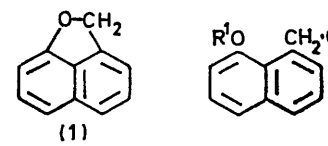
2*H*-Naphtho[1,8-*bc*]furan and 8-Hydroxy-1-naphthaldehyde

By **D. Berry** and **D. C. C. Smith,*** Department of Chemistry, The University, Manchester M13 9PL

Syntheses of 2*H*-naphtho[1,8-*bc*]furan (1) are described. It is *C*-protonated, as are its nitrogen analogues, forming a stable salt; and it is oxidised by air to 8-hydroxy-1-naphthaldehyde. Solvent shifts in the spectra of this aldehyde and related compounds are interpreted in terms of conformational changes caused by hydrogen bonding. Naphthofuran (1) is oxidised by lead tetra-acetate; one of the four products isolated is a dialdehyde (21) structurally similar to gossypol (22).

2*H*-NAPHTHO[1,8-*bc*]FURAN (1) is a heterocyclic analogue of phenalene, a hydrocarbon (RH) noted for its ability to form a stable delocalised radical (R·) and ions (R^+ and R^-).[1] Attempts to prepare this naphthofuran (1) by acidic cyclisation of 8-hydroxymethyl-1-naphthol (2),[2] yielded only polycondensation product, probably because ring strain in the naphthofuran (1) makes any cyclisation in acid reversible. Therefore a final cyclisation under basic conditions seemed essential. Use of *p*-tolylsulphonyloxy as leaving group for such a cyclisation, called for selective tosylation of the primary hydroxy-group of diol (2); the di-anion, if formed from this diol in strongly basic conditions, might be expected to be tosylated first at this position since here the negative charge would be more concentrated. Treatment of the diol with potassium t-butoxide (2 equiv.) in dimethyl sulphoxide, followed by toluene-*p*-sulphonyl chloride (1 equiv.), afforded only 8-hydroxymethyl-1-naphthyl toluene-*p*-sulphonate, suggesting that this medium is not basic enough to generate the di-anion; however use of 2 equiv. of sodium methylsulphonylmethanide in dimethyl sulphoxide, followed by 1 equiv. of toluene-*p*-sulphonyl chloride, gave, in 70% yield, the required naphthofuran (1).

Partial acetylation of diol (2) in aqueous alkali gave a monoacetate, shown by its u.v. spectrum to be compound (3); this was unexpected but presumably the acetyl group, unlike the tosyl group, can migrate intramolecularly from the phenolic oxygen atom. As expected, the same monoacetate is also formed on partial alkaline hydrolysis of the diacetate (4); the hydrolysate also contains traces of the naphthofuran (1), showing that acetoxy can act here as a leaving group in elimination. In sodium hydroxide solutions this elimination to give the naphthofuran cannot compete with saponification



(1)

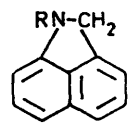
(2) $R^1 = R^2 = H$
(3) $R^1 = H, R^2 = Ac$
(4) $R^1 = R^2 = Ac$
(5) $R^1 = Me, R^2 = H$

[1] D. H. Reid, *Quart. Rev.*, 1965, **19**, 274.
[2] R. J. Packer and D. C. C. Smith, *J. Chem. Soc.* (*C*), 1967, 2194.

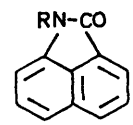
to give the diol, but steam distillation from concentrated potassium carbonate solution converts diacetate (4) quantitatively into the naphthofuran (1), which distils over.

2*H*-Naphtho[1,8-*bc*]furan (1) and 2,2-dimethyl-2*H*-naphtho[1,8-*bc*]furan [2] form stable colourless solutions in cold concentrated sulphuric acid, whence they can be recovered unchanged on dilution. Among methoxynaphthalenes, only the 1,3-isomer shows this property,[3] the others being quickly destroyed. The sulphuric acid solutions of both the naphthofurans give similar u.v. spectra, and analysis of their n.m.r. spectra indicates that the sulphate salts (6) and (7) are formed (Table 1). These two naphthofurans may owe their exceptionally basic character to relief of ring strain on *C*-protonation. The dihydrobenzo[*cd*]indazoles, with a ring system geometrically similar to that of these naphthofurans, exist in the *C*-protonated indazole tautomeric forms in preference to the *N*-protonated naphthalene tautomers.[4,5]

If ready *C*-protonation of these naphthofurans is due to relief of ring strain, then one can expect that the nitrogen analogues, 1,2-dihydrobenz[*cd*]indole (8) and 1,2-dihydro-1-methylbenz[*cd*]indole (9) might also be protonated on carbon rather than on nitrogen in acid. The tertiary amine (9) was prepared by reduction with lithium aluminium hydride of the corresponding lactam (10),[6] as reported previously for the amine (8).[7] Both the indolines (8) and (9) are unstable in air, turning dark blue immediately on silica, but their solutions in tri-



(8) R = H
(9) R = Me



(10)

TABLE 1

Chemical shifts (τ) and u.v. parameters [$\lambda_{max.}$ /nm (log ε)] of salts

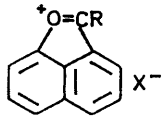
Positions of protons:	1	2	3, 4, 5	6	7	8	$\lambda_{max.}$	λ_{sh}
(6) $^{+}O\text{-}CH_2$ HSO_4^-		3·3 [a]	1·3—2·0	5·25 [a]	1·1 [b,c]	2·2 [d,e]	250 (3·85) 311 (3·90)	348 (3·46)
(7) $^{+}O\text{-}CMe_2$ HSO_4^-		7·6	1·4—1·9	5·1 [a]	1·0 [b,f]	2·05 [d,g]	243 (4·07) 255 (3·96) 310 (3·98)	340 (3·61)
(13) $^{+}MeN\text{-}CH_2$ $CF_3CO_2^-$	6·1	4·65 [a]	1·9—2·4	5·8 [a]	*h*	2·75 [i]	297 (3·91) [j]	
(11) $^{+}HN\text{-}CH_2$ $CF_3CO_2^-$	−0·4 [k]	4·55 [a]	1·9—2·4	5·75 [a]	*h*	2·7	270 (3·69) 280 (3·79) 287 (3·77)	300 (3·59)
(12) $^{+}H_2N\text{-}CH_2$ $CF_3CO_2^-$	0·1 [k]	4·65 [a]	6H m at 1·9—2·4					
1-Naphthylammonium^{+} $CF_3CO_2^-$	0·9 [l]		7H m at 1·9—2·5				268 (3·09) 277 (3·14) 284 (3·00)	

[a] br,s. [b] dt, *J* 10 and 3 Hz. [c] Double irradiation at τ 5·25 caused the signal at 1·1 to become a sharp doublet, *J* 10 Hz. Double irradiation at τ 2·2 caused the signal at 1·1 to become a triplet, *J* 3 Hz. [d] dt, *J* 10 and 1 Hz. [e] Double irradiation at τ 1·1 caused the signal at 2·2 to become a singlet. [f] Double irradiation at τ 5·1 caused the signal at 1·0 to become a sharp doublet, *J* 10 Hz, and the signal at 2·05 to become a sharper doublet. [g] Double irradiation at τ 1·0 caused the signal at 2·05 to become a singlet, and the broad singlet at 5·1 to become sharper. [h] With aromatic multiplet. [i] dt, *J* 10 and 1·5 Hz. [j] There is a strong band below 260 nm, but solvent (trifluoracetic acid) absorption obscures the maximum. [k] vbr; assignments for (11) and (12) could be reversed. [l] vbr.

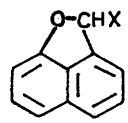
[3] A. J. Birch, M. Salahud-Din, and D. C. C. Smith, *Tetrahedron Letters*, 1964, 1623.
[4] S. Bradbury, C. W. Rees, and R. C. Storr, *Chem. Comm.*, 1969, 1429.
[5] R. W. Alder, G. A. Niazi, and M. C. Whiting, *J. Chem. Soc.* (*C*), 1970, 1693.
[6] N. S. Dokunikhin and L. A. Gaeva, *J. Gen. Chem.* (*U.S.S.R.*), 1958, **28**, 2698.
[7] A. Stoll, T. Petrzilka, and J. Rutschmann, *Helv. Chim. Acta*, 1950, **33**, 2254.

fluoroacetic acid are stable and exhibit clear u.v. and n.m.r. spectra. In Table 1 these are compared with those of salts (6) and (7). The solution of the indoline (8) has bands indicating approximately equal amounts of *C*-protonation, giving salt (11), and *N*-protonation, giving salt (12). The solution of the indoline (9) however gives only the bands characteristic of salt (13), and there is no detectable *N*-protonation.

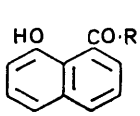
An objective in synthesising 2*H*-naphtho[1,8-*bc*]furan was to try conversion by hydride or hydrogen abstraction into products with structure (14) or (15) that could then by hydrolysis give the unknown 8-hydroxy-1-naphthaldehyde (16). Hydride abstraction seemed promising because 1-oxonia-acenaphthylene salts such as (14) but with R = Me, are stable in sulphuric acid.[2] Treatment of the naphthofuran (1) with triphenylmethyl perchlorate in acetonitrile, conditions similar to those used to abstract hydride from phenalene,[8] gave a blue product from which, on hydrolysis, triphenylmethane but no 8-hydroxy-1-naphthaldehyde could be isolated. When



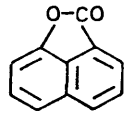
(14) R = H



(15)



(16) R = H
(17) R = Me



(18)

this aldehyde had been prepared by other routes, it was found that it did not give a stable solution of the salt (14; X = HSO_4^-) in cold sulphuric acid.

The initially colourless crystals of 2*H*-naphtho[1,8-*bc*]-furan turn yellow in air: t.l.c. shows that the only abundant product is the yellow aldehyde (16). Auto-oxidation of the aldehyde is not appreciable, but attempts to prepare this aldehyde by bubbling air through the naphthofuran just above its m.p. showed that the conversion stops at about 1%, so perhaps the aldehyde, being phenolic, may act as an auto-oxidation inhibitor.

Another approach to the aldehyde (16) is oxidation of protected compounds derived from the diol (2): the methyl ether (5) with manganese dioxide in benzene gave 8-methoxy-1-naphthaldehyde, which was demethylated by aluminium chloride to the aldehyde (16).

Since the aldehyde (16) is a possible intermediate in rapid reduction of the strained lactone (18) to the diol (2) by sodium borohydride in bis-(2-methoxyethyl) ether,[2] reduction with limited amount of sodium borohydride was examined: a compound was isolated whose spectra indicate it to be one of the two possible 8-hydroxy-1-naphthoate esters of diol (2). Like other 8-hydroxy-1-naphthoyl compounds,[2] this ester shows characteristic changes in its u.v. and i.r. spectra according to whether solvents permit its hydroxy and carbonyl substituents, in *peri*-relationship, to form intra- or inter-molecular hydrogen bonds.

Hitherto no aldehydes of this type have been examined for such solvent shifts. Known *peri*-hydroxynaphthaldehydes include only examples with two or more hydroxy-groups,[9] and the analogue, 8-mercapto-1-naphthaldehyde exists exclusively as the tricyclic hemimercaptal tautomer.[10] 8-Hydroxy-1-naphthaldehyde (16) is found to show marked u.v. solvent shifts and these are summarised in Table 2. The aldehyde (16)

TABLE 2

U.v. data [$\lambda_{max.}$/nm (log ε)]

In cyclohexane: [a]

Aldehyde (16): 262 (4·23), 274 (4·22), 330 (3·18), 394 (3·52)
Ketone (17): 255 (4·16), 325 (3·92), 372 (3·37)

In water–methanol (3 : 1): [b]

Aldehyde (16): 241 (4·24), 256 (4·21), 324 (3·48), 350 (3·45)
Ketone (17): 223 (4·39), 300 (3·64), 309 (3·63), 323 (3·55)

In aqueous 0·1N-sodium hydroxide: [c]

Aldehyde (16): 257 (4·23), 341 (3·56), 380 (3·34)
Ketone (17): 250 (4·29), 340 (3·80)

[a] Spectra in chloroform, except where the solvent absorbs, were similar, showing only minor differences. [b] Spectra in tetrahydrofuran, except where the solvent absorbs, were similar, showing only minor differences. [c] Spectra in N-sodium hydroxide were identical.

absorbs at significantly longer wavelengths than the analogous ketone (17), and this may be attributed to a greater resonance interaction between the carbonyl group and the aromatic nucleus in the aldehyde, permitted by the smaller steric requirements of a formyl group relative to an acetyl group. This effect is apparent in both the intramolecularly hydrogen-bonded state (in cyclohexane or chloroform) and in the intermolecularly hydrogen-bonded states (in aqueous methanol or tetrahydrofuran). The spectra of the anions derived from the aldehyde (16) and ketone (17) are rather more alike. The carbonyl bands in the i.r. spectra also reflect the change-over from intra- to inter-molecular hydrogen bonding: aldehyde (16) has two bands at 1660 and 1680 cm^{-1} when dissolved in tetrahydrofuran, but only one band at 1660 cm^{-1} when dissolved in chloroform. The related aldehyde (21), described below, showed the same behaviour.

The n.m.r. spectra of aldehyde (16) in deuteriochloroform and in tetrahydrofuran also show large solvent shifts (Table 3); in each solvent the spectra show two low-field singlets due to the formyl and phenolic protons: they can be distinguished by exchange with deuterium

[8] W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 1959, 2773.
[9] G. T. Morgan and D. C. Vining, *J. Chem. Soc.*, 1921, **119**, 177; R. Adams and D. E. Burney, *J. Amer. Chem. Soc.*, 1941, **63**, 1103.
[10] D. G. Hawthorne and Q. N. Porter, *Austral. J. Chem.*, 1966, **19**, 1909.

oxide, but care is needed in interpreting the tetrahydrofuran results since deuterium oxide is miscible with this solvent and moves the formyl resonance downfield in proportion to the amount added. In deuteriochloroform the hydroxy-proton of aldehyde (16) resonates at much lower field than it does in tetrahydrofuran, as expected for a proton that is part of an intramolecular hydrogen bond. In tetrahydrofuran the formyl proton resonates

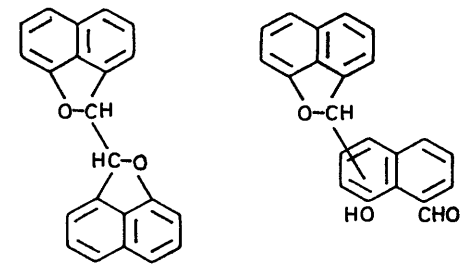
TABLE 3

Chemical shifts (τ)

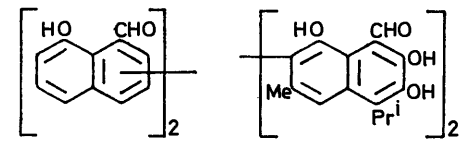
	CHO	OH
Aldehyde (16) in $CDCl_3$	+0·24	−1·60
in tetrahydrofuran	−0·39	−0·72
Aldehyde (20) in $CDCl_3$	+0·16	−2·30
in tetrahydrofuran	+0·06	−2·38
Aldehyde (21) in $CDCl_3$	+0·08	−1·73
in tetrahydrofuran	−0·58	−0·68

at lower field than in deuteriochloroform, perhaps because when the formyl group is freed from the intramolecular hydrogen bond it rotates, putting the formyl proton nearer to the plane of the aromatic nucleus.

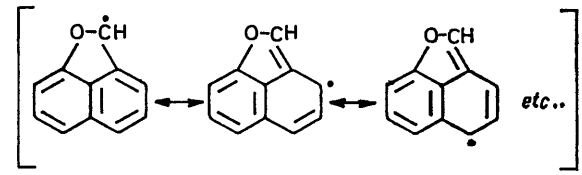
2*H*-Naphtho[1,8-*bc*]furan (1) reacts with lead tetra-acetate in acetic acid, consuming 1 mol. equiv. of oxidant in 2 h at room temperature. The major product is 2-acetoxy-2*H*-naphtho[1,8-*bc*]furan (15; X = OAc), but it was found convenient before attempting to separate other products, to saponify this and other esters present, and then to separate the product into neutral and phenolic fractions. Steam distillation of the neutral fraction gave in the distillate recovered naphthofuran (1) and in the residue a mixture of two diastereoisomeric compounds (19a and b). These were partly separable by t.l.c. and distinguishable by the slightly different chemical shifts of their benzylic protons. The phenolic fraction yielded aldehyde (16) [52% from (1), making this the most convenient preparation of (16)] and two other aldehydes that could be separated by chromatography. The first eluted was shown to have the partial structure (20); in its u.v., i.r., and n.m.r. spectra, it does not show the solvent shifts that are characteristic of aldehydes (16) and (21) (for example see Table 3), an observation that might be explained if the naphthofuran ring were attached *ortho* to the hydroxy-group or to the formyl group, so sterically preventing disruption by tetrahydrofuran of the intramolecular hydrogen bond between these groups. The presence in its n.m.r. spectrum of a low-field signal from *two* aromatic protons, as seen also in the spectrum of aldehyde (16), makes linkage *ortho* to the formyl group seem unlikely. The last eluted aldehyde has the partial structure (21). In its spectra and solvent shifts it closely resembles aldehyde (16), the simplicity of its n.m.r. spectrum suggesting that it is a symmetrical dimer, and the presence of a low-field signal from *two* aromatic protons only, suggesting that the point of attachment is *ortho* or *para* to the formyl groups. However such evidence for the position of linkage of the naphthalene residues ignores the shielding effects of one naphthalene nucleus upon the other.



(19a and b) (20)



(21) (22)



(23)

The formation of compounds (19)—(21) after saponification indicates that dehydro-dimers of naphthofuran (1) were formed by oxidative coupling, and then acetoxylated, like naphthofuran (1) itself, at the methylene groups. The oxidative coupling is noteworthy because it is reported that there are no dimerisation products formed in the reaction of toluene with lead tetra-acetate.[11] The different products from the naphthofuran might be formed by different coupling reactions of the same mesomeric radical (23), which is a heterocyclic analogue of the phenalenyl radical. But 1-methoxynaphthalene, with lead tetra-acetate in acetic acid, slowly yields the 4,4′-bisdehydro-compound.[12] Therefore the dimeric products formed from the naphthofuran do not necessarily constitute evidence for intermediacy of radical (23).

The dialdehyde (21) has a structure reminiscent of the gossypol (22),[13] which is likewise a binaphthyl with hydroxy-groups *peri* to the formyl groups, and this raises the question of whether gossypol arises by oxidation of a naphtho[1,8-*bc*]furan precursor.

[11] R. Criegee, in ' Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, 1965, p. 316.

[12] F. Wessely, J. Kotlan, and W. Metlesics, *Monatsh.*, 1954, **85**, 69.

[13] R. Adams, T. A. Geissman, and J. D. Edwards, *Chem. Rev.*, 1960, **60**, 555; T. J. King and L. B. de Silva, *Tetrahedron Letters*, 1968, 261.

EXPERIMENTAL

8-Hydroxymethyl-1-naphthyl Toluene-p-sulphonate.—8-Hydroxymethyl-1-naphthol (1·0 g)[2] and potassium t-butoxide (1·52 g) were covered with dimethyl sulphoxide and stirred while toluene-*p*-sulphonyl chloride (1·18 g; dissolved in acetone) was added. The clear solution resulting was diluted with aqueous sodium hydroxide, and slowly deposited solid (1·06 g) which formed *plates*, m.p. 132—135° (from benzene) (Found: C, 66·6; H, 5·2; S, 9·2. $C_{18}H_{16}O_4S$ requires C, 65·9; H, 4·9; S, 9·8%).

2H-Naphtho[1,8-bc]*furan* (1).—(*a*) 8-Hydroxymethyl-1-naphthol (0·94 g) in tetrahydrofuran (10 ml) was added under nitrogen to a stirred solution prepared at 70° under nitrogen from dimethyl sulphoxide (10 ml) and sodium hydride (0·33 g). The stirred mixture was treated dropwise with a solution of toluene-*p*-sulphonyl chloride (1·44 g) in tetrahydrofuran (20 ml). Aqueous 4% sodium hydroxide was added and the mixture was extracted with pentane, giving an oil which was distilled from glass wool giving *2H-naphtho*[1,8-bc]*furan* (0·60 g), b.p. 74° at 0·01 mmHg, as crystals, m.p. 53—54° (from methanol) (Found: C, 84·7; H, 5·3. $C_{11}H_8O$ requires C, 84·7; H, 5·2%); $\nu_{max.}$ ($CHCl_3$) 2940, 1625, 1604, 1385, and 1105 cm^{-1}; $\lambda_{max.}$ (EtOH) 300, 310, and 325 nm (log ε 3·78, 3·80, and 3·78); τ ($CDCl_3$) 2·4—2·9 (5H, m), 3·35 (1H, d, *J* 7 Hz), and 4·30 (2H, s); *m/e* 156 (100%), 155 (93%), 128 (51%), 127 (64%); *picrate*, m.p. 146—152° (from methanol) (Found: C, 52·8; H, 3·1; N, 10·8. $C_{17}H_{11}N_3O_8$ requires C, 53·0; H, 2·9; N, 10·9%).

(*b*) 8-Hydroxymethyl-1-naphthol (19·2 g), sodium acetate (5 g), and acetic anhydride (100 ml) were boiled under reflux for 1 h. The solution was then cooled slightly and while still hot, diluted with ethyl acetate (500 ml), washed with warm water, dried (Na_2SO_4), and concentrated under reduced pressure so as to remove excess of acetic anhydride, leaving a solid residue. [In a separate experiment this was recrystallised from benzene–light petroleum (60—80°) giving the *diacetate*, m.p. 81—83° (Found: C, 70·2; H, 5·7. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·5%); $\nu_{max.}$ (CS_2) 1770 and 1740 cm^{-1}; $\lambda_{max.}$ (EtOH) 285 nm (log ε 3·71).] The total product was covered with a saturated aqueous solution prepared from potassium carbonate (200 g), and steam-distilled: the product came over in 2·5 l of water and was isolated with ether, giving *2H*-naphtho[1,8-*bc*]furan (17·5 g, 100%), m.p. 49—53°.

8-Acetoxymethyl-1-naphthol.— 8-Hydroxymethyl-1-naphthol (126 mg) was dissolved in aqueous sodium hydroxide (0·15N; 5·7 ml) and stirred while acetic anhydride (100 mg) in acetone (5 ml) was added; additional sodium hydroxide solution was then added to give a pink colour with phenolphthalein indicator. Ether extraction and drying ($MgSO_4$) afforded a gum (148 mg), giving prisms (79 mg) from benzene, m.p. 113—114° (Found: C, 72·4; H, 5·6. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%); $\nu_{max.}$ (CS_2) 3350 and 1710 cm^{-1}, $\lambda_{max.}$ (CCl_4) 301, 314, and 328 nm (log ε 3·66, 3·59, 3·48).

1-Methylbenz[cd]*indol-2*(1H)*-one* (10; R = Me).—Benz[*cd*]indol-2(1*H*)-one (10; R = H) (10 g), potassium carbonate (200 g), acetone (200 ml), and methyl iodide (20 ml) were agitated for 16 h, then filtered. The filtrate and acetone washings of the solids were concentrated then diluted with water. The product was isolated with benzene as yellow needles (11·0 g), m.p. 79—80° [from benzene–light petroleum (b.p. 60—80°)] (lit.,[6] m.p. 77—79·2°).

1,2-Dihydro-1-methylbenz[cd]*indole* (9).—1-Methylbenz-[*cd*]indol-2(1*H*)-one (1·0 g) in *N*-ethylmorpholine was stirred under nitrogen while lithium aluminium hydride (0·56 g) was added. After the exothermic reaction had subsided, the mixture was kept at 55° for 0·5 h, then cooled in ice, and treated gradually with water dissolved in *N*-ethylmorpholine followed by excess of water. The product was isolated with ether as an oil, initially pale yellow, but turning green as soon as the solvent had been removed, solidifying in an ice-bath but remelting at room temperature (1·07 g). Short-path distillation gave a blue residue and the *product* as a distillate (b.p. 100—150° at 0·01 mmHg), of pale yellow crystals, turning blue soon after admission of air, m.p. 40—46° (Found: C, 82·6; H, 6·5; N, 8·1. $C_{12}H_{11}N$ requires C, 85·2; H, 6·5; N, 8·3%). It was possible to detect the lactam used as starting material in this product [*ca.* 5% by n.m.r. spectroscopy: methyl singlet at τ 6·7 ($CDCl_3$) or 6·3 (trifluoroacetic acid)]. The product otherwise had $\lambda_{max.}$ (EtOH) 252 and 343 nm (log ε 4·17 and 3·91); τ ($CDCl_3$) 2·6—3·3 (6H, m), 3·9 (1H, d, *J* 8 Hz), 5·4 (2H, s), and 7·0 (3H, s).

Auto-oxidation of 2H-*naphtho*[1,8-bc]*furan.*—This compound (5·3 g), melted in a bath held at 70—75°, was aerated with some losses due to sublimation, and at intervals weighed samples (*ca.* 40 mg) were withdrawn and partitioned between ether and dilute sodium hydroxide solution. 8-Hydroxy-1-naphthaldehyde was recovered from the alkaline layer by acidification, taken up in carbon tetrachloride, and estimated by measuring its extinction at 400 nm. Reaction times and conversions into aldehyde (16) were as follows: 3 h (0·54%); 24 h (0·88%). During a subsequent 24 h, several small additions of benzoyl peroxide, were made, causing the apparent conversion to rise to 4·1%. The product (4·38 g) was diluted with ether and extracted with aqueous N-sodium hydroxide (100 ml). From the ether extract, starting material (4·13 g; m.p. 48—51°) was recovered, and after acidification of the alkaline extract, the product was recovered with ether as orange crystals (157 mg), m.p. 63—83°. Chromatography on silica and elution with ether (5%) in benzene gave *8-hydroxy-1-naphthaldehyde* (101 mg), m.p. 85—96°, orange plates from pentane, m.p. 92—96° (Found: C, 76·3; H, 4·8. $C_{11}H_8O_2$ requires C, 76·7; H, 4·7%); $\nu_{max.}$ ($CHCl_3$) 2770 and 1660 cm^{-1}; $\nu_{max.}$ (tetrahydrofuran) 3150, 1680, and 1660 cm^{-1}; τ ($CDCl_3$) −1·60 (1H, s, exchangeable with D_2O), 0·24 (1H, s), 2·0 (1H, dd, *J* 8 and 1 Hz), 2·1 (1H, dd, *J* 6 and 1 Hz), 2·5—2·8 (3H, m), and 2·9 (1H, dd, *J* 7 and 2 Hz).

8-Hydroxymethyl-1-naphthyl Methyl Ether.—A solution of 8-hydroxymethyl-1-naphthol (5·0 g) and sodium hydroxide (1·2 g) in water (40 ml) was treated gradually with dimethyl sulphate (2·7 ml), stirred at 100° for 1 h, then cooled. Ether extraction gave the product (5·22 g); crystals from benzene, m.p. 88—90° (lit.,[14] 88—89°) (Found: C, 76·4; H, 6·3. Calc. for $C_{12}H_{12}O_2$: C, 76·6; H, 6·4%).

8-Methoxy-1-naphthaldehyde.— 8-Hydroxymethyl-1-naphthyl methyl ether (1·89 g) was added during 3 min to a stirred suspension of activated manganese dioxide in benzene (500 ml) [made[15] from wet manganese dioxide (53 g)]. The mixture was stirred for 1 h then filtered; concentration of the filtrate afforded *8-methoxy-1-naphthaldehyde* (1·64 g), m.p. 88—90° (from methanol) (Found: C, 77·3; H, 5·4. $C_{12}H_{10}O_2$ requires C, 77·4; H, 5·4%); $\nu_{max.}$ ($CHCl_3$) 2800, 1680, and 1624 cm^{-1}; $\lambda_{max.}$ (EtOH) 253

[14] D. C. Kleinfelter and P. H. Chen, *J. Org. Chem.*, 1969, **34**, 1741.

[15] I. M. Goldman, *J. Org. Chem.*, 1969, **34**, 1979.

and 330 nm (log ε 4·39 and 3·63); τ ($CDCl_3$) −1·03 (1H, s), 2·1 (2H, m), 2·6 (3H, m), 3·1 (1H, dd, *J* 6 and 2 Hz), and 6·0 (3H, s).

8-Hydroxy-1-naphthaldehyde.— 8-Methoxy-1-naphthaldehyde (515 mg) in benzene (120 ml) under nitrogen was treated with aluminium chloride (1·44 g). The mixture was boiled for 5 min, cooled, and shaken with water, and the separated organic layer was extracted with aqueous 4% sodium hydroxide. On acidification, 8-hydroxy-1-naphthaldehyde was recovered with ether as orange crystals (416 mg), m.p. 80—95°.

Partial Reduction of the Lactone (17).—The lactone of 8-hydroxy-1-naphthoic acid (798 mg) [16] in bis-(2-methoxyethyl) ether (5 ml) was stirred while a mixture of bis-(2-methoxyethyl) ether (20 ml) and 1·18M-sodium borohydride in the same solvent (1 ml) was added dropwise during 30 min. The mixture was stirred with enough water to precipitate a gum, which was triturated with fresh batches of water until it solidified (472 mg). Recrystallisation from chloroform afforded an 8-hydroxy-1-naphthoate monoester of 8-hydroxymethyl-1-naphthol (40 mg), as light yellow prisms, m.p. 168—170° (Found: C, 75·9; H, 4·8. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%); $\nu_{max.}$ ($CHCl_3$) 3550sh, 3200br, and 1670 cm^{-1}; $\nu_{max.}$ (tetrahydrofuran) 3200br, 1735s, and 1670w cm^{-1}; $\lambda_{max.}$ (EtOH) 237, 303, 314, and 328 nm (log ε 4·75, 3·96, 3·95, and 3·92) [in cyclohexane these peaks are of lower intensity and shoulders are observed at 255 and 350 nm (log ε 4·29 and 3·53)]; τ [$(CD_3)_2CO$] 0·26 (1H, s, exchangeable), 0·81 (1H, s, exchangeable), 2·0—2·8 (10H, m), 3·0 (2H, m), and 3·81 (2H, s); *m/e* (70 eV) 344 (0·8%), 326 (2·2%), 188 (29%), 174 (25%), 171 (34%), 170 (99%), 156 (73%), 128 (31%), 127 (40%), and 114 (100%); *m/e* (12 eV) 344 (100%), 206 (18%), and 188 (25%).

Oxidation of 2H-*Naphtho*[1,8-bc]*furan with Lead Tetra-acetate.*—2*H*-Naphtho[1,8-*bc*]furan (9·35 g) dissolved in warm acetic acid, was added to acetic acid (1·34 l) containing lead tetra-acetate (0·063 mol as determined iodometrically). The solution was kept for 4 h at room temperature, concentrated under reduced pressure, then partitioned between water and ether. The organic layer was washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and concentrated to an orange gum. {In a separate experiment a portion of this gum was taken up in ether, washed with dilute aqueous sodium hydroxide, dried ($MgSO_4$), concentrated, and purified by preparative t.l.c.; the principle zone on elution had $\nu_{max.}$ (CCl_4) 1740 cm^{-1}; τ (CCl_4) 2·3—2·8 (6H, m), 3·33 (1H, dd, *J* 6 and 1 Hz), and 8·00 (3H, s), showing it to consist of 2-acetoxy-2*H*-naphtho[1,8-*bc*]furan (15; X = OAc)}. The total product was triturated with warm methanol (100 ml) and aqueous 8% sodium hydroxide (100 ml) for 30 min, then partitioned between ether and water. The organic layer was concentrated, then steam-distilled, and ether was used to isolate (from the distillate) unchanged naphthofuran (1) (1·91 g) [R_F 0·8 on silica t.l.c. developed with carbon tetrachloride–benzene (1 : 4)], and (from the residue) a viscous gum (0·43 g) (two spots, R_F 0·55 and 0·50 in the same system), believed to consist of the diastereoisomers (19a and b) on the basis of the following evidence. A sample (118 mg) gave two fractions on preparative t.l.c., the first crystallising though darkening rapidly in air, showing only one spot (R_F 0·50); τ (CCl_4) 2·4—3·1 (10H, m), 3·4 (1H, d, *J* 6 Hz), 3·55 (1H, d, *J* 7 Hz), and 4·35 (2H, s); *m/e* 311 (36%), 310 (M^+, 100%), 309 (84%), and 308 (14%). The other fraction had the same mass spectrum but still showed two spots on t.l.c. (R_F 0·16 and 0·50); τ (CCl_4) exactly as the other fraction except for the last peak which was accompanied by another of equal intensity at 4·25 (each 1H).

The alkaline extract was neutralised with carbon dioxide and the precipitate was collected with ether as an orange gum which crystallised (7·32 g). Repeated extraction with boiling pentane gave 8-hydroxy-1-naphthaldehyde as orange crystals (3·44 g), m.p. 94—97° [from ether–light petroleum (b.p. 40—60°)]. The residue from pentane extraction (4·09 g) was chromatographed on silica (200 g). Benzene eluted first the aldehyde (20) (600 mg), light orange prisms from chloroform, m.p. 175—177° (Found: C, 81·3; H, 4·4. Calc. for $C_{22}H_{14}O_3$: C, 81·0; H, 4·3%); $\nu_{max.}$ ($CHCl_3$) 2820, 2730, 2650, 1660, and 1620 cm^{-1}; $\nu_{max.}$ (tetrahydrofuran) 1660 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 279, 327, and 390 nm (log ε 4·33, 4·00, and 3·61); $\lambda_{max.}$ (tetrahydrofuran) 275, 327, and 384 nm (log ε 4·31, 4·03, and 3·56); $\lambda_{max.}$ (N-NaOH) 263, 326, and 346 nm (log ε 4·27, 4·00, and 3·86); τ ($CDCl_3$) −2·30 (1H, s, exchangeable with D_2O), 0·16 (1H, s), 2·00 (2H, d, *J* 7 Hz), 2·3—2·8 (9H, m), 3·2 (1H, d, *J* 6 Hz); *m/e* 327 (32%), 326(M^+, 86%), 325 (25%), 324 (18%), 323 (11%), 297 (75%), and 156 (100%). Despite its phenolic group, aldehyde (20) dissolves only very slowly in aqueous alkali.

Further elution with benzene yielded 8-hydroxy-1-naphthaldehyde (1·92 g), m.p. 87—96° [from ether–light petroleum (b.p. 40—60°)]; and ether (5%) in benzene eluted crude aldehyde (21); this was purified by preparative t.l.c. [ethyl acetate–benzene (1 : 9)], giving aldehyde (21) (0·29 g), minute orange prisms from benzene, m.p. 200—205° (Found: C, 77·2; H, 4·1. Calc. for $C_{22}H_{14}O_4$: C, 77·2; H, 4·1%); $\nu_{max.}$ ($CHCl_3$) 2780, 2650, and 1660 cm^{-1}; $\nu_{max.}$ (tetrahydrofuran) 3130, 1680, and 1660 cm^{-1}; $\lambda_{max.}$ ($CHCl_3$) 262, 280sh, 334, and 404 nm (log ε 4·55, 4·47, 3·71, and 3·97); $\lambda_{max.}$ (tetrahydrofuran) 257, 334, and 350sh nm (log ε 4·55, 3·97, and 3·94); $\lambda_{max.}$ (N-NaOH) 259, 349, and 384sh nm (log ε 4·51, 3·99, and 3·87); τ ($CDCl_3$) −1·73 (2H, s, exchangeable with D_2O), 0·08 (2H, s), 2·0 (2H, dd, *J* 6 and 1 Hz), and 2·3—2·9 (8H, m); *m/e* 343 (26%), 342 (M^+, 100%), 341 (8%), and 340 (11%).

We thank the S.R.C. for a studentship (to D. B.).

[1/1826 *Received*, 6*th October*, 1971]

[16] A. J. Birch, M. Salahud-Din, and D. C. C. Smith, *J. Chem. Soc.* (*C*), 1966, 523.