145. *Covalent Alkaline Derivatives of Di-2-hydroxy-1-naphthyl Sulphide and of Di-2-hydroxy-1-naphthylmethane.*

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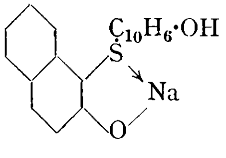
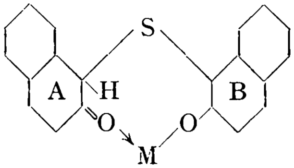
ATTEMPTS to isolate the disodium salt of di-2-hydroxy-1-naphthyl sulphide from aqueous alkaline media yielded an insoluble and stable *monosodium* salt (compare Lesser and Gad, *Ber.*, 1925, **58**, 2557). Further examination of this substance showed that, isolated from aqueous media, it has the composition $C_{20}H_{13}O_2SNa,4H_2O$; it melts at 255°, is insoluble in water, moderately soluble in warm benzene or chloroform, and is strikingly characterised by its high solubility in ether. These properties show that the substance contains the metal in the covalent state (Sidgwick and Plant, J., 1925, **127**, 209; Sidgwick and Brewer, *ibid.*, p. 2379). In assigning a structure to the compound the alternatives (I) and (II) must be considered, but the former is rejected since di-2-hydroxy-1-naphthylmethane (II; S replaced by CH_2) yields a *monosodium* derivative of analogous composition and closely similar properties. The structure (II) is therefore adopted; it is further supported by the facts: (1) The monomethyl ether, obtained from this monosodium derivative by methylation or by synthesis from 2-naphthol and 1-bromothiol-2-methoxynaphthalene (Warren and Smiles, J., 1931, 918), is only slightly soluble in warm dilute aqueous sodium hydroxide and no sodium salt has been obtained from it; also in other reactions which will be described later it gives evidence of the structure indicated. (2) The dehydro-derivative (III) (Warren and Smiles, J., 1930, 956) is quantitatively formed from the monosodium derivative by oxidation (J., 1914, **105**, 1750). (3) Simple aromatic di-*o*-hydroxy-sulphides such as di-4-hydroxy-*m*-tolyl sulphide, which do not yield monomolecular dehydro-derivatives (compare III), do not under similar conditions give sodium derivatives of this character. The influence of substitution in the aromatic nuclei on the behaviour of sulphides of this type will be discussed on a future occasion. Facts similar to those mentioned in (1), (2) and (3) have been observed with derivatives of the analogous methane series.

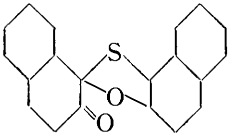
Experiments have been extended to the derivatives of di-2-hydroxy-1-naphthyl sulphide and di-2-hydroxy-1-naphthylmethane containing other metals; the former yielded



(I.)



(II.)



(III.)

covalent *monoalkali* derivatives (II; M as metal) with lithium ($4H_2O$ and $2H_2O$), sodium ($4H_2O$), potassium ($2H_2O$), and rubidium ($2H_2O$ and anyhdrous), and the latter gave the lithium ($4H_2O$), sodium ($4H_2O$) and potassium ($2H_2O$) derivatives. With the exception of the rubidium derivative mentioned, none of these could be dehydrated completely by heating at 100° or by other means.

The apparently anomalous composition of the tetrahydrates of the lithium derivatives requires further comment. It is suggested that the inclusion of the two additional water molecules by these substances is required for the easy attainment of the crystalline state; this view is supported by experiments made with the lithium derivative of the sulphide, which showed a reluctance to crystallise as a dihydrate. For example, the crystalline tetrahydrate of this substance is readily formed in presence of excess of water, but when a warm dilute solution of the tetrahydrate in benzene is rapidly cooled, a gelatinous material of indefinite composition is deposited; the crystalline dihydrate was obtained only by slow cooling of this solution. All the metallic derivatives mentioned are very soluble in ether; some evidence has been obtained of the presence of etherates in these solutions and of the formation of additive products with esters, but a closer examination of these has not yet been made.

One of the more interesting features of this series of covalent derivatives is the relative stability of the 8-membered co-ordinate ring which they contain; moreover, a certain flexibility of this ring seems evident from the formation of both the rubidium derivative of the sulphide and the lithium derivative of dihydroxynaphthylmethane. In seeking an explanation of this circumstance it may be noted that the stereochemical relation of the sulphur atom (or CH_2) to each naphthalene nucleus in (II) is different and it is suggested that this condition, by permitting a non-coplanar arrangement, facilitates chelation and enhances the stability of the ring which is then formed. Attemps to obtain, under the conditions described, similar covalent derivatives from 2 : 2′-dihydroxy-1 : 1′-dinaphthyl and from di-2-hydroxy-1-naphthyl disulphide have been unsuccessful; the behaviour of the disulphide seems the more interesting, since it is known (Stevenson and Smiles, J., 1930, 1745) that this substance yields a dehydro-derivative (III; S replaced by $-\text{S}\cdot\text{S}-$) on oxidation in alkaline solution and is therefore present in such media in the hydroxy-ketonic state required for the formation of the chelate ring.

In structures (II) of the type now encountered it is clear that a resonant condition of the system containing the metallic atom implies the facile attainment of the extreme phases, $\text{A}{=}\text{O}\rightarrow\text{Na}-\text{O}{-}\text{B}$ and $\text{A}{-}\text{O}-\text{Na}\leftarrow\text{O}{=}\text{B}$, which differ from each other not only in the sequence of the various linkages but also in the alternate situation of the 1-hydrogen atom at the nucleus A or B respectively. Resonance of the system $=\text{O}\rightarrow\text{M}-\text{O}-$ would thus appear also to require resonance of hydrogen between the two α-positions. There are several evident reasons for regarding this condition as impossible; perhaps the chief of these is that a change in the stereochemical arrangement of members of the ring would be involved; it is therefore concluded that co-ordinate linkage of the alkali metals in these substances is established without resonance of the systems formed. These considerations are of interest in view of the work of Sidgwick (*Ann. Reports*, 1933, 112; 1934, 40), who has shown that there are fundamental reasons for concluding that the co-ordination of hydrogen requires resonance of the system in which it occurs and thus differs from the mechanism of co-ordination by metals. No definite evidence concerning the structure of the parent hydroxy-compounds can at present be adduced, but it is worth notice that in the case of 2-hydroxy-1-naphthyl sulphide all the alkali derivatives examined are characterised by their high solubility in moist ether, whereas the parent hydroxy-compound is only slightly soluble in this medium.

EXPERIMENTAL.

Unless otherwise stated, all the metallic derivatives described were dried before examination in a current of nitrogen at 25—35°; they were readily soluble in cold ether and moderately soluble in hot benzene, toluene or chloroform. In hot solvents such as those mentioned, partial dehydration sometimes occurred. The m. p.'s recorded must be regarded as approximate and as depending to a certain extent on the rate of heating; in nearly all cases water was lost before the m. p. was reached.

*Derivatives of Di-2-hydroxy-*1*-naphthyl Sulphide.*—*Sodium derivative.* A suspension of the finely powdered sulphide (1 mol.) in 5% sodium hydroxide solution (2 mols.) was stirred and warmed until all had dissolved. The desired *product* separated in pale yellow plates from the cooled solution. It was dried for analysis in a current of air at 25°. It lost some water at about 100° and finally melted at 255°; attempts completely to dehydrate the substance by heating in a vacuum (115°) over phosphoric oxide were unsuccessful (Found: C, 58·8; H, 5·3; Na, 5·5. $C_{20}H_{13}O_2SNa,4H_2O$ requires C, 58·3; H, 5·1; Na, 5·5%). It was also analysed by determining the sulphide liberated after treatment with dilute sulphuric acid (Found: sulphide, 76·5. $C_{20}H_{13}I_2O_2SNa,4H_2O$ requires sulphide, 77·1%). The monomethyl ether of di-2-hydroxy-1-naphthyl sulphide separated when methyl alcohol containing this sodium derivative and methyl iodide was boiled (1 hour). It had m. p. 155° and was identical with the product previously (J., 1931, 918) obtained by synthesis (Found: C, 75·5; H, 4·9. Calc.: C, 75·9; H, 4·8%). The dimethyl ether was obtained by boiling (3 hours) a solution of the sulphide (1 mol.), sodium methoxide (3 mols.), and methyl iodide in methyl alcohol. It formed colourless prisms, m. p. 184°, not depressed by the yellow product (m. p. 185°) obtained (J., 1913, **103**, 345) from 2-methoxynaphthalene and sulphur chloride (Found: C, 76·7; H, 4·9. Calc.: C, 76·3; H, 5·2%).

The *lithium* derivative separated in the crystalline state when a solution of the sulphide (1 mol.) in hot aqueous lithium hydroxide (5%; 2 mols.) was cooled (Found: C, 60·8; H, 5·4. $C_{20}H_{13}O_2SLi,4H_2O$ requires C, 60·6; H, 5·3%). The monomethyl ether of the sulphide was obtained from this substance by reaction with methyl iodide in hot methyl alcohol. When a dilute solution of this tetrahydrate in hot benzene was slowly cooled, the *dihydrate* was obtained in prisms (Found: C, 66·9; H, 4·7. $C_{20}H_{13}O_2SLi,2H_2O$ requires C, 66·7; H, 4·7%).

The *potassium* derivative was obtained in the crystalline state when a hot solution of the sulphide (1 mol.) in aqueous potassium hydroxide (4·5%; 2 mols.) was slowly cooled. After being dried as usual, it had m. p. 230° (Found: C, 61·1; H, 4·4; K, 9·7. $C_{20}H_{13}O_2SK,2H_2O$ requires C, 61·2; H, 4·3; K, 9·9%). Dehydration was incomplete after heating (120°) in nitrogen (2 hours).

The *rubidium* derivative was obtained by shaking the finely powdered sulphide (1 mol.), aqueous rubidium hydroxide (2 mols.; 6%) and rubidium chloride with a little ether. The crystalline material, which separated when the ethereal solution was kept, was purified from warm benzene; the product, after being dried in nitrogen at 80°, was the *dihydrate*, which had m. p. 210° (Found: C, 55·1; H, 3·5; Rb, 19·4. $C_{20}H_{13}O_2SRb,2H_2O$ requires C, 54·7; H, 3·9; Rb, 19·5%). Further dehydration was effected by heating in a current of nitrogen at 120°. The *anhydrous* material then obtained had m. p. 212° (Found: C, 60·4; H, 3·5. $C_{20}H_{13}O_2SRb$ requires C, 59·6; H, 3·2%).

*Di-3-bromo-2-hydroxy-*1*-naphthyl Sulphide.*—The *sodium* derivative was obtained by stirring the sulphide (1 mol.) with aqueous sodium hydroxide (3 mols.; 4%) and rapidly filtering the mixture. When the clear solution was kept, the product separated in pale yellow needles, m. p. 300° after being dried as usual (Found: C, 45·3; H, 2·8. $C_{20}H_{11}O_2Br_2SNa,2H_2O$ requires C, 44·9; H, 2·8%).

*Di-2-hydroxy-*1*-naphthylmethane.*—The *sodium* derivative was obtained as leaflets by cooling a solution of the dihydroxynaphthylmethane (1 mol.) in warm aqueous sodium hydroxide (2 mols.; 5%). This product, after some loss of water at 100°, had m. p. 255° (Found: C, 63·3; H, 5·4; Na, 5·8. $C_{21}H_{15}O_2Na,4H_2O$ requires C, 63·9; H, 5·8; Na, 5·8%). In hot methyl alcohol it was converted by methyl iodide or methyl sulphate into the *monomethyl* ether of di-2-hydroxy-1-naphthylmethane, which formed needles, m. p. 142°, sparingly soluble in cold alcohol and only slightly soluble in warm 2*N*-sodium hydroxide (Found: OMe, 9·9. $C_{22}H_{18}O_2$ requires

OMe, 9·9%). With acetic anhydride (100°, 30 mins.), it furnished an *acetyl* derivative, which formed needles from acetic acid, m. p. 131—133° (Found : C, 80·5; H, 5·7; OMe, 8·5. $C_{24}H_{24}O_3$ requires C, 80·9; H, 5·6; OMe, 8·7%). This acetyl derivative is also formed by prolonged interaction of hot acetic anhydride and di-2-methoxy-1-naphthylmethane, m. p. 148—149° (Kohn and Ostersetzer, *Monatsh.*, 1918, **39**, 302).

The *lithium* derivative separated in the crystalline state when a hot solution of the dihydroxynaphthylmethane (1 mol.) in aqueous lithium hydroxide (2 mols.; 3%) was cooled (Found : C, 66·5; H, 6·0; Li, 1·8. $C_{21}H_{15}O_2Li,4H_2O$ requires C, 66·7; H, 6·1; Li, 1·8%). The substance, like the lithium derivative of the sulphide, had no melting point, apparently passing into the electrovalent state at high temperatures. It yielded the monomethyl ether by reaction with methyl iodide in methyl alcohol, and when the cold solution in moist ether was mixed with benzene it was recovered (Found : C, 66·3; H, 6·2%).

The *potassium* derivative separated in needles when a hot solution of di-2-hydroxy-1-naphthylmethane (1 mol.) in aqueous potassium hydroxide (2 mols.; 4·5%) was cooled (Found : C, 66·9; H, 4·9; K, 10·0. $C_{21}H_{15}O_2K,2H_2O$ requires C, 67·4; H, 5·1; K, 10·4%). It lost some water at 100° and then melted at 245°. Di-2-hydroxynaphthylmethane is also soluble in a more dilute, hot solution of potassium hydroxide (1·4 mols.; 1·5%); when this solution was cooled, a different and more complex *potassium* derivative separated. This had m. p. 170° and was very soluble in moist ether (Found : C, 73·8; H, 4·9; K, 5·5. $C_{21}H_{15}O_2K,C_{21}H_{16}O_2,2H_2O$ requires C, 74·8; H, 5·2; K, 5·8%).

A further examination of this group of substances is being made.

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