192. *Halogen Derivatives of Dehydro-2-naphthol 1-Disulphide.*

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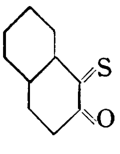
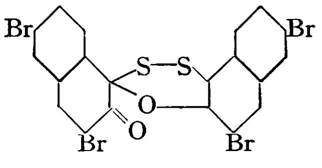
During experiments directed to the synthesis of dehydro-2-naphthol sulphide it was found (J., 1930, 1740) that removal of hydrogen bromide from 1-bromothiol-2-naphthol yielded the dehydro-derivative of 2-naphthol 1-disulphide (compare I). The formation of this substance was regarded as due to the unsymmetrical polymerisation of 1-thio-2-naphthaquinone (I) which may be expected to be liberated at the initial stage of the process. Taking this view, it appeared possible that appropriate substitution of the naphthalene nucleus would modify the activity of the corresponding thioquinones sufficiently to permit their isolation or existence in equilibrium with the dehydro-disulphides.

Experiments on this question have been begun by a study of the 3 : 3′- and 6 : 6′-*dibromo-* and 3 : 3′ : 6 : 6′*-tetrabromo-disulphides.* An improved method of obtaining these substances by alkaline hydrolysis of the 1-thiocyanates renders the preliminary isolation of the thiol unnecessary (compare *loc. cit.*, p. 1743). The corresponding *dehydro-disulphides* have been obtained from them by the following methods: (1) from the action of pyridine on the 1-bromothiol, (2) by oxidation with ferricyanide in aqueous alkaline solution, (3) by oxidation with bromine in presence of sodium acetate in acetic acid. The third of these methods is generally to be preferred.

Further study of dehydro-2-naphthol 1-disulphide has confirmed the results of preliminary experiments (*loc. cit.*) by showing the tendency of the dithio-system to lose half the sulphur; the products are generally those obtained from the dehydro-monosulphides.

(I.)





(II.)

For example, the unsubstituted dehydro-disulphide (compare II) on reduction yields the *iso*-sulphide of 2-naphthol, with acetyl chloride chloro-αββ′α′-dinaphthathioxin is formed, and reaction with bromine yields 3 : 4-dibromodehydro-2-naphthol sulphide. The behaviour of the bromo-derivatives with the two last-named reagents under conditions effective with the parent substance shows the restriction in activity to be expected with substitution in the 3-position. The 6 : 6′-dibromoquinol yields the chlorothioxin with acetyl chloride, but is hardly attacked by bromine, whilst the 3 : 3′-dibromo- and 3 : 3′ : 6 : 6′-tetrabromo-derivatives are not attacked by either reagent.

None of these dehydro-disulphides gave evidence of dissociation; their molecular weights in boiling benzene are normal and their solutions in hot anisole do not show the reversible changes of colour which might be expected. Moreover the 1-bromothiols of 3-bromo- and 3 : 6-dibromo-2-naphthols gave the dehydro-disulphides in good yield by treatment with alkaline media; the monothio-quinones were not detected in the products. It is evident, if the isolation of monothio-quinones is attainable by this method, that substituents of a character different from that of bromine are required.

The preparation of unsymmetrically substituted derivatives of 2-naphthol 1-disulphide has been attempted with a view to obtaining from them the dehydro-disulphides and examining the possibility of resolving the latter by hot solvents into mixtures of symmetrical components. The method used, reaction of a bromothiol with a thiol, has been successfully applied by Lecher (*Ber.*, 1920, **53**, 583) to simpler cases, but with the disulphides now in question mixtures were obtained and the difficulty of resolving them rendered continuation of the work impracticable. Attention is directed to the conversion of 2-naphthol 1-disulphide and its derivatives into the monosulphides by reaction with the corresponding 2-naphthol in alkaline solution. Two examples are recorded, but further investigation of the process has not been made.

EXPERIMENTAL.

2-*Naphthol* 1-*Disulphide.*—2-Naphthol 1-thiocyanate, prepared and isolated from 2-naphthol (33·5 g.), bromine, and sodium thiocyanate as previously described (*loc. cit.*), was hydrolysed (90—100°; ½ hour) by a solution of sodium hydroxide (50 g.) in water (500 c.c.). Addition of dilute sulphuric acid to the filtered solution liberated the required disulphide (75% yield).

6 : 6′-*Dibromo*-2-*naphthol* 1-*Disulphide*, $(C_{10}H_5Br{\cdot}OH)_2S_2$.—Acetic acid (120 c.c.) containing bromine (12 c.c.) was slowly (¼ hour) added to a cooled and stirred solution of 6-bromo-2-naphthol (52 g.) and sodium thiocyanate (72 g.) in acetic acid (600 c.c.). The thiocyanate, isolated by dilution (2000 c.c.), was hydrolysed as described; the *disulphide*, liberated by dilute sulphuric acid, after being recrystallised from acetic acid, formed yellow needles, m. p. 174° (70% yield) (Found: C, 46·8; H, 2·5; Br, 31·6. $C_{20}H_{12}O_2Br_2S_2$ requires C, 47·2; H, 2·3; Br, 31·5%).

6-*Bromo*-2-*naphthylene* 1-*thiolcarbonate*, $C_{10}H_5Br{<}\overset{S}{\underset{O}{}}{>}CO$, was obtained from the thiocyanate by means of zinc and acetic acid. It separated from alcohol in needles, m. p. 167° (Found: C, 46·7; H, 2·0; S, 11·7. $C_{11}H_5O_2BrS$ requires C, 47·0; H, 1·8; S, 11·4%).

3 : 3′-*Dibromo*-2-*naphthol* 1-*disulphide* was prepared by the method used for the 6-bromo-derivative. It was found necessary further to purify the crude material as the sodium salt by addition of brine to the alkaline solution. Liberated from this by dilute sulphuric acid and recrystallised from acetic acid, the substance formed yellow needles, m. p. 176° (Found: C, 46·9; H, 2·6%).

3 : 3′ : 6 : 6′-*Tetrabromo*-2-*naphthol* 1-*disulphide* was prepared in a similar manner from 3 : 6-dibromo-2-naphthol. Further purification of the crude product was effected by crystallisation of the sodium salt from warm aqueous sodium hydroxide. The required disulphide formed yellow needles, m. p. 221°, from benzene (Found: C, 35·8; H, 1·5; Br, 47·8. $C_{20}H_{10}O_2Br_4S_2$ requires C, 36·0; H, 1·5; Br, 48·0%).

When 2-naphthol 1-disulphide or the 6-bromo-derivative was kept (2 hours, 90—100°) in 10% aqueous sodium hydroxide with 2-naphthol or 6-bromo-2-naphthol (2 mols.) respectively, the corresponding monosulphide was formed and isolated in almost theoretical amount. These products were identified with authentic specimens.

Dehydro-2-*naphthol* 1-*Disulphide.*—Acetic acid (16 c.c.) containing bromine (1·6 g.) was slowly added to a stirred suspension of the disulphide (3·5 g.) and sodium acetate (5 g.) in the same solvent. Unchanged disulphide was removed from the crystalline precipitate by means of aqueous sodium hydroxide; the insoluble material (70%) separated from benzene in yellow prisms, m. p. 170°, which were identical with material obtained (*loc. cit.*, p. 1745) from the bromothiol or by oxidation with ferricyanide. When this dehydro-disulphide was treated (½ hour) with excess of boiling acetyl chloride an almost theoretical yield of chloro-$\alpha\beta\beta'\alpha'$-dinaphthathioxin (m. p. 173°) was obtained (compare J., 1912, **101**, 715). When a solution of bromine (2—3 mols.) in acetic acid was added to acetic acid containing the dehydro-disulphide (1 mol.) in suspension, the latter dissolved and was replaced by a precipitate of the tribromo-derivative of the dehydro-monosulphide (J., 1932, 639); this gave as usual the 3 : 4-dibromo-dehydro-sulphide (m. p. 208°) on treatment with pyridine.

6 : 6′-*Dibromodehydro*-2-*naphthol* 1-*disulphide*, prepared in a similar manner from the disulphide with bromine and sodium acetate in acetic acid, formed yellow prisms, m. p. 190°, from benzene (Found : C, 47·5; H, 2·3; S, 12·4; *M*, in boiling benzene at various concentrations, 506, 502, 512. $C_{20}H_{10}O_2Br_2S_2$ requires C, 47·4; H, 2·0; S, 12·6%; *M*, 506).

3 : 3′-*Dibromodehydro*-2-*naphthol* 1-*disulphide* was prepared : (*a*) by oxidation of the disulphide with bromine in presence of sodium acetate as usual (70% yield), and (*b*) the 1-bromothiol prepared from the disulphide (4 g.) by treatment with the theoretical amount of bromine in cooled dry carbon tetrachloride was suspended anew in this solvent (50 c.c.), and the mixture kept (1 hour) at room temperature before being washed with water. The residue obtained from the carbon tetrachloride and the product from (*a*) were purified from benzene. The substance formed yellow prisms, m. p. 184—185° (Found : C, 47·0; H, 2·2; S, 12·4%; *M*, 492, 489, 495).

3 : 3′ : 6 : 6′-*Tetrabromodehydro*-2-*naphthol* 1-*Disulphide* (II).—The bromothiol obtained from the disulphide (6·7 g.) was treated (1 hour) in carbon tetrachloride (100 c.c.) with pyridine (3 g.) at room temperature. After removal of excess of the base and its hydrobromide by the usual method the *dehydro*-derivative was isolated (75% yield) from the solution. It separated from benzene and light petroleum in yellow prisms, m. p. 189° (Found : C, 35·9; H, 1·3; S, 9·4; *M*, 665, 682. $C_{20}H_8O_2Br_4S_2$ requires C, 36·1; H, 1·2; S, 9·6%; *M*, 664).

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