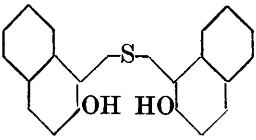
XXIX.—*A Synthesis of* iso*Naphthathioxin.*

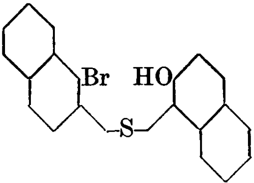
By Aaron Cohen and Samuel Smiles.

Dehydration of 2-naphthol 1-sulphide (I) gives αβα′β′-naphthathioxin (Mauthner, *Ber.*, 1906, **39**, 1346), and similar treatment of *iso*-β-naphthol sulphide yields *iso*naphthathioxin (J., 1913, **103**, 347, 909), which is also obtained from dehydro-β-naphthol sulphide by means of acetyl iodide (J., 1914, **105**, 1741). For many reasons which need not be here enumerated, the constitutions assigned to *iso*-β-naphthol sulphide (Lesser and Gad, *Ber.*, 1923, **56**, 963) and to dehydro-β-naphthol sulphide (Hinsberg, *J. pr. Chem.*, 1915, **91**, 307) are unsatisfactory. In seeking further information concerning them it seemed necessary as a first step to determine the structure of *iso*naphthathioxin, since this substance is simply related to both. αβα′β′-Naphthathioxin being known, syntheses of the αββ′α′- and βαβ′α′-derivatives were required for comparison of these materials with *iso*naphthathioxin. A preliminary account of experiments directed to the synthesis of αββ′α′-naphthathioxin has already been communicated (J., 1926, 957), since attempts having the same object were recorded elsewhere (Lesser and Gad, *Ber.*, 1925, **58**, 2557) while the work was in progress.

All attempts to sulphurate 1 : 2′-dinaphthyl oxide having failed, di-1-iodonaphthyl 2-disulphide was heated with sodium 2-naphthoxide in presence of copper; but the expected 2-disulphide of 1 : 2′-dinaphthyl oxide was not obtained, the only definite product encountered being the dinaphthathianthren which results from the action of copper on the disulphide alone (J., 1928, 1149). Attention was therefore directed to the derivatives of 1 : 2′-dinaphthyl sulphide. Dehydration of a 2 : 1′-dihydroxy-derivative (J., 1926, 957) was tried without success, but it was expected that halogen acid might be removed from 1-bromo-2′-hydroxy-2 : 1′-dinaphthyl sulphide (II).

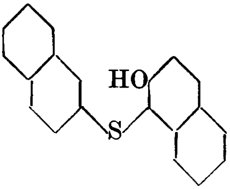
(I.)

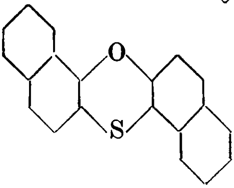




(II.)

(III.)





(IV.)

Previous experience (J., 1926, 1723) had shown that 2′-hydroxy-2 : 1′-dinaphthyl sulphide (III) is smoothly formed from sodium 2-naphthoxide and 2-naphthyl disulphoxide. 1-Bromonaphthalene-2-sulphinic acid was therefore prepared from 1-bromo-β-naphthylamine or from α-naphthylamine-2-sulphonic acid by the usual methods, but the conversion of this acid into the required disulphoxide could not be effected, the corresponding disulphide being obtained when the usual reagents were employed. Bromination of 2-naphthyl disulphoxide in acetic acid also gave this disulphide owing to reduction by the hydrogen bromide liberated (compare Fries, *Ber.*, 1914, **47**, 1196), but even when this was avoided by operating in pyridine the chief product was 2-naphthyl disulphide. Evidently before bromination took place the thiolsulphonate group was ruptured. Finally it was found that careful bromination of the hydroxy-sulphide (III) led to the desired material (II). The situation of halogen in this product was proved by synthesis, though in poor yield and quality, from the fusion of β-naphthol and 1-bromonaphthalene-2-sulphinic acid according to a reaction studied by Hinsberg (*Ber.*, 1903, **36**, 108) in other simpler cases. When the sodium derivative of this bromohydroxy-sulphide (II) was heated in presence of copper acetate a good yield of the required αββ′α′-naphthathioxin (IV) was isolated; this product was identical with the *iso*naphthathioxin obtained from *iso*-β-naphthol sulphide or from the dehydro-derivative.

It is evident that this result has an important bearing on the structures to be assigned to the "iso-" and "dehydro-" sulphides, but a discussion of this question is deferred until further evidence has been collected from experiments now in progress. One interesting feature which is now clear in the relations between these substances is that during the conversion of 2-naphthol 1-sulphide (I) *via* the dehydro-sulphide into the αββ'α'-naphthathioxin (IV) the situations of oxygen and sulphur in one naphthalene nucleus have become interchanged.

EXPERIMENTAL.

1-*Bromonaphthalene*-2-*sulphinic Acid*, $C_{10}H_6Br{\cdot}SO_2H$.—(a) *From α-naphthylamine*-2-*sulphonic acid.* The moist diazo-compound prepared as usual from the amino-acid (25 g.) was gradually added to a boiling solution of cuprous bromide (10 g.) in hydrobromic acid (100 c.c. of 36 %). When reaction was complete, the bromosulphonic acid was collected from the cooled liquid and purified by recrystallisation (charcoal) of the sodium salt (yield, 50%). This was converted into the sulphonyl chloride by treatment (20 g.) with an equal weight of phosphorus pentachloride (1 hour). 1-*Bromonaphthalene*-2-*sulphonyl chloride* separated from acetic acid in needles, m. p. 93—94° (Found: Cl + Br, 37·8. $C_{10}H_6O_2ClBrS$ requires Cl + Br, 37·8%). When this sulphonyl chloride was shaken (1 hour) with a concentrated alkaline solution of sodium sulphite it dissolved and from the clear solution sulphuric acid (60%) liberated the required sulphinic acid (yield, 60%).

(b) *From* 1-*bromo*-β-*naphthylamine.* The hydrochloride of the base (10 g.) was suspended in hydrochloric acid (100 c.c. of 15%) and diazotised at 0° (3 g. of sodium nitrite in 25 c.c. of water). The clear solution was slowly added to a stirred mixture of copper paste (50 g.) and a saturated solution of sulphur dioxide (150 c.c.), a current of the gas being maintained during the process. When decomposition was complete the solid was mixed with aqueous sodium hydroxide. The purified solution (charcoal) of the sodium salt was mixed with sulphuric acid (60 %), the required *sulphinic acid* being liberated (yield, about 60%). The sulphinic acid obtained by these methods was very sparingly soluble in water; it separated from aqueous acetone in needles, m. p. 146° (Found: C, 44·4; H, 2·4. $C_{10}H_7O_2BrS$ requires C, 44·3; H, 2·6%). When dissolved in pure warm thionyl chloride it yielded a relatively stable chloride. 1-*Bromonaphthalene*-2-*sulphinyl chloride*, $C_{10}H_6Br{\cdot}SOCl$, separated from dry benzene in yellow prisms, m. p. 110° (Found: Cl + Br, 39·7. $C_{10}H_6OClBrS$ requires Cl + Br, 39·9%).

Di-1-*bromonaphthyl* 2-*Disulphide*, $(C_{10}H_6Br{\cdot}S{\cdot})_2$.—A solution of the sulphinic acid in hot alcohol was saturated with sulphur dioxide and mixed with a few drops of hydriodic acid (*d* 1·7). Reduction was soon complete, the required *disulphide* separating from the liquid (yield, 90%). It was very sparingly soluble in alcohol or acetic acid and separated in plates, m. p. 161°, from benzene–

acetic acid (Found: C, 50·1; H, 2·6; *M*, 461. $C_{20}H_{12}Br_2S_2$ requires C, 50·4; H, 2·5%; *M*, 476). This disulphide was also obtained in almost quantitative yield by slowly adding a solution of bromine in acetic acid to 2-naphthyl disulphoxide in the same solvent.

1-*Bromo*-2′-*hydroxydinaphthyl* 2 : 1′-*Sulphide* (II).—(a) Acetic acid containing the theoretical amount of bromine was slowly added to a warm solution of 2′-hydroxydinaphthyl 2 : 1′-sulphide (III) in the same solvent. The reaction, which began at once, was completed by warming the mixture (50°). The product (yield, 95%), isolated by addition of water, crystallised from acetic acid (charcoal) in leaflets, m. p. 154° (Found: C, 62·7; H, 3·6. $C_{20}H_{13}OBrS$ requires C, 63·0; H, 3·4%).

(b) A molten mixture of 1-bromonaphthalene-2-sulphinic acid (5 g.) and β-naphthol (2·6 g.) was kept at 95—100° during 2½ hours. The dark violet product was boiled with dilute aqueous sodium hydroxide (8%), and the hot solution, freed from a small quantity of insoluble material, was mixed with a suitable amount of sodium hyposulphite (charcoal). On cooling, the sodium derivative of the required naphthol separated in the crystalline state (2·2 g.); it was purified from hot dilute sodium hydroxide solution. The naphthol generated from this salt and purified as previously indicated had m. p. 154° and this was not depressed by mixture with a sample obtained by bromination (method a). The substance gave a green solution in warm sulphuric acid. The sparingly soluble sodium salt separated from hot water in small shining plates. This bromonaphthol sulphide occurs in two forms. Sometimes method (a) yielded a product which after purification had m. p. 135—136°; but the molten substance resolidified a few degrees above this and finally melted at 154°. Mixture of this material (m. p. 135°) with that of m. p. 154° did not depress this m. p. More precise conditions of the relative stability of these materials were not determined.

1-*Bromo*-2′-*acetoxydinaphthyl* 2:1′-*sulphide*, prepared from the foregoing hydroxy-compound and acetic anhydride, was purified from dilute acetic acid. When rapidly separated from this medium, it was obtained in the amorphous state, but if allowed to separate slowly from dilute solution it formed needles, m. p. 116—117° (Found: C, 62·4; H, 3·5. $C_{22}H_{15}O_2BrS$ requires C, 62·4; H, 3·5%).

αββ′α′-*Naphthathioxin* (IV).—A mixture of the dry sodium derivative of 1-bromo-2′-hydroxydinaphthyl 2 : 1′-sulphide (II), obtained by either of the methods described, and a little copper acetate was heated under diminished pressure (1 mm.). Reaction began at 140—150°, the mixture then became pasty and the product slowly sublimed. The process was more rapid at 160—170° (yield, *ca.* 50%). The crude sublimed product had m. p. 151—152°, and after purification from alcohol was obtained in yellow needles, m. p. 154° (Found : C, 79·8; H, 4·2. Calc.: C, 80·0; H, 4·0%). This material did not depress the melting point of a sample of *iso*naphthathioxin obtained from the sources already mentioned. The identification was also effected by comparison of the picrates (m. p. 177—178°) and dibromo-derivatives (m. p. 245°) of these materials.

In conclusion we desire to thank Dr. Child for information concerning 1-bromonaphthalene-2-sulphonic acid and its derivatives.

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