

Friedel-Crafts Reactions. Part XXIV.† Diacylations of 2,7-Dimethylnaphthalene. Deuterium-labelling as an Aid to Structural Determinations

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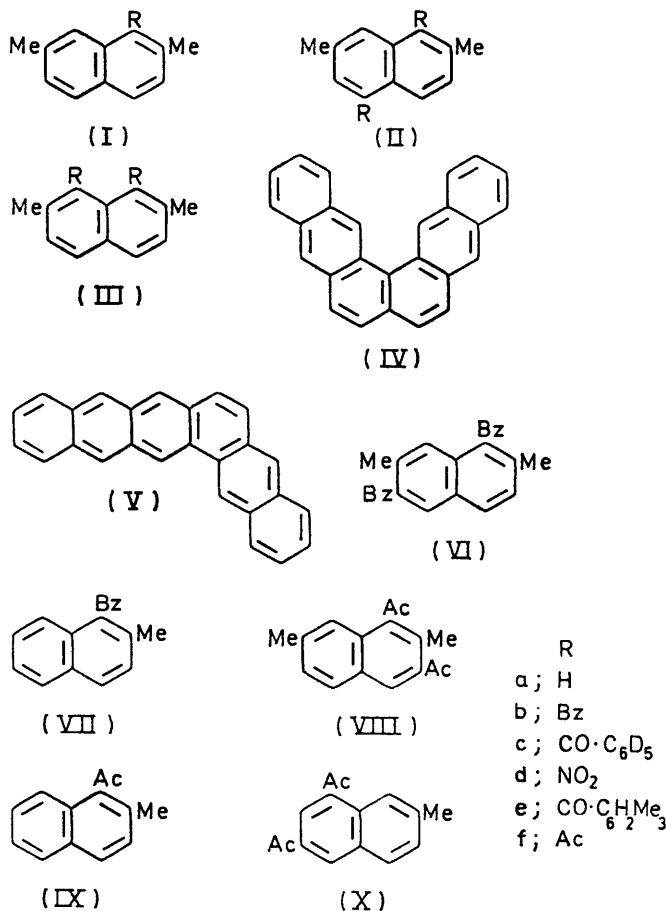
Friedel-Crafts diacetylation of 2,7-dimethylnaphthalene gives mixtures of 1,3- and 1,5-diacetyl-derivatives, the latter usually predominating. A corresponding benzoylation afforded a mixture of 1,5- and 1,8-dibenzoyl-derivatives, with the latter predominating. The structures of the dibenzoyl derivatives followed from the ^1H n.m.r. spectra of ketones deuterium-labelled in the phenyl rings. Stereochemical aspects of the diacylation reactions and products are discussed.

DETAILS of the monoacylation of 2,7-dimethylnaphthalene (Ia) have recently been reported.¹ In 1929 Clar, Wallenstein, and Avenarius² effected the dibenzoylation of this hydrocarbon (Ia) by a Friedel-Crafts reaction with an excess of benzoyl chloride and aluminium chloride in carbon disulphide suspension. The product, which could not be crystallised, was considered to be a mixture of 1,5- (IIb) and 1,8-dibenzoyl-2,7-dimethylnaphthalene (IIIb). As evidence for the orientation of (IIIb) was advanced the formation from it (by an Elbs condensation at 300°) of a new hydrocarbon, anthra-[1,2-*a*]anthracene (IV), for whose structure no evidence was, however, advanced. Similarly, the report of the formation of the diketone (IIb) was mere supposition. On the basis solely of its electronic absorption spectrum Clar, in 1940,³ deduced a different structure (V) (hexaphene) for the hydrocarbon obtained in 1929. Since rearrangements prior to cyclisation had been reported,⁴ especially in the case of cisoid angular structures like (IV), it was evident that no firm structural conclusions relating to ketonic intermediates could be drawn from the structures of aromatic hydrocarbons derived from them. Nevertheless in 1964 Clar⁵ suggested that his hydrocarbon (V) could have been formed from 1,6-dibenzoyl-2,7-dimethylnaphthalene (VI) present in his original acylation product. Clar also sought here⁵ to perpetuate the fiction that attempts to prepare the hydrocarbon (IV) from the diketone (IIIb) were unsuccessful.

We now report our investigations of the diacetylation, dibenzoylation, and attempted dimesitylation of 2,7-dimethylnaphthalene (Ia).

Dibenzoylation and Dimesitylation.—When 2,7-dimethylnaphthalene (Ia) was dibenzoylated, precisely as described previously,² an oily mixture of ketones was obtained. One component (A), m.p. 193° , of this mixture was readily obtained by crystallisation, and two others, 1-benzoyl-2,7-dimethylnaphthalene (Ib), m.p. 89° , and (B), m.p. 176° , could be purified by chromatography. The 1-benzoyl compound is invariably the main product ($>93\%$) in monobenzoylations of 2,7-

dimethylnaphthalene.¹ The ketones (A) and (B) were isomeric dibenzoyl-2,7-dimethylnaphthalenes. The



carbonyl stretching frequencies of these ketones did not indicate unambiguously the location of benzoyl groups. The ^1H n.m.r. spectrum showed a single methyl signal at τ 7.87 for ketone (A), showing that the two benzoyl groups were symmetrically disposed. For ketone (B) two separate methyl signals were obtained, τ 7.77 and 7.82. The aromatic signals, however, were too complex

¹ P. H. Gore and A. S. Siddiquei, *J.C.S. Perkin I*, 1972, 1442.

² E. Clar, H. Wallenstein, and R. Avenarius, *Ber.*, 1929, **62**, 950.

³ E. Clar, *Ber.*, 1940, **73**, 81; 'Aromatische Kohlenwasserstoffe,' Springer Verlag, Berlin, 2nd edn., 1952, 245.

⁴ J. W. Cook, *J. Chem. Soc.*, 1930, 1087; E. Clar and F. John, *Ber.*, 1931, **64**, 981; E. Clar, F. John, and R. Avenarius, *Ber.*, 1939, **72**, 2139.

⁵ E. Clar, 'Polycyclic Hydrocarbons,' Academic Press, London and New York, vol. 1, 1964, 416.

† This series results from the amalgamation of two previous series, the titles and last parts of which were as follows: 'Friedel-Crafts Acylations of Aromatic Hydrocarbons,' Part XV, *J.C.S. Perkin I*, 1972, 1781, and 'The Friedel-Crafts Acylation of Aromatic Halogen Derivatives,' Part V, *J. Chem. Soc. (C)*, 1971, 2362. The new series also incorporates the following papers, not previously part of a series: R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc. (C)*, 1966, 181; P. C. Doolan and P. H. Gore, *ibid.*, 1967, 211; and P. H. Gore, G. H. Smith, and S. Thorburn, *ibid.*, 1971, 650.

for analysis [Figure 1(a)], since there was superposition of resonances of ten phenyl protons on those of four naphthalenic protons.

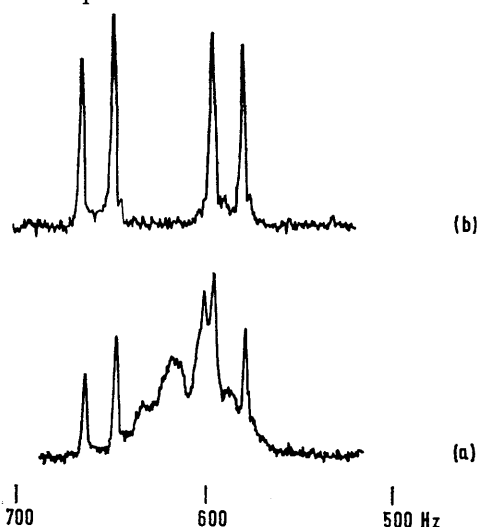


FIGURE 1 ^1H N.m.r. spectra (CHCl_3 solution; Me_4Si internal standard) of (a) the ketone (IIIb) and (b) the ketone (IIIc) at 60 MHz

However, the pattern of substitution in the ketones (A) and (B) was revealed clearly by studying the dibenzoyl-2,7-dimethylnaphthalenes obtained by a Friedel-Crafts reaction with pentadeuteriobenzoyl chloride.

much simpler (Figure 2), and proved to be that of 1,5-bis(pentadeuteriobenzoyl)-2,7-dimethylnaphthalene (IIc). The alternative structure (VI) for isomer (B) is ruled out because of the multiplicity of the 8-H signal, and because the singlet at τ 2.68 must belong to a β -naphthyl proton.

We have therefore confirmed Clar's original² claim that ketones (IIIb) and (IIb) are formed in the ratio of *ca.* 3 : 2. Both ketones are evidently derived from the initially formed ketone (Ib). Polarisability studies⁶ have shown that in carbon tetrachloride solution the preferred conformation of 1-benzoyl-2-methylnaphthalene (VII) probably exhibits a carbonyl group twisted 70° (or more) away from coplanarity with the naphthalene system, and $90^\circ \pm 15^\circ$ away from coplanarity with the phenyl ring. The extent to which this conformation will be altered when the carbonyl oxygen atom, during the acylation reaction, is co-ordinated with the aluminium chloride⁷ is uncertain. However, sufficient space must remain available at the *peri*- (8-) position of the intermediate (Ib) for entry of a second benzoyl group. Dinitration of the hydrocarbon (Ia) has been reported to give 1,8-dinitro-2,7-dimethylnaphthalene (IIIId).⁸

It proved possible to introduce a mesityl group into the 1-position of 2,7-dimethylnaphthalene (Ia) to give the ketone (Ie). The reaction is much slower than the corresponding benzoylation, probably mainly for steric

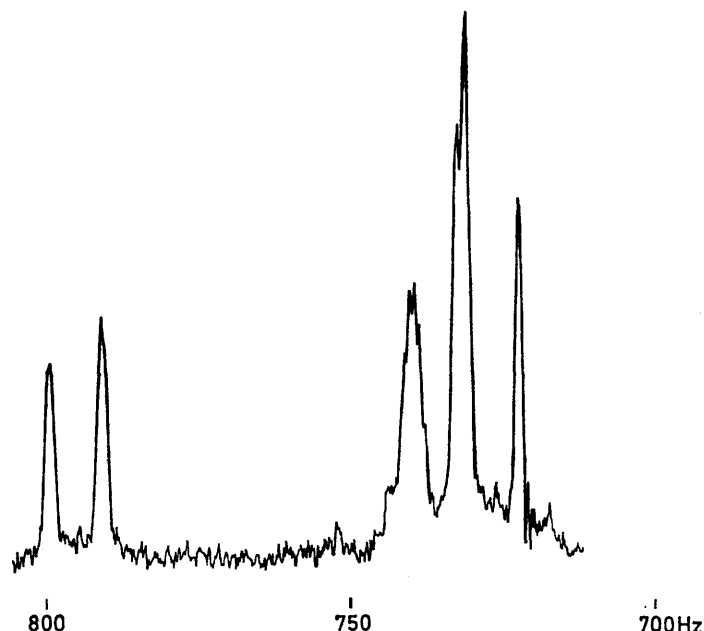


FIGURE 2 ^1H N.m.r. spectrum (CDCl_3 solution; Me_4Si internal standard) of the ketone (IIc) at 100 MHz

The simple AA'BB' pattern of the ^1H n.m.r. signals of the deuteriated ketone (A) [Figure 1(b)] showed it to be 1,8-bis(pentadeuteriobenzoyl)-2,7-dimethylnaphthalene (IIIc). The spectrum of the isomer (B) likewise was

⁶ C. L. Cheng, G. L. D. Ritchie, and P. H. Gore, *J.C.S. Perkin II*, 1973, 1368.

⁷ N. N. Greenwood and K. Wade, in 'Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, vol. 1, 1963, pp. 573, 585.

reasons. Analogously, benzoylation of mesitylene (in nitromethane solution) is *ca.* 3000 times as fast as its mesitylation.⁹ By analogy with the known conformations of dimesityl ketone¹⁰ and mesityl 1-naphthyl

⁸ J. B. Ashton, U.S.P. 3,145,235/1964.

⁹ P. H. Gore, J. A. Hoskins, and S. Thorburn, *J. Chem. Soc. (B)*, 1970, 1343.

¹⁰ P. H. Gore, J. A. Hoskins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. (B)*, 1967, 741.

ketone¹¹ it is likely that both bulky aryl systems of the ketone (Ie) are twisted substantially away from coplanarity with the carbonyl function. This should result in additional encroachment on the space available at the *peri*-position, in comparison with the 1-benzoyl derivative (Ib). Attempts at effecting dimesitylation of the hydrocarbon (Ia), *i.e.* by using reagents in excess in boiling carbon disulphide suspension for 14 days, failed to give either diketone (IIe) or (IIIe).

Non-coplanarity of the carbonyl function in the ketone (Ib) with the naphthalene system implies that reasonably stable *cis*- and *trans*-isomers of 1,8-dibenzoyl-2,7-dimethylnaphthalene (IIIb) could exist. On the present

The isomer of m.p. 100° was similarly shown to be 1,3-diacetyl-2,7-dimethylnaphthalene (VIII). The carbonyl stretching bands of its acetyl groups occurred at 1688 (1-Ac) and 1670 cm⁻¹ (3-Ac), respectively. The chemical shifts of the four methyl signals are here especially characteristic. The 2-methyl signal is shifted substantially downfield by its two neighbouring electro-negative groups. Further, the chemical shifts for the hindered α -acetyl group (τ 7.39) and the hindered β -acetyl group (τ 7.35) are as expected¹ for structure (VIII).

Acylation in all naphthalene derivatives generally occurs predominantly at α -positions. In the case of

TABLE 1
Acetylation of 2,7-dimethylnaphthalene

Solvent	Conditions			Yield (%) ^b	Products (%)			
	Molar proportions of reactants ^a	Temp. (°C)	Time (h)		Monoketones	Diketones (IIf) (VIII)		Isomer ratio (IIf)/(VIII)
C ₂ H ₄ Cl ₂	2 : 2 : 1	85	3	88	43	39	18	2.15
C ₂ H ₄ Cl ₂	6 : 4 : 1	85	4	90	0	51	49	1.05
CS ₂	6 : 4 : 1	45	4	86	0	61	39	1.55

^a Aluminium chloride : acetyl chloride : 2,7-dimethylnaphthalene. ^b Overall yield (w/w).

TABLE 2
¹H N.m.r. spectra of acyl derivatives of 2,7-dimethylnaphthalene

Derivative	Chemical shifts (τ) ^a							<i>J</i> /Hz						
	3-H	4-H	5-H	6-H	8-H	Ph	1-Ac	3-Ac	5-Ac	2-Me	7-Me	3,4	5,6	6,8
(Ia) ^b	2.82(dd)	2.35(d)	2.35(d)	2.82(dd)	2.54br ^c					7.54	7.54	8.4	8.4	1.5
(IIf)	2.66(d)	2.24(d)		2.68(m)	1.88br		7.35		7.29	7.45	7.46			
(VIII)		1.81	2.21(d)	2.72(d)	2.61		7.39	7.35		7.40	7.60			
(Ib)	2.75(d)	2.24(d)	2.29(d)	2.79(d)	2.79(m)	2.0—2.9(m)				7.67	7.76	8.7	8.7	
(IIb)	2.73(d)	2.05(d)		2.68	2.60(m)	2.2—2.8(m)				7.77	7.82	8.6		1.3
(IIIb)	2.68(d)	2.11(d)	2.11(d)	2.68(d)		2.2—2.8(m)				7.87	7.87	8.5	8.5	
(Ie) ^d	2.90(d)	2.35(d)	2.30(d)	2.81(dd)	2.29(m)	3.20 ^e				7.63	7.76	8.4	8.0	1.5

^a Unless otherwise denoted signals were singlets. ^b Redetermined. ^c Same value for 1-H resonance. ^d Chemical shifts for mesityl group: 2-(6)-Me 7.92; 4-Me 7.84. ^e Phenyl *m*-protons.

evidence we cannot assign a particular configuration to our compound.

Diacetylation.—Use of reagents in excess in the Perrier acetylation procedure applied to 2,7-dimethylnaphthalene (Ia) afforded two diacetyl derivatives, m.p. 108 and 100°, separable by fractional crystallisation and g.l.c. The relative proportions formed under various conditions are given in Table 1.

The isomer of m.p. 108° had two carbonyl absorptions in the i.r. spectrum, indicating the presence of one α -acetyl group twisted out of the plane of the naphthalene rings by interaction with an *ortho*-methyl group (1685 cm⁻¹), and another (1673 cm⁻¹) which could be either an unhindered α -acetyl group or a hindered β -acetyl group.^{1,12} The ¹H n.m.r. spectrum (Table 2) confirmed the presence of two different acetyl groups. One signal (τ 7.35) must be that of a hindered α -acetyl and the other (τ 7.29) that of an unhindered α -acetyl group. The chemical shifts and multiplicities of the aromatic proton resonances confirm the structure as that of 1,5-diacetyl-2,7-dimethylnaphthalene (IIf).

¹¹ C. L. Cheng, G. L. D. Ritchie, P. H. Gore, and M. Jehangir, *J. C. S. Perkin II*, 1972, 1432.

¹² P. H. Gore and M. Yusuf, *J. Chem. Soc. (C)*, 1971, 2586.

1-acetylnaphthalene, electronic effects ($-I$, $-M$) preferentially deactivate the substituted ring; also, inductive and steric effects tend to lower the reactivity at the 8-position. The predominant formation of diacetyl derivatives having a 1,5-orientation is therefore predictable. This reasoning agrees with data obtained for the diacetylation of 2,3-dimethylnaphthalene,¹³ 2,6-dimethylnaphthalene,¹² and naphthalene itself.¹⁴ Where initial substitution leads to a derivative of 1-acetyl-2-methylnaphthalene (IX) a further steric factor operates. It has been shown that in the preferred conformation of the ketone (IX), the proximity of a *peri*-hydrogen atom and an *ortho*-methyl group to the 1-acetyl group, cause the latter to take up a position almost at right angles to the naphthalene rings.⁶ The effective size, however, of the substituent will be maintained by complexation with the catalyst (see before), and considerable steric hindrance is offered to further acetylation at the *peri*-position. The qualitative difference in comparison with the successful *peri*-benzoylation of hydrocarbon (Ia) (see

¹³ P. H. Gore, C. K. Thadani, and S. Thorburn, *J. Chem. Soc. (C)*, 1968, 2502.

¹⁴ G. Lock, *Monatsh.*, 1950, **81**, 850; R. Stephen, *Chem. Ber.*, 1957, **90**, 296; W. Carruthers, personal communication.

before) resides in the larger steric requirements of the acetylation reagent.¹⁵

The non-coplanarity of the 1-acetyl group at the same time will reduce sharply the electron demand by the conjugative $-M$ mechanism on the naphthalene ring system. This situation closely resembles that in certain hindered homologues of benzene, *e.g.* mesitylene¹⁶ and pseudocumene,¹⁷ which form 1,3-diacetyl derivatives fairly readily. The isomer (VIII) was formed to its largest extent when an excess of aluminium chloride was used (Table 1), *i.e.* when effective formation of the initial ketone-catalyst complex was most likely.

The ketone (VIII) is the first authentic example to be reported of a diacylated naphthalene in which both acyl groups have entered the same ring. A report of the formation¹⁸ of 1,3-diacetyl-7-methylnaphthalene (X) from 2-methylnaphthalene could not be confirmed.¹⁹

EXPERIMENTAL

I.r. spectra were measured for potassium bromide discs, or for solutions in chloroform. ¹H N.m.r. spectra were obtained at 60 or 100 MHz for solutions in deuteriochloroform, with tetramethylsilane as internal standard. G.l.c. analyses were performed with a stainless steel column (1/8 in int. diam.) packed with Apiezon L (3.5%) on Celite (60–70 mesh), with nitrogen as carrier gas at 182°, on a Perkin-Elmer F11 instrument fitted with a flame-ionisation detector. Kováts²⁰ retention indices (*I*) for the diacetyl derivatives, and slopes (*b*) of the plots of log(retention volume) *vs.* carbon number for the *n*-alkanes, are given in Table 3.

TABLE 3

Kováts retention indices (*I*) and slopes (*b*) for diacetyl-2,7-dimethylnaphthalenes at 182°

Ketone	<i>I</i>	<i>b</i>
(VIII)	2030	0.21
(III)	2050	0.21

Diacetylation of 2,7-Dimethylnaphthalene.—Acetylations were carried out by the Perrier procedure, *i.e.* with final addition of the hydrocarbon to a mixture of the other components in the chosen solvent. The experimental details are summarised in Table 1; the scale of the acylations was based on use of 0.03 mol of 2,7-dimethylnaphthalene. The reaction mixtures were cooled and added to hydrochloric acid and ice, and the ketones were isolated in the usual way and analysed by g.l.c. Monoacetyl derivatives could be separated from diacetyl derivatives by chromatography on alumina (benzene as eluant). The more strongly absorbed diketone fractions were recrystallised several times to give 1,5-diacetyl-2,7-dimethylnaphthalene, m.p. 108° (from ethanol) (Found: C, 79.6; H, 6.6. C₁₆H₁₆O₂ requires C, 80.0; H, 6.7%); ν_{\max} (KBr) 1685 and 1673 cm⁻¹ (C=O). The mother liquors afforded 1,3-diacetyl-2,7-dimethylnaphthalene, m.p. 100° (methanol) (Found: C, 79.8; H, 6.6; *M*⁺, 240.1146. C₁₆H₁₆O₂ requires *M*, 240.1150); ν_{\max} (KBr) 1688 and 1670 cm⁻¹ (C=O).

¹⁵ H. J. Brown, G. Marino, and L. M. Stock, *J. Amer. Chem. Soc.*, 1959, **81**, 3310.

¹⁶ P. H. Gore and J. A. Hoskins, *J. Chem. Soc. (C)*, 1970, 517.

¹⁷ L. I. Smith and C. Guss, *J. Amer. Chem. Soc.*, 1937, **59**, 804;

cf. G. S. Hammond and M. F. Hawthorne, in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, 175.

Dibenzoylation of 2,7-Dimethylnaphthalene (Method of Clar *et al.*)²¹.—The oily product slowly deposited crystals at 5°; recrystallisation (ethanol) gave 1,8-dibenzoyl-2,7-dimethylnaphthalene, m.p. 192–193° (Found: C, 85.3; H, 5.3. C₂₆H₂₀O₂ requires C, 85.7; H, 5.5%); ν_{\max} (KBr) 1660 cm⁻¹. Preparative t.l.c. of the residue from the mother liquors (silica gel G; benzene) afforded 1,5-dibenzoyl-2,7-dimethylnaphthalene, m.p. 175.5–176° (from ethanol) (Found: C, 85.5; H, 5.5%).

Mesitylation of 2,7-Dimethylnaphthalene.—Aluminium chloride (4 g) was added in portions during 25 min to a stirred mixture of 2,4,6-trimethylbenzoyl chloride (3.4 g) and 2,7-dimethylnaphthalene (1.4 g) in carbon disulphide (50 ml) at 0°. The dark green mixture was then gently boiled for 72 h. The oily product was isolated in the usual way; crystallisation (ethanol) afforded 2,7-dimethyl-1-naphthyl 2,4,6-trimethylphenyl ketone (2.8 g), m.p. 104–105° (Found: C, 87.4; H, 7.3. C₂₂H₂₂O requires C, 87.4; H, 7.3%); ν_{\max} (CHCl₃) 1655 cm⁻¹ (C=O); *R_F* 0.8.

A slow-moving band (*R_F* 0.2) on preparative t.l.c. gave 2,4,6-trimethylbenzoic acid (rel. yield 15%), m.p. and mixed m.p. 151°.

Bromopentadeuteriobenzene.—This compound was obtained by bromination (bromine; trace of pyridine) of hexadeuteriobenzene (>99% isotopic purity), as an oil, b.p. 148–150° (33° at 0.3 mmHg).

Pentadeuteriobenzoic Acid.—The acid, obtained by carbonylation of the Grignard reagent from bromopentadeuteriobenzene, formed crystals, m.p. 118–119°; τ -0.41 (exchanged in D₂O).

Pentadeuteriobenzoyl Chloride.—Pentadeuteriobenzoic acid was heated gently under reflux with an excess of thionyl chloride. Removal of the excess of reagent by distillation then gave the chloride, which was used directly for the following acylation.

Acylation of 2,7-Dimethylnaphthalene with Pentadeuteriobenzoyl Chloride.—The experimental conditions were precisely those of the earlier benzoylation experiment, except that an appropriate weight of pentadeuteriobenzoyl chloride was used. The oily product was separated by preparative t.l.c. (benzene) into three main fractions: (i) 1,8-bis(pentadeuteriobenzoyl)-2,7-dimethylnaphthalene, *R_F* 0.33, m.p. 189–190° [Found: C, 82.5; H(D), 5.5 (by thermal conductivity). C₂₆H₁₀D₁₀O₂ requires C, 83.4%. C₂₆H₂₀O requires H, 5.5%], ν_{\max} 1667 cm⁻¹, relative yield 50%; (ii) 1,5-bis(pentadeuteriobenzoyl)-2,7-dimethylnaphthalene, *R_F* 0.66, m.p. 176° [Found: C, 83.2; H(D), 5.5%], ν_{\max} 1662 cm⁻¹, relative yield 34%; (iii) 1-pentadeuteriobenzoyl-2,7-dimethylnaphthalene, *R_F* 0.95, m.p. 89.5° (lit.¹ m.p. for 1-benzoyl-2,7-dimethylnaphthalene 92°) [Found: C, 85.3; H(D), 6.1. C₁₉H₁₁D₅O requires C, 85.8%. C₁₉H₁₆O requires H, 6.2%], ν_{\max} (CHCl₃) 1662 cm⁻¹ (C=O), relative yield 16%.

We thank the British Council for a grant (to A. Y. M.) and the S.R.C. for some measurements carried out at the P.C.M.U.

[3/1211 Received, 11th June, 1973]

¹⁸ K. Dziewonski and M. Brand, *Roczniki Chem.*, 1932, **12**, 693; *Bull. Acad. polon. Sci., Ser. Sci. chim.*, 1933, 99.

¹⁹ P. H. Gore, A. S. Siddiquei, and S. Thorburn, *J.C.S. Perkin I*, 1972, 1781.

²⁰ E. Kováts, *Helv. Chim. Acta*, 1958, **41**, 1915; 1959, **42**, 2709; L. S. Etre, *Analyt. Chem.*, 1964, **36**, 31A.