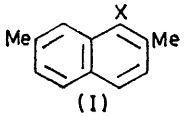
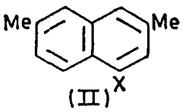
# Friedel–Crafts Acylations of Aromatic Hydrocarbons. Part XIV.[1] Mono-acetylation and Monobenzoylation of 2,7-Dimethylnaphthalene

By **P. H. Gore** * and **A. S. Siddiquei,** School of Chemistry, Brunel University, Kingston Lane, Uxbridge, Middlesex

The Friedel–Crafts acetylation or benzoylation of 2,7-dimethylnaphthalene gives mixtures of three isomers, the 1-isomer usually predominating. In acetylations in nitro-solvents equal amounts of the 1- and the 3- (β) isomers are formed. Competitive acetylation experiments in chloroform solution give the following positional reactivities of naphthalene and derivatives: 1- 1·00, 2- 0·31, 2,7-dimethyl-1- 39, 3,6-dimethyl-2- 6·0, and 3,6-dimethyl-1- 3·5; the values for the corresponding benzoylations are 1·00, 0·40, 230, 9·7, and 7·5, respectively.

CONTINUING our investigations[1,2] of the aromatic substitution reactions (acylations, formylations) of alkylnaphthalenes we have studied Friedel–Crafts acylations of 2,7-dimethylnaphthalene (Ia). The hydrocarbon (Ia) has been reported[3] to give, on sulphonation, a mixture of 2,7-dimethyl-4- (IIb) and -3-sulphonic acids (IIIb). Nitration has been shown[4] to afford either 1-nitro-2,7-dimethylnaphthalene (Ic) or 1,8-dinitro-2,7-dimethylnaphthalene (IVc). Bromination was reported[5] to give the 1-bromo-isomer (Id), but no proof of structure was offered; the corresponding 1-iodo-compound (1h) was similarly obtained.[5,6] More recently, a quantitative study of the bromination of hydrocarbon (Ia) revealed the formation of 98·6% of the 1-bromo-isomer (Id) and 1·4% of 1-bromo-3,6-dimethylnaphthalene (IId).[7] In another quantitative study, of the nitration of hydrocarbon (Ia), isomer proportions (Ic) (75·2%), (IIc) (20·9%), and (IIIc) (3·9%) were reported;[8] however, the identities of these isomers were not properly established.


(I)


(II)

X

a; H

b; SO$_3$H

c; NO$_2$

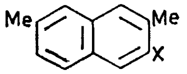
d; Br

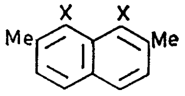
e; Ac

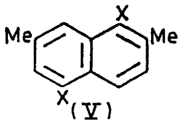
f; Bz

g; CN

h; I


(III)


(IV)


(V)

A Friedel–Crafts acetylation of 2,7-dimethylnaphthalene (Ia) was reported[9] to give a mixture, the main component of which was given as 1-acetyl-2,7-dimethylnaphthalene (Ie), but no proof of structure was offered. Benzoylation,[10] according to the Perrier addition procedure,[11a] afforded 1-benzoyl-2,7-dimethylnaphthalene (If), the structure of which followed from the result of an Elbs cyclisation, which gave 2-methylbenz[*a*]anthracene.[12] Dibenzoylation of hydrocarbon (Ia) was also effected,[13] giving a liquid mixture (unseparated) of what were believed to be 1,5-dibenzoyl- (Vf) and 1,8-dibenzoyl-2,7-dimethylnaphthalene (IVf). We report here our results on the mono-acetylation and -benzoylation of 2,7-dimethylnaphthalene (Ia); diacylations will be reported separately.

*Syntheses.*—The ketones (Ie) and (IIIe) were obtained by independent syntheses. Bromination[5] of the hydrocarbon (Ia) afforded 1-bromo-2,7-dimethylnaphthalene (Id), the orientation of which follows from its $^1$H n.m.r. spectrum. The ketone (Ie) was obtained *via* the nitrile (Ig) by a standard procedure,[2a] as a liquid. Its carbonyl stretching frequency ($\nu_{max}$ 1690 cm$^{-1}$) is consistent with its non-planar configuration.[2b]

Crude sodium 3,6-dimethylnaphthalene-2-sulphonate (IIIb)[3] on fusion with potassium cyanide afforded a mixture of carbonitriles, consisting mainly of isomer (IIIg) together with a small amount of isomer (IIg). The pure nitrile (IIIg), m.p. 158°, obtained by t.l.c., was converted in the usual way[2a] into 2-acetyl-3,6-dimethylnaphthalene (IIIe), m.p. 77°.

1-Acetyl-3,6-dimethylnaphthalene (IIe), m.p. 79°, obtained by preparative g.l.c. from mixtures of ketones, was identified on the basis of its $^1$H n.m.r. and i.r. spectra.

The benzoyl derivatives (If), m.p. 92°, and (IIIf), m.p. 77°, were obtained analogously to the acetyl compounds, from the corresponding carbonitriles.

*Friedel–Crafts Acetylations.*—The results of acetylation experiments on 2,7-dimethylnaphthalene (Ia) are summarised in Table 1. The isomer proportions were determined by quantitative g.l.c. analysis. Each of the

---

[1] Part XIII, F. A. Aslam, P. H. Gore, and M. Jehangir, *J.C.S. Perkin I*, 1972, 892.

[2] (*a*) P. H. Gore, C. K. Thadani, and S. Thorburn, *J. Chem. Soc.* (*C*), 1968, 2502; (*b*) P. H. Gore and M. Yusuf, *J. Chem. Soc.* (*C*), 1971, 2586; (*c*) P. H. Gore and M. Yusuf, *Chem. Comm.*, 1969, 1487.

[3] R. Weissgerber and O. Kruber, *Ber.*, 1919, **52**, 346.

[4] J. B. Ashton, U.S.P. 3,145,235/1964.

[5] E. Clar and H. Wallenstein, *Ber.*, 1931, **64**, 2076.

[6] H. O. Wirth, O. Königstein, and W. Kern, *Annalen*, **1960**, **634**, 84.

[7] J. B. Kim, C. Chen, J. K. Krieger, K. R. Judd, C. C. Simpson, and E. Berliner, *J. Amer. Chem. Soc.*, 1970, **92**, 910.

[8] A. Davies and K. D. Warren, *J. Chem. Soc.* (*B*), 1969, 873.

[9] E. Clar, personal communication in E. Clar, ' Aromatische Kohlenwasserstoffe,' 2nd edn., Springer Verlag, Berlin, 1952.

[10] J. W. Cook, *J. Chem. Soc.*, 1931, 490.

[11] P. H. Gore, in ' Friedel–Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, vol. III, (*a*) p. 4; (*b*) p. 64.

[12] J. W. Cook, *J. Chem. Soc.*, 1932, 456.

[13] E. Clar, H. Wallenstein, and R. Avenarius, *Ber.*, 1929, **62**, 950.

three monoacetyl derivatives (Ie), (IIIe), and (IIe) was formed in every reaction. The proportions varied with the nature of the solvent used.[2a,14] In the chlorinated hydrocarbon solvents, and carbon disulphide, which are so-called ' normal ' Friedel–Crafts solvents,[11b] the 1-position of hydrocarbon (Ia) is substituted to the greatest extent.

Table 1

Acetylation of 2,7-dimethylnaphthalene at 20° for 24 h (Perrier procedure)

| Solvent | Overall yield (%) | Isomer proportions (%) (Ie) | (IIIe) | (IIe) |
|---|---|---|---|---|
| $CHCl_3$ | 95 | 80·5 | 12·5 | 7·0 |
| $C_2H_4Cl_2$ | 97 | 85·5 | 8·0 | 6·5 |
| $CH_2Cl_2$ | 92 | 82·5 | 12·5 | 5·0 |
| $CS_2$ | 87 | 74 | 16 | 10 |
| $MeNO_2$ | 88 | 41·5 | 42·5 | 16 |
| $PhNO_2$ | 29 | 40 | 42 | 18 |

This is a naphthalene α-position, flanked by a methyl group, which in related systems appears to offer considerable steric hindrance to attack by the bulky acetylation reagent. Thus, in 2,3-dimethylnaphthalene,[2a] 2,6-dimethylnaphthalene,[2b,c] and 2-methylnaphthalene,[15] the corresponding 1-positions are not predominantly attacked in Friedel–Crafts acetylations.

In nitromethane or nitrobenzene solutions approximately equal yields of the 1-isomer (Ie) and the 3-isomer (IIIe) are formed. A naphthalene β-position is normally preferred in Friedel–Crafts acetylations carried out in nitro-solvents.[11b] The proportions of the unhindered α-isomer (IIe), albeit invariably low, are increased when nitro-solvents are used.

*Friedel–Crafts Benzoylations.*—Benzoylations of 2,7-dimethylnaphthalene (Ia) by the Perrier addition procedure [11a] gave high overall yields of mixtures of the monoketones (If), (IIf), and (IIIf) (Table 2). The proportion of the 1-isomer (If) invariably exceeded 93%; the other isomers were formed only in traces. These results again illustrate that Friedel–Crafts benzoylations are highly selective and normal substitution reactions; they do not, in contrast to acetylations, vary appreciably with the solvent (*cf.* refs 2 and 16).

Table 2

Benzoylation of 2,7-dimethylnaphthalene at 20° for 24 h (Perrier procedure)

| Solvent | Overall yield (%) | Isomer proportions (%) (If) | (IIIf) | (IIf) |
|---|---|---|---|---|
| $CHCl_3$ | 80 | 93 | 4·0 | 3·0 |
| $C_2H_4Cl_2$ | 75 | 94 | 3·3 | 2·7 |
| $CH_2Cl_2$ | 70 | 93·5 | 4·3 | 2·3 |
| $CS_2$ | 83 | 97 | 1·7 | 1·3 |
| $CS_2$[a] | 88 | 97·5 | 1·5 | 1·0 |
| $MeNO_2$ | 78 | 97 | 3·1 | $<0·3$ |
| $PhNO_2$ | 38 | 94 | 4·6 | 1·2 |

[a] Conditions: 6 h at 0—5° (method of ref. 12).

*Competitive Acylations.*—The reactivity of 2,7-dimethylnaphthalene (Ia) was compared in chloroform solution with that of the parent naphthalene by the method of competitive acylations. The molar ratios of ketones (acylnaphthalenes to acyl-2,7-dimethylnaphthalenes) formed from equimolar amounts of the hydrocarbon substrates were 1 : 21·6 for acetylations and 1 : 89·6 for benzoylations. A comparison of positional reactivities (Table 3) shows for acetylations a 40-fold enhancement in reactivity at the 1-position of hydrocarbon (Ia), relative to the 1-position in naphthalene. The corresponding rate enhancements for the related 1-positions in 2,3-dimethylnaphthalene [2a] and 2,6-dimethylnaphthalene [2b] had been found to be much smaller (1·6 and 4·1, respectively). It is evident that activation of the nuclear positions depends on the substituent action of *both* methyl groups. The 1-position of hydrocarbon (Ia) is thus of high reactivity towards acetylation reagents, despite probable steric hindrance (*cf.* ref. 2). It is also significant that the reactivity of the 3-position of hydrocarbon (Ia) has been increased by a factor of *ca.* 20, although Friedel–Crafts acetylations do not readily occur at positions *ortho* to methyl groups.[2b,17]

Table 3

Relative reactivities of nuclear positions in competitive acylations of 2,7-dimethylnaphthalene and naphthalene in chloroform solution

| Naphthalene position | Relative reactivities Acetylation | Benzoylation |
|---|---|---|
| 1- | 1·00 | 1·00 |
| 2- | 0·31 | 0·40 |
| 2,7-Dimethyl-1- | 39 | 230 |
| 3,6-Dimethyl-2- | 6·0 | 9·7 |
| 3,6-Dimethyl-1- | 3·5 | 7·5 |

The 1-position of 2,7-dimethylnaphthalene (Ia) exhibits a relative benzoylation rate about six times as great as for acetylation. This observation, which is in line with earlier results,[2a,b] points to the lower reactivity and greater selectivity of the benzoylation reaction in these systems.

*¹H N.m.r. Spectra.*—Details of the spectra of the hydrocarbon (Ia) and eight of its derivatives are given in Table 4. The naphthalenic proton signals were generally satisfactorily resolved except where phenyl resonances, as in derivatives (If) and (IIIf), were superimposed.

The relative positions of the acetyl resonances are characteristic. In the 1-isomer (Ie) the *ortho*-methyl group, acting through the short 1,2-naphthalene bond,[18] exerts a strong inductive (+*I*) effect, thereby pushing

---

[14] (*a*) P. H. Gore and C. K. Thadani, *J. Chem. Soc.* (*C*), 1967, 2619; (*b*) R. E. Girdler, P. H. Gore, and J. A. Hoskins, *ibid.*, 1966, 181, 518; P. H. Gore and C. K. Thadani, *ibid.*, p. 1729; 1967, 1498.

[15] P. R. Wells and P. G. E. Alcorn, *Austral. J. Chem.*, 1963, **16**, 1109; P. H. Gore, A. S. Siddiquei, and S. Thorburn, unpublished work.

[16] P. H. Gore and J. A. Hoskins, *J. Chem. Soc.*, 1964, 5666; P. A. Goodman and P. H. Gore, *J. Chem. Soc.* (*C*), 1968, 966.

[17] H. C. Brown, G. Marino, and L. M. Stock, *J. Amer. Chem. Soc.*, 1959, **81**, 3310.

[18] D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc. A*, 1960, **258**, 270.

the acetyl signal upfield (τ 7·40). In the isomer (IIIe) the inductive effect is transmitted through the longer 2,3-naphthalene bond,[18] and a signal at lower field (τ 7·32) results. The corresponding signal for isomer (IIe), possessing only distant methyl groups, occurs at still lower field (τ 7·26). Resonance effects may also contribute to the position of these signals. A similar sequence was observed, but not commented on, with the acetyl resonances of related methyl naphthyl ketones.[2]

The spectra in general provide strong supporting evidence for the structures proposed.

## EXPERIMENTAL

I.r. spectra were measured for potassium bromide discs, for films, or for solutions in chloroform. $^1$H N.m.r. spectra were obtained at 60 or 100 MHz for solutions in deuteriochloroform (tetramethylsilane as internal standard).

TABLE 4

$^1$H N.m.r. spectra of derivatives of 2,7-dimethylnaphthalene

| Derivative | Chemical shifts (τ) [a] | | | | | | | | | | J/Hz | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1-H | 3-H | 4-H | 5-H | 6-H | 8-H | Aryl H | Ac | 2-Me | 7-Me | 3,4 | 5,6 | 6,8 |
| (Ia) [b] | 2·54(d) | 2·83(dd) | 2·34(d) | 2·34(d) | 2·83(dd) | 2·54(d) | | | 7·37 | 7·37 | 8·2 | 8·2 | 1·4 |
| (Id) | | 2·79(d) | 2·37(d) [c] | 2·41(d) [c] | 2·76(dd) | 1·97(m) | | | 7·42 | 7·47 | 8·2 | 8·2 | 1·7 |
| (Ig) | | 2·74(d) | 2·30(d) | 2·17(d) | 2·68(dd) | 2·09(m) | | | 7·30 | 7·46 | 8·1 | 8·4 | 1·5 |
| (Ie) | | 2·82(d) | 2·33(d) | 2·33(d) | 2·76(d) | 2·67(m) | | 7·40 | 7·54 | 7·61 | 8·4 | 8·3 | *ca.* 1·8 |
| (If) | | | | | | | 2·0—2·9 | | 7·66 | 7·73 | | | |
| (IIe) [d] | 2·31br | 2·45 | | 1·42(d) | 2·63(dd) | 2·31br | | 7·26 | 7·45 | 7·48 | | 8·7 | 1·8 |
| (IIIg) [d] | 1·79 | | 1·49 | 2·21(d) | 2·32(dd) | 2·19 | | | 7·30 | 7·44 | | *ca.* 8 | |
| (IIIe) [d] | 2·49 | | 1·85 | 2·27(d) | 2·73(dd) | 2·50br | | 7·32 | 7·35 | 7·49 | | 8·1 | 1·5 |
| (IIIf) [d] | | | | | | | 2·0—2·9 | | 7·55 | 7·74 | | | |

[a] Unless otherwise denoted signals were singlets. [b] Reported 2(7)-Me signals at τ ($CCl_4$) 7·54 (Foch Fu-Hsie Yew, R. J. Kurland, and B. J. Mair, *Analyt. Chem.*, 1964, **36**, 843). [c] The assignment may be the reverse. [d] Numbered as a 2,7-dimethylnaphthalene

*Gas Chromatography.*—Analyses were performed (A) for acetylations: with a glass column (5 ft × ¼ in int. diam.) packed with Bentone 34 (3·5%) and Carbowax 20M (1·5%) on Celite (80—100 mesh) with nitrogen as carrier gas at 167°; or (B) for benzoylations: with a stainless-steel tube (2 m × 2·2 mm int. diam.) packed with SE 30 (10%), coated with silicone elastomer, on Celite (100—200 mesh) at 237°. The instruments used were (A) Pye model 104, and (B) Perkin-Elmer model F 11, fitted with flame-ionisation detectors. Detector mass responses were determined for the various ketones, and were applied as appropriate. Kováts[19] retention indices (*I*) for the ketones are given in Table 5, which also includes the slopes (*b*) of the graphs of log (retention volume) *vs.* carbon number for the n-alkane.

TABLE 5

Kováts retention indices (*I*) and slopes (*b*) for ketones from 2,7-dimethylnaphthalene

| Methyl series [column (A), 167°] | *I* | *b* | Phenyl series [column (B), 237°] | *I* | *b* |
|---|---|---|---|---|---|
| (Ie) | 2210 | 0·195 | (If) | 2258 | 0·134 |
| (IIe) | 2507 | 0·194 | (IIf) | 2365 | 0·133 |
| (IIIe) | 2410 | 0·195 | (IIIf) | 2388 | 0·134 |

2,7-*Dimethylnaphthalene*-1-*carbonitrile* (Ig).—1-Bromo-2,7-dimethylnaphthalene[5] (5·0 g) was heated with copper(I) cyanide (2·5 g) and dry pyridine (10 ml) at 190° (bath) for 6 h. The crude product was worked up as described before,[25] to give the off-white *nitrile* (2·9 g, 50%), m.p. 93·5—94° (Found: C, 86·4; H, 6·2; N, 7·5. $C_{13}H_{11}N$ requires C, 86·2; H, 6·1; N, 7·7%), $\nu_{max.}$ (KBr) 2205 cm$^{-1}$ (C≡N).

1-*Acetyl*-2,7-*dimethylnaphthalene* (Ie).—A solution of 2,7-dimethylnaphthalene-1-carbonitrile (0·9 g) in dry benzene was rapidly added to methylmagnesium iodide [from magnesium (1·2 g) and iodomethane (7·1 g)] in ether; the mixture was boiled for 24 h. To the cooled solution a saturated solution of ammonium chloride was added with stirring. The organic layer was separated, washed with water, and evaporated. The residue was then boiled under reflux with 3N-sulphuric acid (100 ml) for 24 h. The cooled solution was extracted with ether and the extract was washed with water and dried. Evaporation then gave the crude ketone, which was purified by passage through a short column of alumina (benzene as eluant) and removing the solvent *in vacuo*. 1-*Acetyl*-2,7-*dimethylnaphthalene* (0·25 g, 30%) was a pale yellow liquid (Found: C, 85·0; H, 6·9. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%), $\nu_{max.}$ (film) 1690 cm$^{-1}$ (C=O).

1-*Benzoyl*-2,7-*dimethylnaphthalene* (If).—This compound, prepared like the ketone (Ie) from phenylmagnesium bromide, had m.p. 92° (Found: C, 87·8; H, 6·1. Calc. for $C_{19}H_{16}O$: C, 87·7; H, 6·2%), $\nu_{max.}$ (KBr) at 1660 cm$^{-1}$ (C=O), and was identical (mixed m.p., i.r. spectrum) with that obtained from the Friedel–Crafts reactions.

3,6-*Dimethylnaphthalene*-2-*carbonitrile* (IIIg).—An intimate mixture of sodium 3,6-dimethylnaphthalene-2-sulphonate[3] (8·0 g) and potassium cyanide (4 g) was gently heated over a flame until vapours were no longer given off. 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 (0·6 g). This was chromatographed on alumina (from benzene) to give the *nitrile* (0·35 g, 6%), m.p. 157—158° (Found: C, 86·2; H, 6·3; N, 7·7. $C_{13}H_{11}N$ requires C, 86·2; H, 6·1; N, 7·7%), $\nu_{max.}$ (KBr) 2233 cm$^{-1}$ (C≡N).

2-*Acetyl*-3,6-*dimethylnaphthalene* (IIIe).—Prepared from the nitrile (IIIg) by the method described for the isomer (Ie), the yellow *ketone* (38%) had m.p. 76—77° (from ethanol) (Found: C, 84·4; H, 7·3. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%), $\nu_{max.}$ (KBr) 1670 cm$^{-1}$ (C=O), and was identical with that obtained from a Friedel–Crafts acetylation carried out in nitromethane solution (see later).

2-*Benzoyl*-3,6-*dimethylnaphthalene* (IIIf).—Obtained from

---

[19] E. Kováts, *Helv. Chim. Acta*, 1958, **41**, 1915; 1959, **42**, 2709; L. S. Ettre, *Analyt. Chem.*, 1964, **36**, 31A.

the nitrile (IIIg) by the action of phenylmagnesium bromide, the *ketone* (21%) had m.p. 76—77° (from ethanol) (Found: C, 87·5; H, 6·3. $C_{19}H_{16}O$ requires C, 87·7; H, 6·2%), $\nu_{max.}$ (KBr) 1655 cm$^{-1}$ (C=O), and was identical with the minor product, obtained by fractional crystallisation, from the Friedel–Crafts benzoylation in nitromethane.

*Friedel–Crafts Acylations.*—The experimental procedures are those employed previously; [2a] the scale of the acylations was usually 0·02M.

1-*Acetyl*-3,6-*dimethylnaphthalene* (IIe).—From an acetylaction carried out in nitrobenzene 1-*acetyl*-3,6-*dimethylnaphthalene* was obtained by preparative g.l.c. as crystals, m.p. 78—79° (Found: C, 84·7; H, 7·2. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%), $\nu_{max.}$ (film) 1673 cm$^{-1}$ (C=O).

*Competitive Acylations of* 2,7-*Dimethylnaphthalene and Naphthalene.*—These were carried out by Perrier addition in chloroform solution, at 20°, on 0·02M scale, by the method described earlier.[14a]

We thank Mr. S. Thorburn for advice, the S.R.C. for facilities provided at the P.C.M.U., and The Sun Oil Company for a gift of 2,7-dimethylnaphthalene.

[2/062 *Received*, 12*th January*, 1972]