448. *The Elimination of Non-angular Alkyl Groups in Aromatisation Reactions. Part IV.**

By Wesley Cocker, L. O. Hopkins, (Mrs.) L. Mabrouk, (Miss) J. McCormick, and T. B. H. McMurry.

New di-, tri-, and tetra-alkylnaphthalenes have been synthesised, including two completely substituted in the *peri*-positions. Their infrared spectra are recorded. Spectroscopic characteristics of the last two compounds show no abnormalities which could arise from overlap of the alkyl groups.

Two cases of the loss of ethyl group during dehydrogenation with selenium and with palladised charcoal are reported.

The fifteen polyalkylnaphthalenes (Ia—r) have been synthesised by conventional methods shown by the formulæ. We have also synthesised 1-methoxy-8-methylnaphthalene (Iu) and 8-methyl-1-naphthol (Iv).

All the benzoylpropionic acids (II; R* = H) were known compounds, and the stages leading to the naphthalenes are well characterised. However, we prepared 1-ethyl-3-methylnaphthalene (Ia) by two routes, namely, from methyl β-benzoyl-α-methylpropionate (IIa), obtained from benzene and methylsuccinic anhydride,[1] and from β-benzoyl-β-methylpropionic acid (IIb) obtained by the condensation of α-bromopropiophenone and ethyl sodiomalonate. In the first route the ethyl group was introduced at the (IIa ⟶ IIIa) stage, and in the second route this group was introduced at the (Vb ⟶ VIIa) stage.

Methyl β-benzoyl-α-ethylpropionate (IIc) was the starting material for the synthesis of 3-ethyl-1-methylnaphthalene (Ib). We prepared the acid by the aluminium chloride-catalysed condensation of benzene and ethylsuccinic anhydride in methylene chloride. The position of the ethyl group was established by the ready formation of the benzylidene derivative (IId). Its position conforms with earlier work [2,3] on the reaction of unsymmetrical succinic anhydrides with aromatic hydrocarbons in ionising solvents. It might be added that the acid corresponding to (IIc) has previously [4] been prepared by other routes.

We found that conversion of the keto-esters (II) into the unsaturated acids (III) in good yield required use of boiling toluene and an excess of Grignard reagent. Under these conditions the predominant product was always the acid and not the corresponding ester.

---

* Part III, *J.*, 1954, 2420.

[1] Mayer and Stamm, *Ber.*, 1923, **56**, 1424.

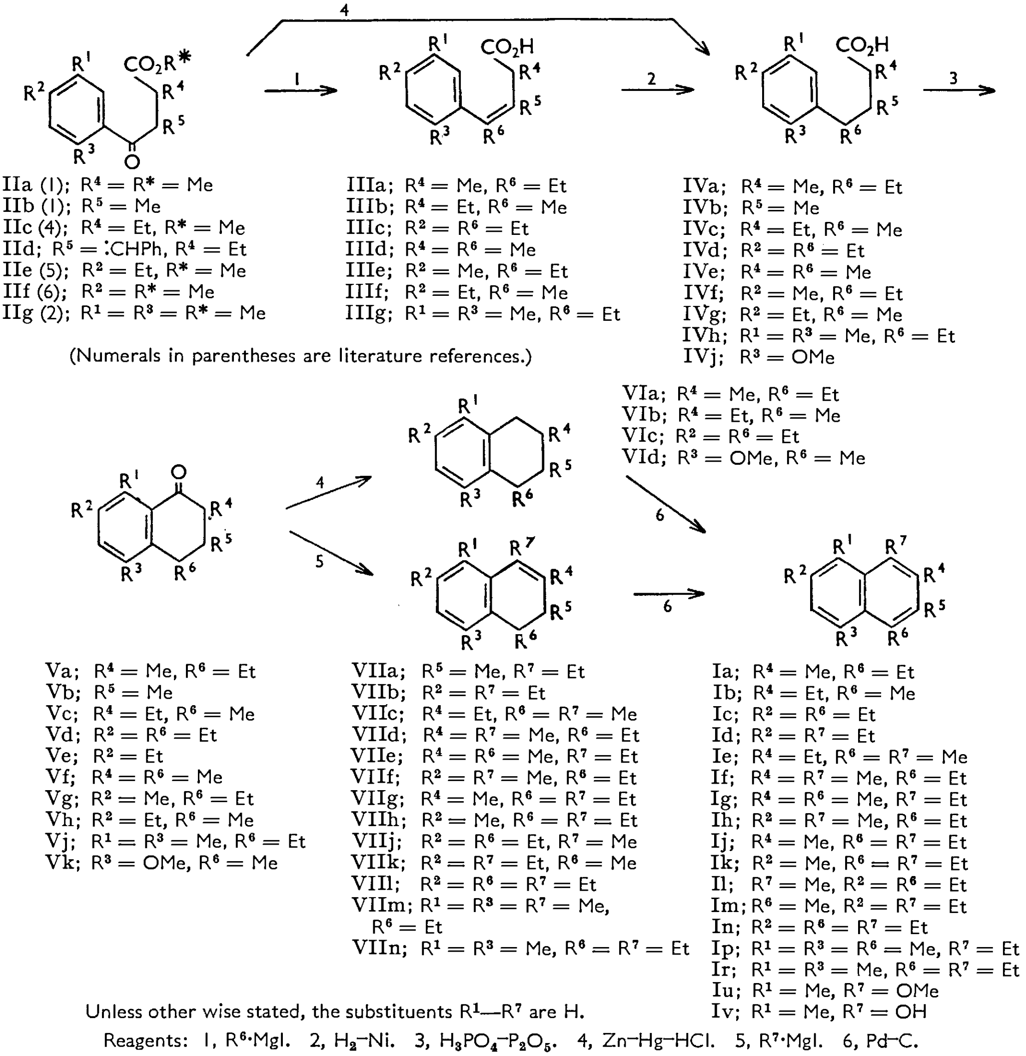
[2] Berliner, *Org. Reactions*, 1949, **5**, 242, 275.

[3] Cocker, Cross, Fateen, Lipman, and Whyte, *Chem. and Ind.*, 1949, 641; Cocker, Cross, Fateen, Lipman, Stuart, Thompson, and Whyte, *J.*, 1950, 1781; Cocker, Fateen, and Lipman, *J.*, 1951, 926; cf. Baddar, Fahim, and Fleifel, *J.*, 1955, 2199.

[4] Buchta and Haagner, *Chem. Ber.*, 1948, **81**, 251, who also give references to earlier work.

The de-esterifying reagent is probably MgI·OH liberated in the formation of the double bond.

Palladised charcoal was used for dehydrogenation of the reduced naphthalenes (VI) and (VII). We encountered two cases where an alkyl group was eliminated during this reaction: when we heated 4,5,8-triethyl-1,2-dihydronaphthalene (VIII) with palladised charcoal at 260—280° we obtained 1,4-diethylnaphthalene; and when 1,5,8-triethyl-1,2,3,4-tetrahydronaphthalene (IX) was heated with selenium at 340° 1,4-diethylnaphthalene was again obtained. Neither palladised charcoal nor sulphur effected the latter dehydrogenation, the tetrahydro-compound being recovered unchanged. These results confirm the experience of Cocker *et al.*[7] We also found that 1,2,3,4-tetrahydro-5-methoxy-4-methylnaphthalene (VId; see below) was partly demethoxylated when heated with



IIa (1); R^4 = R* = Me
IIb (1); R^5 = Me
IIc (4); R^4 = Et, R* = Me
IId; R^5 = :CHPh, R^4 = Et
IIe (5); R^2 = Et, R* = Me
IIf (6); R^2 = R* = Me
IIg (2); R^1 = R^3 = R* = Me

IIIa; R^4 = Me, R^6 = Et
IIIb; R^4 = Et, R^6 = Me
IIIc; R^2 = R^6 = Et
IIId; R^4 = R^6 = Me
IIIe; R^2 = Me, R^6 = Et
IIIf; R^2 = Et, R^6 = Me
IIIg; R^1 = R^3 = Me, R^6 = Et

IVa; R^4 = Me, R^6 = Et
IVb; R^5 = Me
IVc; R^4 = Et, R^6 = Me
IVd; R^2 = R^6 = Et
IVe; R^4 = R^6 = Me
IVf; R^2 = Me, R^6 = Et
IVg; R^2 = Et, R^6 = Me
IVh; R^1 = R^3 = Me, R^6 = Et
IVj; R^3 = OMe

(Numerals in parentheses are literature references.)

VIa; R^4 = Me, R^6 = Et
VIb; R^4 = Et, R^6 = Me
VIc; R^2 = R^6 = Et
VId; R^3 = OMe, R^6 = Me

Va; R^4 = Me, R^6 = Et
Vb; R^5 = Me
Vc; R^4 = Et, R^6 = Me
Vd; R^2 = R^6 = Et
Ve; R^2 = Et
Vf; R^4 = R^6 = Me
Vg; R^2 = Me, R^6 = Et
Vh; R^2 = Et, R^6 = Me
Vj; R^1 = R^3 = Me, R^6 = Et
Vk; R^3 = OMe, R^6 = Me

VIIa; R^5 = Me, R^7 = Et
VIIb; R^2 = R^7 = Et
VIIc; R^4 = Et, R^6 = R^7 = Me
VIId; R^4 = R^7 = Me, R^6 = Et
VIIe; R^4 = R^6 = Me, R^7 = Et
VIIf; R^2 = R^7 = Me, R^6 = Et
VIIg; R^4 = Me, R^6 = R^7 = Et
VIIh; R^2 = Me, R^6 = R^7 = Et
VIIj; R^2 = R^6 = Et, R^7 = Me
VIIk; R^2 = R^7 = Et, R^6 = Me
VIIl; R^2 = R^6 = R^7 = Et
VIIm; R^1 = R^3 = R^7 = Me, R^6 = Et
VIIn; R^1 = R^3 = Me, R^6 = R^7 = Et

Ia; R^4 = Me, R^6 = Et
Ib; R^4 = Et, R^6 = Me
Ic; R^2 = R^6 = Et
Id; R^2 = R^7 = Et
Ie; R^4 = Et, R^6 = R^7 = Me
If; R^4 = R^7 = Me, R^6 = Et
Ig; R^4 = R^6 = Me, R^7 = Et
Ih; R^2 = R^7 = Me, R^6 = Et
Ij; R^4 = Me, R^6 = R^7 = Et
Ik; R^2 = Me, R^6 = R^7 = Et
Il; R^7 = Me, R^2 = R^6 = Et
Im; R^6 = Me, R^2 = R^7 = Et
In; R^2 = R^6 = R^7 = Et
Ip; R^1 = R^3 = R^6 = Me, R^7 = Et
Ir; R^1 = R^3 = Me, R^6 = R^7 = Et
Iu; R^1 = Me, R^7 = OMe
Iv; R^1 = Me, R^7 = OH

Unless other wise stated, the substituents R^1—R^7 are H.

Reagents: 1, R^6·MgI. 2, H_2–Ni. 3, H_3PO_4–P_2O_5. 4, Zn–Hg–HCl. 5, R^7·MgI. 6, Pd–C.

---

[5] Baddar and Warren, *J.*, 1939, 944.

[6] Barnett and Sanders, *J.*, 1933, 434.

[7] Cocker, Cross, Edward, Jenkinson, and McCormick, *J.*, 1953, 2355.

palladised charcoal. This also accords with our previous experience. Thus 1-ethyl-1,2,3,4-tetrahydro-8-methoxy-5,7-dimethylnaphthalene loses its methoxyl group on dehydrogenation with palladised charcoal, as also does 1-ethyl-1,2,3,4-tetrahydro-5-methoxy-7,8-dimethylnaphthalene.[7]

Table 1 shows that the polyalkylnaphthalenes have the characteristic absorption of naphthalenic hydrocarbons,[8] with the expected progressive shift of the maxima to longer wavelengths [9] with increasing substitution.

As expected the two naphthalenes completely substituted in the *peri* positions (Ip and Ir) do not show any change in naphthalenic absorption. There may be some distortion of the nucleus from the planar form arising from interference between the alkyl groups, but this would certainly not be so great as in octamethylnaphthalene where the non-planar nucleus [10] shows no abnormal spectroscopic properties.[9] It appears that some out-of-plane distortion of the naphthalene nucleus is permissible without loss of resonance between the nuclei.

Relatively few polyalkylnaphthalenes have been studied in the infrared region. The spectra of a few monosubstituted [11] and polysubstituted [12] alkylnaphthalenes have been recorded.

For purposes of correlation, the infrared spectra of naphthalenes may be divided into five regions, namely, (*a*) 4000—2000, (*b*) 2000—1650, (*c*) 1650—1300, (*d*) 1300—950, and (*e*) 950—650 cm.$^{-1}$. Region (*a*) contains the =CH stretching vibrations,[13] and Table 2 shows that, whilst there is some slight variation in the position of this band with change in substitution pattern, there seems to be no regularity about it. We have not measured the weak bands which occur in region (*b*). Region (*c*) may be divided into two groups, those in the 1500—1600 and those in the 1380—1460 cm.$^{-1}$ range.

TABLE 1. *Ultraviolet-light absorption of polyalkylnaphthalenes* (*measured in ethanol*).

No.	Naphthalene	$\lambda_{max.}$ (Å) (intensity, log ε, in parentheses)
Ia	1-Et-3-Me	2240(4·95), 2760—2800(3·80), 3210(2·65)
Ib	3-Et-1-Me	2300(4·87), 2870(3·83), 3230(2·91)
Ic	1,6-Et$_2$	2270(4·85), 2790(3·62), 3210(2·75)
Id	1,7-Et$_2$	2280(5·35), 2800(3·83), 3210(2·58)
If	4-Et-1,2-Me$_2$	2310(4·97), 2910(3·83), 3250(2·91)
Ig	1-Et-2,4-Me$_2$	2310(4·93), 2910(3·93), 3250(2·96)
Ih	1-Et-4,6-Me$_2$	2300(4·85), 2900(3·87), 3240(2·94)
Ij	1,4-Et$_2$-2-Me	2300(4·82), 2910(3·85), 3250(2·84)
Ik	1,4-Et$_2$-6-Me	2310(4·91), 2900(3·95), 3250(3·09), 3555(2·33)
Il	1,6-Et$_2$-4-Me	2300(4·86), 2890(3·66), 3240(2·57)
Im	4,6-Et$_2$-1-Me	2320(4·83), 2900(3·82), 3240(2·85)
In	1,4,6-Et$_3$	2310(4·82), 2880(3·83), 3240(2·84)
Ip	1-Et-4,5,8-Me$_3$	2335(4·85), 2920—2930(3·74), 3290(3·05)
Ir	1,4-Et$_2$-5,8-Me$_2$	2340(4·95), 2910(3·83), 3270(2·77)

The trisubstituted naphthalenes can be divided into two groups for comparison purposes. The first group consists of 4-ethyl-1,2-dimethyl- (If), 1-ethyl-2,4-dimethyl- (Ig), and 1,4-diethyl-2-methyl-naphthalene (Ij), and the second of 1-ethyl-4,6-dimethyl- (Ih), 1,4-diethyl-6-methyl- (Ik), 1,6-diethyl-4-methyl- (Il), 4,6-diethyl-1-methyl- (Im), and 1,4,6-triethyl-naphthalene (In).

The naphthalenes of both groups have a relatively strong band at 1620—1625 cm.$^{-1}$ and most of them have a weaker band in the 1600—1610 cm.$^{-1}$ region. In the cases of 1-ethyl-4,6-dimethyl- (Ih) and 1,4,6-triethyl-naphthalene (In), however, the latter band is at 1593 cm.$^{-1}$. Most of the naphthalenes also have a weak band at, or around, 1578 cm.$^{-1}$,

---

[8] Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy," Arnold, London, 2nd edn., 1957, p. 136.

[9] Abadir, Cook, and Gibson, *J.*, 1953, 8.

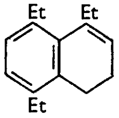
[10] Donaldson and Robertson, *J.*, 1953, 17.

[11] Broomfield, *J. Inst. Petroleum*, 1952, **38**, 424.

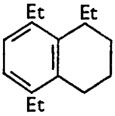
[12] Cannon and Sutherland, *Spectrochim. Acta*, 1951, **4**, 373; Mosby, *J. Amer. Chem. Soc.*, 1952, **74**, 2564.

[13] Fox and Martin, *J.*, 1939, 318; *Proc. Roy. Soc.*, 1940, **175**, *A*, 208.

but for (Ih) and (In) this band is displaced to the lower wave number of 1572 and 1567 cm.$^{-1}$ respectively. A further band in the 1504—1516 cm.$^{-1}$ range is common to all the trialkylnaphthalenes, but it is significant that 1,4,6-triethylnaphthalene once again has its band at the bottom of this wave-number range. The last compound also has a more detailed spectrum in the 1500—1600 cm.$^{-1}$ range than the other naphthalenes.



(VIII)



(IX)

It is perhaps significant that the three trisubstituted naphthalenes (If), (Ig), and (Ij), which have the three alkyl groups in the same nucleus, have a band at 1468—1478 cm.$^{-1}$ which is absent from the spectra of the other trialkylnaphthalenes. Otherwise all the trialkylnaphthalenes have reasonable similarity of spectrum in the 1370—1460 cm.$^{-1}$ range.

The naphthalenes show a pair of close bands in the 1450—1470 cm.$^{-1}$ region due to $-CH_3$. In some cases this appears as a broad band with a shoulder as for example in the spectrum of (Il).

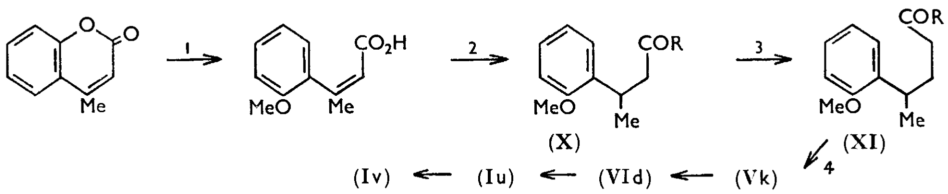
The two tetrasubstituted naphthalenes are, as expected, very similar in spectrum at both ends of region (*c*), and need no special comment.

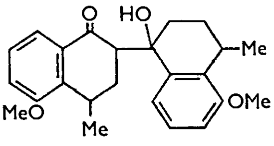
Region (*d*) is characterised by relatively weak bands shown by aromatic compounds. In general the position of the bands varies with the type of benzenoid substitution pattern,[14] although data refer largely to substituted benzenes only. In the region (*e*) the bands are due to the out-of-plane deformation vibrations of the hydrogen atoms remaining on the ring; [14] again published data are largely for substituted benzenes, and our interpretations in Table 2 are therefore somewhat speculative.

During this investigation we prepared 1-methoxy-8-methylnaphthalene (Iu) and 8-methyl-1-naphthol which were required for another purpose. The method adopted was as shown in annexed formulæ.

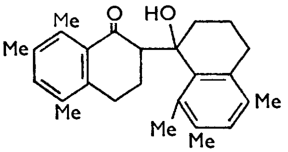
β-*o*-Methoxyphenylbutyryl chloride (X; R = Cl) was obtained by a two-stage process from 4-methylcoumarin. The chloride was converted by the Arndt–Eistert process into γ-*o*-methoxyphenylvaleramide (XI; R = NH_2) which was then hydrolysed with alkali to the corresponding acid (XI; R = OH). The two-stage process was found to give more satisfactory yields than the direct conversion of the chloride into the homologous acid. Ring-closure of the acid with polyphosphoric acid afforded the tetralone (Vk).

A second compound to which we assign structure (XII) was obtained, in not insignificant yield, as a by-product of the cyclisation of the acid (XI; R = OH). Its analysis and molecular weight indicated formula $C_{22}H_{22}O_2(OMe)_2$. In the ultraviolet spectrum it gave a single maximum at 2750 Å (log ε 4·43) and in the infrared region it showed bands at





(XII)



(XIII)

Reagents: 1, OH^-, then Me_2SO_4. 2, H_2–Pt. 3, Arndt–Eistert. 4, H_3PO_4–P_2O_5.

---

[14] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 75.

TABLE 2. *Infrared spectra* (*cm.*$^{-1}$) *of substituted naphthalenes* (*liquid films*)

Naphthalene	Aromatic =C–H 3000	C–Me 3000—2850	C=C 1600—1500	C–Me 1450—1370	Benzenoid substitution pattern 1280—950	Adjacent free H atoms 950—700
Ia 1-Et-3-Me	3107, 3006	2839	1634, 1612, 1516	1459, 1404, 1378	1278, 1228, 1137, 959 (1,2-di) 1047 (1,2,3,5-tetra)	872, 852, 819 (1 free H) 787, 747 (4 adj. H)
1,4-Et$_2$	3080, 2967	2933, 2866	1600, 1556w, 1517	1467, 1453, 1376	1269, 1216, 1113, 1038, 956 (1,2-di-) 1164, 1065, 994w (1,2,3,4-tetra-)	875w, 841 (2 adj. H) 789, 775w, 763, 750 (4 adj. H)
Ic 1,6-Et$_2$	3034, 3000	2966, 2894	1628, 1600, 1572w, 1506	1447, 1370	1256, 1204, 1159, 1050 (1,2,3-tri-) 1084w, 1000 (1,2,4-tri-) 955, 947	885, 870 (1 free H) 819 (2 adj. H) 790, 747 (3 adj. H)
Id 1,7-Et$_2$	3040, 2956	2928, 2870	1630, 1602, 1580w, 1514	1453, 1377	1260, 1236, 1207, 1147, 1062 (1,2,3-tri-) 1162, 1078, 1016 (1,2,4-tri-) 953, 964	880 (1 free H) 831 (2 adj. H) 752 3 adj. H
If 4-Et-1,2-Me$_2$	3116, 3000	2917	1616, 1585, 1528	1472, 1424w, 1390	1256, 1227, 1178, 1168, 1090, 1031, 1000, 953 (1,2-di-) 1065, 1040w (1,2,3,4,5-penta)	884, 862w (1 free H) 759 (4 adj. H) 942, 812, 784w, 778w
Ig 1-Et-2,4-Me$_2$	3120, 3000	2979 2920	1620 1605w, 1578w, 1514w	1478, 1449, 1400, 1378	1270, 1165, 1153, 1031, 1009 (1,2-di-) 1214, 1050 (1,2,3,4,5-penta-) 952	890, 867, 853w (1 free H) 750 (4 adj. H) 804, 783, 695
Ih 1-Et-4,6-Me$_2$	3050, 3000	2925	1625, 1594, 1572, 1564, 1553, 1508	1460, 1444, 1430, 1372	1262, 1223, 1208, 1159, 1128, 1070, 1050, 1025 (1,2,4-tri-)	884 (1 free H) 860, 812 (2 adj. H) 785, 764, 740
Ij 1,4-Et$_2$-2-Me	3000	2964, 2893	1622, 1609, 1578w 1520ms	1468, 1459, 1422w 1390, 1378	1266, 1178, 1165w, 1093, 1040, 970 (1,2-di-) 1219, 1072, 1062 (1,2,3,4,5-penta-) 968	884 (1 free H) 766 (4 adj. H) 816, 850w, 753, 714
Ik 1,4-Et$_2$-6-Me	3000	2985	1625, 1600, 1512	1463, 1453	1266, 1240, 1215, 1165, 1145, 1080, 1070, 995 (1,4-di- and 1,2,4-tri-) 962	891, 880 (1 free H) 840, 825 (2 adj. H) 793, 782, 758
Il 1,6-Et$_2$-4-Me	3015	2958, 2893	1612, 1600, 1575w, 1506	1448 s, br, 1373, 1336	1266, 1189, 1055, 1027, 962 (1,2,4-tri-) 1208, 1156, 1136 (1,2,3,4-tetra-)	872 (1 free H) 822 (2 adj. H) 928, 779, 747, 700
Im 4,6-Et$_2$-1-Me	3015	2984, 2912	1629, 1604, 1585w, 1515	1454, 1430, 1379	1270, 1166, 1106, 1078, 1025w, 963 (1,2,4-tri-) 1213, 1144 (1,2,3,4-tetra-)	878 (1 free H) 831 (2 adj. H) 813w, 778, 697

TABLE 2. (*Continued.*)

	Aromatic =C–H	C–Me	C=C	C–Me	Benzenoid substitution pattern	Adjacent free H atoms
Naphthalene	3000	3000—2850	1600—1500	1450—1370	1280—950	950—700
In 1,4,6-Et_3	3000	2966, 2903	1621, 1593, 1567w, 1550w, 1531w, 1504	1456, 1447, 1367	1260, 1160w, 1075w, 1056w, 1026, 990 (1,2,4-tri-) 1200w, 1141 (1,2,3,4-tetra-) 953	873 (1 free H) 825 (2 adj. H) 781
Ip 1-Et-4,5,8-Me_3	2980	2937, 2886	1623, 1605, 1578w, 1513w	1465, 1453, 1406, 1384	1272w, 1216, 1153, 1142w, 1095w, 1070w, 1057, 1037, 1021w (1,2,3,4-tetra- and 1,4-di-)	817 (2 adj. H) 928w, 890w, 862, 847w, 765
Ir 1,4-Et_2-5,8-Me_2	3080, 3000	2953, 2898	1619w, 1608, 1588w, 1502w	1456, 1465, 1412w, 1381, 1320w	1214, 1152, 1057, 1035 (1,2,3,4-tetra- and 1,4-di-)	819 (2 adj. H) 907w, 884, 875, 855, 760w

1673 (Ar•CO) and at 1605, 1578, and 1504 cm.$^{-1}$ (C=C). Hydroxyl infrared absorption varied with the medium. In chloroform where hydrogen bonding is unlikely, the substance showed a band at 3583 cm.$^{-1}$ and in Nujol at 3450 cm.$^{-1}$ indicative of hydrogen bonding. Models show that hydrogen bonding in (XII) is possible. Attempts to dehydrate this compound with boiling acetic anhydride, and with phosphorus oxychloride, both of these alone and in pyridine, left the compound unaffected.

The spectra and properties of compound (XII) are reminiscent of those of the analogue (XIII) described by Cocker and Jenkinson,[15] and we feel justified in suggesting structure (XII), with its highly hindered and hydrogen-bonded carbonyl group, for the by-product.

EXPERIMENTAL

Ultraviolet spectra refer to ethanol solutions, and infrared spectra of oils to liquid films and of solids to Nujol mulls.

1-*Ethyl*-3-*methylnaphthalene* (Ia).—(i) 2-*Methyl*-4-*phenylhex*-3-*enoic acid* (IIIa). β-Benzoyl-α-methylpropionic acid [1] (cf. IIa; but R* = H) (38 g.) with diazomethane in methanol–ether gave *methyl* β-*benzoyl*-α-*methylpropionate* (IIa) (37 g.) as prisms (from light petroleum), m. p. 56° (Found: C, 69·9; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). (*a*) Ethylmagnesium iodide, from ethyl iodide (39 g.) and magnesium (6 g.) in dry ether (86 c.c.), was slowly added with stirring to a solution of the ester (5 g.) in ether (20 c.c.), and the mixture was refluxed for 1 hr. and set aside overnight. Decomposition of the complex with ice-cold hydrochloric acid afforded *methyl* 2-*methyl*-4-*phenylhex*-3-*enoate* (0·5 g.), b. p. 165°/17 mm., n_D^{20} 1·5194, $\lambda_{max.}$ 2435 Å (log ε 3·24), $\nu_{max.}$ 1770 cm.$^{-1}$ (CO_2Me) (Found: C, 77·0; H, 8·0. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%). (*b*) Methyl β-benzoyl-α-methylpropionate (IIa) (20·6 g., 0·1 mole) in dry ether (100 c.c.) was added dropwise with stirring to ethylmagnesium iodide (0·138 mole) [from ethyl iodide (21·5 g.)] in dry ether (50 c.c.), the mixture being kept at 0°. After 30 min. it was allowed to warm to room temperature and dry toluene (30 c.c.) was added. Ether was removed by distillation, and the residue was heated at 100° for 6 hr. and then worked up in the usual way. The required *acid* was obtained as a colourless oil (16 g.), b. p. 183°/17 mm., $\lambda_{max.}$ 2390 Å (log ε 3·91), $\nu_{max.}$ 1716 cm.$^{-1}$ (CO_2H) (Found: C, 76·2; H, 7·6. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%). Its S-*benzylisothiouronium salt* (colourless needles) had m. p. 126° (Found: C, 68·1; H, 6·4. $C_{21}H_{26}O_2N_2S$ requires C, 68·1; H, 7·1%).

(ii) 2-*Methyl*-4-*phenylhexanoic acid* (IVa). The acid (IIIa) (15 g.) was reduced in methanol (60 c.c.) with Raney nickel (1 g.) at 100°/70 atm. of hydrogen. The required *acid* (14·2 g.) distilled as a colourless oil (12·4 g.), b. p. 183°/17 mm., $\nu_{max.}$ 1706 cm.$^{-1}$ (Found: C, 76·0; H, 8·8. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%).

(iii) 4-*Ethyl*-1,2,3,4-*tetrahydro*-2-*methyl*-1-*oxonaphthalene* (Va). 2-Methyl-4-phenylhexanoic

---

[15] Cocker and Jenkinson, *J.*, 1954, 2420.

acid (12·4 g.) was added with stirring to cold polyphosphoric acid prepared by heating 90% phosphoric acid (33·4 c.c.) with phosphoric oxide (35·3 g.) at 165° for 1 hr. The mixture was heated at 165° for 5 min., cooled, and poured into cold water. The *tetralone* was extracted with ether, and the ether was washed with sodium carbonate solution, and distilled, giving an oil (8·5 g.), b. p. 101°/1 mm., $\nu_{max.}$ 1691 cm.$^{-1}$ (Ar·CO) (Found: C, 83·0; H, 8·5. $C_{13}H_{16}O$ requires C, 82·9; H, 8·6%).

(iv) 4-*Ethyl*-1,2,3,4-*tetrahydro*-2-*methylnaphthalene* (VIa). A mixture of the tetralone (Va) (3 g.), toluene (60 c.c.), acetic acid (5 c.c.), hydrochloric acid (200 c.c.), water (45 c.c.), and amalgamated zinc (80 g.) was refluxed for 60 hr. The toluene layer was separated, the aqueous layer was extracted with ether, and the combined extracts were dried and distilled, giving 4-*ethyl*-1,2,3,4-*tetrahydro*-2-*methylnaphthalene* (VIa) (1 g.), b. p. 71°/1 mm. (Found: C, 89·8; H, 9·9. $C_{13}H_{18}$ requires C, 89·6; H, 10·4%).

(v) 1-*Ethyl*-3-*methylnaphthalene* (Ia). The preceding compound (0·9 g.) was heated at 260—280° for 4 hr. with palladised charcoal (0·9 g.). The product, collected in ether, distilled from sodium as a colourless oil (0·2 g.), b. p. 140°/22 mm., n_D^{24} 1·5969 (Found: C, 91·6; H, 8·4. $C_{13}H_{14}$ requires C, 91·7; H, 8·3%). Its *picrate* consisted of brick-red needles (from methanol), m. p. 112·5° (Found: C, 57·6; H, 4·4. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·3%). Its *styphnate* crystallised as yellow needles (from acetic acid), m. p. 119·5° (Found: C, 54·8; H, 4·4. $C_{19}H_{17}O_8N_3$ requires C, 54·9; H, 4·1%). Its *trinitrobenzene adduct* (lemon needles from methanol) had m. p. 115° (Found: C, 59·2; H, 4·4. $C_{19}H_{17}O_6N_3$ requires C, 59·5; H, 4·4%). Its *trinitrotoluene adduct* (lemon needles from methanol) had m. p. 75° (Found: C, 59·3; H, 4·9. $C_{20}H_{19}O_6N_3$ requires C, 60·4; H, 4·8%).

β-*Benzoylbutyric Acid* (IIb).—α-Bromopropiophenone (45·5 g.) was added to a suspension of ethyl sodiomalonate, from sodium (6 g.) and ethyl malonate (45·5 g.) in dry benzene (200 c.c.). The mixture was heated at 100° for 6 hr., and the resulting ester was then hydrolysed with excess of methanolic potassium hydroxide. In this way (1-benzoylethyl)malonic acid (15 g.), m. p. 158°, was obtained. It was heated at 160° until effervescence had ceased and the product triturated with light petroleum, β-benzoylbutyric acid (5·5 g.), m. p. 56°, being obtained. It crystallised from water as colourless prisms, m. p. 58° (lit.,[1] m. p. 56—59°).

β-*Methyl*-γ-*phenylbutyric Acid* (IVb).—The preceding compound (IIb) was refluxed for 40 hr. with concentrated hydrochloric acid (20 c.c.), water (9 c.c.), toluene (12 c.c.), and amalgamated zinc (16 g.). The toluene layer was separated and the aqueous layer was extracted several times with ether. From the combined extracts β-methyl-γ-phenylbutyric acid (IVb) was obtained as an oil [16] (3·5 g.), b. p. 172°/15 mm. (Found: C, 73·4; H, 7·6. Calc. for $C_{11}H_{14}O_2$: C, 74·1; H, 7·9%). In the infrared spectrum it showed peaks at 1716 (CO_2H) and at 1794w cm.$^{-1}$, the latter probably due to the presence of some 3-methyl-4-phenylbut-3-en-1,4-olide.

1,2,3,4-*Tetrahydro*-3-*methyl*-1-*oxonaphthalene* (Vb).—The acid (IVb) (2·4 g.) was heated with concentrated sulphuric acid (16 c.c.) at 90° for 10 min., and the mixture was then poured into water. The tetralone was extracted with ether which was washed with sodium carbonate solution and then distilled. It was collected as an oil [17] (1 g.), b. p. 128°/14 mm. (Found: C, 81·5; H, 7·4. Calc. for $C_{11}H_{12}O$: C, 82·5; H, 7·55%).

1-*Ethyl*-3,4-*dihydro*-3-*methylnaphthalene* (VIIa).—The tetralone (0·9 g.) in ether (20 c.c.) was added to ethylmagnesium iodide [from ethyl iodide (5 c.c.)] in ether (30 c.c.) and the mixture was refluxed for 3 hr. Decomposition of the complex and collection of the product in ether afforded 1-ethyl-3,4-dihydro-3-methylnaphthalene (VIIa) (0·6 g.), b. p. 136°/14 mm.

3-*Ethyl*-1-*methylnaphthalene* (Ib).—(i) *Ethylsuccinic anhydride*. We found the following method to be preferable to the methods of Wren and Crawford [18] and of Smith and Horwitz.[19] Diethyl ethylmalonate (188 g.) was added slowly with stirring to sodium ethoxide, from sodium (23 g.) in ethanol (50 c.c.). The mixture was cooled in ice, and sodium iodide (1 g.) was added and followed by ethyl chloroacetate (122·5 g.) dropwise with stirring. The mixture was then refluxed for 20 hr. with stirring. Alcohol was removed by distillation, and the residue was diluted with water and extracted several times with ether from which triethyl butane-1,2,2-tricarboxylate was obtained as an oil (150 g.), b. p. 193°/60 mm. The ester was refluxed with

---

[16] Cf. Anschütz and Motschmann, *Annalen*, 1915, **407**, 84.
[17] Cf. von Braun and Stuckenschmidt, *Ber.*, 1923, **56**, 1724.
[18] Wren and Crawford, *J.*, 1937, 230.
[19] Smith and Horwitz, *J. Amer. Chem. Soc.*, 1949, **71**, 3418.

excess of concentrated hydrochloric acid until a clear solution was obtained which was then evaporated in a vacuum, giving ethylsuccinic acid (60 g.), m. p. 94°. A sample crystallised from benzene–ether had m. p. 97°. The acid of m. p. 94° (60 g.) was distilled and the fraction of b. p. 235—250° was collected. Redistillation gave ethylsuccinic anhydride (45 g.), b. p. 146°/25 mm.

(ii) β-*Benzoyl*-α-*ethylpropionic acid* (cf. IIc; but R* = H). Aluminium chloride (180 g.) was added with stirring to ethylsuccinic anhydride (74 g.) in ice-cold benzene (65 c.c.) and methylene chloride (225 c.c.), and the mixture was stirred for 18 hr. The required acid (78 g.; m. p. 81°) was obtained from the mixture in the usual way. It crystallised from light petroleum as needles,[4] m. p. 85° (Found: C, 70·4; H, 6·6. Calc. for $C_{12}H_{14}O_3$: C, 69·9; H, 6·8%). Its *methyl ester* (IIc) (prepared by use of methanolic sulphuric acid) distilled at 132°/1 mm. and had $\nu_{max.}$ 1730 (CO_2Me) and 1685 cm.$^{-1}$ (Ar·CO) (Found: C, 70·4; H, 7·2. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

(iii) 3-*Benzoyl*-2-*ethyl* 4-*phenylbut*-3-*enoic acid* (IId). A solution of benzaldehyde (1·06 g.) in methanol (15 c.c.) was added to a solution of the above ester (1 g.) and sodium methoxide (0·54 g.) in methanol (5 c.c.). The solution was heated at 40° for 10 min. and set aside overnight. Methanol was then removed, and the residue acidified with dilute hydrochloric acid and extracted with ether. The ethereal extract was washed with sodium bisulphite solution, dried, and distilled. The residue, crystallised from light petroleum, gave the *benzylidene derivative* (IId) (1·5 g.) as needles, m. p. 123°, $\nu_{max.}$ 1702 (CO_2H), 1651 (CO–C=C), 1600 cm.$^{-1}$ (C=C) (Found: C, 77·1; H, 6·1. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%).

(iv) 2-*Ethyl*-4-*phenylpent*-3-*enoic acid* (IIIb).—The method adopted was that used for the preparation of (IIa). Using methyl β-benzoyl-α-ethylpropionate (IIc) (30 g.) and methylmagnesium iodide [from methyl iodide (27·43 g.)] afforded the *acid* (IIIb) (19 g.), b. p. 135°/1 mm., m. p. 48—49°, which crystallised from light petroleum as needles, m. p. 50—51°, $\nu_{max.}$ 1700 (CO_2H) (Found: C, 76·6; H, 7·8. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%).

(v) α-*Ethyl*-γ-*phenylvaleric acid* (IVc). The preceding acid (32 g.) was hydrogenated over Raney nickel in methanol at 100°/80 atm., giving the methyl ester of acid (IVc). This was hydrolysed with 7·5% methanolic potassium hydroxide to the *acid* (IVc) (17 g.), b. p. 139°/1 mm., $\nu_{max.}$ 1700 (CO_2H) (Found: C, 75·2; H, 9·1. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%).

(vi) 2-*Ethyl*-1,2,3,4-*tetrahydro*-4-*methyl*-1-*oxonaphthalene* (Vc). Cyclisation of the previous compound (IVc) (17 g.) with polyphosphoric acid, from phosphoric acid (90%; 46 c.c.) and phosphorus pentoxide (4 g.), as described for compound (Va) gave the *tetralone* (Vc) (9 g.), b. p. 123°/1 mm., $\lambda_{max.}$ 2480 and 2890 Å (log ε 4·98 and 4·16 respectively), $\nu_{max.}$ 1680 cm.$^{-1}$ (Ar·CO) (Found: C, 82·3; H, 8·9. $C_{13}H_{16}O$ requires C, 82·9; H, 8·6%).

(vii) 3-*Ethyl*-1,2,3,4-*tetrahydro*-1-*methylnaphthalene* (VIb).—The tetralone (Vc) (3 g.), reduced as described for its analogue (VIa), gave the *tetralin* (VIb) (1 g.), b. p. 77°/1 mm. (Found: C, 89·0; H, 10·9. $C_{13}H_{18}$ requires C, 89·6; H, 10·4%).

(viii) 3-*Ethyl*-1-*methylnaphthalene* (Ib). The preceding tetralin (0·6 g.) was heated with palladised charcoal (0·6 g.) for 4·5 hr. at 260—270°, and the product was extracted with benzene. Distillation gave 3-ethyl-1-methylnaphthalene (Ib) as an oil in small yield. Its *picrate* (orange needles from methanol) had m. p. 83° (Found: C, 57·4; H, 5·0. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·3%).

1,6-*Diethylnaphthalene* (Ic).—(i) *Methyl* β-p-*ethylbenzoylpropionate* (IIe). β-*p*-Ethylbenzoyl propionic acid [5] (cf. IIe; but R* = H) (30 g.), when refluxed for 2 hr. with methanol (50 c.c.) and concentrated sulphuric acid (5 c.c.), gave the *keto-ester* (IIe) (28·8 g.), b. p. 134°/1 mm., m. p. 33°, $\nu_{max.}$ 1754 cm.$^{-1}$ (CO_2Me and Ar·CO) (Found: C, 70·4; H, 7·0. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

(ii) 4-p-*Ethylphenylhex*-3-*enoic acid* (IIIc). Ethylmagnesium iodide [from ethyl iodide (30·2 g.)] in ether (60 c.c.) was added to the ester (IIe) (28·8 g.) in dry ether (100 c.c.), and the reaction was completed as described for the preparation of the acid (IIIa). 4-p-*Ethylphenylhex*-3-*enoic acid* (IIIc) was obtained as an oil (12·5 g.), b. p. 182°/1 mm., $\nu_{max.}$ 1715 cm.$^{-1}$ (CO_2H) (Found: C, 77·2; H, 8·4. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%).

(iii) 4-p-*Ethylphenylhexanoic acid* (IVd). The unsaturated acid (IIIc) (12·5 g.) in methanol (100 c.c.) was hydrogenated over Raney nickel at 100°/110 atm., giving a mixture of saturated acid and ester, which was refluxed with 5% methanolic potassium hydroxide (50 c.c.) for 2 hr. The required *acid* (IVd) distilled as an oil (5·5 g.), b. p. 132—133°/1 mm., $\nu_{max.}$ 1700 cm.$^{-1}$ (CO_2H) (Found: C, 76·7; H, 9·4. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·15%).

(iv) 1,6-*Diethyl*-1,2,3,4-*tetrahydro*-4-*oxonaphthalene* (Vd). The previous compound (IVd) (12 g.) was cyclised with polyphosphoric acid, from phosphoric acid (90%; 33·4 c.c.) and phosphoric oxide (35·3 g.), at 165° for 3 min. The mixture was poured into water, and the product was extracted with ether, giving the required *tetralone* (Vd) (9·0 g.), b. p. 117—118°/1 mm., $\nu_{max.}$ 1680 cm.$^{-1}$ (Ar·CO) (Found: C, 83·2; H, 9·0. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%).

(v) 1,6-*Diethyl*-1,2,3,4-*tetrahydronaphthalene* (VIc). The tetralone (3·3 g.) in toluene (60 c.c.) was refluxed for 42 hr. with amalgamated zinc (80 g.), concentrated hydrochloric acid (100 c.c.), acetic acid (5 c.c.), and water (45 c.c.). 1,6-*Diethyl*-1,2,3,4-*tetrahydronaphthalene* (VIc) was produced as an oil (1·2 g.), b. p. 92°/1 mm. (Found: C, 89·4; H, 10·6. $C_{14}H_{20}$ requires C, 89·3; H, 10·7%).

(vi) 1,6-*Diethylnaphthalene* (Ic). The preceding compound (VIc) (1 g.), heated with palladised charcoal (1 g.) for 4 hr. at 260—280°, gave 1,6-*diethylnaphthalene* (Ic) (0·8 g.), b. p. 76°/1 mm., n_D^{21} 1·5806 (Found: C, 90·6; H, 9·0. $C_{14}H_{16}$ requires C, 91·25; H, 8·75%). Its picrate (orange needles from methanol) had m. p. 70°.

1,7-*Diethylnaphthalene* (Id).—(i) 1,7-*Diethyl*-3,4-*dihydronaphthalene* (VIIb). 7-Ethyl-1,2,3,4-tetrahydro-1-oxonaphthalene [20] (Ve) (7·7 g.) in ether (25 c.c.) was added to ethylmagnesium iodide [from ethyl iodide (12·3 g.)], and the mixture was refluxed for 3 hr. The product, consisting partly of alcohol and partly of dihydronaphthalene, was set aside with anhydrous formic acid (20 c.c.) for 2 hr. The mixture was poured into water and extracted with ether, giving 1,7-*diethyl*-3,4-*dihydronaphthalene* (VIIb) (5·7 g.), b. p. 79°/1 mm. (Found: C, 90·3; H, 9·6. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

(ii) 1,7-*Diethylnaphthalene* (Id). Dehydrogenation of the preceding compound (3 g.) with palladised charcoal at 260—270° for 4 hr. gave 1,7-*diethylnaphthalene* (Id) (2·5 g.), b. p. 87°/1 mm., n_D^{20} 1·5858 (Found: C, 91·2; H, 8·8. $C_{14}H_{16}$ requires C, 91·25; H, 8·75%). Its *picrate* (orange needles from methanol) had m. p. 78° (Found: C, 58·55; H, 4·8. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6%).

2-*Ethyl*-1,4-*dimethylnaphthalene* (Ie).—(i) 3-*Ethyl*-1,2-*dihydro*-1,4-*dimethylnaphthalene* (VIIc). 2-Ethyl-1,2,3,4-tetrahydro-4-methyl-1-oxonaphthalene (Vc) (1 g.) in dry ether (10 c.c.) was added with stirring to an ice-cold solution of methylmagnesium iodide, from methyl iodide (3·5 g.) in ether (25 c.c.). The mixture was refluxed for 7 hr. and set aside overnight. Decomposition of the complex with ice and ammonium chloride gave the *dihydronaphthalene* (VIIc) (0·6 g.), b. p. 75°/1 mm. (Found: C, 90·2; H, 10·0. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

(ii) 2-*Ethyl*-1,4-*dimethylnaphthalene* (Ie). The dihydronaphthalene (0·4 g.), heated at 260—280° for 4·5 hr. with palladised charcoal, gave an oil which was directly converted into its *trinitrobenzene adduct*. This crystallised from methanol as yellow needles, m. p. 123° (Found: C, 59·6; H, 4·5. $C_{20}H_{19}O_6N_3$ requires C, 60·4; H, 4·8%).

4-*Ethyl*-1,2-*dimethylnaphthalene* (If).—4-Ethyl-1,2,3,4-tetrahydro-2-methyl-1-oxonaphthalene (Va) (2·5 g.) in dry ether (10 c.c.) was added, with stirring, to an ice-cold solution of methylmagnesium iodide, from methyl iodide (3·8 g.), in ether (40 c.c.). After 2 hours' refluxing the complex was decomposed with ice and ammonium chloride, and the solution was extracted with ether, from which 4-*ethyl*-1,2,3,4-*tetrahydro*-1-*hydroxy*-1,2-*dimethylnaphthalene* was isolated. A sample crystallised from light petroleum as hexagonal prisms, m. p. 73° (Found: C, 82·3; H, 9·8. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%). The remainder of the tetralol was set aside for 2 hr. with anhydrous formic acid (10 c.c.) and then diluted with water. Extraction with ether gave 1-*ethyl*-1,2-*dihydro*-3,4-*dimethylnaphthalene* (VIId) which distilled from sodium as a colourless oil (1·4 g.), b. p. 150°/1 mm. (Found: C, 89·9; H, 9·65. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

This dihydro-compound (1·3 g.) was heated with palladised charcoal (1·3 g.) for 4 hr. at 260—280°, and the product was extracted with methanol, giving 4-*ethyl*-1,2-*dimethylnaphthalene* (If) (0·8 g.), b. p. 136°/1 mm., n_D^{23} 1·6021 (Found: C, 91·3; H, 8·7. $C_{14}H_{16}$ requires C, 91·25; H, 8·75%). Its *picrate* (orange needles from methanol) had m. p. 117° (Found: C, 57·6; H, 4·6. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6%). Its *trinitrobenzene* adduct (golden needles from methanol) had m. p. 118° (Found: C, 60·3; H, 4·7. $C_{20}H_{19}O_6N_3$ requires C, 60·45; H, 4·8%). Its *styphnate* (orange needles from acetic acid) had m. p. 119° (Found: C, 55·3; H, 4·6. $C_{20}H_{19}O_8N_3$ requires C, 55·9; H, 4·5%).

1-*Ethyl*-2,4-*dimethylnaphthalene* (Ig).—(i) 2-*Methyl*-4-*phenylpent*-3-*enoic acid* (IIId).

---

[20] Krollpfeiffer and Schäfer, *Ber.*, 1923, **56**, 620; Levy, *Ann. Chim.* (*France*), 1938, **9**, 75.

Methyl β-benzoyl-α-methylpropionate (IIa) (14 g.) in dry ether (75 c.c.) was added to methylmagnesium iodide [from methyl iodide (13·3 g.)], then refluxed for 3 hr. and set aside for 18 hr. The complex was decomposed, the mixture was extracted with ether, and the ethereal solution was washed with 5% sodium carbonate from which 2-*methyl*-4-*phenylpent*-3-*enoic acid* (IIId) was isolated by acidification as an oil (3 g.), b. p. 150°/1 mm., $\nu_{\text{max.}}$ 1712 cm.$^{-1}$ (CO_2H) (Found: C, 75·6; H, 7·0. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%). The ethereal extract afforded a neutral compound as a pale yellow oil (6·5 g.), b. p. 118°/1 mm., $\nu_{\text{max.}}$ 1778 cm.$^{-1}$ (CO_2Me or lactone). Hydrolysis of the oil with 5% methanolic potassium hydroxide (36 c.c.) for 3 hr. gave the required acid (IIId) (5 g.).

(ii) α-*Methyl*-γ-*phenylvaleric acid* (IVe). The unsaturated acid (12 g.) in methanol (50 c.c.) was hydrogenated over Raney nickel (1 g.) at 100°/70 atm., giving the saturated ester which was not isolated. Hydrolysis with 5% methanolic potassium hydroxide (100 c.c.) for 2 hr. gave α-*methyl*-γ-*phenylvaleric acid* (IVe) (10 g.), b. p. 125°/1 mm., $\nu_{\text{max.}}$ 1713 cm.$^{-1}$ (CO_2H). (Found: C, 74·6; H, 8·4. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%).

(iii) 1,2,3,4-*Tetrahydro*-2,4-*dimethyl*-1-*oxonaphthalene* (Vf). The previous compound (4·8 g.) was heated at 165° for 3 min. with polyphosphoric acid prepared from phosphoric acid (16·7 c.c.) and phosphoric oxide (17·6 g.). The required *tetralone* (Vf) was obtained as a colourless oil (2·6 g.), b. p. 88—89°/1 mm., $\nu_{\text{max.}}$ 1694 cm.$^{-1}$ (Ar·CO) (Found: C, 82·4; H, 8·1. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%).

(iv) 4-*Ethyl*-1,2-*dihydro*-1,3-*dimethylnaphthalene* (VIIe). The tetralone (Vf) (1·4 g.) in dry ether (10 c.c.) was added to ethylmagnesium iodide [from ethyl iodide (3·8 g.)] in ether (40 c.c.) and refluxed for 3 hr. The complex was decomposed with ice and ammonium chloride and extracted with ether from which 4-*ethyl*-1,2-*dihydro*-4-*hydroxy*-1,3-*dimethylnaphthalene* was obtained (0·9 g.) as hexagonal prisms, m. p. 85° (from light petroleum) (Found: C, 81·9; H, 9·5. $C_{14}H_{20}O$ requires C, 82·3; H, 9·9%). This alcohol was set aside for 2 hr. in anhydrous formic acid (10 c.c.), giving 4-*ethyl*-1,2-*dihydro*-1,3-*dimethylnaphthalene* (VIIe) (0·7 g.), b. p. 95°/1 mm. (Found: C, 89·5; H, 9·3. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

(v) 1-*Ethyl*-2,4-*dimethylnaphthalene* (Ig). The preceding compound (0·6 g.) was heated with palladised charcoal (0·6 g.) for 3 hr. at 260—280°. The mixture, extracted with benzene, afforded 1-*ethyl*-2,4-*dimethylnaphthalene* (1 g.) (0·4 g.), b. p. 109°/2 mm., n_D^{23} 1·5975 (Found: C, 91·5; H, 8·8. $C_{14}H_{16}$ requires C, 91·25; H, 8·75%). Its *picrate* (orange needles from methanol) had m. p. 94° (Found: C, 57·8; H, 4·6. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6%).

1-*Ethyl*-4,6-*dimethylnaphthalene* (Ih).—(i) 4-p-*Tolylhex*-3-*enoic acid* (IIIe). Methyl β-p-toluoylpropionate (cf. ref. 6) (IIf) [$\nu_{\text{max.}}$ 1722 (CO_2Me), 1675 cm.$^{-1}$ (Ar·CO)] (41 g.) in ether (100 c.c.) was slowly treated with ethylmagnesium iodide [from ethyl iodide (43 g.)] in ether (160 c.c.), and the reaction was completed as described for the preparation of (IIIa). 4-p-*Tolylhex*-3-*enoic acid* (IIIe) was obtained as a colourless oil (15 g.), b. p. 137—141°/1 mm., $\nu_{\text{max.}}$ 1710 cm.$^{-1}$ (CO_2H) (Found: C, 75·6; H, 7·6. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%).

(ii) 4-p-*Tolylhexanoic acid* (IVf). The unsaturated acid (20 g.), when hydrogenated in methanol (75 c.c.) over Raney nickel (2 g.) at 100°/80 atm., gave *methyl* 4-p-*tolylhexanoate* (20 g.), b. p. 99°/1 mm., $\nu_{\text{max.}}$ 1740 cm.$^{-1}$ (CO_2Me) (Found: C, 76·5; H, 9·1. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·15%). Hydrolysis of the ester with 5% methanolic potassium hydroxide (120 c.c.) gave 4-p-*tolylhexanoic acid* (IVf) (17 g.), b. p. 155°/1 mm., m. p. 36° (Found: C, 75·1; H, 8·9. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%).

(iii) 4-*Ethyl*-1,2,3,4-*tetrahydro*-7-*methyl*-1-*oxonaphthalene* (Vg). The preceding compound (IVf) (16 g.) was heated at 165° with polyphosphoric acid, from phosphoric acid (90%; 44·5 c.c.) and phosphoric oxide (48 g.), for 5 min. The mixture was extracted with ether, giving the required *tetralone* (Vg) (15 g.), b. p. 134°/2 mm., $\lambda_{\text{max.}}$ 2540 and 2950 Å (log ε 4·21 and 3·74 respectively), $\nu_{\text{max.}}$ 1683 cm.$^{-1}$ (Ar·CO) (Found: C, 83·3; H, 8·5. $C_{13}H_{16}O$ requires C, 83·0; H, 8·6%). Its *semicarbazone* (rhombs from dilute alcohol) had m. p. 165—166° (Found: C, 68·2; H, 8·0. $C_{14}H_{19}ON_3$ requires C, 68·5; H, 7·8%).

(iv) 1-*Ethyl*-1,2-*dihydro*-4,6-*dimethylnaphthalene* (VIIf). 4-Ethyl-1,2,3,4-tetrahydro-7-methyl-1-oxonaphthalene (Vg) (5 g.) in ether (25 c.c.) was added to methylmagnesium iodide [from methyl iodide (7·1 g.)] in ether (50 c.c.), and the mixture was refluxed for 3·5 hr. The complex was decomposed with ice and ammonium chloride, giving the *dihydro-compound* (VIIf) (3 g.), b. p. 115°/1 mm. (Found: C, 89·6; H, 9·3. $C_{14}H_{18}$ requires C, 90·3; H, 9·7%).

(v) 1-*Ethyl*-4,6-*dimethylnaphthalene* (Ih). The preceding compound (2 g.) was heated with palladised charcoal (2 g.) at 260—280° for 4 hr., and the product was extracted with benzene.

1-*Ethyl*-4,6-*dimethylnaphthalene* (Ih) distilled from sodium as a colourless oil (1·3 g.), b. p. 85°/1 mm. (Found: C, 91·6; H, 8·4. $C_{14}H_{16}$ requires C, 91·25; H, 8·75%). Its *picrate* (orange needles from methanol) had m. p. 85° (Found: C, 57·4; H, 4·2. $C_{20}H_{19}O_7N_3$ requires C, 58·1; H, 4·6%). Its *trinitrobenzene adduct* (yellow needles from methanol) had m. p. 109° (Found: C, 60·7; H, 4·5. $C_{20}H_{19}O_6N_3$ requires C, 60·4; H, 4·8%).

1,4-*Diethyl*-2-*methylnaphthalene* (Ij).—4-Ethyl-1,2,3,4-tetrahydro-2-methyl-1-oxonaphthalene (Va) (2·9 g.) in ether (15 c.c.) was added to ethylmagnesium iodide [from ethyl iodide (4·1 g.)] in ether (40 c.c.), and the mixture was refluxed for 4 hr. The complex, decomposed with ice and ammonium chloride, gave a colourless oil consisting largely of alcohol. This was set aside for 2 hr. in anhydrous formic acid (10 c.c.), then poured into water and extracted with ether from which 1,4-*diethyl*-1,2-*dihydro*-3-*methylnaphthalene* (VIIg) was obtained as a colourless oil (1·5 g.), b. p. 140°/1 mm. (Found: C, 89·5; H, 9·8. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%).

This product (9·4 g.) was heated with palladised charcoal (1·4 g.) for 4 hr. at 260—280°, giving 1,4-*diethyl*-2-*methylnaphthalene* (Ij) (0·8 g.), b. p. 142°/1 mm., n_D^{21} 1·5935 (Found: C, 91·2; H, 8·8. $C_{15}H_{18}$ requires C, 90·85; H, 9·15%). Its *picrate* (orange-red needles from methanol) had m. p. 62° (Found: C, 59·1; H, 4·9. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·95%). Its *trinitrobenzene adduct* (golden-yellow needles from methanol) had m. p. 97° (Found: C, 61·1; H, 4·9. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·15%). Its *trinitrotoluene adduct* (yellow needles from methanol) had m. p. 68° (Found: C, 61·8; H, 5·2. $C_{22}H_{23}O_6N_3$ requires C, 62·2; H, 5·45%).

1,4-*Diethyl*-6-*methylnaphthalene* (Ik).—4-Ethyl-1,2,3,4-tetrahydro-7-methyl-1-oxonaphthalene (Vg.) (5 g.) in ether (25 c.c.) was added to ethylmagnesium iodide [from ethyl iodide (7·8 g.)] in ether (50 c.c.), and the mixture was refluxed for 4 hr. Decomposition of the complex with ice and ammonium chloride gave the *dihydro-compound* (VIIh) which distilled from sodium as a colourless oil (2·7 g.), b. p. 123°/2 mm (Found: C, 90·1; H, 10·0. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%).

The dihydro-compound (2 g.) was heated with palladised charcoal (2 g.) at 260—280° for 4 hr., and the product was extracted with benzene. Distillation from sodium gave 1,4-*diethyl*-6-*methylnaphthalene* (Ik) (1·2 g.), b. p. 112°/1 mm. (Found: C, 90·2; H, 9·1. $C_{15}H_{18}$ requires C, 90·85; H, 9·15%). Its *picrate* (orange needles from methanol) had m. p. 71—72° (Found: C, 59·2; H, 5·3. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·95%). Its *trinitrobenzene adduct* (yellow needles from methanol) had m. p. 101° (Found: C, 61·1; H, 5·3. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·15%).

1,6-*Diethyl*-4-*methylnaphthalene* (Il).—1,6-Diethyl-1,2,3,4-tetrahydro-4-oxonaphthalene (Vd) (3·3 g.) in ether (10 c.c.) was added to methylmagnesium iodide [from methyl iodide (2 c.c.)] in ether (50 c.c.), and the mixture was refluxed for 2 hr. The product, largely the alcohol, was set aside in anhydrous formic acid (12 c.c.) for 2 hr., giving 1,6-*diethyl*-1,2-*dihydro*-4-*methylnaphthalene* (VIIj) (3 g.), b. p. 89°/1 mm. (Found: C, 89·8; H, 9·9. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%).

This product (1·4 g.), heated for 4 hr. with palladised charcoal (1·4 g.) at 260—280°, gave 1,6-*diethyl*-4-*methylnaphthalene* (Il) (1·1 g.), b. p. 90°/1 mm., n_D^{21} 1·5859 (Found: C, 91·0; H, 9·1. $C_{15}H_{18}$ requires C, 90·85; H, 9·15%). Its *picrate* (orange needles from methanol) had m. p. 56° (Found: C, 59·1; H, 6·0. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·95%). Its *trinitrobenzene adduct* (lemon needles from methanol) had m. p. 80° (Found: C, 60·9; H, 5·0. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·15%).

4,6-*Diethyl*-1-*methylnaphthalene* (Im).—(i) 4-p-*Ethylphenylpent*-3-*enoic acid* (IIIf). Methyl β-*p*-ethylbenzoylpropionate (IIe) (84·4 g.) in ether (250 c.c.) was treated with methylmagnesium iodide [from methyl iodide (75·2 g.)] in ether (150 c.c.), and the reaction completed by 5 hours' refluxing. 4-p-*Ethylphenylpent*-3-*enoic acid* (IIIf) was obtained as an oil (6·5 g.), b. p. 138°/1 mm., $\nu_{max.}$ 1719 cm.$^{-1}$ (CO_2H) (Found: C, 76·7; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%). The product of the Grignard reaction before fractionation showed evidence of substantial amounts of a lactone ($\nu_{max.}$ 1778 cm.$^{-1}$), probably γ-methyl-γ-*p*-ethylphenylbutyrolactone.

(ii) γ-p-*Ethylphenylvaleric acid* (IVg). The crude product (10 g.) of the previous reaction was hydrogenated for 6 hr. in methanol (50 c.c.) over Raney nickel (1 g.) at 100°/110 atm., and then hydrolysed with 5% methanolic potassium hydroxide (100 c.c.). The required γ-p-*ethylphenylvaleric acid* (IVg) was isolated as an oil (9·5 g.), b. p. 137°/1 mm., $\nu_{max.}$ 1706 cm.$^{-1}$ (CO_2H) (Found: C, 76·0; H, 8·7. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·8%).

(iii) 6-*Ethyl*-1,2,3,4-*tetrahydro*-1-*methyl*-4-*oxonaphthalene* (Vh). γ-*p*-Ethylphenylvaleric acid (6 g.), cyclised with polyphosphoric acid [from phosphoric acid (90%; 25·1 c.c.) and phosphoric oxide (26·5 g.)] at 165° for 5 min., gave the *tetralone* (Vh) (4·5 g.), b. p. 113°/1 mm., $\nu_{max.}$ 1682 cm.$^{-1}$ (Found: C, 82·8; H, 8·7. $C_{13}H_{16}O$ requires C, 82·9; H, 8·6%).

(iv) 4,6-*Diethyl*-1,2-*dihydro*-1-*methylnaphthalene* (VIIk). The tetralone (Vh) (2·5 g.) in ether (15 c.c.) was added to ethylmagnesium iodide [from ethyl iodide (6·7 g.)] in ether (20 c.c.), and the mixture was refluxed for 4 hr. The product was set aside for 2 hr. in anhydrous formic acid (10 c.c.), giving 4,6-*diethyl*-1,2-*dihydro*-1-*methylnaphthalene* (VIIk) (1·6 g.), b. p. 96°/1 mm. (Found: C, 89·75; H, 10·0. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%).

(v) 4,6-*Diethyl*-1-*methylnaphthalene* (Im). The preceding compound (1·2 g.) was heated for 4 hr. with palladised charcoal (1·2 g.) at 260—270°. 4,6-*Diethyl*-1-*methylnaphthalene* (Im) was obtained as a colourless oil (0·9 g.), b. p. 110°, n_D^{26} 1·5808 (Found: C, 91·1; H, 9·2. $C_{15}H_{18}$ requires C, 90·85; H, 9·15%). Its *picrate* (orange needles from methanol) had m. p. 76·5° (Found: C, 59·05; H, 5·0. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·95%).

1,4,6-*Triethylnaphthalene* (In).—1,6-Diethyl-1,2,3,4-tetrahydro-4-oxonaphthalene (Vd) (4 g.) in ether (12 c.c.) was added to ethylmagnesium iodide [from ethyl iodide (3·3 c.c.)] in ether (50 c.c.), and the mixture was refluxed for 2 hr. The product was set aside for 2 hr. in anhydrous formic acid (10 c.c.), giving 1,4,6-*triethyl*-1,2-*dihydronaphthalene* (VIIl) (3·1 g.), b. p. 119°/1 mm. (Found: C, 89·9; H, 10·1. $C_{16}H_{22}$ requires C, 89·65; H, 10·35%).

This product (2·9 g.) was heated with palladised charcoal (2·9 g.) at 260—280° for 4 hr., giving 1,4,6-*triethylnaphthalene* (In) (2 g.), b. p. 128°/2 mm., n_D^{25} 1·5770 (Found: C, 90·4; H, 9·4. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%). Its *picrate* (red-orange needles from methanol) had m. p. 53° (Found: C, 59·9; H, 5·0. $C_{22}H_{23}O_7N_3$ requires C, 59·9; H, 5·25%).

1-*Ethyl*-4,5,8-*trimethylnaphthalene* (Ip).—(i) *Methyl* β-(2,5-*dimethylbenzoyl*)*propionate* (IIg) (21 g.) was obtained as an oil, b. p. 148°/1 mm., n_D^{19} 1·5202, $\nu_{max.}$ 1754 cm.$^{-1}$ (CO_2Me) (Found: OMe, 14·0. $C_{13}H_{16}O_3$ requires OMe, 14·1%), when the corresponding acid [6] (30 g.) was refluxed for 2 hr. with methanol (60 c.c.) and sulphuric acid (3 c.c.).

(ii) 4-(2,5-*Dimethylphenyl*)*hex*-3-*enoic acid* (IIIg). The ester (IIg) (15 g.) in ether (20 c.c.) was treated with ethylmagnesium iodide [from ethyl iodide (14·3 g.)] in ether (60 c.c.), and the reaction was completed during 18 hr. as described for the preparation of (IIIa). The required *acid* (IIIg) was obtained as an oil (5 g.), b. p. 146°/1 mm., $\nu_{max.}$ 1715 cm.$^{-1}$ (Found: C, 76·5; H, 8·1. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%), along with recovered keto-acid.

(iii) 4-(2,5-*Dimethylphenyl*)*hexanoic acid* (IVh).—The unsaturated acid (30 g.) was hydrogenated in methanol (80 c.c.) over Raney nickel (2 g.) at 100°/120 atm., giving *methyl* 4-(2,5-*dimethylphenyl*)*hexanoate* (32 g.), b. p. 133°/1 mm., $\nu_{max.}$ 1745 cm.$^{-1}$ (Found: C, 77·6; H, 8·9. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%). The ester was refluxed for 6 hr. with 5% methanolic potassium hydroxide (160 c.c.), giving the required *acid* (IVh) (22·5 g.), b. p. 149°/1 mm., $\nu_{max.}$ 1715 cm.$^{-1}$ (Found: C, 76·8; H, 8·9. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·15%).

(iv) 1-*Ethyl*-1,2,3,4-*tetrahydro*-5,8-*dimethyl*-4-*oxonaphthalene* (Vj). The preceding compound (12·4 g.) was heated at 165° for 5 min. with polyphosphoric acid [from phosphoric acid (90%; 33·4 g.) and phosphoric oxide (35·3 g.)], giving the *tetralone* (Vj) (7·8 g.), b. p. 121°/1 mm., $\nu_{max.}$ 1675 cm.$^{-1}$ (Ar·CO) (Found: C, 83·1; H, 8·3. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%).

(iii) 1-*Ethyl*-1,2-*dihydro*-4,5,8-*trimethylnaphthalene* (VIIm). The tetralone (3 g.) in ether (15 c.c.) was added to methylmagnesium iodide [from methyl iodide (4·2 g.)] in ether (40 c.c.), and the mixture was refluxed for 14 hr., giving the 1,2-*dihydro-compound* (VIIm) (0·4 g.), b. p. 120°/1 mm. (Found: C, 89·6; H, 10·0. $C_{15}H_{20}$ requires C, 89·9; H, 10·1%).

(iv) 1-*Ethyl*-4,5,8-*trimethylnaphthalene* (Ip). This dihydro-compound (0·4 g.), heated for 3 hr. with palladised charcoal (0·4 g.) at 260—280°, gave 1-*ethyl*-4,5,8-*trimethylnaphthalene* (Ip) (0·2 g.), b. p. 118°/3 mm., n_D^{19} 1·5841 (Found: C, 90·5; H, 9·2. $C_{15}H_{18}$ requires C, 90·85; H, 9·15%). Its *picrate* (brick-red needles from methanol) had m. p. 110° (Found: C, 59·1; H, 4·3. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·95%).

1,4-*Diethyl*-5,8-*dimethylnaphthalene* (Ir).—1-Ethyl-1,2,3,4-tetrahydro-5,8-dimethyl-4-oxonaphthalene (Vj) (5 g.) in ether (25 c.c.) was added to ethylmagnesium iodide [from ethyl iodide (7·7 g.)] in ether (60 c.c.), and the mixture was refluxed for 9 hr. The product was set aside for 2 hr. in anhydrous formic acid (20 c.c.), giving 1,4-*diethyl*-1,2-*dihydro*-5,8-*dimethylnaphthalene* (VIIn) (1·7 g.), b. p. 101°/1 mm. (Found: C, 89·5; H, 9·9. $C_{16}H_{22}$ requires C, 89·65; H, 10·35%).

This product (1·3 g.) was heated for 4 hr. at 260—280° with palladised charcoal (1·3 g.), giving 1,4-*diethyl*-5,8-*dimethylnaphthalene* (Ir) (1 g.), b. p. 107°/1 mm., n_D^{20} 1·5844 (Found: C, 90·6; H, 9·3. $C_{16}H_{20}$ requires C, 90·5; H, 9·5%). Its *picrate* (orange needles from methanol) had m. p. 135° (Found: C, 59·8; H, 5·1. $C_{22}H_{23}O_7N_3$ requires C, 59·9; H, 5·25%).

1-*Methoxy*-8-*methylnaphthalene* (Iu) *and* 8-*Methyl*-1-*naphthol* (Iv).—(i) β-o-*Methoxyphenylbutyryl chloride* (X; R = Cl). β-*o*-Methoxyphenylbutyric acid [21] (X; R = OH) (25 g.) was refluxed for 1 hr. with thionyl chloride (20 c.c.) and the product distilled. The acid chloride was collected as a golden-yellow oil (24·7 g.), b. p. 144—145°/3 mm.

(ii) γ-o-*Methoxyphenylvaleramide* (XI; R = NH_2). The acid chloride (X; R = Cl) (26·1 g.) in ether (150 c.c.) was slowly added to a stirred, ice-cold solution of diazomethane (12·1 g.) in ether (700 c.c.), and the mixture was set aside for 2 days. The solvent was then removed, the residue was dissolved in dioxan (257 c.c.) at 50°, a mixture of 30% aqueous ammonia (150 c.c.) and 10% aqueous silver nitrate (40 c.c.) was rapidly added and the whole was then heated on the water-bath for 2 hr. After filtration, the dioxan and water were removed under reduced pressure, and the oily residue was collected in ether, dried, and recovered. It was triturated with light petroleum, giving γ-o-*methoxyphenylvaleramide* (XI; R = NH_2) (16·2 g.) which crystallised from benzene as needles, m. p. 76° (Found: C, 69·6; H, 8·4. $C_{12}H_{17}O_2N$ requires C, 69·5; H, 8·3%).

(iii) γ-o-*Methoxyphenylvaleric acid* (XI; R = OH). The amide (16·2 g.) was refluxed for 5 hr. with 15% aqueous potassium hydroxide (100 c.c.), then acidified and extracted with ether, giving the *acid* (16 g.) which recrystallised from light petroleum as prisms, m. p. 66—67° (Found: C, 69·5; H, 7·8. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%).

(iv) 1,2,3,4-*Tetrahydro*-5-*methoxy*-4-*methyl*-1-*oxonaphthalene* (Vk). The preceding compound (15 g.) was heated at 165° for 5 min. with polyphosphoric acid, from phosphoric acid (90%; 52·6 c.c.) and phosphoric oxide (63·2 g.). The mixture was cooled, poured on ice, and extracted with ether. The extract was washed with water, 5% sodium carbonate solution, and water, and then dried. When the solvent was removed a solid and an oil remained. The solid (XII) was collected and crystallised from ethyl acetate as colourless needles (4·1 g.), m. p. 242° (Found: C, 75·5; H, 7·2; OMe, 16·25. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4; OMe, 16·3%). The oil from the filtrate was distilled, giving 1,2,3,4-*tetrahydro*-5-*methoxy*-4-*methyl*-1-*oxonaphthalene* (Vk) (5·5 g.), b. p. 107°/1 mm., $\nu_{max.}$ 1686 cm.$^{-1}$ (Ar·CO) (Found: C, 75·9; H, 7·5. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

(v) 1,2,3,4-*Tetrahydro*-5-*methoxy*-4-*methylnaphthalene* (VId). The tetralone (Vk) (5·5 g.) was reduced during 30 hr. with amalgamated zinc (69 g.) in concentrated hydrochloric acid (69 c.c.), water (42 c.c.), acetic acid (1·5 c.c.), and toluene (20 c.c.). The *methoxytetralin* (VId) distilled from sodium as a colourless oil (3·3 g.), b. p. 78° (Found: C, 82·2; H, 8·9. $C_{12}H_{16}O$ requires C, 81·8; H, 9·15%).

(vi) 1-*Methoxy*-8-*methylnaphthalene* (Iu). (*a*) The methoxytetralin (3·4 g.), heated for 4 hr. at 260—280° with palladised charcoal (3·4 g.), yielded a mixture of 1-methylnaphthalene (2·1 g.), b. p. 60°/1 mm. (Found: C, 93·1; H, 7·0. Calc. for $C_{11}H_{10}$: C, 92·9; H, 7·1%) (picrate, m. p. and mixed m. p. 143°), and 1-*methoxy*-8-*methylnaphthalene* (Iu) (0·1 g.), b. p. 98°/1 mm. [*picrate* (red-orange needles from methanol), m. p. 154° (Found: C, 53·5; H, 3·7. $C_{18}H_{15}O_8N_3$ requires C, 53·9; H, 3·8%)]. (*b*) The tetralin (2·2 g.) was heated for 3 hr. with sulphur (0·4 g.) at 220—230°, giving 1-methoxy-8-methylnaphthalene (Iu) (1·2 g.), b. p. 105°/2 mm., n_D^{26} 1·5625, $\lambda_{max.}$ 2290, 2800, 2920, and 3260 Å (log ε 4·48, 3·54, 3·55, and 2·98 respectively), whose picrate was identical with that described above.

(vii) 8-*Methyl*-1-*naphthol* (Iv). 1-Methoxy-8-methylnaphthalene (Iu) was refluxed for 2 hr. with hydriodic acid (*d* 1·7; 30 c.c.) and acetic acid (33 c.c.). The solution was cooled, diluted, and extracted with ether. The ether extract was washed with water and then extracted with 10% sodium hydroxide solution. The alkaline extract was acidified and the product was collected in ether from which the naphthol was obtained as an oil (0·3 g.), b. p. 110°/4 mm. Its *picrate* (red-orange needles from methanol) had m. p. 190° (Found: C, 52·3; H, 3·3. $C_{17}H_{13}O_8N_3$ requires C, 52·7; H, 3·3%).

The authors thank the Government of the Republic of Ireland for Research Maintenance Grants awarded to L. O. H. and J. McC.

University Chemical Laboratory,
Trinity College, Dublin.

[*Received, November* 19*th*, 1959.]

---

[21] Woodruff, *Org. Synth.*, 1944, **24**, 69.