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383. Covalent Alkaline Derivatives of Di-2-hydroxy-1-naphthyl Selenide and Allied Substances.

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Further investigation of covalent alkali derivatives of type (I) has been made; those derived from di-2-hydroxy-1-naphthyl selenide are described and shown to have compositions analogous to those of the methane and the sulphide series. In the sulphide and the methane series potassium derivatives of an "acid" type may be obtained, but under the same conditions sodium derivatives of "normal" composition are isolated. The study of the covalent alkali derivatives of substituted di-2-hydroxy-1-phenyl sulphides has been extended and additional illustration is given of the influence of the 6-methyl group in favouring the formation of these and of dehydro-derivatives. Further examples of an eight-membered non-coplanar ring containing co-ordinated alkali metal have been found in the lithium, sodium, and potassium derivatives of salicylideneacetophenone and of 4-salicylidene-1-methylcyclohexan-3-one (XIII), confirmation of the structure (I) assigned to the derivatives of o-hydroxy-sulphides and -methanes being thus obtained.

PREVIOUS experiments showed that di-2-hydroxy-1-naphthyl sulphide and di-2-hydroxy-1-naphthylmethane and their substitution products yielded covalent mono-alkali derivatives (Evans and Smiles, J., 1937, 727) to which the structure (I; X = S or CH₂; M = alkali metal) was assigned. Further examples of the non-coplanar ring indicated (I) have been found in the series of alkali derivatives of di-2-hydroxy-1-naphthyl selenide (I, X = Se), which have the same order of stability as that of the sulphide and the methane series; they are characterised by a similar high solubility in moist ether and separate when warm aqueous solutions of the electrovalent salts are cooled. Methylation of the sodium derivative gave the monomethyl ether of the selenide and oxidation with ferricyanide led to the dehydro-selenide (II); further analogy with the sulphide and the methane series was found in the similar degree of hydration of the sodium (4H₂O), potassium (2H₂O) and lithium (4H₂O) derivatives, the anomalous degree of hydration of the lithium derivative being noteworthy. Some evidence of instability of the ring in these selenides is given by the dehydration of the sodium derivative in hot chloroform solution, which yielded an anhydrous salt of electrovalent character.



Attempts to obtain covalent alkali derivatives from di-2-hydroxy-1-naphthyl sulphoxide or sulphone under conditions effective with the sulphide were unsuccessful. In these cases where the thio-group is replaced by thionyl or sulphonyl, suppression of the necessary hydroxy-ketonic state and a consequent diminished stability of the covalent derivatives may be expected. Renewed experiments to obtain covalent alkali derivatives from the corresponding disulphide have confirmed the previous conclusion (Evans and Smiles, *loc. cit.*) that the nine-membered ring which would be required for the formation of these substances is unstable or attained with difficulty. Examination of the 6:6'-dibromo- and 3:6:3':6'tetrabromo-derivatives, whose salts are less soluble than those of the parent substance, led to monosodium derivatives of covalent character, but owing to their instability they were not further investigated. Suitable derivatives of di-2-hydroxyphenyl sulphide or di-2hydroxyphenylmethane also are capable of yielding covalent mono-alkali compounds. In previous studies (McClement and Smiles, J., 1937, 1016; Shearing and Smiles, *ibid.*, p. 1933) it was found that this property and the formation of dehydro-derivatives, which evidently depend on the ability of the phenol to assume the hydroxy-ketonic structure,

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are shown only by sulphides and methanes containing the 6-methyl goup. Some further evidence of this influence of the 6-methyl group has now been obtained.

5-Chloro-o-4-xylenol and sulphur chloride yielded the sulphide (III). An isomeride, which was obtained by chlorinating di-4-hydroxy-o-5-xylyl sulphide (IV), evidently has the alternative structure (V). Of these sulphides, (III) yielded a covalent monosodium and a dehydro-derivative, but neither (IV) nor (V) gave these products. m-5-Xylenol, according to its usual behaviour on substitution (compare Lesser and Gad, Ber., 1923, 56, 974), may be expected to yield mainly the sulphide (VI) together with a smaller quantity of (VII) and perhaps the unsymmetrical sulphide containing both these structures. After removal of the chief product (VI) the residue was found to contain a sulphide, which was isolated by the solubility of its sodium salt in wet ether; the structure (VII) is therefore assigned to it.



Previous examination of the sulphides (McClement and Smiles, *loc. cit.*) derived from 2-chloro-*m*-5-xylenol (VIII), 5-chloro-*p*-2-xylenol (IX), and ψ -cumenol (X) was restricted to the isolation of their covalent monosodium derivatives. A more complete study of their mono-alkali compounds, including those derived from di-6-chloro-3-hydroxy-2-cymyl sulphide (XI), has been made. Compared with the derivatives of 2-naphthol (I), the chief features of this series are a lower stability of the tetrahydrates of the sodium and lithium compounds and in some cases a greater tendency to revert to the electrovalent state



by dehydration. For example, the sodium derivatives of (VIII), (IX), (X), and (XI) have been obtained as dihydrates and some evidence of less stable tetrahydrates was found in the cases of (IX), (X), and (XI). Also the lithium derivatives of (VIII), (IX), (X), and (XI) were isolated as dihydrates, evidence of unstable tetrahydrates being obtained only with (IX) and (X). None of the derivatives of (VIII) showed a melting point, although they had the usual high solubility in moist ether. The potassium, sodium, and lithium compounds of (XI) separate as liquids from the aqueous media of their preparation : this characteristic behaviour is also shown by the lithium and potassium derivatives of the selenide (I, X = Se).

All the alkali compounds now discussed may be regarded as the "normal" mono-alkali derivatives. The only example of an "acid" type hitherto encountered had the composition $C_{21}H_{14}(OH) \cdot OK$, $C_{21}H_{14}(OH)_2$, $2H_2O$ and was obtained (Evans and Smiles, *loc. cit.*) from di-2-hydroxy-1-naphthylmethane with aqueous potassium hydroxide of greater dilution and in smaller molecular proportion than that leading to the "normal" derivative. Under the same conditions di-2-hydroxy-1-naphthyl sulphide gave a potassium derivative of analogous composition, but it is remarkable that both this sulphide and di-2-hydroxy-1-naphthylmethane with aqueous sodium hydroxide under these conditions gave the "normal" derivative, *e.g.*, $C_{21}H_{14}(OH) \cdot ONa$, $4H_2O$. At present no well-founded explanation of this different behaviour of the two alkali metals can be given, but it seemed probable that the reluctance of sodium to form the acid type of derivative in aqueous media might be due to the greater stability of these in the case of the potassium derivatives, which have only been observed as dihydrates. This view appears to be confirmed by the behaviour of (VIII) in presence of sodium hydroxide; the tetrahydrate of this sodium derivative.

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tive has not been isolated; in fact the dihydrate is somewhat unstable, and with the more dilute alkali the "acid" type of sodium compound was formed.

Since covalent alkali derivatives of type (I) are comparatively stable and are readily formed even in aqueous solutions of the salts, it may be expected that further examples of an eight-membered non-coplanar ring should be obtained from substances offering similar intramolecular conditions. The structure which has been assigned to these sulphides and di-2-hydroxy-1-naphthylmethanes (I) requires for its establishment three chief conditions in the parent substance: the ability to assume the hydroxy-ketonic state, a suitably close approach of the oxygen atoms concerned, and a configuration which permits the formation of a non-coplanar ring. Investigation has been extended to other types which appear to offer these essential intramolecular features; among these the salicylidene derivatives of The ease with which these substances are acetone and acetophenone are prominent. converted by acids into the benzopyrylium salts indicates their *cis*-configurations and the close approach of hydroxyl and carbonyl in them. Assuming these conditions, it is evident that the metal in their alkali salts, if inclined to form a co-ordinate link with carbonyl oxygen, could be accommodated between the oxygen atoms with little strain by suitable rotatory displacement of the phenoxyl or acyl groups, a non-coplanar eight-membered ring being then formed (XII). 4-Salicylidene-1-methylcyclohexan-3-one, which readily yields xanthylium salts (Borsche, Annalen, 1912, 393, 39), offers conditions similar to those in (XII). In alkali salts of this substance, the facile inclusion of the metal in a chelate ring would mainly depend on adjustment of phenoxyl, the carbonyl group by its inclusion



in the cyclohexane ring being deprived of free mobility. Covalent lithium, sodium, and potassium derivatives of both these types (XII and XIII) are readily obtained; like those derived from (I), they separate from aqueous media and contain two or four molecules of water, but they lack the high solubility in moist ether characteristic of the latter class. The sodium derivatives of type (XII, R = Ph or Me) yield adducts with salicylaldehyde and thus differ from the naphthol derivatives (I, M = Na), which are decomposed by the reagent. The isolation of these derivatives (XII and XIII) evidently supports the structure (I) assigned to the covalent alkali derivatives of the hydroxy-sulphides, -selenides, and -methanes.

Brief attempts to isolate copper derivatives of (I) showed that these exist but are far less stable than either the alkali compounds now recorded or the copper derivatives containing a seven-membered non-coplanar ring obtained by Brady (J., 1933, 1227) from o-diphenol.

EXPERIMENTAL.

Derivatives of Di-2-hydroxy-1-naphthyl Selenide.—The dehydro-derivative (II) separated in an amorphous condition when a solution of potassium ferricyanide (2·2 mols.) was gradually added to a cooled and shaken solution of the selenide (1 mol.) in aqueous potassium hydroxide. It was collected in chloroform and, after the solution had been dried, the solvent was evaporated (15°). The viscous residue slowly crystallised in contact with alcohol, in which it was sparingly soluble; the product, a red-brown crystalline powder, had m. p. 145° (Found : C, 66·3; H, 3·1. $C_{20}H_{12}O_2$ Se requires C, 66·1; H, 3·3%).

The monomethyl ether. Methanol (100 c.c.) containing the tetrahydrate of the monosodium derivative (3.6 g.) and methyl sulphate (2 mols.) was warmed (35°, $\frac{1}{2}$ hour). The product, which separated when the mixture had been cooled, formed prisms, m. p. 148°, from aqueous acetone (Found : C, 66.4; H, 4.0. $C_{21}H_{16}O_2$ Se requires C, 66.4; H, 4.2%).

The *potassium* derivative separated as a heavy yellow liquid when a solution of the selenide in warm N-potassium hydroxide (2 mols.) was cooled. The product subsequently formed yellow prisms; these, after being dried in air (15°) , became paler in colour, yielding the *dihydrate*, which had m. p. 170° and was soluble in ether, toluene or chloroform. Analysis was effected by determining the selenide liberated after treatment with dilute sulphuric acid (Found : K, 8.9; selenide, 82.4. $C_{20}H_{13}O_2$ SeK,2H₂O requires K, 8.9; selenide, 83.1%).

The sodium derivative, prepared under similar conditions, separated from the aqueous medium in yellow prisms, which, after being dried in air (15°), had m. p. 270° with previous loss of water, and were soluble in ether, toluene or chloroform (Found : Na, 4.9; selenide, 80.0. $C_{20}H_{13}O_2SeNa_4H_2O$ requires Na, 5.0; selenide, 79.5%). When a solution of this *tetrahydrate* in chloroform was boiled, the colourless anhydrous sodium salt separated in the crystalline state; this did not melt and was insoluble in dry ether (Found : Na, 5.9. $C_{20}H_{13}O_2SeNa$ requires Na, 5.9%).

The *lithium* derivative, prepared under similar conditions, separated from the aqueous medium as an oil forming a thick emulsion. Since the product did not crystallise when the mixture was kept, it was collected in ether. The deep yellow oil remaining after the solvent had been removed (15°) from the dried solution was triturated with benzene; the tetrahydrate then separated in needles, which were soluble in the usual solvents. Like the lithium derivatives of the sulphide and di-2-hydroxy-1-naphthylmethane, this selenide did not melt when heated (Found : Li, 1.6; selenide, 83.4. $C_{20}H_{13}O_2SeLi,4H_2O$ requires Li, 1.6; selenide, 82.4%).

Derivatives of Di-2-chloro-5-hydroxy-m-4-xylyl Sulphide (VIII).—The potassium derivative was prepared by stirring a suspension of the sulphide in hot N-potassium hydroxide (2 mols.), exactly sufficient alcohol being finally added to obtain complete solution. When the mixture had been cooled, the crystalline product separated and this, dried in air (15°), yielded the *dihydrate*, which was readily soluble in moist ether and sparingly in hot toluene or chloroform (Found : C, 46.7; H, 4.5; K, 9.2. $C_{16}H_{15}O_2Cl_2SK, 2H_2O$ requires C, 46.0; H, 4.6; K, 9.4%).

The sodium derivative, prepared under similar conditions, formed needles, which were easily soluble in moist ether and after being dried in nitrogen (26°) consisted of the *dihydrate* (Found : C, 47.5; H, 4.8; Na, 5.6. C₁₆H₁₈O₂Cl₂SNa,2H₂O requires C, 47.9; H, 4.7; Na, 5.7%). Complete dehydration of this material was effected at 115° in a vacuum (Found : Na, 6.3. Calc. : Na, 6.3%) as recorded by McClement and Smiles (*loc. cit.*).

The *lithium* derivative was prepared under the same conditions; it separated as a gelatinous mass from the rapidly cooled solution and as needles when the mixture was slowly cooled. The product was collected in ether, in which it was very soluble, and was isolated as usual. After being dried in air (15°), the product consisted of the *dihydrate* (Found : C, 50·0; H, 5·0; Li, 1·7. C₁₆H₁₅O₂Cl₂SLi,2H₂O requires C, 49·9; H, 5·0; Li, 1·8%). None of these derivatives melted.

A sodium derivative of "acid" type was obtained when the sulphide was dissolved in hot aqueous sodium hydroxide (1·1 mols.; 1·5%). It separated from the cooled solution and was dried at 115° (Found : Na, 3·4. $C_{16}H_{15}O_2Cl_2SNa,C_{16}H_{16}O_2Cl_2S$ requires Na, 3·2%). For comparison with this behaviour di-2-hydroxy-1-naphthyl sulphide was dissolved in hot aqueous sodium hydroxide (1·3 mols.; 1·5%); the tetrahydrate of the "normal" monosodium derivative separated when the solution was cooled (Found : Na, 5·5. Calc. : Na, 5·4%). Di-2-hydroxy-1-naphthylmethane gave an analogous result (Found : Na, 5·8. Calc. : Na, 5·8%). On the other hand, a solution of di-2-hydroxy-1-naphthyl sulphide in hot aqueous potassium hydroxide (1·2 mols.; 1·5%) yielded, when cooled, needles of the "acid" dihydrate. These were soluble in ether, hot benzene or chloroform, had m. p. 200°, and were dried in nitrogen (26°) (Found : C, 66·7; H, 3·9; K, 5·8. $C_{20}H_{13}O_2SK,C_{20}H_{14}O_2S.2H_2O$ requires C, 67·6; H, 4·3; K, 5·5%). The similar behaviour of the corresponding methane with aqueous potassium hydroxide has already been recorded (Evans and Smiles, *loc. cit*.).

Derivatives of Di-6-chloro-3-hydroxy-p-2-xylyl Sulphide (IX).—The potassium derivative, prepared under the same conditions as those adopted with the sulphide (VIII), formed pale yellow needles of the *dihydrate*, m. p. 260°, which were soluble in ether and sparingly soluble in toluene (Found : C, 46.6; H, 4.5; K, 9.2. $C_{16}H_{15}O_2Cl_2SK, 2H_2O$ requires C, 46.0; H, 4.6; K, 9.4%).

The sodium derivative was obtained by similar treatment of the sulphide; it separated from the cooled medium in long needles of the tetrahydrate, m. p. 255° after some loss of water (Found: Na, 5·3. Calc.: Na, 5·3%). This tetrahydrate was previously isolated (McClement and Smiles, *loc. cit.*) by extraction of the solution of the sulphide in excess of aqueous alkali with ether. It was readily soluble in ether and moderately in chloroform. The crystals of the tetrahydrate, when kept (16°), slowly disintegrated and were finally dried in nitrogen (26°), the *dihydrate*, m. p. 255°, being then obtained (Found: C, 48·8; H, 4·4; Na, 5·7. C₁₆H₁₅O₂Cl₂SNa,2H₂O requires C, 47·9; H, 4·7; Na, 5·7%). When the chloroform solution

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was boiled, the anhydrous salt separated as a flocculent mass of needles, which did not melt (Found : C, 52.2; H, 4.1; Na, 6.1. $C_{16}H_{15}O_2Cl_2SNa$ requires C, 52.7; H, 4.1; Na, 6.3%).

The lithium derivative, similarly prepared, separated from the cooled medium in pale yellow needles of the *tetrahydrate*; these were dried in air (15°), had m. p. 200°, and were soluble in ether, chloroform or benzene (Found : C, 45.5; H, 5.3; Li, 1.7. $C_{16}H_{15}O_2Cl_2SLi,4H_2O$ requires C, 45.6; H, 5.4; Li, 1.6%). When the tetrahydrate was kept in a current of dry nitrogen (26°), water was lost, the *dihydrate* being formed (Found : loss of H_2O , 8.2. Conversion of tetra-into di-hydrate requires loss of H_2O , 8.5%).

Derivatives of Di-5-hydroxy-6- ψ -cumyl Sulphide (X).—The sulphide was completely soluble in the usual alkaline media (2 mols.; N), the addition of alcohol being unnecessary. With potassium hydroxide, the sulphide showed exceptional behaviour. After the solution in this reagent had been kept (4 days, 15°), the insoluble product was collected in ether; after being isolated in the usual manner (15°), it formed pale yellow needles of the "acid" dihydrate, m. p. 223°, soluble in chloroform or toluene (Found: C, 63·7; H, 6·7; K, 5·6. $C_{18}H_{21}O_2SK, C_{18}H_{22}O_2S, 2H_2O$ requires C, 63·8; H, 6·9; K, 5·7%). When the chloroform solution was boiled, a crystalline product separated; this was not closely examined.

The sodium derivative separated as a mass of thin needles when the usual aqueous alkaline medium was cooled. These were collected in ether and after removal of the solvent (15°) the impure *tetrahydrate* remained as needles, m. p. 245° with previous loss of water (Found : C, 55.7; H, 7.5. C₁₈H₂₁O₂SNa,4H₂O requires C, 54.6; H, 7.3%). By drying in nitrogen (26°), this material was easily converted into the *dihydrate*, which was soluble in toluene or ether (Found : C, 60.1; H, 6.8; Na, 6.2. C₁₈H₂₁O₂SNa,2H₂O requires C, 60.0; H, 6.9; Na, 6.4%).

The lithium derivative was obtained in thick needles when the usual alkaline solution was kept (15°, 4 days); these after isolation gradually changed in appearance and when dried in air (15°) evidently consisted of the impure *tetrahydrate* (Found : C, 58.9; H, 7.1; Li, 1.8. $C_{18}H_{21}O_2SLi,4H_2O$ requires C, 56.8; H, 7.6; Li, 1.8%), which was converted into the *dihydrate* by drying in nitrogen at 26° (Found : C, 63.2; H, 7.0; Li, 2.1. $C_{18}H_{21}O_2SLi,2H_2O$ requires C, 62.8; H, 7.3; Li, 2.0%). The latter was soluble in ether, chloroform or toluene and had an indefinite m. p. 150° after previous loss of water. For comparison with this, the *lithium* derivative of di-5-hydroxy-6- ψ -cumyl methane (X, S replaced by CH₂) was prepared. After being dried in air (15°), it formed needles of the *tetrahydrate*, which were soluble in ether or toluene (Found : C, 62.2; H, 8.8; Li, 1.9. $C_{19}H_{23}O_2Li,4H_2O$ requires C, 63.0; H, 8.6; Li, 1.9%). This tetrahydrate was evidently more stable than that of the sulphide.

Derivatives of Di-6-chloro-3-hydroxy-2-cymyl Sulphide (XI).—The potassium derivative separated from the cooled alkaline medium as a yellow liquid, which subsequently set to a jelly. This was collected in ether and, after the usual process, colourless prisms of the *dihydrate* were obtained; these had m. p. 206° and were soluble in ether, chloroform or toluene (Found : C, 50.4; H, 5.4; K, 8.4. $C_{20}H_{23}O_2Cl_2SK, 2H_2O$ requires C, 50.7; H, 5.7; K, 8.2%).

The sodium derivative separated as a yellow oil, which solidified, forming a mass of large prisms. These evidently consisted of an unstable tetrahydrate; they disintegrated in the air (15°) and when dried in nitrogen were converted (26°) into the *dihydrate*, which had m. p. 125° and was soluble in the usual organic media (Found : C, 52.0; H, 6.0; Na, 4.9. $C_{20}H_{23}O_2Cl_2SNa, 2H_2O$ requires C, 52.5; H, 6.0; Na, 5.0%).

The *lithium* derivative, also, separated as a liquid; this solidified, yielding the *dihydrate*, which formed yellow plates, m. p. 95° (Found : C, 53.8; H, 5.9; Li, 1.5. $C_{20}H_{23}O_2Cl_2SLi_2H_2O$ requires C, 54.5; H, 6.1; Li, 1.6%).

Di-5-chloro-4-hydroxy-o-3-xylyl Sulphide (III).—A solution of the chloroxylenol (10 g.), sulphur chloride ($3\cdot 5$ g.), and aluminium chloride (10 g.) in carbon disulphide (50 c.c.) was kept (24 hrs., 16°). The residue obtained after removal of the solvent and unchanged chloro-xylenol was dried, triturated with light petroleum, and crystallised from acetic acid. The product was dissolved in warm aqueous sodium hydroxide, and the sodium derivative precipitated with brine. The sulphide liberated from this product crystallised from acetic acid in prisms, m. p. 154° (Found : C, 56·2; H, 4·8. C₁₆H₁₆O₂Cl₂S requires C, 55·9; H, 4·6%).

The *dehydro*-derivative was obtained by adding aqueous sodium hypochlorite (2%) to a solution of the sulphide in excess of alkali. The insoluble orange product was purified from aqueous acetone and then had m. p. 115° (approx.) (Found : C, 56.8; H, 4.5. $C_{16}H_{14}O_2Cl_2S$ requires C, 56.3; H, 4.1%).

The sodium derivative was prepared from the sulphide in the usual way (2 mols. of N-sodium hydroxide) and was collected in ether, in which it was easily soluble. After the usual treatment the solution yielded long yellow needles, sparingly soluble in chloroform or toluene, which

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evidently consisted of the tetrahydrate (Found: Na, 5.4. C18H15O2Cl2SNa,4H2O requires Na, 5.3%).

Di-4-hydroxy-0-5-xylyl Sulphide (IV).—This was obtained from the reaction of sulphur chloride (1 mol.) with o-4-xylenol (2 mols.) in chloroform; it crystallised from acetic acid in prisms, m. p. 157° (Found : C, 70.5; H, 6.8. C₁₆H₁₈O₂S requires C, 70.1; H, 6.6%). When a solution of sulphuryl chloride (9 g.) in chloroform (20 c.c.) was gradually added (15°) to a solution of this sulphide (9.1 g.) in the same solvent, di-3-chloro-4-hydroxy-0-5-xylyl sulphide (V) was formed. This was isolated by removal of the solvent and solution of the residue in 2N-sodium hydroxide. The material liberated from this solution in the usual way crystallised from acetic acid in prisms, m. p. 145° (Found : C, 56.4; H, 4.9. C16H16O2Cl2S requires C, 56.0; H, 4.7%). A mixture of this sulphide with (III) had m. p. 130° (approx.).

Di-5-hydroxy-m-2-xylyl Sulphide (VI) .- This sulphide, obtained from m-5-xylenol and sulphur chloride in chloroform, separated from the reacting mixture and, purified from acetic acid, had m. p. 265° (Found : C, 70.5; H, 6.8. C16H18O2S requires C, 70.1; H, 6.6%). After a further small quantity of this sparingly soluble sulphide had been removed from the motherliquor, the solvent was evaporated, the residue dissolved in N-sodium hydroxide, and the clear solution, after the addition of brine, shaken with ether. This solvent removed a sodium derivative which yielded an isomeride of (VI), evidently di-5-hydroxy-m-6-xylyl sulphide (VII); it formed prisms from acetic acid, m. p. 149° (Found : C, 70.4; H, 6.7%). Alkaline ferricyanide converted this sulphide into an orange dehydro-derivative, but this was not closely examined. A covalent sodium derivative of " acid " type was obtained by adding brine to a solution of the sulphide (VII) (1 mol.) in N-sodium hydroxide (2 mol.) and shaking the solution with ether. The pale yellow, crystalline product isolated from the ethereal solution did not melt after being dried (Found : Na, 4.2. C₁₆H₁₇O₂SNa,C₁₆H₁₈O₂S requires Na, 4.0%); it was sparingly soluble in moist chloroform or toluene.

Derivatives of Salicylideneacetophenone (XII, R = Ph).—When a solution of the hydroxyketone (1 mol.) in N-potassium hydroxide (1 mol.) was kept (15°, 12 hrs.), the dihydrate of the potassium derivative separated as a mass of orange needles; these had m. p. 175° and were sparingly soluble in ether, soluble in hot toluene, and readily soluble in hot chloroform, from which the substance may be purified (Found : C, 60.2; H, 5.2; K, 13.2. C₁₅H₁₁O₂K,2H₂O requires C, 60.4; H, 5.0; K, 13.1%).

The sodium derivative, prepared in a similar manner, rapidly separated from aqueous solution in long orange needles of the dihydrate; these were dried in nitrogen (26°) (Found: C, 63.5; H, 5·3; Na, 7·9. C₁₅H₁₁O₂Na,2H₂O requires C, 63·8; H, 5·3; Na, 8·1%). The substance did not melt and was sparingly soluble in hot chloroform. When mixed with salicylaldehyde (15°) , it formed a bright yellow, crystalline *adduct*. This was washed with ether and dried in air (15°) (Found : Na, 6.9. C₁₅H₁₁O₂Na,C₇H₆O₂ requires Na, 6.3%). Prolonged washing with ether or treatment with hot toluene, in which the adduct was sparingly soluble, yielded the red sodium derivative of the hydroxy-ketone. For comparison with this behaviour the sodium derivative of p-hydroxybenzylideneacetophenone was examined. This was very soluble in water and was isolated as an orange crystalline mass by evaporating (15°) the solution to dryness; it was insoluble in the usual organic solvents and did not yield an adduct with salicylaldehyde, being decomposed by the reagent.

The lithium derivative separated when a warm solution of the hydroxy-ketone in N-lithium hydroxide (1 mol.) was cooled. The product, after being washed with ether, crystallised from chloroform in a mass of slender orange needles, m. p. 250° (decomp.). The dihydrate was obtained after drying in nitrogen (26°) ; this also was soluble in ether or hot toluene (Found : H, 5.6; Li, 2.6. $C_{15}H_{11}O_2Li$, 2H₂O requires H, 5.6; Li, 2.6%). Evidence of the existence of a less stable higher hydrate was obtained.

The sodium derivative of salicylideneacetone (XII, R = Me) was isolated by adding ether to an alcoholic solution of the hydroxy-ketone and sodium ethoxide (1 mol.) (Harries, Ber., 1891, 24, 3180). The red oil which quickly separated was discarded and red prisms were obtained by keeping the solution. These, washed with ether and dried in air (15°) , formed the *tetra*hydrate (Found : C, 46.8; H, 6.4; Na, 9.0. C₁₀H₉O₂Na,4H₂O requires C, 46.9; H, 6.6; Na, 9.0%), which was sparingly soluble in ether, hot toluene, or chloroform and decomposed at 100° (approx.). With salicylaldehyde, a yellow crystalline adduct was formed (Found : Na, 7.9. $C_{10}H_9O_2Na, C_7H_6O_2$ requires Na, 7.5%), which was decomposed by heating, boiling chloroform, or by a large excess of ether, yielding the red sodium derivative of the hydroxy-ketone.

Derivatives of 4-Salicylidene-1-methylcyclohexan-3-one (XIII).—When saturated aqueous potassium chloride was added to a solution of the hydroxy-ketone in N-potassium hydroxide

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(1.5 mols.), the *potassium* derivative at once separated in the crystalline state. The product, purified from hot chloroform, formed orange needles, m. p. 95° (approx.), sparingly soluble in ether and readily soluble in hot toluene. After drying in air (15°), the *dihydrate* was obtained (Found : K, 13.2. $C_{14}H_{15}O_2K$, 2H₂O requires K, 13.4%).

The sodium derivative separated in thin orange plates when a solution of the hydroxyketone in N-sodium hydroxide was cooled and kept (1 hr.). These, dried in air, formed the *tetrahydrate*, m. p. 190° after some loss of water (Found: C, 54.9; H, 7.2; Na, 7.4. $C_{14}H_{15}O_2Na, 4H_2O$ requires C, 54.2; H, 7.4; Na, 7.4%). The substance was readily soluble in hot toluene or chloroform, from which it separated as an orange jelly.

The lithium derivative separated as yellow needles when a solution of the hydroxy-ketone in aqueous lithium hydroxide was kept. After being dried in air (15°), the product consisted of the *tetrahydrate*, m. p. 235° (approx.); this was soluble in ether, toluene or chloroform (Found : C, 57.4; H, 7.8; Li, 2.3. $C_{14}H_{15}O_2Li_4H_2O$ requires C, 57.1; H, 7.8; Li, 2.3%). When these solutions were heated, partial dehydration occurred, a less soluble gelatinous material being formed.

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