A Comparison of Friedel–Crafts Acylations of Acenaphthene and 1,8-Dimethylnaphthalene. Methyl Migration and Acyl Rearrangements accompanying Acylations

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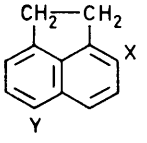
Acylations of acenaphthene afford mixtures of 5- and 3- (but no 4-) acylacenaphthenes. The 5-acylacenaphthene : 3-acylacenaphthene ratio varies from 2 to 40 for acetylations, and from 3 to 13 for benzoylations, according to the solvent used. From benzoylations of 5-acetylacenaphthene two isomeric diketones could be isolated: 6-acetyl-3-benzoyl- and 3-acetyl-6-benzoyl-acenaphthene, the latter a product of acyl rearrangement. 1,8-Dimethylnaphthalene affords mixtures of 2-, 3-, and 4-acetyl-1,8-dimethylnaphthalenes, together with two isomeric ketones, 3- and 4-acetyl-1,7-dimethylnaphthalenes, which result from methyl migration of the substrate. From competitive acetylations, the relative positional reactivities could be estimated for chloroform solution at 20 °C: 1-naphthyl 1.0, 2-naphthyl 0.45, 1,8-dimethyl-4-naphthyl 60, 3-acenaphthenyl 6.4, and 5-acenaphthenyl 94.

FRIEDEL–CRAFTS acetylations of acenaphthene (1a) have been reported to give 5-acetylacenaphthene (1b),[1a,2] sometimes with small amounts of 3-acetylacenaphthene (1c).[3,4] Benzoylations are said to give only 5-benzoylacenaphthene (1d).[1a,5,6] Diacylations result in the formation mainly of 3,6-diacylacenaphthenes (1e or f).[1a,7-9] For the related *peri*-dialkylnaphthalene, 1,8-dimethylnaphthalene (2a) the sole Friedel–Crafts acylation reported involves attack at the 4-position, *para* to alkyl groups.[10]

We now report our quantitative results on the Friedel–Crafts acetylation and benzoylation of the two hydrocarbons (1a) and (2a).



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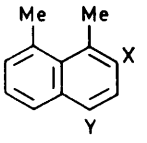

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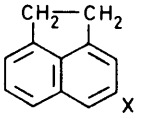

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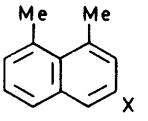

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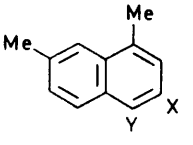

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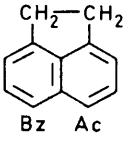

(6)

	X	Y		X	Y
a;	H	H	g;	Ac	
b;	H	Ac	h;	alkyl	
c;	Ac	H	j;	Bz	H
d;	H	Bz	k;	Bz	
e;	Ac	Ac	l;	Ac	Bz
f;	Bz	Bz	m;	Bz	Ac

RESULTS AND DISCUSSION

Acetylations of Acenaphthene.—A series of acetylations was carried out, using mainly the Perrier addition procedure,[1b,11] which avoids contact of the substrate with the catalyst, and equimolar proportions of reactants. The results obtained are collected in Table 1. 5- (1b) and 3-acetylacenaphthenes (1c) are invariably formed, but in no experiment was the 4-isomer (3g) detected. The proportions of the 5-isomer (1b) were highest in chloroalkane solvents, and lowest for the more basic nitro-solvents. Non-formation here of the 4-isomer (3 g) agrees with other electrophilic substitutions of the hydrocarbon (1a),[12,13] but contrasts with Friedel–Crafts alkylations for which 4-alkylacenaphthenes (3h) have been claimed in yields up to 63%.[14]

Acetylations of 1,8-*Dimethylnaphthalene.*—Acetylations of the hydrocarbon (2a) proved more complex. All the three normal acylation products, 2- (2c), 3- (4g), and 4-acetyl-1,8-dimethylnaphthalene (2b), were formed, though not in every solvent (Table 2). In addition two further isomeric ketones were obtained, in several reactions in considerable amounts. They were identified as 3- (5c) and 4-acetyl-1,7-dimethylnaphthalene (5b), *i.e.* ketones formally derived from the isomeric hydrocarbon 1,7-dimethylnaphthalene (5a). The evidence for the structure of these ketones is, in summary: (*a*) the two ketones are formed as major products in the acetylation of substrate (5a) under comparable reaction conditions (Table 3). They were isolated from the reaction mixtures, had identical g.l.c. retention characteristics to ketones obtained from 1,8-dimethylnaphthalene (2a), and were identified by elementary analysis, mass spectrometry and ^{1}H n.m.r. spectroscopy. (*b*) 1,8-Dimethylnaphthalene (2a), in the presence of boron fluoride–hydrogen fluoride is known to rearrange rapidly (by an α→β-methyl shift) to its isomers 1,7- (5a) and

TABLE 1

Friedel–Crafts acylations [a] of acenaphthene at 20 °C

	Acetylation products [b,c]				Benzoylation products [d]			
Solvent	Yield [e] (%)	(1b) (%)	(1c) (%)	(1b) : (1c)	Yield [e] (%)	(1d) (%)	(1j) (%)	(1d) : (1j)
$MeNO_2$	77	64	36	1.8	73	79	21	3.3
$PhNO_2$	83	78	22	3.6	91	86	14	6.0
$C_2H_4Cl_2$ [f]	90	80	20	4.0				
CS_2	71	93	6.8	14	83	93	7.2	13
$CHCl_3$	88	94	6.3	15	78	83	17	4.8
CH_2Cl_2	90	96	4.2	23	90	88	12	7.2
$C_2H_4Cl_2$	87	98	2.4	41	98	89	11	8.0
C_6H_6 [g]					85	87	13	6.7

[a] Unless otherwise stated: Perrier addition procedure (final addition of substrate), substrate : acyl chloride : aluminium chloride in mol ratios 1 : 1 : 1. [b] The 4-isomer (3g) or (3k) was not detected, *i.e.* <0.1% formation in any of these reactions. [c] Duration 2 h. [d] Duration 6 h. [e] Yield after column chromatography; includes any unreacted hydrocarbon (normally <10%). [f] Method (refs. 4 and 9) uses acetic anhydride at 10 °C. [g] Method (ref. 6) uses final addition of catalyst (Elbs addition procedure, ref. 1*b*).

TABLE 2

Friedel–Crafts acetylations [a] of 1,8-dimethylnaphthalene

	Temperature	Yield [b]	Ketones (%)					Ratio of
Solvent	(°C)	(%)	(2c)	(4g)	(2b)	(5b)	(5c)	ketones [c]
CH_2Cl_2	40	97	17		71	12		7.3 : 1
CS_2	47	82	0.9	8.2	69	22		3.6 : 1
$CHCl_3$	61	79			77	23		3.3 : 1
$C_2H_4Cl_2$ [d]	83	92	1.2	6.8	88	2.0	2.0	24 : 1
$MeNO_2$	100	77	2.8	26	69	2.5		39 : 1
$PhNO_2$	100	67	5.1	29	47	4.1	15	4.3 : 1

[a] Perrier addition procedure; substrate : acetyl chloride : aluminium chloride, mol ratio 1 : 1 : 1; reactions were carried out at the temperature stated normally for 6 h. [b] Yield after column chromatography; includes any unreacted hydrocarbon(s) (normally <10%). [c] [Normal ketones] : [abnormal ketones], *i.e.* [(2c) + (4g) + (2b)] : [(5b) + (5c)]. [d] Duration 3 h.

TABLE 3

Friedel–Crafts acetylations [a] of 1,7-dimethylnaphthalene

	Temperature	Duration	Yield [b]	Ketones (%) [c]					
Solvent	(°C)	h	(%)	(*A*)	(*B*)	(*C*)	(*D*)	(5b)	(5c)
$CHCl_3$	61	16	74	1.3		0.4	0.8	78	20
$C_2H_4Cl_2$	83	4	82	0.8			0.7	76	22
$MeNO_2$	102	8	68		1.1	0.4	4.0	48	46

[a] Perrier addition procedure; substrate : acetyl chloride : aluminium chloride, mol ratio 1 : 1 : 1. [b] Yield after column chromatography; includes any unreacted hydrocarbon (5a) (<10%). [c] Isomeric ketones (all M^+ 198), listed in the sequence of their g.l.c. retention times.

2,7-dimethylnaphthalenes.[15] The position of equilibrium depends on the concentration of the catalyst, but favours the 2,7-isomer; the 1,8-isomer (2a) is not present at equilibrium. The 1,8-→2,7-dimethylnaphthalene isomerisation could also be effected in the presence of aluminium chloride (see Experimental section).[16] The three acetyl-2,7-dimethylnaphthalene isomers were available,[17] and were found to have different properties from any of the products of acetylation of either hydrocarbon (2a) or (5a). Methyl migration preceding Friedel–Crafts acetylations, even in the absence of 'free' aluminium chloride, has been observed once before, in the 1-methylnaphthalene system.[18,19] (*c*) On the basis of experimentally determined positional reactivities [18] of 1- and 2-methylnaphthalenes in Friedel–Crafts acetylations one can calculate, assuming perfect additivity, the percentage of isomers to be expected in the acetylations of 1,7-dimethylnaphthalene (5a) (Table 4). A similar application of additivity, using partial rate factors, had proved successful in recent predictions of reactivity in dimethylnaphthalene systems.[13,20] It is predicted here that in chloroform solution 1,7-dimethylnaphthalene (5a) will give mainly the 4-isomer (5b), with the 3-isomer (5c) next in abundance; for nitromethane solution this order is reversed. These predictions match up with our experimental results (Table 3) satisfactorily.

For 1,8-dimethylnaphthalene (2a) the sequence of reactivities predicted for nitromethane solution, *i.e.* 4- (2b) > 3- (4g) > 2- (2c) agrees with experiment (Table 2). The sequence of the less reactive positions seems to vary in the different chloroalkane solvents, but the sequence predicted for chloroform solution, *i.e.* 4- > 2- > 3-, seems to fit with the results observed at least in dichloromethane solution. The formation of abnormal ketones derived from a rearranged hydrocarbon is also in agreement with the predicted data on the overall reactivities (Table 4). Acetylation of 1,8-dimethylnaphthalene (2a), if slow, would be accompanied by a rearrangement to the 1,7-isomer (5a), which is then acylated much more rapidly than the initial substrate in chloroform solution, or at a comparable rate in nitromethane solution.

Benzoylations of Acenaphthene.—Friedel–Crafts benzoylations of acenaphthene (1a) afforded mainly 5-benzoylacenaphthene (1d), varying small proportions of

the 3-isomer (1j) but no 4-isomer (3k) (Table 1). A sample of supposed 4-benzoylacenaphthene,[21] having m.p. 97—98.5 °C,[6] proved to be the 5-isomer (1d); the authentic 4-ketone (3k) melts at 56—57 °C.

Diacylations of Acenaphthene.[19]—Results obtained from a Friedel–Crafts acetylation of 5-benzoylacenaphthene (1d) and of benzoylations of 5-acetylacenaphthene (1b) are given in Table 5. An acylation of acenaphthene (1a) employing acetylation and benzoylation reagents simultaneously confirms the higher reactivity of the former, as seen from the significant extent of formation of 3,6-diacetylacenaphthene (1l).

shown to take place with aluminium chloride as the catalyst.[19] However, the formation (albeit in low yield) of 3,6-diacetylacenaphthene (1e) (Table 5) suggests that some deacetylation can occur with acetylacenaphthene (1b), at least in other solvents.

(*B*) (1b)→(6)→(1d)→(1l). This route requires the intermediate formation of 5-acetyl-6-benzoylacenaphthene (6). A *peri*-diacylnaphthalene has been reported in the benzoylation of 2,7-dimethylnaphthalene,[23] though this may be a favourable case. In the acetylation of 5-acetylacenaphthene (1b) small yields were believed to be formed of 5,6-diacetylacenaphthene,[24]

TABLE 4

Experimental and predicted positional reactivities of 1- and 2-methyl- and 1,7- and 1,8-dimethylnaphthalenes, in Friedel–Crafts acetylations [a]

Methylnaphthalene	Ketone isomers (%) 1-	2-	3-	4-	5-	6-	7-	8-	Overall reactivity ratio: substrate/naphthalene
(*a*) In $CHCl_3$									
1- [b]		0.28	0.16	99.4	0.026	0.032	0.090	0	10.8
2- [b]	30.0		0.80	3.62	0.52	18.3	4.65	42.1	6.69
1,7-di- [c]		2.33	5.26	92.2	0.17	0.046		0	2.33
1,8-di- [c]		0.49	0.10	49.4	49.4	0.10	0.49		0.347
(*b*) In $MeNO_2$									
1- [b]		0.87	4.50	88.7	0.72	1.94	3.25	0	7.85
2- [b]	2.49		3.93	2.23	0.39	63.9	11.8	15.3	3.73
1,7-di- [c]		3.02	84.1	10.2	0.47	2.23		0	20.5
1,8-di- [c]		1.89	5.79	42.3	42.3	5.79	1.89		18.9

[a] Each reactant (hydrocarbon, acetyl chloride, aluminium chloride) at 0.0625 mol dm^{-3}. [b] Experimental results (ref. 18). [c] Data predicted.

TABLE 5

Friedel–Crafts diacylations of acenaphthene

Substrate	Reagent [a]	Conditions	Yield [c] (%)	Products (%) [b] (1b)	BzAN [a]	(1e)	(1l) + (1m) [d]
BzAN [a]	AcCl,$AlCl_3$	CS_2; 48 °C, 8 h	16		53		42 [e]
(1b)	BzCl,$AlCl_3$	$CHCl_3$; 64 °C, 5 h	20	23			72 [e]
(1b)	BzCl,$AlCl_3$	CS_2; 48 °C, 8 h	73	76		0.8	14 [f]
(1b)	BzCl,$AlCl_3$	$PhNO_2$; 0 °C, 1.5 h; 20 °C, 24 h; 50 °C, 3 h	56	71		0.6	26
(1a)	AcCl,$AlCl_3$ + BzCl,$AlCl_3$	$C_2H_4Cl_2$; 85 °C, 5 h		42	14	5.1	36

[a] Abbreviations used: AcCl = acetyl chloride, BzCl = benzoyl chloride, BzAN = mixture of benzoylacenaphthenes [(1d) : (1j) = 93 : 7]. [b] Products listed in the sequence of their g.l.c. retention times; in each reaction another product (2.5—8.5%) was formed, whose identity was not established; dibenzoylacenaphthenes [*e.g.* (1f)] were absent (t.l.c.). [c] Yield of mixed ketones, after column chromatography. [d] Ketones (1l) and (1m) were not separated on the g.l.c. column. [e] Ketone (1l) was isolated by crystallisation. [f] Ketone (1m) was isolated by crystallisation.

Substantial amounts of 'mixed' 3,6-diacylacenaphthenes were formed in these acylations, a result similar to that obtained in the mesitylene series.[22] A quite unexpected result was the formation in small yield of 3-acetyl-6-benzoylacenaphthene (1l) from a benzoylation of 5-acetylacenaphthene (1b) in chloroform solution, *viz.* a homogeneous reaction, with no 'free' catalyst present. The proportions of the diketones (1l) and (1m) formed could not be determined, as they did not separate on g.l.c. For the anomalous formation of diketone (1l), formally involving an acyl rearrangement, the following alternative paths may be envisaged.

(*A*) (1b)→(1a)→(1d)→(1l). This path requires an initial protiodeacylation at an α-naphthyl position, yet neither with 1-acetylnaphthalene itself, nor with related α-acetyl compounds, has this ever been unambiguously not, however, the supposed '5,6'-isomer originally believed to be formed as the major product in these diacylations (and later shown to have, in fact, the 3,6-orientation).[1a] If diketone (6) were indeed formed its deacetylation to ketone (1d) is considered feasible, as such an acetyl group in particular is quite hindered,[19,23] and is unable to gain significant resonance-stabilisation due to its non-coplanarity with the naphthalene moiety.[25]

(*C*) (1b)→(1c)→(1l). This path involves 3-acetylacenaphthene (1c) as an intermediate. Formation of this ketone *either* by an intramolecular rearrangement (no such rearrangement has ever been reported), *or via* the hydrocarbon (1a) (attack at the 3-position on re-acetylation is kinetically not favoured), is considered highly improbable.

Relative Reactivities.—The positional reactivities of the two hydrocarbons (1a) and (2a) were estimated for acetylation reactions in chloroform solution by the method of competitive acylations [26] (Table 6). Here

TABLE 6

Relative reactivities of naphthyl positions in Friedel–Crafts acetylation in chloroform at 20 °C

Naphthyl *	Relative reactivity
1-	1.0
2-	0.45
1-methyl-4-	62
1-methyl-3-	0.10
1-methyl-2-	0.18
1,8-dimethyl-4-	60
5-AN	94
4-AN	<0.20
3-AN	6.4

* AN = acenaphthenyl.

acenaphthene (1a) was compared in chloroform solution with another reactive substrate, 2,7-dimethylnaphthalene, whose reactivity is known relative to naphthalene.[17] A comparison of the two hydrocarbons in nitromethane solution proved abortive, as *ca.* 99% of the ketones formed derived from acenaphthene (1a) only. The reactivity of 1,8-dimethylnaphthalene (2a) was similarly determined relative to 2-methylnaphthalene, whose reactivity in turn had been measured relative to naphthalene.[18] At the lower concentration (*ca.* 0.06 mol dm^{-3}) used for the competitive acetylations compared to preparative reactions (*ca.* 0.4 mol dm^{-3}), concurrent formation of abnormal products, *i.e.* mainly ketone (5b), was reduced to <2%, and could be ignored.

From the data in Table 6 it is evident that a *para*-alkyl group is strongly activating for each of the three α-alkylnaphthalenes. The 4-position of 1,8-dimethylnaphthalene (2a) can be considered to be the least accessible to the three different *para*-positions to the acetylating species, which is a reagent possessing large steric requirements.[27] This reduced reactivity is due to distortions of the naphthalene framework,[28] arising from the overcrowding of the two *peri*-methyl groups. A comparison of the effect of *ortho*-alkyl groups is equally instructive. The 3-position of acenaphthene is some 140 times as reactive as a 2-naphthyl position, due to the favourable geometry of the *ortho*-position.[13,29] The 2-position of 1-methylnaphthalene is only 0.40 times as reactive as a 2-naphthyl position, whilst the corresponding position in 1,8-dimethylnaphthalene (2a) is too low in reactivity for measurement.

^{1}H *N.m.r. Spectra.*—Acenaphthenes possessing a 3-substituent exhibit separate signals for the methylene groups of the CH_2CH_2 bridge. For 4- or 5-substituted acenaphthenes or for 4-acetyl-1,8-dimethylnaphthalene (2b) the methylene (or methyl) signals coalesce as sharp singlets. Acenaphthenes possessing strong electronegative 5-substituents [(1b); further examples are given in Supplementary Publication No. SUP 22534] exhibit, like the corresponding α-acylnaphthalenes,[30] a downfield signal for the *peri*- (6-) hydrogen of the neighbouring ring. For 5-benzoylacenaphthene (1d) the corresponding signal is *ca.* τ 0.7 more upfield than for the acetyl compound (1b). This difference is illustrated by ketones (1l) and (1m), and is an aid to their identification: the most downfield signals (5-H) occur at τ 1.99 and 1.19, respectively. The methyl signals for 1,7-dimethylnaphthalene (5a) and the two ketones (5b) and (5c) are well separated (Δτ 0.13—0.16); for 2-, 6-, and 8-acetyl-1,7-dimethylnaphthalenes the corresponding chemical-shift difference would be very different.[31]

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were recorded for samples as KBr discs, unless otherwise stated. ^{1}H N.m.r. spectra were obtained at 60 or 100 MHz in deuteriochloroform solution, with tetramethylsilane as internal standard. Full n.m.r. data and Kovàts retention indices [32] are available in Supplementary Publication No. SUP 22534 (5 pp.).*

G.l.c.—Analyses of mixtures of ketones were carried out as follows: (1) for acetylations, using a glass column (5 ft × 0.25 in internal diameter) filled with Bentone (3.5%) and Carbowax 20M (1.5%) on Celite (80—100 mesh) at 180 °C and N_2 as carrier gas, with a flame-ionisation detector (f.i.d.); (2) for benzoylations, using a glass column (2m × 2 mm internal diameter) filled with OV-17 (3%) on Chromosorb G (60—72 mesh) at 222 °C and N_2 as carrier gas, with a f.i.d.; (3) for the competitive acetylations, using a glass column filled with SE 30 (10%) on Celite (100—120 mesh) at 210 °C and as carrier gas N_2, with a f.i.d. The column materials were pretreated with hexamethyldisilazane. Peak areas were evaluated by triangulation, or by tracing the peak area and weighing. Detector mass-responses were determined, and corrections applied as appropriate.

3-Acetylacenaphthene (1c) [9,33] had m.p. 102 °C (lit.,[9] m.p. 103.5—104.5 °C); ^{1}H n.m.r. at τ 2.45(d, 4-H), 2.09(d, 5-H), 2.39(dd, 6-H), 6.64(m, 1-CH_2), and 6.28(m, 2-CH_2), $J_{4,5}$ 8.5, $J_{6,7}$ 8.0, and $J_{6,8}$ 1.5 Hz; $\nu_{max.}$ ($CHCl_3$) at 1 670 cm^{-1} (C=O). 5-Acetylacenaphthene (1b) [4] had m.p. 70 °C (lit.,[34] m.p. 75 °C); ^{1}H n.m.r. signals (CCl_4) at τ 2.79(d, 3-H), 2,10(d, 4-H), 1.34(d, 6-H), 2.54(t, 7-H), 2.86 (d, 8-H), and 6.66(s, CH_2); $J_{3,4}$ 7.2, and $J_{6,7}$ 8.6 Hz; $\nu_{max.}$ at 1 654 cm^{-1} (C=O). 5-Benzoylacenaphthene (1d) [6] had m.p. 100 °C (lit.,[6] m.p. 100—102 °C); ^{1}H n.m.r. at τ 2.73(d, 3-H), 1.97(d, 6-H), 2.81(d, 8-H), and 6.60(s, CH_2); $J_{3,4}$ 7.2, $J_{6,7}$ 8.5, and $J_{7,8}$ 7.2 Hz; $\nu_{max.}$ at 1 645 cm^{-1} (C=O). 3,6-Diacetylacenaphthene (1e) [7] has m.p. 146—147 °C (lit.,[7] m.p. 149 °C); ^{1}H n.m.r. signals at τ 2.06(d, 4-H), 1.23(d, 5-H), 1.94(d, 7-H), 2.71(m, 8-H), 6.29(m, 2-CH_2), and 6.63(m, 1-CH_2); $J_{4,5}$ 9.0 and $J_{7,8}$ 7.2 Hz; $\nu_{max.}$ at 1 660 cm^{-1} (C=O). 3,6-Dibenzoylacenaphthene (1f) [35] had m.p. 149—150 °C (lit.,[35] m.p. 148.5—149.5 °C); ^{1}H n.m.r. at τ 1.83 (d, 5-H) and 6.2—6.7 (complex, CH_2); $\nu_{max.}$ at 1 650 cm^{-1} (C=O).

4-Acetylacenaphthene (3g).—To a solution of methylmagnesium iodide [prepared from magnesium (0.24 g) and methyl iodide (1.4 g) in dry ether] 4-cyanoacenaphthene [6] (0.18 g) dissolved in dry benzene (15 ml) was added and the mixture gently boiled for 6 h. The mixture was cooled, and a saturated solution of ammonium chloride added with stirring. The organic layer on evaporation gave a crude ketimine, which was boiled for 48 h with 5N-sulphuric acid (20 ml). The product was taken up in

* For details see *J.C.S. Perkin I*, 1978, Index issue.

chloroform, the extract washed with water, dried ($MgSO_4$), and evaporated to give crude ketone (0.2 g). Purification was achieved by chromatography on alumina from benzene, giving yellow 4-*acetylacenaphthene* (22 mg, 11%), m.p. 85 °C (ethanol) (Found: C, 85.9; H, 5.85. $C_{14}H_{12}O$ requires C, 85.7; H, 6.15%); ^{1}H n.m.r. at τ 2.40(br, 3-H), 1.80(br, 5-H), and 6.54(s, CH_2); $\nu_{max.}$ ($CHCl_3$) at 1 678 cm^{-1} (C=O).

4-*Benzoylacenaphthene* (3k).—By a method analogous to the preparation of ketone (3g), 4-cyanoacenaphthene (0.24 g) was converted into 4-*benzoylacenaphthene* (80 mg, 23%), m.p. 56—57 °C (methanol) (claimed [6] m.p. 97—98.5 °C) (Found: C, 88.2; H, 5.2. $C_{19}H_{14}O$ requires C, 88.3; H, 5.5%); ^{1}H n.m.r. at τ 1.97(d, 5-H) and 6.55(s, CH_2); $J_{3.5}$ 1.3 Hz; $\nu_{max.}$ ($CHCl_3$) at 1 660 cm^{-1} (C=O).

3-*Benzoylacenaphthene* (1j).—A mixture of acenaphthene-3-carboxylic acid [36] (68 mg) and thionyl chloride (5 ml) was boiled for 2 h; the excess of the latter was then removed by distillation: dry benzene (20 ml) was then added, followed by aluminium chloride (0.5 g) in portions, with stirring. The crude ketone, isolated in the usual way, was chromatographed from benzene on alumina, to give 3-*benzoylacenaphthene* (72 mg, 85%), m.p. 30 °C (Found: C, 88.2; H, 5.3%; M^+, 258.320. $C_{19}H_{14}O$ requires C, 88.3; H, 5.5%; *M*, 258.320); ^{1}H n.m.r. at τ 1.82(d, 5-H) and 6.15—6.75 (complex CH_2); $J_{4.5}$ 8.5 Hz; $\nu_{max.}$ ($CHCl_3$) at 1 658 cm^{-1} (C=O).

2-*Acetyl*-1,8-*dimethylnaphthalene* (2c).—This ketone was obtained from 1,8-dimethylnaphthalene-2-carboxylic acid [37] by use of an excess of methyl-lithium in ether. Isolated in the usual way, and purified by chromatography over alumina from benzene, 2-*acetyl*-1,8-*dimethylnaphthalene* formed a semi-solid, m.p. *ca.* 25 °C (Found: C, 84,5; H, 7.1. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%); *m/e* (with relative abundances): 91 (100), 183 (86), 198 (M^+, 55), 155 (45), 43 (32), and 199 (9.0); $\nu_{max.}$ at 1 690 cm^{-1} (C=O).

3-*Acetyl*-1,8-*dimethylnaphthalene* (4g).—Prepared from 1,8-dimethylnaphthalene-3-carboxylic acid [37] as for isomer (2c), 3-*acetyl*-1,8-*dimethylnaphthalene* formed crystals, m.p. 176 °C (ethanol) (Found: C, 84.6; H, 7.0. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%); *m/e* (with relative abundances): 183 (100), 43 (100), 198 (M^+, 54), 155 (21), 139 (12), and 199 (8.5); $\nu_{max.}$ at 1 680 cm^{-1} (C=O).

Friedel–Crafts Acylations.—(i) *General.* The acylations summarised in Tables 1—3 and 5 were generally carried out using equimolar quantities of substrate, acyl chloride, and aluminium chloride. The scale was in the range 0.002—0.02 mol, and concentrations used were: for reactions with acenaphthene 0.4 mol dm^{-3}, for 1,8-dimethylnaphthalene 0.08 mol dm^{-3}, and for 1,7-dimethylnaphthalene 0.067 mol dm^{-3}. The reactions were conducted, and the products isolated, as described earlier. Aliquots of the reaction products were passed through a column of alumina, and exhaustively eluted with benzene. The solvent was then removed, and the residue examined by g.l.c.

(ii) 4-*Acetyl*-1,8-*dimethylnaphthalene* (2b). This ketone was isolated from acetylations of 1,8-dimethylnaphthalene carried out in chloroform solution. The crude product was chromatographed over alumina (benzene), and the viscous product subjected to preparative g.l.c. 4-*Acetyl*-1,8-*dimethylnaphthalene* was a liquid, n_D^{22} 1.606 (Found: C, 84.5; H, 7.1. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%); ^{1}H n.m.r. signals at τ 2.36(d, 3-H), 1.55(m, 5-H), 7.07 (Me), and 7.31 (COMe); $J_{2.3}$ 7.3 Hz; $\nu_{max.}$ at 1 680 cm^{-1} (C=O).

(iii) 4-*Acetyl*-1,7-*dimethylnaphthalene* (5b) *and* 3-*acetyl*-1,7-*dimethylnaphthalene* (5c). 1,7-Dimethylnaphthalene was prepared essentially by the literature method,[38] except that the dehydrogenation step was effected by use of chloranil; the hydrocarbon was purified *via* the picrate, m.p. 120 °C (lit.,[38] m.p. 120 °C), and had b.p. 84—86 °C at 1 mmHg (lit.,[38] b.p. 258 °C); ^{1}H n.m.r. signals at τ 2.29—2.85 complex, aromatic-H), 7.43 (1-Me), and 7.55 (7-Me).

To a stirred solution of aluminium chloride (2.66 g) and acetyl chloride (1.57 g) in nitromethane was added at room temperature, during 15 min, a solution of 1,7-dimethylnaphthalene (3.12 g) in nitromethane. The mixture was boiled gently for 19 h, then cooled, treated with ice and 10N-hydrochloric acid, and worked-up in the usual way, to give a brown product (4.0 g), which was subjected to preparative g.l.c. Two isomers were thus obtained: 4-*acetyl*-1,7-*dimethylnaphthalene* (86 mg), m.p. 71 °C (ethanol) (Found: C, 84.5; H, 6.9. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%); *m/e* (with relative abundances): 198 (M^+, 100), 183 (100), 155 (94), 152 (63), 128 (42), 139 (34), 127 (31), and 199 (30); ^{1}H n.m.r. at τ 2.76(m, 2-H), 2.26(d, 3-H), 1.30(d, 5-H), 2.61(dd, 6-H), 2.25(br, 8-H), 7.35 (1-Me), 7.51 (7-Me), and 7.35 (COMe); $J_{2.3}$ 7.2, $J_{5.6}$ 9.0, and $J_{6.8}$ 1.8 Hz; $\nu_{max.}$ at 1 682 cm^{-1} (C=O), and 3-*acetyl*-1,7-*dimethylnaphthalene*, an oil (Found: C, 84.6; H, 7.0. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%); ^{1}H n.m.r. at τ 1.99(br, 2-H), 1.57(br, 4-H), 1.98(d, 5-H), 2.44(m, 6-H), 2.11(br, 8-H), 7.30 (1-Me), 7.43 (7-Me), and 7.31 (COMe); $J_{5.6}$ 8.5 Hz; $\nu_{max.}$ at 1 680 cm^{-1} (C=O).

(iv) *Acetylation of benzoylacenaphthene.* To a stirred mixture of aluminium chloride (6.6 g) and benzoyl chloride (7.0 g) in carbon disulphide (70 ml) was added during 15 min a solution of acenaphthene (7.7 g) in carbon disulphide (30 ml). After stirring the mixture for 24 h at room temperature, aluminium chloride (9.9 g) was then added at 0 °C, followed by addition of acetyl chloride (3.9 g) during 15 min. The mixture was again stirred for 8 h at room temperature, then treated with 10N-hydrochloric acid (50 ml) and ice, and the product (2.2 g) isolated in the usual way. A sample was passed through a column of alumina in benzene; the eluate afforded a brown solid, which was analysed by g.l.c. (Table 5). Repeated crystallisation (benzene–light petroleum) afforded 3-*acetyl*-6-*benzoylacenaphthene*, m.p. 152.5—153 °C (Found: C, 84.2; H, 5.4. $C_{21}H_{16}O_2$ requires C, 84.0; H, 5.4%); ^{1}H n.m.r. at τ 2.12(d, 4-H), 1.99(d, 5-H), 6.61(m, 1-CH_2), 6.26(m, 2-CH_2), and 7.32 (COMe), $J_{4.5}$ 8.5 and $J_{7,8}$ 7.5 Hz; $\nu_{max.}$ at 1 650 (benzoyl C=O) and 1 678 (acetyl C=O) cm^{-1}.

(v) *Benzoylation of* 5-*acetylacenaphthene.* (a) *In chloroform.* A complex of aluminium chloride (3.4 g) and benzoyl chloride (3.5 g) in chloroform (50 ml) was added over 20 min at room temperature to a stirred mixture of 5-acetylacenaphthene (4.4 g) and aluminium chloride (3.4 g) in chloroform (100 ml). The reaction mixture was then boiled gently for 5 h, cooled, and treated with 10N-hydrochloric acid and ice. On working-up a thick black liquid (1.1 g) was obtained, which after chromatography (alumina eluting with benzene), and then crystallisation afforded 3-acetyl-6-benzoylacenaphthene (30 mg), identical (mixed m.p., i.r., ^{1}H n.m.r.) with the product obtained under (iv) above.

(b) *In carbon disulphide.* To a stirred mixture of 5-acetylacenaphthene (8.8 g) and aluminium chloride (6.8 g) in carbon disulphide (150 ml) was added over 15 min a mixture of aluminium chloride (6.8 g) and benzoyl chloride

(7.0 g) in carbon disulphide (100 ml). The mixture was boiled for 8 h, then cooled and 10N-hydrochloric acid and ice were added. The crude product was distilled *in vacuo*, when unreacted 5-acetylacenaphthene (6.0 g) distilled over, b.p. 145 °C at 0.5 mmHg, m.p. 66—68 °C. The distillation residue (0.5 g) was extracted with alcohol, and the extract crystallised, to give 6-*acetyl*-3-*benzoylacenaphthene* (85 mg), m.p. 151—153 °C (Found: C, 84.2; H, 5.4. $C_{21}H_{16}O_2$ requires C, 84.0; H, 5.4%); ^{1}H n.m.r. at τ 2.19(d, 4-H), 1.19(d, 5-H), 1.80(d, 7-H), 6.25—6.8 (complex, CH_2), and 7.25 (COMe); $J_{4,5}$ 8.5 and $J_{7,8}$ 7.5 Hz; $\nu_{max.}$ at 1 650 (benzoyl C=O) and 1 675 (acetyl C=O) cm^{-1}.

(c) *In nitrobenzene.* From a reaction carried out in nitrobenzene solution [35] the only readily crystallisable product proved to be unchanged 5-acetylacenaphthene (33%).

(vi) *Combined acetylation and benzoylation of acenaphthene.* Solutions of acetyl chloride (3.9 g) and aluminium chloride (6.6 g) in 1,2-dichloroethane (50 ml), and of benzoyl chloride (7.0 g) and aluminium chloride (6.6 g) in 1,2-dichloroethane (50 ml) were mixed. To this solution acenaphthene (7.6 g) in 1,2-dichloroethane (50 ml) was added, and the mixture boiled gently for 5 h, then cooled, and 10N-hydrochloric acid and ice added. A portion of the black residue was chromatographed over alumina from benzene, and the eluate was evaporated. The sample was then analysed (Table 5).

(vii) *Competitive acylations.* A mixture of the two hydrocarbons to be compared (acenaphthene and 2,7-dimethylnaphthalene, *or* 1,8-dimethylnaphthalene and 2-methylnaphthalene, respectively) in chloroform solution was added rapidly to a stirred mixture of aluminium chloride and acetyl chloride in more chloroform at 20 °C, and the reaction allowed to proceed for *ca.* 10 min. Equimolar amounts of the reactants were used, and the concentrations were 0.133 mol dm^{-3} or 0.0571 mol dm^{-3} for the two systems, respectively. A total of *ca.* 10% of ketones were formed in this time. The products were isolated in the usual way, and then analysed by g.l.c.

Isomerisation of 1,8-*Dimethylnaphthalene.*—1,8-Dimethylnaphthalene (0.31 g) was added to a mixture of aluminium chloride (0.26 g) in nitrobenzene (2 ml), and the solution was boiled under reflux for 6 h. The product, isolated in the usual way, was shown by g.l.c. [column (3) used at 130 °C] to contain unchanged 1,8-dimethylnaphthalene together with 2,7-dimethylnaphthalene (0.7%). No other hydrocarbon could be detected.

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