8-Hydroxy-1-naphthoyl Compounds

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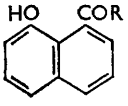
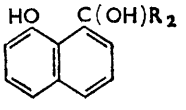
The lactone of 8-hydroxy-1-naphthoic acid reacts with nucleophilic reagents to give a variety of 8-hydroxy-1-naphthoyl compounds. In these an intramolecular hydrogen bond unites the hydroxy- and carbonyl functions and strongly affects ultraviolet and visible spectra, but only in non-basic solvents. The reactions of these compounds in strong acid, and their mass spectra, are also dependent on *peri*-ring closures.

EXCEPT for 8-hydroxy-1-naphthoic acid (Ia),[1] and its methyl ester (Ib),[2] compounds of the general type (I) have not been described. Since they possess a carbonyl and a hydroxy-group in close proximity, special reactivity might be expected; and they are potentially precursors of *peri*-fused tricyclic systems. We report the preparation of a dozen compounds of this structural type [(Ib)—(Im)] from the lactone (V). This lactone represents a tricyclic aromatic system and its reactions might not be entirely typical of γ-lactones; its nucleus is probably strained, since the C(1)–C(8) distance in naphthalene is nearly twice the length of the single C–O bond in esters, and the naphthalene nucleus can be distorted in *peri*-disubstituted compounds;[3a] consequently the lactone ring in (V) might be exceptionally easy to cleave. This is so; the lactone reacts rapidly with sodium borohydride to give 8-hydroxymethyl-1-naphthol (IIa), whereas γ-lactones are not usually reduced by this reagent.[3b] Ring strain in lactone (V) also explains the failure of 8-hydroxy-1-naphthoic acid to lactonise in acidic solutions, even though it is a γ-hydroxy-acid; in contrast, 8-amino-1-naphthoic acid dehydrates to give a lactam in solution.[3b] Consequently, 8-hydroxy-1-naphthoic acid cannot be an intermediate in the preparation of lactone (V) by diazotisation of 8-amino-1-naphthoic acid,[1] and the carboxy-group of the latter must directly displace nitrogen from the diazonium grouping during the decomposition of the diazonium salt (IV) in water.



(I)

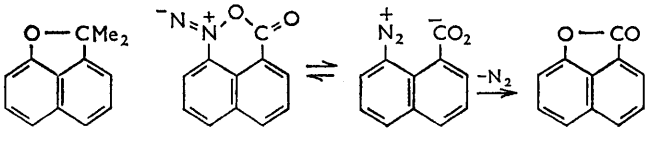
R	
a;	OH
b;	OMe
c;	OEt
d;	OPr^i
e;	OBu^t
f;	*N*-Pyrrolidinyl)



(II)

R	
a;	H
b;	Ph
c;	Me

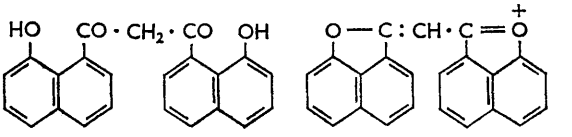
R	
g;	Ph
h;	Me
i;	CH_2·SO·Me
j;	CH_2·CO_2Et
k;	CH_2·CO_2H
l;	CH_2·Ac
m;	CH_2·Bz



(III) (IV) (V)

Lactone (V) undergoes easy and complete methanolysis in acidic conditions to give the ester (Ib); the ethyl and isopropyl ester (Ic and d) can be prepared analogously. t-Butyl 8-hydroxy-1-naphthoate (Ie) was prepared by the reaction of lactone (V) with potassium t-butoxide, and analogous cleavage with pyrrolidine gave *N*-(8-hydroxy-1-naphthoyl)pyrrolidine (If).

No 8-hydroxy-1-naphthyl ketones have been prepared previously, and it was thought that treatment of the lactone (V) with limited amounts of Grignard reagents might afford these compounds rather than tertiary alcohols. With phenylmagnesium bromide (1 mol.) the lactone yielded 8-benzoyl-1-naphthol (Ig) (47%), though an excess of reagent gave the diol (IIb). Lactone (V) was treated with methylmagnesium iodide, but decomposition of the initial product with acid gave an intractable product. When the reaction mixture was decomposed instead with a neutral solution of sodium ethylenediaminetetra-acetate, a solid yellow magnesium complex was formed, which when hydrolysed gave bis-(8-hydroxy-1-naphthoyl)methane (VI). This compound gives intense blue solutions with hydrochloric acid in acetic acid, presumably owing to formation of the cation (VII). The remainder of the reaction product contained unreacted lactone (V) and 8-acetyl-1-naphthol (Ih); the presence of diol (IIc), suggested by chromato-



(VI) (VII)

graphic analysis, was confirmed by n.m.r. spectroscopy and by isolation of the product of its spontaneous dehydration, the cyclic ether (III). Table 1 shows the effect of varying the procedure on the amounts of products.

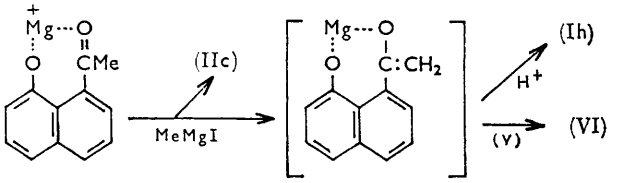
TABLE 1

	Molar yields from lactone (V)			
	(V)	(VI)	(Ih)	(IIc)
Methylmagnesium iodide (1 mol.) added gradually to the lactone (V)	0·37	0·14	0·43	0·10
Lactone (V) added gradually to methylmagnesium iodide (5 mol.)	0	0	0·07	0·54

From this it appears that an intermediate magnesium complex (VIII) can react in two ways. The presence

[1] A. G. Ekstrand, *Ber.*, 1886, **19**, 1131.
[2] A. J. Birch, M. Salahud-Din, and D. C. C. Smith, *J. Chem. Soc.* (*C*), 1966, 523.
[3] V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, (*a*) 567; (*b*) 604.

of enolate (IX) is suggested by the formation of a substantial amount of ketone (Ih) even when an excess of Grignard reagent gave a homogeneous solution.



(VIII) (IX)

Side reactions leading to diol (IIc) and diketone (VI) limit the Grignard method as a means of preparing 8-acetyl-1-naphthol. An alternative route involves acylation of dimethyl sulphoxide.[4] Sodium methanesulphinylmethylide converted the lactone (V) into 8-(methanesulphinylacetyl)-1-naphthol (Ii), but reductive cleavage of this with deactivated Raney nickel gave only a poor yield of 8-acetyl-1-naphthol. An efficient synthesis of 8-acetyl-1-naphthol used the Reformatski reaction of ethyl bromoacetate with lactone (V). The Reformatski synthesis of β-oxo-esters gives good yields only from exceptionally electrophilic esters, such as formates and oxalates.[5] In accordance with its exceptional reactivity already noted, lactone (V) reacted smoothly with zinc and ethyl bromoacetate, to give ethyl 8-hydroxy-1-naphthoylacetate (Ij) (69% after recrystallisation). This was saponified to give the acid (Ik) which when decarboxylated in hot water gave 8-acetyl-1-naphthol (Ih) quantitatively.

Other nucleophilic additions to the lactone (V) included Claisen condensations in dimethylsulphoxide with the sodium enolates of acetone and acetophenone, which gave 8-(3-oxobutyryl)-1-naphthol (Il) and 8-(2-benzoylacetyl)-1-naphthol (Im), respectively.

Infrared Spectra of 8-Hydroxy-1-naphthoyl Compounds.—The compounds in Table 2 all show two carbonyl bands: one (b) at the frequency expected by analogy with naphthoyl compounds with *peri*-substituents but no free hydroxy-group, such as those in Table 3; and one (a) a much lower frequency. The relative intensities of the bands depend critically on the solvent; bands (a) are favoured in inert solvents, and bands (b) are predominant in solvents that can accept hydrogen bonds from hydroxy-groups. The magnitude of the frequency differences between the bands (a) and (b) (*ca.* 40 cm.$^{-1}$ in chloroform, and *ca.* 60 cm.$^{-1}$ in tetrahydrofuran) is of the same order as the shift usually observed in intramolecular hydrogen bonding,[6] which suggests that bands (a) are characteristic of conformer (X). Measurements of concentration dependence (Table 4) suport this view. The higher frequency band (b) of 8-acetyl-1-naphthol, which is only a minor feature in dilute solutions in the inert solvent carbon tetrachloride, becomes much stronger as the concentration of 8-acetyl-1-naphthol increases; it is therefore attributable to 8-acetyl-1-naphthol molecules associated by intermolecular hydrogen bonds. The intramolecular hydrogen bond competes in very dilute solutions, and in accordance with this interpretation, the broad hydroxy-band of 8-acetyl-1-naphthol in carbon tetrachloride shifts with decreasing concentration from 3300 to 3100 cm.$^{-1}$. The carbonyl bands of t-butyl 8-hydroxy-1-naphthoate in tetrahydrofuran show no significant concentration dependence; presumably neither of the conformers responsible for the two carbonyl bands in this solvent involves intermolecular association of solute molecules. If the lower-frequency band is due to conformer (X), which seems likely as its frequency does not vary significantly between solvents, then the higher-frequency band must be due to a conformer with a solute–tetrahydrofuran hydrogen bond, which would leave the

TABLE 2

Infrared absorption: carbonyl bands (cm.$^{-1}$) of 8-hydroxy-1-naphthoyl compounds (I)

R (in I)		Solvent: Carbon tetrachloride	Chloroform	Chloroform–ethanol (4 : 1)	Tetrahydrofuran
OH	α	1659	(1660)	1666	1671
	β	1694	1687	(1705)	1732
	α:β	3:4*	1:2	2:1	3:2
C_4H_8N–	a	1608	1583	1612	1590
	b	—	—	—	1642
	a:b	—*	—*	—*	1:2*
OMe	a	1687	1679	1682	1680
	b	—	1721	1722	1741
	a:b	—	5:1	1:2	1:4
OEt	a	1677	1676	1674	1675
	b	—	1720	1718	1737
	a:b	—	8:1	2:3	1:2
OPr^i	a	1674	1665	1669	1669
	b	—	1710	1708	1730
	a:b	—	10:1	2:3	1:5
OBu^t	a	1674	1670	1672	1671
	b	—	1710	1709	1729
	a:b	—	8:1	4:5	1:5
Me	a	1660	1660	—	—
	b	1694	1698	1698	1708
	a:b	6:1	3:1	—†	—
Ph	a	1639	1637	—	—
	b	1678	1673	1673	1681
	a:b	4:1*	1:1	—	—

a:b and α:β are relative peak heights on a scale of optical density [$D = 2 - \log$ (% transmission)].

* Measurements were made on 0·5% solutions in a 1 mm. cell except for those marked with an asterisk, for which solutions were saturated and weaker than 0·5%. † In chloroform–ethanol (50:1): a, 1657, b, 1695; a:b = 1:1.

Figures in brackets refer to inflexions and are therefore only rough estimates.

[4] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1345.

[5] R. L. Shriner, *Org. Reactions*, 1942, **I**, 1.

[6] J. C. D. Brand and G. Eglinton, 'Applications of Spectroscopy to Organic Chemistry,' Oldbourne Press, London, 1964, pp. 126, 140.

TABLE 3

Infrared absorption: carbonyl bands ($cm.^{-1}$) of model compounds

		Acetylnaphthalenes			Benzoylnaphthalenes	
	8-Substituent	H	OAc	OMe	OAc	OMe
Solvent	Carbon tetrachloride	1690	1708 (1782)*	1708	1680 (1780)	1679
	Chloroform	1677	1697 (1775)	1696	1671 (1770)	1670
	Ethanol–chloroform (1:4)	1682	1699 (1775)	1699	1675 (1769)	1669
	Tetrahydrofuran	1682	1704 (1781)	1703	1680 (1781)	1678

* Numbers in brackets refer to ester carbonyl groups. Measurements were made on 0·5% solutions in a 1 mm. cell.

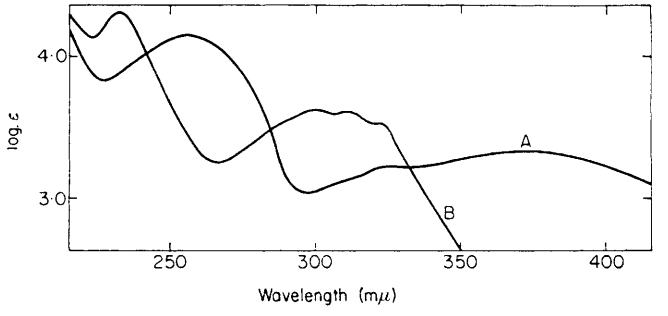
carbonyl groups unbonded. That the frequencies of of the higher-frequency bands are all significantly higher in tetrahydrofuran confirms the view that the carbonyl groups are not hydrogen-bonded in this solvent.

TABLE 4

Infrared absorption: concentration dependence of carbonyl bands

	Concentration (mg./ml.)	$\nu_{max.}$ ($cm.^{-1}$) a	b	Relative peak heights (a: b) (optical density)
8-Acetyl-1-naphthol in carbon tetrachloride	2·3	1660	(1708)	11:1
	5·2	1660	1693	6:1
	50·4	1660	1690	1:1
t-Butyl 8-hydroxy-1-naphthoate in tetrahydrofuran	2·2	1673	1728	1:5·0
	5·0	1673	1727	1:4·4
	50·1	1672	1729	1:4·8

8-Hydroxy-1-naphthoic acid shows two carbonyl bands (α and β in Table 2) in each solvent used; but since this compound differs from the others under consideration in having two hydroxy-groups per molecule,



Ultraviolet spectrum of 8-acetyl-1-naphthol; (A) in cyclohexane (B) in water–methanol (3:1)

these bands cannot be assigned to specific conformations. The ultraviolet spectra of the compound indicate, however, that it contains an intramolecular hydrogen bond as in conformation (X).

Ultraviolet Spectra of 8-Hydroxy-1-naphthoyl Compounds.—Colour effects were noted with 8-hydroxy-1-naphthoyl compounds. Except for the carboxylic acids (Ia and k), and the partly enolic diketones (Im) and (VI), which form yellow or orange crystals and solutions, these compounds are colourless or nearly so when crystallised or when dissolved in alcohols and ethers. However, when melted or when dissolved in inert solvents they exhibit, with the exception of amide (If), striking yellow colours. As shown in Table 5, there are solvent shifts in their ultraviolet spectra. These shifts correspond to the effects on the carbonyl bands described before, and we conclude that the conformer (X) is responsible for the absorption curves of type A (Figure). The bathochromic shift when intramolecular hydrogen bonds are formed is characteristic of *ortho*-acylphenols,[7] and the effect is large in some naphthalene derivatives,[8] but the large effect observed here is noteworthy in that the hydroxy- and carbonyl groups are

TABLE 5

Solvent shifts in the ultraviolet spectra of 8-hydroxy-1-naphthoyl compounds (I) *

	R (in I)					
	OH	C_4H_8N–	OMe	OBu^t	Me	Ph
Cyclohexane	A	AB	A	A	A	A
Carbon tetrachloride	A	AB	A	A	A	A
Chloroform	A	AB	A	A	A	A:B (1:2)
Tetrahydrofuran	A:B (3:1)	B	B	B	B	B
Water–methanol (3:1)	B	B	B	B	B	B

* Spectra classified according to which curve they resemble in the Figure; quantitative details are listed in the Experimental section.

TABLE 6

Ultraviolet spectra of 8-acyl-1-naphthyloxide anions

8-Substituent	$\lambda_{max.}$ (mμ) (log ε)
Bz	247 (4·44), 337 (3·79)
Ac	250 (4·29), 340 (3·80)
CO_2Bu^t	250 (4·36), 338 (3·84)
CO_2Me	250 (4·39), 338 (3·83)
$C_4H_8N{\cdot}CO$	251 (4·38), 339 (3·86)
CO_2^-	248 (4·34), 337 (3·89)

Data were identical for both N- and 0·1N-sodium hydroxide solutions in methanol–water (3:1).

not formally conjugated through the aromatic nucleus, and in that they are probably not coplanar with the nucleus.

Table 6 shows the anion spectra of the same compounds: ionisation results in a bathochromic shift with respect to the B-type spectrum and an increase in extinction, but the solutions are almost colourless.

Certain of the compounds described form stable highly coloured solutions in aqueous sulphuric acid that probably contain aromatic oxonia-acenaphthylene salts [(VII) and (XIa—d)]. Their colours and absorption spectra are listed in Table 7.

[7] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1940, 1347.
[8] M. Oki, M. Hirota, and S. Hirofuji, *Spectrochim. Acta*, 1966, **22**, 1537.

Since there is a possibility of, though no evidence for, ring–chain tautomerism in 8-hydroxy-1-naphthoyl compounds, giving rise to a hemiketal (XII), acetylation

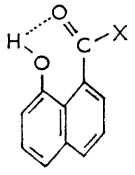
TABLE 7

Ultraviolet spectra of oxonia-acenaphthylene sulphates in 80% sulphuric acid †

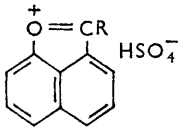
	Colour	$\lambda_{max.}$ (mμ) (log ε)
(VII)	Blue	224 (4·41), 267 (4·13), 553 (4·31),* 591 (4·67), 632 (4·89)
(XIa)	Yellow	244 (3·91), 252 (3·89), 313 (3·92),* 323 (4·02), 399 (4·05)
(XIb)	Orange	235 (4·02), 257 (3·89), 267 (3·87), 280 (3·78), 289 (3·82), 339 (3·99), 441 (4·20),* 485 (4·35)
(XIc)	Yellow-green	233 (4·26), 274 (4·15),* 280 (4·24), 322 (4·06), 464 (4·39)
(XId)	Orange-pink	245 (4·23), 290 (3·90), 338 (4·11), 510 (4·73),* 532 (4·76)

† The spectra in 60% sulphuric acid were almost the same.
* Inflexion.

and methylation of 8-acetyl-1-naphthol and 8-benzoyl-1-naphthol were studied. Acetylation and methylation of the anions gave normal derivatives. Boiling acidified methanol did not methylate these compounds, but

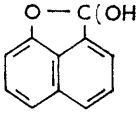


(X)

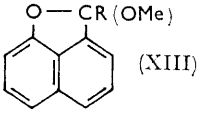


(XI)

a; R = Me
b; R = Ph
c; R = CH:C(OH)Me
d; R = CH:C(OH)Ph



(XII)



(XIII)

a; R = Me b; R = Ph

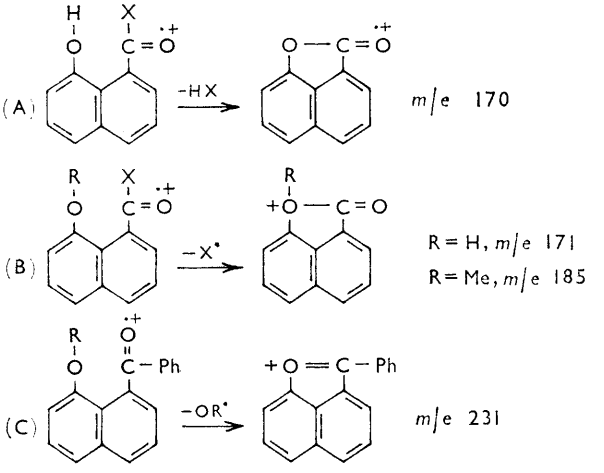
with methyl orthoformate they gave cyclic ketals (XIIIa and b).

Mass Spectra of 8-Hydroxy-1-naphthoyl Compounds.—The mass spectrum of lactone (V) exhibits three metastable peaks which delineate a pathway of fragmentation: *m/e* 170 (100%, M^+) —118·6*→ *m/e* 142 (7%) —91·5*→ *m/e* 114 (46%) —67·9*→ *m/e* 88 (6%).

The spectra of 8-hydroxy-1-naphthoyl compounds are summarised in Table 8. The first eleven examples have a base peak at *m/e* 170 and peaks at *m/e* 142 and 114 characteristic of the lactone; for these compounds the predominant mode of fragmentation (A) is probably a cyclisation to give the molecular ion of lactone (V). A thermal elimination followed by electron impact could also give this result, but could not explain the metastable peaks observed in the spectra of 8-hydroxy-1-naphthoic acid and 8-hydroxy-1-naphthoylacetone, *m/e* 153·7 (= 170²/188) and 126·7 (= 170²/228), respectively.

A fragment at *m/e* 171 is also characteristic of these spectra, and indicates a second mode of fragmentation (B); with 8-acetyl-1-naphthol and its methyl ether this predominates, to give base peaks at *m/e* 171 and 185, respectively, and is confirmed for 8-acetyl-1-naphthol by a metastable peak at *m/e* 157·2.

In the spectra of 8-benzoyl-1-naphthol and its methyl ether, fragmentations by modes (A) and (B) are apparent, together with another type of fragmentation (C), to the



2-phenyloxonia-acenaphthylene cation, *m/e* 231. This last process is confirmed, for the methyl ether, by a metastable peak, *m/e* 203·7.

The sulphoxide (Ii) shows a more complex mass spectrum, and has in addition to peaks at *m/e* 170 and 114, attributable to cleavage by mode (A), and peaks at *m/e* 171 and 115 attributable to cleavage by mode (B), a base peak at *m/e* 184 which could result from the elimination of methylsulphenic acid from the molecular ion, a process which has been reported for other methyl sulphoxides.[9] One peak at *m/e* 232 represents simple loss of oxygen at the moleculear ion, and there are several strong peaks (*m/e* 230, 183, 155, and 127) which can be explained in more than one way, though they may be part of a single pathway of fragmentation involving successive loss of methylthio-radical and two molecules of carbon monoxide.

EXPERIMENTAL

8-Hydroxymethyl-1-naphthol (IIa).—A cooled solution of the lactone of 8-hydroxy-1-naphthoic acid (10 g.),[2] in diglyme (100 ml.) was treated with sodium borohydride (3 g.). After 0·5 hr., the mixture was diluted with water and saturated with carbon dioxide. The crystalline precipitate was dissolved in ether and the solution shaken with 4% sodium hydroxide (200 ml.). The aqueous layer was washed with ether, then saturated with carbon dioxide. *8-Hydroxymethyl-1-naphthol* precipitated as needles (8·45 g.), m. p. 144—146° (from benzene–acetone) (Found: C, 75·9; H, 5·7. $C_{11}H_{10}O_2$ requires C, 75·8; H, 5·8%).

Methanolysis of Lactone (V).—Lactone (V) (1·0 g.) and methanol (60 ml.) containing sulphuric acid (293 mg.;

[9] I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc.* (*C*), 1967, 302.

TABLE 8

Mass spectra of 8-hydroxy-1-naphthoyl compounds and some derivatives

	Standard fragments (relative intensities)						
		m/e					
	M+	171	170	142	115	114	Other fragments [*m/e* (relative intensity)]
(I; R = OH)	29	13	100	8	6	28	
OMe	9	19	100	20	20	71	
OEt	7	14	100	12	8	40	
OPr^i	4	15	100	13	11	15	
OBu^t	3	15	100	13	11	15	
C_4H_8N–	63	24	100	8	24	29	71 (93) 70 (77)
$CH_2{\cdot}CO_2Et$	18	26	100	3	9	7	202 (24)
CH_2Ac	37	47	100	3	34	48	139 (10)
CH_2Bz	29	6	100	15	3	15	120 (22) 105 (30) 77 (15)
Diketone (VI)	2	80	100	11	35	54	186 (45) 168 (19) 139 (6)
(I; R = Ph)	100	60	73	3	19	10	231 (45) 124 (4) 105 (21) 77 (15)
Methyl ether of (I; R = Ph)	100	54	26				231 (34) 185 (76) 127 (14) 105 (19) 78 (15) 77 (24)
(I; R = Me)	81	100	5		62	11	168 (11)
Methyl ether of (I; R = Me)	68	6	45			11	185 (100) 127 (20) 126 (10)
(I; R = $CH_2{\cdot}SO{\cdot}Me$)	26	93	33		33	14	232 (13) 231 (11) 230 (61) 229 (9) 185 (17) 184 (100 183 (79) 157 (10) 156 (7) 155 (42) 129 (10) 128 (10) 127 (24) 126 (17)

TABLE 9

Ultraviolet spectra of 8-hydroxynaphthoyl compounds

	Solvent †	$\lambda_{max.}$ (mμ) (log ε)						
8-Benzoyl-1-naphthol	1	‡	256 (4·31)			324 (3·40)		374 (3·48)
	2	—	—			324 (3·40)	—	374 (3·48)
	3	—	—		309 (3·50)*	323 (3·42)		374 (3·33)
	4	—	279 (3·65)*	287 (3·70)	300 (3·72)	311 (3·69)*	324 (3·59)	345 (2·99)*
	5	229 (4·47)	250 (4·24)*	283 (3·76)		309 (3·63)*	323 (3·50)	345 (3·10)*
8-Acetyl-1-naphthol	1		255 (4·16)					
	2	—	—			325 (3·29)		372 (3·37)
	3	—	—					
	4	—			300 (3·68)	310 (3·64)	324 (3·58)	
	5	233 (4·39)			300 (3·64)	309 (3·63)	323 (3·55)	
t-Butyl 8-hydroxy-1-naphthoate	1		251 (4·32)					
	2	—	—			320 (3·47)*	335 (3·52)	355 (3·47)*
	3	—	—					
	4	—			300 (3·67)	311 (3·65)	324 (3·58)	350 (2·91)*
	5	234 (4·46)			298 (3·70)	308 (3·65)*	322 (3·52)	
Methyl 8-hydroxy-1-naphthoate	1		253 (4·34)				323 (3·43)*	338 (3·51) 352 (3·51)
	2	—	—					
	3	—	—				323 (4·47)*	336 (3·51) 347 (3·51)
	4	—			301 (3·66)	311 (3·65)	324 (3·58)	350 (2·87)*
	5	233 (4·45)			298 (3·69)	308 (3·65)*	322 (3·52)	
N-(8-Hydroxy-1-naphthoyl)pyrrolidine	1	241 (4·45)			299 (3·54)*	314 (3·65)	326 (3·74)	350 (3·25)*
	2	—	—		299 (3·54)*	316 (3·67)	326 (3·75)	350 (3·26)*
	3	—	—		300 (3·64)*	312 (3·67)	323 (3·63)*	350 (3·19)*
	4	—			302 (3·70)	312 (3·69)	325 (3·62)	350 (2·99)*
	5	233 (4·50)			298 (3·73)	309 (3·67)*	323 (3·53)	
8-Hydroxy-1-naphthoic Acid	1		255 (4·26)				324 (3·21)*	337 (3·28)* 361 (3·31)
	2	—	—				326 (3·33)*	338 (3·41)* 361 (3·45)
	3	—	—				325 (3·40)*	344 (3·46)* 350 (3·47)
	4	—			299 (3·34)*	312 (3·44)*	325 (3·48)	335 (3·41)* 350 (3·36)*
	5	234 (4·43)			299 (3·67)	309 (3·64)	322 (3·53)	
	6	236 (4·31)			300 (3·64)*	312 (3·67)	324 (3·65)	

* Inflexion. † 1, Cyclohexane (' special for spectroscopy '); 2, carbon tetrachloride ('AnalaR '); 3, chloroform, filtered through active alumina to reduce its ethanol content; 4, tetrahydrofuran (' stabilised,' kept over sodium); 5, methanol–water (1:3) containing hydrogen chloride (0·1%); 6, methanol–water (1:3) containing potassium hydrogen carbonate (1%). ‡ Horizontal lines indicate regions of the spectrum that could not be scanned owing to insufficient transmission by the solvent.

98%) were boiled under reflux. Sample drops were withdrawn at intervals and analysed by ultraviolet spectroscopy: measurements of the ratio $E(350\ m\mu) : E(300\ m\mu)$ gave the following estimates of % methanolysis: 5 min., 24%; 15 min., 53%; 60 min., 93%. After 3 hr. the mixture was diluted with ice–water and extracted with benzene to give methyl 8-hydroxy-1-naphthoate (Ib) as prisms (1·17 g.), m. p. 93—95° (from benzene).

Ethyl 8-Hydroxy-1-naphthoate (Ic).—Lactone (V) (1·34 g.) and ethanol (60 ml.) containing sulphuric acid (0·3 g.) were boiled under reflux for 5 hr., then poured into ice–water, and extracted with ether. The organic layer was extracted with 8% sodium hydroxide solution (3 × 50 ml.) and the extract was washed with ether and saturated with carbon dioxide. A yellow gum precipitated and eventually crystallised. The *ester* formed prisms (1·03 g.), m. p. 49—50° (from pentane–benzene) (Found: C, 72·2; H, 5·9. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%).

Isopropyl 8-Hydroxy-1-naphthoate (Id).—Lactone (V) (1·03 g.) and propan-2-ol (60 ml.) containing sulphuric acid (0·3 g.) were boiled under reflux for 4 hr., then poured into ice–water, and extracted with ether. The organic layer was extracted with 8% sodium hydroxide (2 × 50 ml.) and the organic layer gave unchanged lactone (V) (0·67 g.). The aqueous layer was saturated with carbon dioxide; the *ester* precipitated as a yellow gum which gave cream prisms, m. p. 66—67° (from benzene–light petroleum) (Found: C, 73·0; H, 6·0. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%).

t-Butyl 8-Hydroxy-1-naphthoate (Ie).—Lactone (V) (2·89 g.) was treated with potassium t-butoxide (5 g.) in dimethyl sulphoxide (50 ml.; distilled from calcium hydride at 0·5 atm.). After 1 hr. the mixture was diluted with ice–water (100 ml.), then saturated with carbon dioxide. The *ester* precipitated as a yellow oil which crystallised (3·45 g.) and gave cream prisms, m. p. 112—113° (from benzene–light petroleum) (Found: C, 74·0; H, 6·7. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%).

N-(8-Hydroxy-1-naphthoyl)pyrrolidine (If).—Lactone (V) (1·03 g.) was treated with pyrrolidine (2 ml.) in benzene (10 ml.) and set aside overnight. The solution was then diluted with benzene and ether, and extracted with 1% sodium hydroxide solution (100 ml.). The red extract was treated with charcoal, filtered, and acidified with carbon dioxide to precipitate the *amide*, which gave cream prisms (0·86 g.), m. p. 236—240° (from methanol) (Found: C, 74·9; H, 6·3; N, 5·7. $C_{15}H_{15}NO_2$ requires C, 74·7; H, 6·3; N, 5·8%).

8-Benzoyl-1-naphthol (Ig).—The Grignard reagent prepared from bromobenzene (4·43 g.) and magnesium (2·5 g.) in tetrahydrofuran (50 ml.) was added dropwise, under nitrogen, to a stirred solution of lactone (V) (4·00 g.), in benzene (100 ml.) during 1 hr. An orange precipitate which had formed dissolved when the mixture was stirred with a solution of ethylenediaminetetra-acetic acid (10 g.) in 4% sodium hydroxide solution (100 ml.). The organic layer was washed with brine, concentrated, and treated with light petroleum to give *8-benzoyl-1-naphthol* as cream prisms (2·73 g.), m. p. 184—187° (from methanol) (Found: C, 81·9; H, 4·9. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·9%).

8-(1-Hydroxy-1-phenylbenzyl)-1-naphthol (IIb).—Lactone (V) (4·00 g.) in benzene (100 ml.) was added dropwise under nitrogen to a stirred Grignard reagent, prepared from bromobenzene (18·5 g.) and magnesium (5·7 g.) in tetrahydrofuran (50 ml.), during 30 min. The clear orange solution was set aside for 1 hr., then decomposed with a solution of ethylenediaminetetra-acetic acid (30 g.) in 4% sodium hydroxide solution (300 ml.). Concentration of the organic layer gave a yellow glass which crystallised on treatment with benzene, and gave the *diol* as cream prisms (6·2 g.), m. p. 177—179° (Found: C, 84·3; H, 5·5. $C_{23}H_{18}O_2$ requires C, 84·7; H, 5·5%).

Reaction of Lactone (V) *with Methylmagnesium Iodide.*—(*a*) The Grignard reagent prepared from methyl iodide (8·4 g.) and magnesium (4 g.) in ether (100 ml.) was added dropwise, under nitrogen, to a stirred solution of lactone (V) (10 g.) in warm benzene (100 ml.) during 5 min. An orange solid separated. After 30 min. the mixture was stirred with a solution ethylenediaminetetra-acetic acid (20 g.) and sodium hydrogen carbonate (35 g.) in water (300 ml.) for 15 min., then filtered. The solid yellow magnesium complex was washed with water and benzene, and stirred with methanol (50 ml.), ether (100 ml.) and N-hydrochloric acid (100 ml.) until it dissolved; the ether layer was washed with sodium hydrogen carbonate solution and shaken with saturated aqueous cupric acetate for 2 hr. to give a green *copper complex*, which was washed with ether and water (2·6 g.) (Found: C, 69·1; H, 4·3; residue of CuO, 9·8. $C_{46}H_{30}O_8Cu,2H_2O$ requires C, 68·2; H, 4·2; CuO, 9·8%). The copper complex was decomposed when shaken with 2N-hydrochloric acid and ether; the organic layer was washed with potassium hydrogen carbonate solution and concentrated to an orange glass (1·60 g.). This gave *bis-(8-hydroxy-1-naphthoyl)methane* (VI) as orange prisms (1·46 g.), m. p. 193—194° (from methanol–chloroform) (Found: C, 77·7; H, 4·6. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%), $\nu_{max.}$ (Nujol) 3380, 1713, 1687, 1630, and 1590 $cm.^{-1}$; τ (hexadeuterioacetone) 0·68 (2H singlet), 1·9—3·1 (12—13H multiplet), 3·68 (0·2H singlet), and 5·39 (1·6H singlet), which indicates that in this solution the diketone is a tautomeric mixture containing *ca.* 20% enol.

The organic layer of the filtrate from the crude magnesium complex was washed and extracted with 4% sodium hydroxide solution (200 ml.). Concentration of the organic layer gave unchanged lactone (V) (3·75 g.). The alkaline extract on acidification with carbon dioxide gave a yellow gum which solidified (5·89 g.) and gave *8-acetyl-1-naphthol* (3·46 g.) as cream prisms, m. p. 81—83° (from benzene) (Found: C, 77·5; H, 5·5. $C_{12}H_{10}O_2$ requires C, 77·4; H, 5·4%). The mother-liquor was later separated into neutral and phenolic fractions, (0·7 g.) and (1·7 g.), respectively. The former was identified as the cyclic ether (III), and the latter was shown (t.l.c.) to consist of 8-acetyl-1-naphthol, and a substance of slightly higher R_F, presumably the diol (IIc); n.m.r. spectroscopy (carbon tetrachloride) showed methyl singlets at τ 7·60 due to 8-acetyl-1-naphthol and at τ 8·37 attributable to the diol (IIc); integration indicated the presence of 1·3 and 0·4 g., respectively.

(*b*) Lactone (V) (4·08 g.) in warm benzene (50 ml.) was added dropwise, under nitrogen, to a stirred Grignard reagent prepared from methyl iodide (17·5 g.) and magnesium (5·8 g.) in ether (100 ml.) during 1·5 hr. The clear yellow solution was stirred for 0·5 hr., then decomposed with a solution of ethylenediaminetetra-acetic acid (40 g.) and sodium hydrogen carbonate (50 g.) in water (300 ml.). Benzene (200 ml.) was added and the mixture was stirred until all solid had dissolved and acidified with carbon dioxide. The organic layer was separated, washed, and extracted with 2% sodium hydroxide solution (400 ml.).

The alkaline solution was washed with ether, then acidified with carbon dioxide. The precipitated gum was extracted with ether and the extract was concentrated to a gum (3·25 g.) shown by t.l.c. to consist only of cyclic ether (III), the diol (IIc), and 8-acetyl-1-naphthol. It was later separated into neutral and acidic fractions (1·62 g.) and (1·17 g.), respectively. The n.m.r. spectrum of the acidic fraction indicated the presence of 8-acetyl-1-naphthol (0·33 g.) and diol (IIc) (0·84 g.). The neutral fraction was distilled to give 2,2-*dimethyl*-2H-*naphtho*[1,8-bc]*furan* (III), b. p. 145—150°/15 mm. (Found: C, 84·5; H, 6·5. $C_{13}H_{12}O$ requires C, 84·3; H, 6·5%). The *picrate* had m. p. 106—107° (from methanol) (Found: C, 55·2; H, 3·8; N, 10·5. $C_{19}H_{15}N_3O_8$ requires C, 55·2; H, 3·7; N, 10·2%).

8-(*Methanesulphinylacetyl*)-1-*naphthol* (Ii).—A 50% oil suspension of sodium hydride (2·4 g.) was freed from oil by washing with pentane, then warmed at 70° under nitrogen with dimethyl sulphoxide (30 ml.). After 45 min., effervescence had ceased and the solution was diluted with tetrahydrofuran, stirred, and cooled in an ice-bath while a solution of lactone (V) (3·4 g.) in tetrahydrofuran (30 ml.) was added dropwise. After 1 hr. at room temperature, the mixture was decomposed with water and acidified with carbon dioxide. The *sulphoxide* (Ii) crystallised out as prisms (5·16 g.), m. p. 196—198° (Found: C, 62·8; H, 4·7; S, 12·1. $C_{13}H_{12}O_3S$ requires C, 62·9; H, 4·9; S, 12·9%).

Desulphurisation of Sulphoxide (Ii).—The sulphoxide (1·0 g.) was boiled under reflux with acetone (50 ml.) and treated portionwise with a suspension of Raney nickel that had been deactivated by boiling with acetone, until t.l.c. showed that no unchanged suphoxide remained. The solution was filtered, concentrated, taken up in ether, and extracted with 4% sodium hydroxide solution. Acidification of the extract with carbon dioxide precipitated a gum which solidified (0·69 g.) and gave 8-acetyl-1-naphthol (0·22 g.), m. p. and mixed m. p. 80—85° (from ether–pentane). The mother-liquor gave only low-melting products.

Ethyl 8-*Hydroxy*-1-*naphthoylacetate* (Ij).—Lactone (V) (4·0 g.) in tetrahydrofuran (50 ml.) was boiled with zinc foil (4·6 g.) under reflux, while a solution of ethyl bromoacetate (7·9 ml.) in tetrahydrofuran (100 ml.) was added gradually during 2·75 hr. The solution was then boiled for a further 0·25 hr., diluted with ether, decanted from unchanged zinc (0·26 g.), washed with 2N-hydrochloric acid, brine, and potassium hydrogen carbonate solution, and concentrated to an orange oil which crystallised (6·51 g.) and gave the *ester* (Ij) as cream prisms from ether–carbon tetrachloride (4·18 g.); m. p. after recrystallisation from benzene–ether, 96—97° (Found: C, 69·3; H, 5·3. $C_{15}H_{14}O_4$ requires C, 69·7; H, 5·5%), τ 1·67 (1H singlet, removed by D_2O), 2·0—3·1 (6H multiplet), 5·85 (2H quartet), 5·98 (2H singlet), and 8·82 (3H triplet).

8-*Hydroxy*-1-*naphthoylacetic Acid* (Ik).—Ester (Ij) (0·40 g.) was warmed on a steam-bath with 4% aqueous sodium hydroxide for 0·5 hr.; the mixture was then cooled and acidified with hydrochloric acid. Ether extraction yielded a gum which gave prisms of the *acid* (259 mg.), m. p. 101—114° (decomp.) (from ether–benzene) (Found: C, 68·1; H, 4·3. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·4%).

8-*Acetyl*-1-*naphthol* (Ih).—Ester (Ij) (1·06 g.) was warmed on a steam-bath with 4% aqueous sodium hydroxide for 0·5 hr. The solution was cooled, diluted to dissolve crystals which formed, acidified with hydrochloric acid, and extracted twice with ether. These extracts were washed with brine, then concentrated *in vacuo* below room temperature. The yellow gum remaining was taken up with warm water (200 ml.) and heated on a boiling water-bath for 5 min.; carbon dioxide was evolved, and 8-acetyl-1-naphthol separated from the cooled solution as cream prisms (0·52 g.), m. p. 82—84°. Extraction of the filtrate with ether gave more naphthol (0·20 g.), m. p. 75—81°.

8-(3-*Oxobutyryl*)-1-*naphthol* (Il).—A solution of sodium methanesulphinylmethylide in dimethyl suphoxide, prepared under nitrogen as previously described from sodium hydride (50%; 2 g.), was mixed with acetone (3 g.) and tetrahydrofuran (10 ml.), then stirred while lactone (V) (2·0 g.) in tetrahydrofuran (10 ml.) was added dropwise during 10 min. After 30 min. the mixture was diluted with ether and extracted with water. Acidification of the aqueous layer with carbon dioxide precipitated the crude diketone as an orange gum (1·22 g.) which was isolated with ether. 8-Hydroxy-1-naphthoic acid (1·14 g.) was isolated with ether from the acidified aqueous layer.

The crude diketone (Il) was shaken with ether and saturated aqueous cupric acetate, to give a *copper salt*, which gave blue-green needles from glacial acetic acid (Found: C, 63·9; H, 4·6; residue of CuO, 14·1. $2C_{28}H_{22}CuO_6,C_2H_4O_2$ requires C, 63·6; H, 4·4; CuO, 14·1%), $\nu_{max.}$ (tetrahydrofuran) 1584, 1618, 1722, and 1747 cm.$^{-1}$; cf. acetic acid in tetrahydrofuran, $\nu_{max.}$ 1724 and 1745 cm.$^{-1}$.

The copper salt was stirred with ether and 2N-hydrochloric acid until it dissolved. The yellow organic layer was washed with brine and concentrated to give the *diketone* (Il) as an orange gum which was purified for n.m.r. spectroscopy by evaporation from solution in carbon tetrachloride; τ (deuteriochloroform) 1·04 (1H singlet, removed by D_2O), 1·9—3·0 (6·5H multiplet), 3·84 (1H singlet, removed by D_2O), 5·98 (0·2H singlet, removed by D_2O), 7·75 (0·4H singlet), and 7·86 (2·6H singlet), which indicates that in this solution, the diketone is a tautomeric mixture containing *ca.* 85% enol.

8-(2-*Benzoylacetyl*)-1-*naphthol* (Im).—The procedure of the previous experiment, with sodium hydride (50%; 1·70 g.), acetophenone (4·66 g.), and lactone (V) (2·00 g.), gave 8-hydroxy-1-naphthoic acid (1·46 g.) and crude diketone as an orange gum (0·91 g.). This gave a brown copper salt which was washed with ether but not recrystallised, then decomposed as before, to give a solid, which gave the *diketone* (Im) as orange prisms (336 mg.), m. p. 95—96° (from carbon tetrachloride) (Found: C, 78·3; H, 4·9. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·9%), τ (deuteriochloroform) 0·93 (1H singlet, removed by D_2O), 1·8—2·9 (12H multiplet), and 3·13 (1H singlet, removed by D_2O), which indicates that in this solution it is in an enolic form.

Derivatives of 8-*Acetyl*-1-*naphthol*.—(*a*) With hydroxylamine hydrochloride and sodium acetate in methanol it gave an *oxime*, isolated with ether, m. p. 174—178° (from ether–light petroleum) (Found: C, 70·7; H, 5·8; N, 7·0. $C_{12}H_{11}NO_3$ requires C, 70·7; H, 5·5; N, 7·0%).

(*b*) When shaken with 4% aqueous sodium hydroxide and acetic anhydride the naphthol gave an *acetate*, isolated with ether, as cream prisms, m. p. 70—71° (from benzene–light petroleum) (Found: C, 73·5; H, 5·2. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·2%).

(*c*) With potassium carbonate and methyl iodide in acetone it gave 1-*acetyl*-8-*methoxynaphthalene*, isolated with ether, m. p. 53—54° (from pentane) (Found: C, 77·6; H, 6·1. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%).

(*d*) With methanol containing sulphuric acid (one drop) and methyl orthoformate after 1 week, the naphthol gave the

cyclic methyl acetal (XIIIa), isolated with ether as an oil, b. p. 100°/0·4 mm. (Found: C, 78·1; H, 6·0. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%).

Derivatives of 8-*benzoyl*-1-*naphthol* were prepared in a similar way: *acetate*, m. p. 114—115° (Found: C, 78·0; H, 4·7. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8%); 1-*benzoyl*-8-*methoxynaphthalene*, m. p. 81—82° (Found: C, 82·5; H, 5·4. $C_{18}H_{14}O_2$ requires C, 81·7; H, 5·4%); *cyclic methyl acetal* (XIIIb), b. p. 120°/0·4 mm. (Found: C, 86·1; H, 5·4. $C_{18}H_{14}O_2$ requires C, 86·2; H, 5·3%).

Thermal Dissociation of Bis-(8-*hydroxy*-1-*naphthoyl*)-*methane* (VI).—This compound (246 mg.) was distilled in a two-bulb apparatus, from a Woods metal-bath at 0·1 mm. The distillate, which came over quickly at 200° leaving very little residue, solidified. It was taken up in ether and separated into neutral (114 mg.) and phenolic (90 mg.) fractions. The former gave lactone (V) (53 mg.) as reddish prisms, m. p. and mixed m. p. 99—101° (from benzene–light petroleum); the latter gave 8-acetyl-1-naphthol (50 mg.) as brownish prisms, m. p. and mixed m. p. 80—81° (from benzene–light petroleum).

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