Friedel–Crafts Acylations of Aromatic Hydrocarbons. Part XV.[1] Acetylation of 2-Methylnaphthalene

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In the Friedel–Crafts acetylation of 2-methylnaphthalene all seven possible isomers are formed, their proportions depending on the experimental conditions. The yields of the isomers vary within the limits given in parentheses: 1- (0·3—33%), 3- (0·8—14%), 4- (0·8—5·5%), 5- (0·4—2·0%), 6- (7·4—73%), 7- (4·2—58%), and 8- (9—59%). Competitive acetylation experiments in chloroform solution at 20° gave the following positional reactivities: 1-naphthyl 1·00, 2-naphthyl 0·31, 2-methyl-1-naphthyl 11·4, 2-methyl-3-naphthyl 0·31, 2-methyl-4-naphthyl 1·37, 2-methyl-5-naphthyl 0·19, 2-methyl-6-naphthyl 7·02, 2-methyl-7-naphthyl 1·78, and 2-methyl-8-naphthyl 16·1; the corresponding values obtained in nitromethane solution were: 1·00, 8·3, 6·9, 10·8, 6·1, 11·0, 177, 32·6, and 42·3, respectively. Overall and positional reactivities of 2,3-, 2,6-, and 2,7-dimethylnaphthalenes were calculated, and compared with results from earlier experiments.

ELECTROPHILIC substitutions of 2-methylnaphthalene (Ia) have been much studied. Bromination, in the presence of catalysts, gave mainly 1-bromo-2-methylnaphthalene (Ib).[2] Under more vigorous conditions a pentabromo-derivative of hydrocarbon (Ia) could be obtained, but its structure was not determined.[3] Recently the isomer distribution in the bromination of substrate (Ia) was investigated:[4] the isomers formed were (Ib) (98·2%), (IIb) (1·00%), (IIIb) (0·51%), and (IVb) (0·27%). In the presence of sunlight chlorination of substrate (Ia) gave the 1-isomer (Ic).[5] Nitration of hydrocarbon (Ia) is more complex, as many early studies

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

[2] (*a*) K. E. Schulze, *Ber.*, 1884, **17**, 1527; (*b*) F. Mayer and A. Sieglitz, *Ber.*, 1922, **55**, 1835; (*c*) R. Adam and L. O. Binder, *J. Amer. Chem. Soc.*, 1941, **63**, 2773.

[3] F. Bodroux and F. Taboury, *Bull. Soc. chim. France*, 1909, [4], **5**, 826.

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

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have shown.[2a,6] A detailed study of the nitration reaction revealed the formation, under various experimental conditions, of mononitro-isomers (Id) (52·7—66·2%), (IId) (13·7—17·4%), (IIId) (8·1—18·7%), (IVd) (6·6—9·0%), (Vd) (1·7—6·6%), and (VId) (0·13—0·6%).[7] Thus, results from halogenation and nitration studies agree on a reactivity sequence of nuclear positions in 2-methylnaphthalene (Ia): 1- > 8- > 4- > 5- > 6- > 3-. In a kinetic study of detritiations in trifluoroacetic acid the reactivity sequence was found to be: 1- ≫ 8- > 4- > 6- > 5- > 3- > 7- (see also below).[8]

Sulphonation, which is generally considered an anomalous aromatic substitution reaction,[9] has been reported to give as main products either the isomer (Ve),[10-12] or (IIe),[11,13,14] or (VIIe),[11] and a low yield of isomer (Ie).[14] A contribution to the sulphonation of hydrocarbon (Ia) will be published elsewhere.[15]

Chloromethylation of substrate (Ia) gave good yields of the 1-isomer (If).[16] Other alkylation methods gave products whose orientation was not determined.[17] Formylation gave exclusively 2-methylnaphthalene-1-carbaldehyde (Ig).[18] Friedel–Crafts acylations of substrate (Ia) using aromatic carboxylic acid derivatives generally give exclusively the 1-acyl derivative (Ih).[19-21] In one case only, that of phthalic anhydride, a small yield (3%) of a second isomer, (IIj) or (VIIj), was also obtained.[21] Aliphatic acyl derivatives, *viz.* propionyl chloride,[22,23] maleic anhydride,[24] succinic anhydride,[25] and methylsuccinic anhydride,[22] have been reported to give solely the 6-derivative [as in (V)]. A mixture of the 6-derivative [as in (V)] and the 8-derivative [as in (II)] has been reported for the reaction with phenylacetyl chloride,[26] or with succinic anhydride.[27] In the reaction with succinic anhydride it was suggested that the 1-isomer (Ik) was first formed and then rearranged to the 6-isomer (Vk).[28] The Friedel–Crafts acetylation of hydrocarbon (Ia) has been studied several times. Dziewoński and Brand[29] effected the acetylation in carbon disulphide suspension using the Elbs addition procedure:[30] a mixture of 1-acetyl-7-methylnaphthalene (IIl) and 2-acetyl-6-methylnaphthalene (Vl) was obtained, separable *via* their oximes. Kon and Weller[23] repeated this reaction, but obtained only the 6-isomer (Vl); they recommended nitrobenzene as solvent for a better overall yield of the ketone. The 6-isomer (Vl) was also obtained by a method which uses isopropenyl acetate as acylating agent.[31] Wells and Alcorn[32] reported the formation in nitrobenzene solution of isomers (Vl) and (IIl) as major components, together with some 1-acetyl-2-methylnaphthalene (Il) and (probably) 1-acetyl-3-methylnaphthalene (IIIl). More recently, Leahey and Praill[33] obtained the isomer (IIl) from a Friedel–Crafts acetylation carried out in chloroform solution. These workers also reported the formation of isomers (IIl), (Vl), and (Il) by the action of acetyl perchlorate on hydrocarbon (Ia) in benzene or nitromethane solution.[33] After the completion of our own work a quantitative study by Bonnier and Rinaudo[34] of the Friedel–Crafts acetylation of hydrocarbon (Ia) in nitrobenzene, carbon disulphide, and chloroform solutions, came to our notice. In this work constant proportions of isomers (IIIl), (IVl), (VIIl), and (IIl) were reported, with isomer (Vl) being formed in greater amounts than isomer (Il) in nitrobenzene solution, and in smaller amounts in the other two solvents (see Table 1, footnotes). The 4- (IIIl) and 5- (IVe) isomers were not able to be separated, and formation of the 3-isomer (VIl) was only indicated, but not proven.[34]

The present paper details our results of the Friedel–Crafts acetylation of hydrocarbon (Ia). The results are

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

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[21] L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 3742; L. F. Fieser and M. Fieser, *ibid.*, 1933, **55**, 3342.

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[33] J. P. Leahey and P. F. G. Praill, personal communication; J. P. Leahey, Ph.D. Thesis, London University, 1967.

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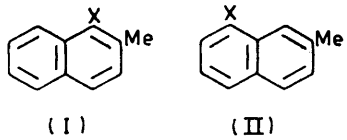
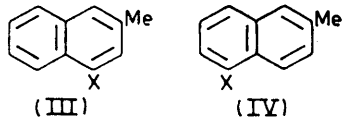
basic to a discussion of the acetylation of dimethylnaphthalenes (carrying β-methyl groups), data on which were published previously.[35-37]

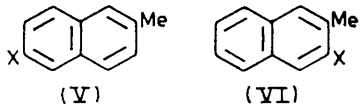
Syntheses.—All the seven isomers of acetyl-2-methylnaphthalenes were obtained by independent syntheses. Carboxylation of the Grignard reagent of 1-bromo-2-methylnaphthalene (Ib) [2b] afforded 2-methyl-1-naphthoic


(I)

(II)


(III)

(IV)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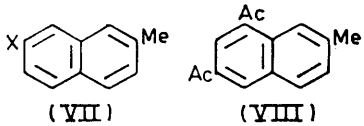

(VII)

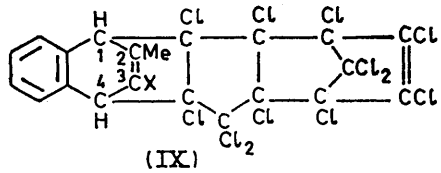
(VIII)

X	X
a; H	j; $COC_6H_4CO_2H$(-*o*)
b; Br	k; $CO[CH_2]_2CO_2H$
c; Cl	l; Ac
d; NO_2	m; CO_2H
e; SO_3H	n; COCl
f; CH_2Cl	o; $COCH(CO_2Et)_2$
g; CHO	p; CN
h; COAr	q; Me
	r; NH_2

acid (Im); [2c] conversion into 1-acetyl-2-methylnaphthalene (Il) was effected by treatment of 2-methylnaphthalene-1-carbonyl chloride (In) with an excess of methylmagnesium iodide.[2c,34] The same ketone (Il) was also prepared by conversion of the bromo-derivative (Ib) into 2-methylnaphthalene-1-carbonitrile (Ip) by the general procedure of Beyer and Fritsch,[38] followed by addition of methylmagnesium iodide, and hydrolysis of the imine intermediate with mineral acid.

2-Acetyl-3-methylnaphthalene (VII) was synthesised by two methods. The bis-hexachlorocyclopentadiene adduct [presumably (IXa); the ^1H n.m.r. spectrum is consistent with this structure] of 2-methylnaphthalene was nitrated according to instructions provided by Dr. J. Hyman.[39] The nitrated adduct (IXd) was heated *in vacuo* in a rotating vessel, which resulted in its dissociation to 2-methyl-3-nitronaphthalene (VId). Conversion, in the usual way ($NO_2 \rightarrow NH_2 \rightarrow CN \rightarrow COCH_3$), gave 2-acetyl-3-methylnaphthalene (VII) in low yield. A more direct route, *via* Friedel–Crafts acetylation of adduct (IXa), and pyrolysis of the ketone (IXl), gave the desired isomer (VII) in 23% yield overall.

1-Acetyl-3-methylnaphthalene (IIIl) was obtained from 3-methyl-1-naphthoic acid (IIIm) *via* the acid chloride (IIIn) by treatment with diethyl magnesiomalonate [40] and acid hydrolysis of the substituted malonic ester (IIIo), using the general procedure of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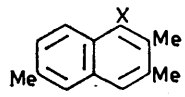
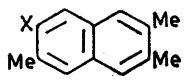

(X)


(XI)

Bowman.[41] 1-Acetyl-6-methylnaphthalene (IVl) was similarly prepared from 6-methyl-1-naphthoic acid (IVm). 2-Acetyl-6-methylnaphthalene (Vl) was isolated, *via* its oxime, from a Friedel–Crafts acetylation product. It was also synthesised independently from 2-methylnaphthalene-6-sulphonic acid (Ve): [11] the sodium salt of acid (Ve) on fusion with potassium cyanide afforded the carbonitrile (Vp), which by the action of methylmagnesium iodide was converted into the ketone (Vl). The 7-isomer (VIIl) was obtained analogously, *via* the carbonitrile (VIIp), from 2-methylnaphthalene-7-sulphonic acid (VIIe).[11] The final isomer, 1-acetyl-7-methylnaphthalene (III) was obtained independently by the general procedure outlined above, from the corresponding sulphonic acid (IIe), as well as isolated directly from mixtures of ketones obtained by the Friedel–Crafts reaction.

Friedel–Crafts Acetylations.—The results of our acetylation experiments on 2-methylnaphthalene (Ia), using aluminium chloride as catalyst and a variety of experimental conditions, are summarised in Table 1. After initial purification of the ketonic products by passage through alumina the proportions of the isomers were determined by quantitative g.l.c. analysis. Good separation of the seven isomers was achieved (see Experimental section); only incomplete resolution was obtained by earlier workers.[34] Table 1 shows that in each case all the seven monoacetyl derivatives of hydrocarbon (Ia) were formed. The proportions of the

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[41] R. E. Bowman, *J. Chem. Soc.*, 1950, 325.

isomers formed depends crucially on the solvent used, and to a lesser extent on the addition procedure employed. The percentages of the individual isomers formed vary within wide limits: (II) (0·3—33%), (VII) (0·8—14%), (IIII) (0·8—5·5%), (IVI) (0·4—2·0%), (VI) (7·4—73%), (VIII) (4·2—58%), and (III) (9—59%). Our findings, therefore, disagree with those of Bonnier and Rinaudo,[34] who reported that yields of the isomers (IIII), (IVI), and (VIII) were not solvent-dependent. In general, solvents which promote formation of the 1-isomer (II) also favour another α-naphthyl-type isomer (III). It is therefore of value to assess the overall position of α- *vs.* β-naphthyl reactivity. The observed α-/β-ratio [ratio of isomers {(II) + (III) + (IIII) + (IVI)}/{(VI) + (VII) + (VIII)}] decreases in the solvent sequence (Table 1): $C_2H_4Cl_2 > CH_2Cl_2 > CHCl_3 > CS_2 > MeNO_2 > PhNO_2$. This same sequence of

In chloroform solution two Perrier acetylations gave rather different results. At 0° a near-quantitative yield of ketones was obtained; comparison of the isomer-distribution with that of the reaction performed at 20° shows a substantially smaller formation of the 1-isomer (II) and increased formation of isomers (VI), (VIII), and (III). One does not normally observe such differences with a 20° temperature change, and it is therefore more likely that the explanation of this difference is connected with reversible acylation of this hindered acetyl group (*cf.* ref. 19*b*, 44, 46). Using the Rousset addition procedure in this solvent causes a severe reduction of the percentage formation of the isomer (II), and an unexpectedly predominant acylation at the 7-position, *viz.* five times as great as under any other conditions. In previous comparisons of the Rousset acetylation procedure (in which free aluminium

TABLE 1

Monoacetylation of 2-methylnaphthalene

Solvent	Addition procedure	Conditions	Overall yield (%)	Isomer proportions (%) [a] 1-(II)	3-(VII)	4-(IIII)	5-(IVI)	6-(VI)	7-(VIII)	8-(III)	Normalised ratio α-/β- [b]
CH_2Cl_2	Perrier	20°, 1 h	76	19	0·9	3·5	1·0	12	4·5	59	3·6
$CHCl_3$	Perrier [c]	20°, 1 h	75	30	0·8	3·6	0·5	18·5	4·6	42	2·4
$CHCl_3$	Perrier [d]	0°, 2 h	98	12·5	0·8	3·6	0·4	27	7·3	48	1·4
$CHCl_3$	Rousset	20°, 1 h	89	1·2	14	0·8	2·0	13	58	11	0·13
$(CH_2Cl)_2$	Perrier	20°, 1 h	74	33	0·8	4·0	0·6	7·4	4·2	50	5·3
CS_2	Perrier [c]	20°, 1 h	70	32	1·2	4·2	1·3	23·5	7·0	31	1·6
CS_2	Elbs [e]	45°, 3 h	50	0·3	1·9	5·5	0·9	53	7·2	32	0·47
$MeNO_2$	Perrier	20°, 1 h	74	2·5	3·9	2·2	0·4	64	12	15	0·19
$PhNO_2$	Perrier [c]	20°, 1 h	65	2·2	2·1	1·5	0·9	73	11·5	9	0·12

[a] Isomers are numbered as derivatives of 2-methylnaphthalene. [b] Ratio of % α-isomers : % β-isomers, normalised to indicate average positional reactivity. [c] Reported (ref. 34) for Perrier acetylations, at ambient temperature for 45 h, mixtures of ketones (i) in chloroform: 44% of 1-, 9% of 4-(+5-), 10% of 6-, 2% of 7-, and 35% of 8-isomer; (ii) in carbon disulphide: 73% yield: 34·5% of 1-, 7·5% of 4-(+5-), 24·5% of 6-, 3% of 7-, and 30·5% of 8-isomer; (iii) in nitrobenzene: 85% yield: 2·5% of 1-, 7% of 4-(+5-), 55·5% of 6-, 3% of 7-, and 32% of 8-isomer. [d] Procedure of Leahey and Praill (ref. 33). [e] Procedure of Dziewoński and Brand (ref. 29).

'orientation by solvent' has been found in the Friedel–Crafts acetylation of other mono-[42] and di-substituted naphthalenes,[35-37] for naphthalene itself,[43] and of phenanthrene.[44] The only exception, that of 2-methoxynaphthalene (for which the α-/β-ratio is $CS_2 > CHCl_3$),[45] can be discounted as it is in part based on the formation of a diacetyl compound. A Perrier acetylation in ethylene chloride gives the highest yield of the 1-isomer (II) (33%), but the 8-isomer (III) is formed therein to the greatest extent. The 3- (VII), 4- (IIII), and 5- (IVI) are throughout formed in low yields only. The 6-isomer (VI) is formed in good yield in Perrier reactions carried out in a nitro-solvent or in an Elbs reaction in carbon disulphide suspension. A Rousset reaction performed in chloroform solution gave nearly 60% of the 7-isomer (VIII), and a Perrier reaction carried out in dichloromethane afforded mainly the 8-isomer (III). These several Friedel–Crafts acylations can all be recommended for the preparations of the appropriate isomers.

chloride is present in the reaction mixture, especially at the beginning of the reaction) with the Perrier acetylation (in which free aluminium chloride is entirely absent) an increase in formation of the hindered 1-isomer,[35,45] or, as here, a decrease of the 1-isomer,[36] has been reported. An Elbs acetylation (in which the free catalyst is again present), carried out in carbon disulphide suspension, likewise afforded a sharp reduction in the yield of isomer (II), this time to the benefit of the 6-isomer (VI). It should be noted, however, that a remarkable increase occurred in the formation of the β-isomer (VII) in the Rousset reaction, and this isomer may be considered also to be somewhat hindered.

Friedel–Crafts diacetylation of hydrocarbon (Ia) has been claimed [29] to give, as main-product (1—3% yield) the diketone (VIII). We have found that in this reaction a complex mixture of diketones is formed, probably containing (as shown by g.l.c.) at least four isomers.

[42] R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc.* (*C*), 1966, 518.
[43] G. Baddeley, *J. Chem. Soc.*, 1949, S 99; H. F. Bassilios and A. Y. Salem, *Bull. Soc. chim. France*, 1952, [5], **19**, 586; H. F. Bassilios, S. M. Makar, and A. Y. Salem, *ibid.*, 1954, [5], **21**, 72.
[44] R. B. Girdler, P. H. Gore, and C. K. Thadani, *J. Chem. Soc.* (*C*), 1967, 2619.
[45] R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc.* (*C*), 1966, 181.
[46] P. H. Gore and J. A. Hoskins, *J. Chem. Soc.* (*C*), 1970, 517.

Competitive Acylations.—The reactivities of 2-methylnaphthalene (Ia) and naphthalene were compared in the usual way [44] by study of competitive acylation reactions carried out in chloroform and in nitromethane solutions. The molar ratios of methyl ketones formed (acetylnaphthalenes : acetyl-2-methylnaphthalenes) were 1 : 7·28 and 1 : 7·40 in chloroform and nitromethane, respectively. The positional reactivities are recorded in Table 2. A wider span of reactivities is in evidence for nitromethane solution. The 3-position in substrate (Ia) is of the same reactivity as is the 2-naphthyl position in chloroform solution, and only slightly greater in nitromethane solution. Thus, whatever electronic activating effect the methyl group might exert is virtually cancelled by a superimposed retarding steric effect. The other β-naphthyl positions are also activated to about the same extent in both media: by factors of *ca.* 22 and *ca.* 5 for the 6- and the 7-position, respectively. Since the 2-position of naphthalene is strongly favoured in nitromethane solution, this results in a very high reactivity (177) for the 2-methyl-6-naphthyl position, relative to the 1-naphthyl position. In both solvents the 8-position of hydrocarbon (Ia) is of greater reactivity (especially in nitromethane) than the 1-position, although it might have been anticipated from the general data on the reactivity of the hydrocarbon (see above) that the 1-position is by far the more reactive.

Factors which may influence the reactivity towards electrophilic reagents of 2-methylnaphthalene comprise (i) polar effects, (ii) resonance effects, and (iii) steric effects. The polar inductive (+*I*) effect of the methyl group will cause an increase in the electron-density in

TABLE 2

Relative reactivities of naphthalene positions

	Relative activities					
Position	Acetylation in chloroform at 20° [a]		Acetylation in nitromethane at 20° [a]		Detritiation in trifluoroacetic acid at 70° [b]	
1-	1·00		1·00		1·00	
2-	0·31	1·00	8·3	1·00	0·130	1·00
2-Methyl-1-	11·4		6·9		300	
2-Methyl-3-	0·31	1·00	10·8	1·30	0·467	3·59
2-Methyl-4-	1·37		6·1		2·75	
2-Methyl-5-	0·19		11·0		1·31	
2-Methyl-6-	7·02	22·6	177	21·3	2·51	19·4
2-Methyl-7-	1·78	5·74	32·6	3·93	0·207	1·59
2-Methyl-8-	16·1		42·3		2·90	

[a] This work. [b] Data from ref. 8.

particular of the neighbouring positions, and to a decreasing extent with an increase in the distance from the methyl group. Recalling that the 2,3-bond (1·415 Å) in naphthalene is longer than its 1,2-bond (1·364 Å),[47] and that the sp^3–sp^2 C–CH_3 bond distance is 1·50 Å,[48] inductive activation by the methyl group should decrease in the order (distance-through-bonds in parentheses): 1- (2·86 Å) ~ 3- (2·92 Å) > 4- (4·28 Å) > 8- (5·71 Å) > 7- (7·07 Å) ~ 5- (7·12 Å) > 6- (8·49 Å).

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

In so far as a methyl group can cause electron-release by a conjugative (+*M*) mechanism the positions in hydrocarbon (Ia) so activated would be the 1-, 3-, 6-, and 8-positions. Of these the 1-position should again be the most activated, and the 3-position probably the least. The combined electronic effects would permit us to predict a reactivity sequence 1- > 8- > 4- ~ 6-. It is therefore evident that in Friedel–Crafts acetylations the reactivity of the 1-position (like the 3-position) is substantially reduced due to steric hindrance. Similar conclusions have been drawn for the acetylations at the 1-position of the related systems 2,3-dimethylnaphthalene (VIq),[35] 2,6-dimethylnaphthalene (Vq),[36] and 2-methoxynaphthalene.[42] For 2,7-dimethylnaphthalene (VIIq) the retardation effect was less significant, in that it did not result in a qualitative change in isomer distribution.[37]

An anomalously low reactivity emerged for the 5-position of 2-methylnaphthalene (Ia). It would appear that an α-naphthyl position is here deactivated by a factor of *ca.* 5, on substitution of a methyl group in the other ring. A possibility exists that the rate of substitution at this position is controlled by encounter,[6b,49] but this seems unlikely for a solvent of low viscosity and a reaction which is comparatively slow.

For comparison the only other complete set of positional reactivities for 2-methylnaphthalene, that of detritiation in trifluoroacetic acid,[8] is included in Table 2. The outstanding difference from our results is the very high reactivity of the 1-position for the hydrogen-exchange reaction. Clearly, in acetylation the reactivity of the 1-position is markedly reduced by steric hindrance, especially in nitromethane solution. The remarkably high reactivity of the 7-position in our systems is also noteworthy.

Reactivity Predictions.—The experimental reactivities of the nuclear positions of 2-methylnaphthalene (Ia) enable one to predict the overall reactivities, and isomer proportions, for acetylations carried out under the same experimental conditions of β-methyl-substituted naphthalenes. For example, the 1-position in 2,3-dimethylnaphthalenes may be regarded as being activated (for chloroform solution) both by a 2-methyl group (×11·4) and a 3-methyl group (×1·37); the positional reactivities thus obtained may be combined to give global reactivities relative to naphthalene, or worked out as isomer percentages (Table 3). The predicted reactivities of the dimethylnaphthalenes relative to naphthalene are seen to be too high by factors of 1·7—3·3; this is outside possible experimental errors. A second β-methyl group is thus less effective than the first substituent and can in fact be *deactivating*. If one places in the appropriate β-position(s) of 2-methylnaphthalene one (or more) imaginary substituents, which exert nil effect on the other positions, the reactivity (relative to naphthalene) 2-methylnaphthalene, initially = 7·28, is lowered to the residual values, which are given in the last column of Table 3. It can be seen that in 2,6-dimethylnaphthalene

[48] G. R. Somayajulu, *J. Chem. Phys.*, 1959, **31**, 919.
[49] M. W. Austin and J. H. Ridd, *J. Chem. Soc.*, 1963, 4204.

(Vq) the second methyl substituent exerts virtually a zero overall activating effect. In 2,7-dimethylnaphthalene (VIIq) the second methyl group causes an overall enhancement of reactivity only about 30% of that expected from the reactivity data for 2-methylnaphthalene. For 2,3-dimethylnaphthalene (VIq), however, one finds a 34% decrease in reactivity, instead of the expected 65% increase. This anomalous effect may be due to the proximity of the methyl groups in this molecule. To relieve the strain of non-bonded interactions, which may in fact be quite small (*cf.* 0·5 kcal mol^{-1} for *o*-xylene [50]), there will be mutual repulsion of the methyl groups with consequent encroachment on the available space at the 1- and 4-positions. A displacement of the methyl groups away from their normal positions will also lower resonance interactions with the acetylation of 2,6-dimethylnaphthalene (Vq) preferred orientation in nitromethane is predicted at the 3-position, whilst an 84% yield of the 4-isomer had been found in nitrobenzene solution.

Predictions are made also for 2,3,6-trimethylnaphthalene (Xa) and 2,3,6,7-tetramethylnaphthalene (XIq), which have not yet been examined experimentally. In chloroform solution substrate (Xa) can be expected to give predominantly the 1-isomer (XI) and in nitromethane solution the 7-isomer (XII).

EXPERIMENTAL

I.r. spectra were measured in chloroform solution or as films (unless otherwise stated). The ^1H n.m.r. spectra were obtained for solutions in deuteriochloroform (unless otherwise stated) at 60 or 100 MHz with tetramethylsilane as

TABLE 3

Reactivities of β-methyl-substituted naphthalenes in Friedel–Crafts acetylations

		Isomer distribution (%)						
		Chloroform		Nitromethane		Relative rate [a]		
Naphthalene	Position	Calc.	Found	Calc.	Found	Calc.	Found	Hypothetical [b]
2,3-Dimethyl- (VIq)	1-	50·0	18·5 [c]	0·67	1·5 [c,d]	11·9	4·75 [c]	7·23
	5-	9·8	59·0	7·4	21			
	6-	40·1	22·5	92·0	78			
2,6-Dimethyl- (Vq)	1-	8·8	33·4 [e]	11·1	11·6 [d,e]	9·46	5·42 [e]	5·97
	3-	2·2	0·4	51·3	4·8			
	4-	89·0	66·2	37·6	84			
2,7-Dimethyl- (VIIq)	1-	98·7	80·4 [f]	12·8	41·5 [f]	71·0	21·5 [f]	6·94
	3-	1·17	12·4	84·2	42·4			
	4-	0·14	7·2	3·0	16·1			
2,3,6-Trimethyl- (Xa)	1-	84·6		2·5		56·8		5·95
	4-	1·0		0·65				
	5-	1·4		4·0				
	7-	1·3		88·2				
	8-	11·7		4·6				
2,3,6,7-Tetramethyl- (XIq)	1-	100		100		36·5		5·60

[a] Ratio of substrate: naphthalene, in chloroform solution. [b] Hypothetical reactivity of a 2-methylnaphthalene molecule, relative to naphthalene, from which the appropriate substituent positions have been removed (see text). [c] Data from ref. 35. [d] Experiment conducted in nitrobenzene solution. [e] Data from ref. 36. [f] Data from ref. 37.

aromatic moiety. The reactivity of the positions contiguous to the methyl groups, and therefore the overall reactivity of the hydrocarbon, would thereby be reduced. This may be considered a further example of the 'buttressing effect'.[51] In agreement with this view is the much lower percentage of the 1-isomer of 2,3-dimethylnaphthalene (VIq) as found in chloroform solution compared to the calculated value (Table 3).

For 2,6- (Vq) and 2,7-dimethylnaphthalene (VIIq) the percentage of isomers found in Friedel–Crafts acetylations in chloroform solution are predicted qualitatively correctly, and this includes the 'anomalous' preferred 4-orientation in 2,6-dimethylnaphthalene (Vq).

The isomer percentages predicted are also qualitatively correct for the acetylations of 2,7-dimethylnaphthalene (VIIq) and 2,3-dimethylnaphthalene (VIq), in nitromethane solution. For hydrocarbon (VIq) experimental data are available only for nitrobenzene solution, which however almost invariably gives closely similar results to nitromethane (*cf.* present work). For the internal standard; the signals were singlets, unless one of the following abbreviations is used: br = broad, d = doublet, dd = doublet of doublets, m = multiplet, c = complex.

Gas Chromatography.—Analyses were performed using a glass column 5 ft × ¼ in (i. diam.) packed with Bentone 34 (3·5%) and Carbowax 20M (1·5%) on Celite (80—100 mesh) (treated with hexamethyldisilazane). Nitrogen was used as carrier gas, at 177°, together with a Pye 104 instrument, fitted with a flame ionisation detector. Peak areas were measured by triangulation. The identity of the peaks were also checked using other chromatographic columns. Mass response of the detector towards different ketones was determined, and corrections applied as appropriate. Kováts [52] retention indices (*I*) are given in Table 4, which also gives the slopes (*b*) of the plots of log (retention volume) *vs.* the carbon number for the n-alkane.

1-Bromo-2-methylnaphthalene (Ib).—This compound was obtained [2c] as an oil (yield 75%), b.p. 128—130° at 3 mmHg

[50] J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, 1958, **90**, 905.

[51] M. Rieger and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1950, **72**, 19; H. A. Karnes, B. D. Kybett, M. H. Wilson, J. L. Margrave, and M. S. Newman, *ibid.*, 1965, **87**, 5554.

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

(Found: C, 59·6; H, 4·2; Br, 36·2. Calc. for $C_{11}H_9Br$: C, 59·7; H, 4·1; Br, 36·2%); ^{1}H n.m.r. signals at τ 7·44 (CH_3) and 1·8—2·7 (arom.-*H*).

2-*Methylnaphthalene*-1-*carbonitrile* (Ip).—The nitrile was obtained [38] (yield 60%) as yellow crystals, m.p. 84° (lit.,[53] m.p. 87°) (Found: C, 86·1; H, 5·4; N, 8·6. Calc. for

TABLE 4

Kováts retention indices (*I*) and slopes (*b*) on Bentone–Carbowax

Ketone	*I*	*b*	Ketone	*I*	*b*
(II)	2185	0·182	(VI)	2408	0·182
(III)	2325	0·183	(VII)	2418	0·182
(VIII)	2368	0·181	(IIII)	2457	0·181
(IVI)	2385	0·182			

$C_{12}H_9N$: C, 86·2; H, 5·4; N, 8·4%); $\nu_{max.}$ (KBr) 2230 cm^{-1} (C≡N); ^{1}H n.m.r. signals at τ 7·27 (CH_3), 1·84 (m, 8-*H*), 2·08 (d, 4-*H*), 2·64 (d, 3-*H*), and 2·1—2·7 (arom.-*H*), $J_{3,4}$ 8·4, $J_{7,8}$ *ca.* 8 Hz.

2-*Methyl*-1-*naphthoic Acid* (Im).—Carboxylation of the Grignard reagent of compound (Ib) afforded [2b] the acid (yield 60%), m.p. 126—127° (lit.,[2c] m.p. 126—127°) (Found: C, 77·2; H, 5·2. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4%); $\nu_{max.}$ (KBr) at 1670 cm^{-1} (C=O); ^{1}H n.m.r. signals at τ 7·32 (CH_3) and 1·7—2·8 (arom.-*H*).

1-*Acetyl*-2-*methylnaphthalene* (II).—(*a*) By treatment of the acid chloride ($SOCl_2$) of compound (Im) with an excess of methylmagnesium iodide [2c,34] the ketone was obtained (yield 50%), as a pale yellow oil, b.p. 118—121° at 0·35 mmHg, n_D^{20} 1·6056 (lit.,[2c] b.p. 125—130° at 3 mmHg, n_D^{20} 1·6037) (Found: C, 84·8; H, 6·6. Calc. for $C_{13}H_{12}O$: C, 84·8; H, 6·6%); $\nu_{max.}$ 1690 cm^{-1} (C=O); ^{1}H n.m.r. signals at τ 7·62 (CH_3), 7·42 ($COCH_3$), and 2·1—2·9 (c, arom.-*H*).

(*b*) The ketone was also prepared (yield 30%) by the action of methylmagnesium iodide on the nitrile (Ip), followed by hydrolysis with 5N-sulphuric acid. It was identical (i.r. spectrum) with the specimen obtained under (*a*).

2-*Methyl*-3-*nitronaphthalene* (VId).—Using the procedure recommended by Hyman.[36] To fuming nitric acid (*d* 1·48, 5·0 g) dichloromethane was added to make up the volume to 10 ml. This mixture was added dropwise with constant stirring to the 2-methylnaphthalene–hexachlorocyclopentadiene adduct [9·0 g; ^{1}H n.m.r. signals at τ 7·63 (CH_3), 6·44 (dd, 3-*H*), 6·11 (1-*H*), 6·03 (d, 4-*H*), and 2·2—3·0 (c, arom.-*H*), $J_{2\text{-}CH_3,3\text{-}H}$ 1·8, $J_{3,4}$ 8·0 Hz]. After 15 min at room temperature the solid was filtered off, washed with water, and dried *in vacuo* (yield 6·8 g); $\nu_{max.}$ (KBr) 1350 cm^{-1} (NO_2).

The nitrated adduct was then heated at 300—320° at 15 mmHg in a rotating glass vessel. The pyrolysed product was taken up in chloroform, and the extract washed with water and dried. On evaporation of the solvent a yellow mass was obtained, affording a yellow solid (1·0 g) on trituration with ice-cold light petroleum. Repeated crystallisation then gave 2-methyl-3-nitronaphthalene (0·35 g, 15%), m.p. 119—119·5° (Hyman [39] reports m.p. 119—119·5°) (Found: C, 70·5; H, 5·0; N, 7·2. Calc. for $C_{11}H_9NO_2$: C, 70·6; H, 4·9; N, 7·5%); $\nu_{max.}$ (KBr) 1352 and 1535 cm^{-1} (NO_2) (Hyman [39] reports $\nu_{max.}$ 1535 cm^{-1}); ^{1}H n.m.r. signals at τ 7·29 (CH_3), 1·50 (4-*H*), 2·28 (1-*H*), and 2·0—2·7 (c, arom.-*H*).

2-*Amino*-3-*methylnaphthalene* (VIr).—Reduction of compound (VId) with tin(II) chloride in hydrochloric acid afforded the amine (VIr) (yield 60%), m.p. 134° (lit.,[54] m.p. 135°); $\nu_{max.}$ 1637, 3410, and 3490 cm^{-1} (N–H).

3-*Methylnaphthalene*-2-*carbonitrile* (VIp).—The nitrile (VIp) was obtained from the amine (VIr) by the Gattermann reaction. Crude yield 50%; $\nu_{max.}$ 2380 cm^{-1} (C≡N).

2-*Acetyl*-3-*methylnaphthalene* (VII).—(*a*) A solution of the adduct of 2-methylnaphthalene with hexachlorocyclopentadiene (27·5 g) in dichloromethane (150 ml) was added dropwise during 15 min to a stirred solution of acetyl chloride (3·1 g) and aluminium chloride (5·34 g) in dichloromethane (50 ml) at 20°. The mixture was stirred at 20° for 24 h, and the acetylated adduct was then isolated as a yellow solid (yield 25·3 g, 90%), m.p. 316—318°; $\nu_{max.}$ 1675 cm^{-1} (C=O).

This adduct was subjected to pyrolysis, under the conditions given for the preparation of compound (VId). The crude product (26%) on crystallisation (ethanol) gave light yellow 2-*acetyl*-3-*methylnaphthalene*, m.p. 76·5—77° (Found: C, 84·8; H, 6·6. $C_{13}H_{12}O$ requires C, 84·8; H, 6·6%); $\nu_{max.}$ 1673 cm^{-1} (C=O); ^{1}H n.m.r. signals at τ 7·34 (CH_3), 7·31 ($COCH_3$), 1·80 (1-*H*), 2·37 (4-*H*), and 2·0—2·7 (c, arom.-*H*).

(*b*) The same ketone (i.r. spectrum) was obtained by addition of methylmagnesium iodide to nitrile (VIp), as given under the preparation of the isomer (II).

1-*Acetyl*-3-*methylnaphthalene* (IIII).—3-Methyl-1-naphthoic acid (0·186 g; kindly supplied by Dr. P. R. Wells) was treated with thionyl chloride (2·0 ml) for 2 h, and excess of the latter was then distilled off. Dry ether (20 ml) was added, followed by an ethereal solution of diethyl magnesiomalonate [41] (0·001M). The mixture was gently boiled under reflux for 2 h, then cooled, and poured into 3N-sulphuric acid (50 ml). The combined ether extracts were evaporated, and the residue was boiled with a mixture of glacial acetic acid (10 ml), conc. sulphuric acid (1·5 ml), and water (10 ml), for 8 h. The cooled mixture was made alkaline, and the product was extracted into ether. Evaporation then gave 1-acetyl-3-methylnaphthalene (20 mg, loss of material) (Found: M^+, 184·0890. Calc. for $C_{13}H_{12}O$: M^+, 184·0888); $\nu_{max.}$ 1670 cm^{-1} (C=O) (Bonnier and Rinaudo [34] gave m.p. 68°; $\nu_{max.}$ 1680 cm^{-1}); ^{1}H n.m.r. signals at τ 7·48 (CH_3), 7·29 ($COCH_3$), 1·36 (8-*H*), 2·24 (m, 2-, 4-, and 5-*H*), 2·47 (m, 7-*H*), and 2·56 (m, 6-*H*), $J_{2,4}$ 1·7, $J_{6,8}$ 1·7, $J_{7,8}$ 8·7, $J_{5,7}$ 1·5 Hz.

6-*Methyl*-1-*naphthoic Acid* (IVm).—This acid was obtained by the method of Price *et al.*[55] as needles, m.p. 176—177° (lit.,[55] m.p. 176—177°) (Found: C, 77·6; H, 5·2. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4%); $\nu_{max.}$ (KBr) 1665 cm^{-1} (C=O); ^{1}H n.m.r. signals (Me_2SO) at τ 7·52 (CH_3), 1·20 (d, 8-*H*), 1·90 (m, 4-*H*), 1·96 (m, 2-*H*), 2·23 (br, 5-*H*), 2·44 (m, 3-*H*), and 2·54 (dd, 7-*H*), $J_{7,8}$ 8·8 Hz.

1-*Acetyl*-6-*methylnaphthalene* (IVI).—This ketone was obtained (yield 60%) by the magnesiomalonate procedure [41] described for the isomer (IIII), as an oil (Found: C, 84·7; H, 6·8. Calc. for $C_{13}H_{12}O$: C, 84·8; H, 6·6%); $\nu_{max.}$ 1664 cm^{-1} (C=O) (reported [34] as an oil, $\nu_{max.}$ 1680 cm^{-1}); ^{1}H n.m.r. signals at τ 7·59 (CH_3), 7·40 ($COCH_3$), 1·34 (d, 8-*H*), 2·26 (m, 4-*H*), *ca.* 2·5 (c, 2-, 3-, and 5-*H*), and 2·76 (d, 7-*H*), $J_{7,8}$ 8·5 Hz.

6-*Methylnaphthalene*-2-*carbonitrile* (Vp).—A mixture of sodium 2-methylnaphthalene-6-sulphonate [11] (Ve) (20 g) and potassium cyanide (10 g) was heated gently over a

[53] H. F. Bassilios, S. M. Makar, and A. Y. Salem, *Bull. Soc. chim. France*, 1958, [5], **21**, 75.

[54] V. Vesely and F. Stursa, *Coll. Czech. Chem. Comm.*, 1934, **6**, 137.

[55] C. C. Price, E. C. Chapin, A. Goldman, E. Krebs, and E. Schafer, *J. Amer. Chem. Soc.*, 1941, **63**, 1857.

direct flame until vapours were no longer evolved. The condensed vapours were taken up in benzene, and the extract was washed with 3N-sulphuric acid and water, and then dried and evaporated. The residue was chromatographed on alumina (from benzene) to give a pale brown liquid (1·7 g, 5%) of the *nitrile* (Found: C, 86·9; H, 5·7%; M^+, 167·0732. $C_{12}H_9N$ requires C, 86·2; H, 5·4%; M^+, 167·0735); $\nu_{max.}$ (KBr) 2250 cm^{-1} (C≡N).

2-*Acetyl*-6-*methylnaphthalene* (Vl).—Addition of an excess of methylmagnesium iodide to the nitrile (Vp), followed by acid hydrolysis, gave the ketone, m.p. 69—70° (lit.,[10] m.p. 70—71°) (Found: C, 84·7; H, 6·6. Calc. for $C_{13}H_{12}O$: C, 84·8; H, 6·6%); $\nu_{max.}$ 1675 cm^{-1} (C=O) (lit.,[34] $\nu_{max.}$ 1680 cm^{-1}); ^1H n.m.r. signals at τ 7·48 (CH_3), 7·32 ($COCH_3$), 1·62 (m, 5-*H*), 2·05 (dd, 7-*H*), 2·17 (d, 4-*H*), 2·25 (d, 8-*H*), 2·39 (m, 1-*H*), and 2·64 (dd, 3-*H*), $J_{1,3}$ 1·7, $J_{5,7}$ 1·5, $J_{3,4} = J_{7,8} = 8·4$ Hz.

The ketone was identical (mixed m.p., i.r. spectrum) with that isolated from Friedel–Crafts acetylations of hydrocarbon (Ia) in carbon disulphide or nitrobenzene solutions (see below).

7-*Methylnaphthalene*-2-*carbonitrile* (VIIp).—This compound was prepared from sodium 2-methylnaphthalene-7-sulphonate,[11] by the method given above for isomer (Vp); the *nitrile* had m.p. 109—110° (Found: C, 86·1; H, 5·5; N, 8·4. $C_{12}H_9N$ requires C, 86·2; H, 5·4; N, 8·4%); $\nu_{max.}$ (KBr) 2234 cm^{-1} (C≡N); ^1H n.m.r. signals (Me_2SO) at τ 7·50 (CH_3), 1·54 (d, 1-*H*), and 1·8—2·6 (c, arom.-*H*).

2-*Acetyl*-7-*methylnaphthalene* (VIIl).—This compound was obtained by the method outlined for the isomer (Vl); the ketone formed a pale yellow liquid (Found: C, 84·9; H, 6·7. Calc. for $C_{13}H_{12}O$: C, 84·8; H, 6·6%); $\nu_{max.}$ 1678 cm^{-1} (lit.,[34] m.p. 95°, $\nu_{max.}$ 1690 cm^{-1}); ^1H n.m.r. signals at τ 7·46 (CH_3), 7·31 ($COCH_3$), 1·62 (1-*H*), and 1·8—2·7 (c, arom.-*H*).

7-*Methylnaphthalene*-1-*carbonitrile* (IIp).—This compound was prepared (yield 5%) from sodium 7-methylnaphthalene-1-sulphonate [11] by the method outlined above for the isomer (Vp); the *nitrile* had b.p. 136—140° at 5 mmHg (Found: C, 87·1; H, 5·7%; M^+, 167·0738. $C_{12}H_9N$ requires C, 86·2; H, 5·4%; M^+, 167·0735); $\nu_{max.}$ 2200 cm^{-1} (C≡N); ^1H n.m.r. signals (Me_2SO) at τ 7·54 (CH_3) and 1·7—2·8 (c, arom.-*H*).

1-*Acetyl*-7-*methylnaphthalene* (IIl).—This compound was obtained as given under the isomer (Vl); the ketone formed a liquid (Found: C, 84·6; H, 6·5. Calc. for $C_{13}H_{12}O$: C, 84·8; H, 6·6%); $\nu_{max.}$ 1675 cm^{-1} (C=O) (lit.,[34] $\nu_{max.}$ 1690 cm^{-1}); ^1H n.m.r. signals at τ 7·53 (CH_3), 7·40 ($COCH_3$), 1·50 (8-*H*), and 2·17—2·93 (c, arom.-*H*).

The ketone was identical (i.r. spectrum) with a sample obtained (see below) from a Friedel–Crafts acetylation of hydrocarbon (Ia) in chloroform solution.

Friedel–Crafts Acetylations.—The procedures were those described in earlier parts of this Series.[35,46,56] The competitive acetylations were carried out by the Perrier method in dilute solutions, for 0·5 h at 20°. G.l.c. analyses gave corrected weight ratios (acetylnaphthalenes: acetylmethylnaphthalenes) for chloroform: 7·77 and 7·96 (mean 7·87), and for nitromethane: 8·04 and 7·96 (mean 8·00).

The product of an acetylation in carbon disulphide was distilled (b.p. 158—160° at 4·5 mmHg; n_D^{20} 1·6222). The mixture of isomers was converted into the oximes, which on repeated crystallisation (benzene) afforded 2-acetyl-6-methylnaphthalene oxime, m.p. 177—178° (lit.,[29] m.p. 181°). Hydrolysis of the oxime with 3N-hydrochloric acid gave the ketone (Vl). The product (b.p. 156—160° at 3 mmHg) from an acetylation in nitrobenzene was converted into the semicarbazones,[23] which afforded 2-acetyl-6-methylnaphthalene semicarbazone, m.p. 227° (reported,[33] m.p. 225°; lit.,[29] m.p. 240°), from which ketone (Vl) could be regenerated with 5N-sulphuric acid. From the same acylation reaction a fraction of diacetyl compounds (b.p. 220—230° at 4 mmHg) was isolated. The product (b.p. 138° at 0·8 mmHg) from an acetylation in chloroform solution afforded 1-acetyl-7-methylnaphthalene semicarbazone, m.p. 176° (reported,[33] m.p. 176°), from which ketone (Ill) was obtained by treatment with 5N-sulphuric acid.

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