CCXXVII.—*β-Naphtha-*1*-thioquinone and Dehydro-*2*-naphthol* 1*-Disulphide.*

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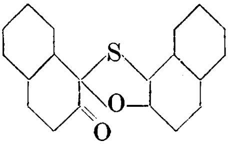
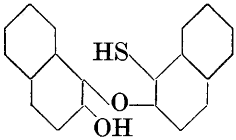
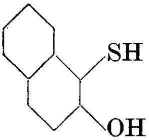
IT has been previously shown that dehydro-2-naphthol 1-sulphide has the structure (I) (this vol., p. 958). Hitherto the only method available for obtaining this substance has been by oxidation of either 2-naphthol 1-sulphide or *iso*-2-naphthol sulphide (II); the experiments now described were undertaken with the object of devising an alternative method of synthesis which would give further opportunity for the study of this type of substance. 1-*Thiol-*2*-naphthol* (III) was obtained from 2-naphthol by the method of Kauffmann (*Ber.*, 1926, **59**, 187; 1929, **62**, 396), the 2-naphthyl 1-thiocyanate being converted by reduction in acid media into a



(I.)



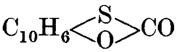
(II.)



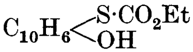
(III.)

mixture of the thiol (III) and the *thiolcarbonate* (IV). The latter resists hydrolysis by acids, but, being easily resolved by alkaline agents, served as a further source of the required thiol or disulphide. Careful hydrolysis of the thiolcarbonate with sodium ethoxide gave the *ethylthiolcarbonate* (V). Attempts to obtain the dehydro-sulphide (I) by reaction of the hydroxy-thiol (III) with β-naphthaquinone were unsuccessful, the normal type of nuclear additive product formed from quinones and thiols (D.R.-P. 175070) being obtained. An alternative method was provided by 1-*bromothiol-2-naphthol* (VII), which was obtained from the corresponding disulphide. This bromothiol (VII) evidently has the usual structure as indicated, since with 2-naphthol it yielded 2-naphthol 1-sulphide and with 6-bromo-2-naphthol and 4-chloro-1-naphthol the corresponding unsymmetrical sulphides (*e.g.*, VIII). The bromothiol thus affords a means of introducing the 1-thio-2-oxynaphthyl group into a suitably substituted naphthalene nucleus. Accordingly the reaction with 1-bromo-2-naphthol was investigated, since there is considerable evidence that substances of this type may react in the keto-methylene form (*e.g.*, VI) (Pummerer and Cherbuliez, *Ber.*, 1919, **52**, 1404; Goldschmidt and Wessbecher, *Ber.*, 1928, **61**, 379; Willstätter and Schuler, *Ber.*, 1928, **61**, 364).

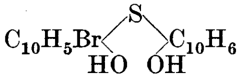
In presence of pyridine the desired dehydro-2-naphthol 1-sulphide was obtained from these reagents, the process evidently taking place as indicated by (VI) and (VII). This mode of synthesis confirms the structure assigned to the dehydro-sulphide on other grounds; moreover, from preliminary experiments it appears to be of wider application and to provide a means of obtaining the dehydro-derivatives of unsymmetrical naphthol sulphides.

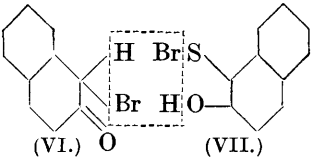

$C_{10}H_6{<}\genfrac{}{}{0pt}{}{S}{O}{>}CO$

(IV.)


$C_{10}H_6{<}\genfrac{}{}{0pt}{}{S\cdot CO_2Et}{OH}$

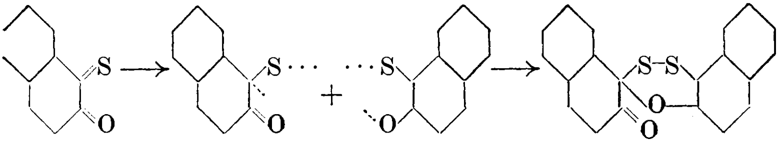
(V.)

(VIII.)

$\underset{HO}{C_{10}H_5Br}{<}\overset{S}{}{>}\underset{OH}{C_{10}H_6}$



(VI.) (VII.)

Another interesting product obtained together with the dehydro-sulphide from this process is formed by withdrawal of the halogen acid from the bromothiol (VII), and is more conveniently obtained from that substance alone with pyridine. The product to be expected from the process is clearly β-naphtha-1-thioquinone (XII), but the substance is in fact a dimeride of this. When it is reduced, half the sulphur is eliminated as hydrogen sulphide and *iso*-2-naphthol sulphide (II) is formed. This difference in character of the two sulphur atoms present, considered together with the structure of the *iso*-sulphide, indicates the "dehydro" structure (IX) for the substance. This view is entirely confirmed by the formation of the compound in the alkaline oxidation of 2-naphthol 1-disulphide. The substance is decomposed by phenylhydrazine with liberation of hydrogen sulphide.



(XII.) (XI.) (X.) (IX.)

The formation of *dehydro-2-naphthol* 1-*disulphide* from the spontaneous polymerisation of β-naphtha-1-thioquinone is interesting. It indicates the general instability of the thioquinones—a class of substance which hitherto has eluded isolation (compare Zincke and Glahn, *Ber.*, 1907, **40**, 3039; Zincke and Frohneberg, *Ber.*, 1909, **42**, 2721)—and also gives information of the character of this individual.

The tautomeric character of quinones which has been demonstrated by Wieland (*Ber.*, 1920, **53**, 1318; 1922, **55**, 1804) in the case of quinone-imines is evidently concerned in the formation of the dehydro-disulphide (IX) from the thionaphthaquinone (XII). The structure of the dehydro-disulphide shows that polymerisation of the thioquinone proceeds unsymmetrically and that in the process the latter assumes the aryloxy (X) and ketonic (XI) forms, which condense as indicated. Regarded in this manner, the case affords evidence of the tautomeric interchange of the ketonic and aryloxy structures and thus confirms the conclusions of Pummerer (*Ber.*, 1919, **52**, 1410), who has claimed a similar interconversion in the radicals liberated from the dehydrogenation of naphthols (see also Goldschmidt and Wessbecher, *loc. cit.*). In fact the polymerisation of β-naphtha-1-thioquinone presents many interesting features in common with those of the conversion of the unstable β-naphtha-1-methylenequinone into dehydrodi-2-naphtholethane (Pummerer and Cherbuliez, *loc. cit.*).

EXPERIMENTAL.

2-*Naphthol* 1-*Disulphide* (compare III).—(*a*) A solution of bromine (12 c.c.) in acetic acid (120 c.c.) was slowly added (¼ hour) to a cooled and stirred solution of 2-naphthol (33·5 g.) and sodium thiocyanate (72 g.) in acetic acid (650 c.c. of 96%). The solution was then mixed with water (2 l.) and the precipitated 2-naphthyl 1-thiocyanate was collected, washed with water, and suspended in acetic acid (250 c.c.) which contained hydrochloric acid (10 c.c.).

The warm mixture was treated with zinc dust (*ca.* 40 g.) until the red colour which appeared at first was removed, more hydrochloric acid being added if necessary to decompose the zinc salt of the thiol, which was inclined to separate. The clear solution was cooled and mixed with water (*ca.* 150 c.c.) and set aside. The thiolcarbonate (IV) separated and was removed, the solution being then treated with sufficient hydrogen peroxide to convert the thiol into the disulphide. The latter (25—30% yield) was purified from acetic acid and had m. p. 168° (Found : C, 68·4; H, 4·3. Calc. : C, 68·6; H, 4·0%); it was identical with a sample of the substance obtained by the method of Henriques (*Ber.*, 1894, **27**, 2998).

(*b*) The same substance was obtained by hydrolysis of the thiolcarbonate (IV). A hot aqueous solution (30 c.c.) of sodium hydroxide (10 g.) was added to a boiling solution of the thiolcarbonate (10 g.) in alcohol (30 c.c.). The deep orange solution was diluted (500 c.c.) and acidified with dilute sulphuric acid. The disulphide separated and was purified (7 g.) from acetic acid which contained a little hydrogen peroxide.

2-*Naphthylene* 1-*thiolcarbonate* (IV) was more conveniently prepared by dissolving the thiocyanate, obtained as previously described (*a*), in acetic acid (300 c.c.) which contained sulphuric acid (30 c.c.). The solution was boiled (¼ hour) and when it was cooled the desired substance separated, a further quantity being obtained by dilution of the liquid (85% yield). It separated from alcohol or acetic acid in long needles, m. p. 106°; these were insoluble in cold aqueous alkali and did not yield the disulphide with hydrogen peroxide (Found : C, 65·1; H, 3·0. $C_{11}H_6O_2S$ requires C, 65·3; H, 3·0%).

2-*Naphthol*-1-*ethylthiolcarbonate* (V).—A solution of sodium ethoxide (1 mol.) in alcohol was added to a cold shaken suspension of naphthylene thiolcarbonate (1 mol.) in alcohol. The yellow solution was mixed with dilute sulphuric acid and water was added until precipitation of the product was complete. The *substance* separated from light petroleum in needles, m. p. 127° (Found : C, 62·6; H, 4·9. $C_{13}H_{12}O_3S$ requires C, 62·9; H, 4·8%). Since it was recovered unchanged from solution in presence of hydrogen peroxide, the substance evidently has the structure indicated and does not contain the thiol group.

1-*Thiol*-2-*naphthol* (III).—A solution of the disulphide (5 g.) in hot acetic acid (50 c.c.) was treated with zinc dust (4 g.), hydrochloric acid being added at intervals to decompose the zinc derivative of the thiol. The *product* (90%) was isolated from the solution by addition of water and was purified from light petroleum. It formed long needles, m. p. 55° (Found : C, 67·8; H, 4·7. $C_{10}H_8OS$ requires C, 68·2; H, 4·5%).

1-*Bromothiol-2-naphthol* (VII).—A 10% solution of bromine (1·6 g.) in carbon tetrachloride was slowly added to a well-cooled and stirred suspension of finely divided 2-naphthol 1-disulphide (3·5 g.) in the same solvent. The disulphide dissolved and stirring was continued until separation of the crystalline *bromothiol* was complete. The substance formed deep red prisms, m. p. 93—95°; these were collected and washed with ether, in which they were sparingly soluble (Found: C, 46·6; H, 2·9; Br, 31·5. $C_{10}H_7OBrS$ requires C, 47·0; H, 2·7; Br, 31·3%).

The following naphthol sulphides were obtained by adding the naphthol concerned (2 mols.), suspended in carbon tetrachloride, to a stirred suspension of the bromothiol prepared as described from the disulphide (1 mol.). Interaction rapidly took place with liberation of hydrogen bromide, the reactants dissolving whilst the desired sulphide separated. From 2-naphthol and the bromothiol, 2-naphthol 1-sulphide was obtained (87% yield). This, after purification from acetic acid, had m. p. 217° and was identical with an authentic specimen. Similarly, 6-bromo-2-naphthol gave (80%) 6-*bromo*-2 : 2′-*dihydroxydi*-1-*naphthyl sulphide* (VIII); this separated from *n*-propyl alcohol in small prisms, m. p. 131° (Found: C, 60·2; H, 3·4. $C_{20}H_{13}O_2BrS$ requires C, 60·4; H, 3·3%). With 4-chloro-1-naphthol, the bromothiol yielded (90%) 4-chloro-1-hydroxy-2-naphthyl 2-hydroxy-1-naphthyl sulphide; this, after purification from benzene, had m. p. 168° and was identical with the substance obtained (J., 1928, 957) from 2-naphthol and 4-chloro-1-naphthyl-2-sulphur bromide (Found: C, 68·1; H, 3·8. Calc.: C, 68·1; H, 3·7%).

Dehydro-2-naphthol 1-*Sulphide* (I).—A solution of 1-bromo-2-naphthol (13·5 g.) in carbon tetrachloride (75 c.c.) was added to a suspension of the bromothiol which had been prepared from the disulphide (3·5 g.) in the same solvent (25 c.c.). After 14 hours (15°), a solution of pyridine (5 g.) in carbon tetrachloride (50 c.c.) was slowly added to the stirred liquid. The semi-solid mass and the solution were separately treated. The former was shaken with carbon tetrachloride (150 c.c.) and dilute aqueous sodium hydroxide until pyridine and phenolic compounds were removed. The carbon tetrachloride solution was dried, the solvent evaporated, and the residue dissolved in a little warm alcohol; when the solution cooled, the yellow dehydro-disulphide present separated in the crystalline state and was removed. The impure dehydro-sulphide remaining in solution was recovered and repeatedly purified from acetic acid, being then obtained in red prisms. The solution obtained from the reaction was treated in a similar manner, but the proportion of dehydro-disulphide present in this was greater. The purified material (yield, *ca.* 30%) had m. p. 155° and was identified by comparison with an authentic specimen of dehydro-2-naphthol 1-sulphide (Found : C, 75·6; H, 3·9. Calc. : C, 75·9; H, 3·8%). Identity with the dehydronaphthol sulphide was also established by comparing the *p*-nitrophenylhydrazone with an authentic specimen.

Dehydro-2-naphthol 1-Disulphide (IX).—(*a*) 2-Naphthol 1-disulphide was converted into the bromothiol in the usual manner. The cooled solution of the substance in carbon tetrachloride (75 c.c.) was mixed with a solution of pyridine (3 g.) in the same solvent (50 c.c.). Subsequently (1 hour) the solution was treated with excess of dilute aqueous sodium hydroxide, washed, and dried. The residue obtained by evaporation of the solvent was purified from hot benzene (65% yield).

(*b*) A stirred solution of 2-naphthol 1-disulphide (3·5 g.) in benzene (300 c.c.) was gradually mixed with an alkaline solution of potassium ferricyanide (2 mols.). The benzene solution was washed with aqueous sodium hydroxide and then with water, the amorphous solid which separated being rejected. The residue obtained after removal of the solvent was purified from benzene (yield, 60%). *Dehydro-2-naphthol 1-disulphide* separated from benzene in orange prisms, m. p. 171° (Found : C, 68·9; H, 3·5; S, 18·2; *M*, 354. $C_{20}H_{12}O_2S_2$ requires C, 69·0; H, 3·4; S, 18·4%; *M*, 348). Phenylhydrazine liberated hydrogen sulphide when it was added to a warm solution of the substance in acetic acid.

iso-2-*Naphthol Sulphide* (II).—A boiling solution of the dehydrodisulphide (0·5 g.) in acetic acid (15 c.c.) which contained zinc dust was treated with a few drops of concentrated hydrochloric acid. Hydrogen sulphide was liberated; when the solution had become colourless it was gradually mixed with water. The crystalline *iso*-2-naphthol sulphide which separated was purified in the usual manner; it had m. p. 156° and was identified by a close comparison with an authentic specimen (Found : C, 75·2; H, 4·5. Calc. : C, 75·5; H, 4·4%).

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