benzoylation of the hydrocarbon (Ia) has been studied under Perrier conditions in carbon disulphide, chloroform and nitrobenzene solution (Table 3). The major product is 1-benzoyl-

TABLE 3

Perrier benzoylation of 2,3-dimethylnaphthalene at 20° for 8 hr.

Solvent	Products (%) (Ib)	(Vg)	(IVf)
CS_2	65	25	10
$CHCl_3$	64	29	7
$PhNO_2$	67	16	17

[19] P. R. Wells and P. G. E. Alcorn, *Austral. J. Chem.*, 1963, **16**, 1109.

[21] (*a*) P. H. Gore and C. K. Thadani, *J. Chem. Soc.* (*C*), 1966, 1729; (*b*) P. H. Gore, *Chem. and Ind.*, 1954, 1385; *Chem. Rev.*, 1955, **55**, 229.

[22] R. B. Girdler, P. H. Gore, and C. K. Thadani, *J. Chem. Soc.* (*C*), 1967, 2619.

[23] R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc.* (*C*), 1966, 181.

[24] K. Dziewonski and M. Brand, *Bull. Intern. Acad. polon. Sci., Classe Sci. Math. Nat., Ser. A*, 1933, 99; G. A. R. Kon and W. T. Weller, *J. Chem. Soc.*, 1939, 792.

[25] J. W. Cook, *J. Chem. Soc.*, 1926, 1282.

[26] P. H. Gore and J. A. Hoskins, *J. Chem. Soc.*, 1964, 5666.

[27] R. Criegee, L. Kraft, and B. Rank, *Annalen*, 1933, **507**, 159; P. H. Gore and J. A. Hoskins, unpublished.

2,3-dimethylnaphthalene (Ib) in each case, and smaller amounts of the other isomers (Vg) and (IVf) are by-products. Only in nitrobenzene solution is a significant yield of the β-ketone (IVf) formed. A high yield of a 'normal' acylation product is a feature of the Friedel–Crafts benzoylation of naphthalene,[28] or of anthracene [26] (whose *meso*-position is sterically analogous to the 1-position of 2,3-dimethylnaphthalene), and thus contrasts with the acetylation of hydrocarbon (Ia) or of anthracene.[21a] The benzoylation reaction is clearly parallel to the predominant 1-acylation reported with phthalic anhydride (see above).[8] This difference in substitution pattern may be ascribed to the lower steric requirements of the benzoylating species when compared with the acetylating species (see below).[29]

The dibenzoylation of 2,3-dimethylnaphthalene (Ia), using the Perrier mode of addition, was also studied (Table 4). Excess of reagents, and a higher reaction

TABLE 4

Perrier benzoylation of 2,3-dimethylnaphthalene at 55—60°

Solvent	Time (hr.)	Mono-ketones	Products (%) (IIIa)	(VIIb)
$(CH_2Cl)_2$	24	12	60	28
$PhNO_2$	24	14	60	26
$(CHCl_2)_2$ [a]	2	40	40	20

[a] Method of Clar (ref. 3).

temperature, led to a substantial degree of diacylation, together with the mixed monobenzoyl derivatives. Analysis by g.l.c. was not here considered feasible, but good separation of the diketones from the mono-ketones could be achieved by t.l.c.[26] Two diketones (C) and (D) were formed in each of three solvents, and their proportions remained constant (*ca.* 2 : 1). The main product (C), m.p. 165—166°, was obtained from 1,5-diacetyl-2,3-dimethylnaphthalene (IIIb), *via* the dicarboxylic acid (IIIc) and a Friedel–Crafts reaction with excess of benzene, and thus had the structure (IIIa). The minor component (D), m.p. 179—180°, was probably identical with the dibenzoyl derivative, m.p. 182—183°, obtained in 66% yield by Clar [3] in tetrachloroethane solution, and the structure of which had been suggested to be (IIa)[3] or (IIIb).[4] Since these two ketones have been shown to melt at 200—201°, and 165—166°, respectively, a more probable structure for (D) is (VIIb). It has not been possible, however, to relate this ketone directly to the diacetyl derivative (B), of probable structure (VIIa).

Reactivity Comparisons.—Competitive acylations were carried out in chloroform solution at 0°, in order to compare the reactivities of the nuclear positions of 2,3-dimethylnaphthalene (Ia) with those of naphthalene. In our experience chloroform is the only reliable solvent for such a comparison.[18,22] In the competitive acetylation experiments the molar ratio of ketones formed was: total acetylnaphthalenes : total acetyl-2,3-dimethylnaphthalene 1 : 4·75. In this product the proportions (76·7% α) of α-acetyl-/β-acetyl-naphthalene compare well with values found earlier, *viz.* 78% [22] or 76% [18], for similar experiments. The mixture of isomeric ketones derived from hydrocarbon (Ia) had the same proportions (58%) of isomer (Ve) as at 25° (Table 1), but an increased proportion (30% at 0°) of isomer (IVd), at the expense of isomer (If). A comparison of the reactivity of individual nuclear positions (Table 5)

TABLE 5

Relative reactivities of nuclear positions in competitive acylations of 2,3-dimethylnaphthalene and naphthalene, in chloroform at 0°

Naphthyl position	Acetylation	Benzoylation
1-	1·00	1·00
2-	0·31	0·04 [a]
2,3-Dimethyl-1-	1·59	172
2,3-Dimethyl-5-	7·14	38·2
2,3-Dimethyl-6-	3·68	7·7

[a] Approximate.

shows a seven-fold reactivity enhancement at the 5-position of 2,3-dimethylnaphthalene, relative to an α-position in naphthalene, and a twelve-fold enhancement at the 6-position, relative to a β-position in naphthalene. The 1-position, on the other hand, although closer to the activating (+*I* effect) methyl groups, is only slightly activated relative to an α-naphthyl position. The results from the competitive benzoylation reaction offer a sharp contrast: the relative rate of naphthalene : 2,3-dimethylnaphthalene is 1 : 89, and this is mirrored in a much greater range of reactivities of the different nuclear positions. At the same time it was observed that the benzoylation proceeded at a slower rate (as gauged from the evolution of hydrogen chloride) than the acetylation. This agrees with the acylations of toluene under comparable conditions, where acetylation is *ca.* 500 times as fast as benzoylation.[29] The main feature of the benzoylation of hydrocarbon (Ia) is the high reactivity of the 1-position; the contrast with the acetylation is clearly due to differences in the nature of the acylating species. It has been shown [29] that in ethylene chloride solution at 25° the partial-rate factor for Friedel–Crafts benzoylation at the *ortho*-position of toluene is *ca.* 7·2 times that for the corresponding acetylation. It was concluded that the steric requirements of the acetylation reagent are larger than those of the benzoylation; [29] this conclusion is in keeping with data from other systems.[21a,22] It would appear that the 1-position of 2,3-dimethylnaphthalene is substituted normally in the Friedel–Crafts benzoylation reaction, but that it offers considerable hindrance to the approach of the acetylating species. An approximate extrapolation shows that in the acetylation of the hydrocarbon (Ia) the reactivity of the 1-position is reduced by a factor of *ca.* 25 by steric factors.

^1H *N.m.r. Spectra.*—Details of the ^1H n.m.r. spectra of derivatives of the hydrocarbon (Ia) are given in

[28] F. R. Jensen, *J. Amer. Chem. Soc.*, 1957, **79**, 1226.
[29] H. C. Brown, G. Marino, and L. M. Stock, *J. Amer. Chem. Soc.*, 1959, **81**, 3310.

Table 6. The naphthalenic protons generally give unresolved multiplets, except with certain compounds possessing a free α-naphthyl position, where a singlet may be observed. In the 1,4-derivatives [(IIc) and (IId)] precise A_2B_2 patterns are observed for the 5—8 H protons.

TABLE 6

^{1}H N.m.r. spectra

Chemical shifts, τ (p.p.m.)

Compound	Methyls	Acetyl	Aromatic multiplet	Aromatic singlet
(Ia)	7·75		2·2—2·8	
(Ib)	7·59, 7·83		2·1—3·0 [a]	
(If)	7·71, 7·80	7·50	2·2—2·8	
(Ig)	7·59, 7·78		1·6—2·8	
(Ih)	7·51, 7·70		1·8—2·8	
(IIa)	7·72		1·8—2·9 [a]	
(IIb)	7·68	7·39	2·2—2·7	
(IIc)	7·38		1·5—2·8 [b]	
(IId)	7·24		1·5—2·4 [b]	
(IIIa)	7·61, 7·80		2·0—2·8 [a]	
(IIIb)	7·57, 7·42	7·32, 7·42	2·1—2·8	1·52 (4-H)
(IVc)	7·53		2·0—2·8	1·83 (5-H)
(IVd)	7·67	7·42	2·0—2·6	1·78 (5-H)
(IVf)	7·58		1·8—2·8 [a]	1·90 (5-H)
(Vc)	7·51, 7·54		1·8—2·8	
(Ve)	7·61, 7·64	7·35	2·1—2·9	1·53 (4-H)
(Vg)	7·58, 7·63		1·9—2·8 [a]	
(VIIa)	7·56, 7·66	7·32, 7·36	1·5—2·7	
(VIIb)	7·55, 7·78		2·1—2·8 [a]	1·82 (5-H)
5,8-Dichloro-6,7-dimethylnaphthalene-1-carboxylic acid [c]	7·38		1·4—2·4	

[a] Includes phenyl protons. [b] A_2B_2 pattern. [c] In deuterioacetone.

Of considerable diagnostic value are the proton resonances of the methyl groups. Substitution at the 1-position causes separation of the methyl proton resonances usually by 10—20 c./sec., and at the 5-position by not more than 5 c./sec.; whilst 6-substituted compounds exhibit only one methyl proton resonance.

EXPERIMENTAL

Melting points are uncorrected. I.r. spectra were measured as KBr dics on a Unicam SP 200 spectrophotometer. The n.m.r. spectra were obtained at 60 MHz in deuteriochloroform (unless otherwise stated), using tetramethylsilane as internal standard.

Gas Chromatography.—Analyses were carried out on stainless-steel columns (3 ft. × 2·2 mm. diam.), packed with Carbowax 20 M (4%) on silanised Chromosorb G, used at 190°, with nitrogen as carrier gas. A flame-ionization detector was used, and mass corrections were applied where appropriate. The following Kovats retention indices [30] (at 200°) were obtained: (If) 2580, (Ve) 2665, (IVd) 2785, (IIb) 3082, (IIIb) 3148, (VIIa) 3278, (Ib) 3244, (Vg) 3336, and (IVf) 3524.

Thin-layer Chromatography.—Analyses of mixtures of dibenzoyl derivatives were carried out using silica gel G (Merck) by a one-dimensional multiple-development technique,[26] with 15% chloroform in benzene.

Friedel–Crafts Acylations.—Monoacylations were carried out using molar equivalents of the reactants and diacylations using 3 moles each of acyl chloride and aluminium chloride per mole of hydrocarbon. In the Perrier [17] procedure the last added component was the substrate, and in the Rousset [16] procedure the mixture of substrate and acyl chloride was added to the mixture of aluminium chloride and the solvent. The products were isolated by addition of crushed ice and 10N-hydrochloric acid and separation of the organic layer (with more solvent when necessary); the extract was then washed with N-hydrochloric acid, N-sodium hydroxide, and water, and finally dried ($MgSO_4$). The solvent was distilled off (or steam-distilled in the case of nitrobenzene), and the residue was dissolved in a minimum of benzene and chromatographed on alumina (to remove polymer). The filtrate was evaporated to dryness, and the product was analysed quantitatively by g.l.c. (or t.l.c. in the case of dibenzoylation). Preparatively, the Rousset procedure (in tetrachloroethane) was used to obtain 1-acetyl-2,3-dimethylnaphthalene, the Perrier diacetylation procedure (in chloroform) for 1-acetyl-6,7-dimethylnaphthalene, the Perrier procedure (in nitrobenzene) for 2-acetyl-6,7-dimethylnaphthalene, and Anderson's method (in carbon disulphide) for 1,5-diacetyl-2,3-dimethylnaphthalene. In the monobenzoylations only 1-benzoyl-2,3-dimethylnaphthalene could readily be obtained by crystallisation. 1,6-Diacetyl-, 1,5-dibenzoyl-, and 1,6-dibenzoyl-2,3-dimethylnaphthalenes could be separated from mixtures by preparative t.l.c. The identity of the ketones was established by comparison of m.p.'s and i.r. spectra with synthetic specimens.

2,3-Dimethylnaphthalene-1-carbonitrile (Ih).—1-Bromo-2,3-dimethylnaphthalene [10] (4 g.) was heated with cuprous cyanide (2 g.) in dry pyridine (5 ml.) at 190—210° (bath) for 6 hr. The cooled residue was taken up in chloroform, washed with dilute ammonia, dilute hydrochloric acid, and water, and the dried (Na_2SO_4) extract was evaporated. The yellow residue (2·4 g.), m.p. 74—77°, was crystallised (charcoal) from ethanol to give *2,3-dimethylnaphthalene-1-carbonitrile* (1·7 g.), m.p. 79·5—80° (Found: C, 86·0; H, 6·4; N, 7·5. $C_{13}H_{11}N$ requires C, 86·2; H, 6·1; N, 7·7%); $\nu_{max.}$ 2220s (C≡N), 1388s (CH_3), and 1382s (CH_3) cm.$^{-1}$ [$\nu_{max.}$ at 1386m cm.$^{-1}$ (CH_3) for 2,3-dimethylnaphthalene].

1-(1-Iminoethyl)-2,3-dimethylnaphthalene (Ij) *and 1-Acetyl-2,3-dimethylnaphthalene* (If).—A solution of 2,3-dimethylnaphthalene-1-carbonitrile (5 g.) in dry benzene (50 ml.) was added slowly to methyl magnesium iodide [prepared from methyl iodide (40 g.) and magnesium (7 g.) in ether] with constant strirring. More benzene (100 ml.) was added and the mixture was boiled for 24 hr.; it was then cooled and treated with saturated ammonium chloride solution. The product was taken up in ether and the extract was washed with water and dried ($MgSO_4$). A stream of dry hydrogen chloride was passed through the solution to precipitate off-white *1-(1-iminoethyl)-2,3-dimethylnaphthalene hydrochloride* (5·86 g.), m.p. 316—317° (Found: C, 72·0; H, 6·6; N, 5·8. $C_{14}H_{16}ClN$ requires C, 71·9; H, 6·9; N, 6·0%). The salt (4·85 g.) was boiled with 5N-sulphuric acid for 4 days after which time the mixture was cooled and extracted with ether; the extract was washed with water, dried ($MgSO_4$), and evaporated to give a brown mobile liquid (3·8 g.). This was chromatographed in benzene on alumina and then crystallised from methanol, to give 1-acetyl-2,3-dimethylnaphthalene (3·5 g.), m.p. 31—32° (Found: C, 84·2; H, 7·0. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%); $\nu_{max.}$ 1678s (C=O) cm.$^{-1}$.

[30] E. Kovats, *Helv. Chim. Acta*, 1958, **41**, 1915; L. S. Ettre, *Analyt. Chem.*, 1964, **36**, 31A.

1-(1-*Iminobenzyl*)-2,3-*dimethylnaphthalene* (Ik) *and* 1-*Benzoyl*-2,3-*dimethylnaphthalene* (Ib).—The method was analogous to that for the preparation of compounds (Ij) and (If). 1-(1-*Iminobenzyl*)-2,3-*dimethylnaphthalene* (yield 47%) formed off-white crystals, m.p. 133·5—134·5° (from methanol) (Found: C, 88·3; H, 6·7; N, 5·6. $C_{19}H_{17}N$ requires C, 88·0; H, 6·6; N, 5·4%). The *hydrochloride* formed yellow crystals, m.p. 248—250°. 1-Benzoyl-2,3-dimethylnaphthalene (yield 31%) formed crystals, m.p. 124—125° (from alcohol) (lit.,[31] 125—126°) (Found: C, 87·9; H, 6·2. Calc. for $C_{19}H_{16}O$: C, 87·7; H, 6·2%), $\nu_{max.}$ 1658s (C=O) cm.$^{-1}$.

6,7-*Dimethylnaphthalene*-1-*carbonitrile* (Vc).— Barium 6,7-dimethylnaphthalene-1-sulphonate [15] (10 g.) was converted into the sodium salt (7·2 g.). An intimate mixture of the sodium salt (3 g.) and potassium cyanide (1 g.) was heated over a low flame, when the product sublimed into the mounted air-condenser. The mixture was extracted with benzene and the extract was washed with N-hydrochloric acid and water, and finally dried ($MgSO_4$); on evaporation a yellow liquid (1·0 g.) was obtained. This was decolourised (charcoal) and crystallised (alcohol) to give 6,7-*dimethylnaphthalene*-1-*carbonitrile*, m.p. 77—78° (Found: C, 86·3; H, 6·3; N, 7·7%), $\nu_{max.}$ 2200s (C≡N) and 1372s (CH_3) cm.$^{-1}$.

1-*Acetyl*-6,7-*dimethylnaphthalene* (Ve).—A solution of 6,7-dimethylnaphthalene-1-carbonitrile (0·5 g.) in benzene (40 ml.) was added to methylmagnesium iodide [prepared from methyl iodide (5 ml.) and magnesium (1·3 g.)] in ether; the mixture was boiled for 22 hr., then cooled, and treated with 3N-sulphuric acid. The acid extract was boiled for 8 hr. to give an oily product which was taken up in chloroform and chromatographed on alumina; elution with benzene gave a product which crystallized (alcohol) to give 1-*acetyl*-6,7-*dimethylnaphthalene* (0·25 g.), m.p. 74—75° (Found: C, 85·1; H, 7·2%), $\nu_{max.}$ 1666s (C=O) cm.$^{-1}$.

6,7-*Dimethylnaphthalene*-1-*carboxylic Acid* (Vf).—A mixture of 1-acetyl-6,7-dimethylnaphthalene (1·5 g.), sodium hydroxide (1 g.), and sodium hypochlorite solution (2% available chlorine; 100 ml.) was boiled for 4 hr., more hypochlorite (50 ml. portions) being added after 1 hr., and after 2 hr., respectively. The cooled solution was acidified and the resultant precipitate was taken up in chloroform; this extract was washed with water and then extracted with 2N-sodium hydroxide. Addition of excess of hydrochloric acid precipitated the product which was filtered off (0·96 g.), m.p. 213—217°, and recrystallized (alcohol) to give 6,7-*dimethylnaphthalene*-1-*carboxylic acid* (0·68 g.), m.p. 220—221° (Found: C, 77·6; H, 6·3. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%).

5,8-*Dichloro*-6,7-*dimethylnaphthalene*-1-*carboxylic Acid*.—The method used was as described above, using hypochlorite (3% available chlorine), and a 5 hr. reaction period. The crude acid (1·2 g.), m.p. 209—212°, was recrystallized (alcohol) to give 5,8-*dichloro*-6,7-*dimethylnaphthalene*-1-*carboxylic acid* (0·6 g.), m.p. 226—227° (Found: C, 58·3; H, 3·8. $C_{13}H_{10}Cl_2O_2$ requires C, 58·0; H, 3·7%).

1-*Benzoyl*-6,7-*dimethylnaphthalene* (Vg).—A mixture of 6,7-dimethylnaphthalene-1-carboxylic acid (0·5 g.) and thionyl chloride (5 ml.) was boiled under reflux for 2 hr. The excess of reagent was distilled off, the brown residue was taken up in dry benzene (15 ml.), and aluminium chloride (0·38 g.) was added. After boiling under reflux for 3 hr., the mixture was cooled, ice and 6N-hydrochloric acid were added, and the product was isolated to give 1-*benzoyl*-6,7-*dimethylnaphthalene* (0·1 g., from alcohol), m.p. 95—96° (Found: C, 87·5; H, 6·4%), $\nu_{max.}$ 1660s (C=O) cm.$^{-1}$.

1-*Benzoyl*-5,8-*dichloro*-6,7-*dimethylnaphthalene*.— This ketone was obtained from the corresponding acid as in the previous reaction; 1-*benzoyl*-5,8-*dichloro*-6,7-*dimethylnaphthalene* (yield 61%), had m.p. 171—172° (Found: C, 68·9; H, 4·4; Cl, 21·2. $C_{19}H_{14}Cl_2O$ requires C, 69·3; H, 4·3; Cl, 21·5%).

6,7-*Dimethylnaphthalene*-2-*carbonitrile* (IVc).—The method of preparation and isolation were as for the isomer (Vc). The 6,7-*dimethylnaphthalene*-2-*carbonitrile* (yield 55%), was isolated as pale yellow crystals, m.p. 191—192° (from alcohol) (Found: C, 86·3; H, 6·2; N, 7·5%).

2-*Acetyl*-6,7-*dimethylnaphthalene* (IVd).—The method of preparation was identical with that used for the isomer (Ve); 2-*acetyl*-6,7-*dimethylnaphthalene* (yield 46%) had m.p. 98—99° (Found: C, 84·2; H, 7·2%), $\nu_{max.}$ 1658s (C=O) cm.$^{-1}$.

6,7-*Dimethylnaphthalene*-2-*carboxylic Acid* (IVe).—The method of preparation was the same as that for the isomer (Vf); 6,7-*dimethylnaphthalene*-2-*carboxylic acid* (30%) had m.p. 269—270° (Found: C, 77·9; H, 5·7%).

2-*Benzoyl*-6,7-*dimethylnaphthalene* (IVf).—This was prepared in an analogous fashion to (Vg); 2-*benzoyl*-6,7-*dimethylnaphthalene* (26%) had m.p. 117—118° (Found: C, 86·9; H, 6·6%), $\nu_{max.}$ 1652s (C=O) cm.$^{-1}$. The 2,4-*dinitrophenylhydrazone*, had m.p. 281—282° (Found: C, 68·2; H, 4·6; N, 12·7. $C_{25}H_{20}N_4O_4$ requires C, 68·2; H, 4·6; N, 12·7%).

1,4-*Dibromo*-2,3-*dimethylnaphthalene* (IIc).—To a stirred solution of 2,3-dimethylnaphthalene (10 g.) in chloroform (50 ml.) at 0° a solution of bromine (21·6 g.) in carbon tetrachloride (30 ml.) was gradually added. The mixture was then set aside for 2 hr. at room temperature, washed with 2N-sodium hydroxide, then with water, and finally dried ($MgSO_4$). Evaporation of the solvent left a white residue of 1,4-*dibromo*-2,3-*dimethylnaphthalene* (22 g.), m.p. 162—163° (alcohol) (Found: C, 46·2; H, 3·2; Br, 50·6. $C_{12}H_{10}Br_2$ requires C, 45·9; H, 3·2; Br, 50·9%).

2,3-*Dimethylnaphthalene*-1,4-*dicarbonitrile* (IId).—A mixture of 1,4-dibromo-2,3-dimethylnaphthalene (3·5 g.), cuprous cyanide (2·5 g.), and dry pyridine (5 ml.) was heated at 200—220° (bath) for 6 hr. The product was isolated by the method described for the nitrile (Ih), to give 2,3-*dimethylnaphthalene*-1,4-*dicarbonitrile* (1·1 g.), m.p. 260·5—261·5° (alcohol) (Found: C, 81·7; H, 4·8; N, 13·5. $C_{14}H_{10}N_2$ requires C, 81·5; H, 4·9; N, 13·6%), $\nu_{max.}$ 2200s (C≡N) cm.$^{-1}$.

1,4-*Diacetyl*-2,3-*dimethylnaphthalene* (IIb).—To a solution of methylmagnesium iodide [prepared from methyl iodide (6·8 g.) and magnesium (1·2 g.)] in ether, 2,3-dimethylnaphthalene-1,4-dicarbonitrile (0·5 g.) in benzene (150 ml.) was added with stirring, and the mixture was boiled under reflux for 21 hr. The mixture was cooled, 3N-sulphuric acid (100 ml.) was added, and the organic solvent was distilled off. The residue was boiled for 18 hr., cooled, and extracted with ether. The extract afforded 1,4-*diacetyl*-2,3-*dimethylnaphthalene* (0·13 g.), m.p. 132—133° (alcohol) (Found: C, 79·9; H, 6·9. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%), $\nu_{max.}$ 1682s (C=O) cm.$^{-1}$.

1,4-*Dibenzoyl*-2,3-*dimethylnaphthalene* (IIa).—The method used for the preparation was similar to that for the ketone

[31] L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 3742.

(IIb); hydrolysis of the intermediate imine was carried on for 3 days in all. 1,4-*Dibenzoyl*-2,3-*dimethylnaphthalene* (yield 4%) had m.p. 202—203° (alcohol) (Found: C, 85·8; H, 5·7. $C_{26}H_{20}O_2$ requires C, 85·7; H, 5·5%), $\nu_{max.}$ 1652s (C=O) cm.$^{-1}$.

2,3-*Dimethylnaphthalene*-1,5-*dicarboxylic Acid* (IIIc).—A mixture of 1,5-diacetyl-2,3-dimethylnaphthalene (1 g.) and sodium hypochlorite solution (60 ml.; 2% available chlorine) was boiled for 5 hr., with addition at hourly intervals of more hypochlorite (4 × 20 ml.). The mixture was acidified and the product was taken up in chloroform; the extract was shaken with 3N-sodium hydroxide to give, on reprecipitation with an excess of hydrochloric acid, 2,3-*dimethylnaphthalene*-1,5-*dicarboxylic acid* (0·66 g.), m.p. 287·5—288·5° (alcohol) (Found: C, 68·7; H, 4·8. $C_{14}H_{12}O_4$ requires C, 68·9; H, 5·0%), $\nu_{max.}$ 3000s (CO_2H), 1674s (C=O), and 1380m (CH_3) cm.$^{-1}$.

1,5-*Dibenzoyl*-2,3-*dimethylnaphthalene* (IIIa).—A mixture of 2,3-dimethylnaphthalene-1,5-dicarboxylic acid (1·2 g.), phosphorus pentachloride (2·2 g.), and chloroform (5 ml.) was boiled gently for 6 hr. The mixture was evaporated under reduced pressure and the residue of crude acid chloride was dissolved in dry benzene (20 ml.) and aluminium chloride (1·3 g.) was added; the mixture was boiled for 4 hr., and worked up to give 1,5-*dibenzoyl*-2,3-*dimethylnaphthalene* (0·3 g.), m.p. 165—166° (alcohol) (Found: C, 85·5; H, 5·7%), $\nu_{max.}$ 1654s (C=O) cm.$^{-1}$.

Acetylation of 1-*Acetyl*-2,3-*dimethylnaphthalene*.—To a stirred mixture of aluminium chloride (1·35 g.) and acetyl chloride (1·58 g.) in chloroform at 0°, 1-acetyl-2,3-dimethylnaphthalene (1 g.) in chloroform (20 ml.) was added, and stirring was continued at 0° for 30 min., and then at 25° for 23·5 hr. The product (0·95 g.) on isolation was shown (g.l.c.) to comprise essentially the unchanged ketone with 1-acetyl-6,7-dimethylnaphthalene (*ca.* 2%), 2-acetyl-6,7-dimethylnaphthalene (*ca.* 1%), 2,3-dimethylnaphthalene (*ca.* 1%), and 1,5-diacetyl-2,3-dimethylnaphthalene (*ca.* 1%).

Analogous reactions carried out with 1-acetyl-2,3-dimethylnaphthalene, and 2-acetyl-6,7-dimethylnaphthalene, respectively, resulted in the recovery of starting materials only.

Deacylation of 1,5-*Diacetyl*-2,3-*dimethylnaphthalene*.—A mixture of 1,5-diacetyl-2,3-dimethylnaphthalene (0·5 g.), glacial acetic acid (27 ml.), and conc. sulphuric acid (3 ml.) was boiled under reflux for 5 hr. The mixture was diluted with water and the product was taken up in chloroform, and purified by chromatography on alumina and crystallisation (alcohol) to give 1-acetyl-6,7-dimethylnaphthalene (0·05 g.).

Additional Data on Ketones.—(a) 1,5-*Diacetyl*-2,3-*dimethylnaphthalene* (IIIb). Crystals of (IIIb) had m.p. 116·5—117·5° (alcohol) (Found: C, 80·0; H, 6·8%), $\nu_{max.}$ 1678s (C=O) and 1656s (C=O) cm.$^{-1}$.

(b) 1,6-*Diacetyl*-2,3-*dimethylnaphthalene* (VIIa). Crystals of (VIIa) had m.p. 113—114° (alcohol) (Found: C, 79·6; H, 6·9%), $\nu_{max.}$ 1675s (C=O) and 1662s (C=O) cm.$^{-1}$.

(c) 1,6-*Dibenzoyl*-2,3-*dimethylnaphthalene* (VIIb). Crystals of (VIIb) had m.p. 179—180° (alcohol) (Found: C, 85·8; H, 5·6%), $\nu_{max.}$ 1640s (C=O) cm.$^{-1}$.

[8/382 *Received, March 18th,* 1968]