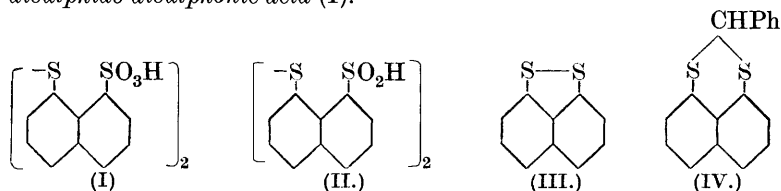


CCCXIII.—*Naphthylene 1 : 8-Disulphide.*

By WILLIAM BENNETT PRICE and SAMUEL SMILES.

THE experiments which have been made on the formation of sulphur ring systems (J., 1922, 121, 87; 1926, 1821, 2265; 1927, 534; this vol., pp. 697, 1142) have now been extended to the inclusion of the *peri*-system of naphthalene in five- and six-membered dithio-ring systems.

1-Naphthylamine-8-sulphonic acid was found to be the most convenient source of the required 1 : 8-dithiolnaphthalene. When naphthalene-1 : 8-diazosulphonate was treated with sulphurous acid in presence of copper the 1 : 8-*sulphino-sulphonic acid* was obtained, and reduction of this acid in aqueous solution with sulphurous acid and dilute hydriodic acid gave a good yield of the corresponding *disulphide-disulphonic acid* (I).



Treatment of the chloride of this acid in the usual way gave 1 : 1'-*dithiodinaphthalene-8 : 8'-disulphonic acid* (II), which finally was

reduced to the required 1 : 8-dithiolnaphthalene. This unstable mercaptan on exposure to air or in solution with mild oxidising agents yielded the orange *disulphide* (III), whilst the simultaneous formation of complex polysulphides was not observed. The ease with which this cyclic system is formed at the *peri*-position of naphthalene accords with the existence of the corresponding sultone and sultan, and also with the stability of *o*-dithiobenzoyl and of diphenyl 2 : 2'-disulphide and -disulphoxide. A further resemblance between the behaviour of 2 : 2'-dithioldiphenyl and that of 1 : 8-dithiolnaphthalene is found in the action of the latter with aldehydes, which furnish the six-membered system in the mercaptals (IV). The results of these experiments amplify the evidence now available from numerous sources of the stability of five- and six-membered dithio-ring systems.

EXPERIMENTAL.

1-Sulphinonaphthalene-8-sulphonic Acid.—A mixture of water (250 c.c.) and the diazosulphonate prepared from 50 g. of 1-naphthylamine-8-sulphonic acid was saturated with sulphur dioxide. After treatment with copper powder in the usual manner, the liquid was warmed and passed through a filter (2 g. of charcoal). When the clear liquid was saturated with salt, the *sodium* salt of the required sulphonic acid separated. A sample was purified from hot water (Found : S, 22.3. $C_{10}H_7O_5S_2Na$ requires S, 21.77%).

1 : 1'-*Dithiodinaphthalene-8 : 8'-disulphonic Acid* (I).—An aqueous solution (400 c.c.) of the mono-sodium salt obtained from the foregoing process, containing hydrogen iodide (3 or 4 drops, *d* 1.7), was kept at 95—100° for 3 hours and treated with a slow current of sulphur dioxide. After the clear liquid had been concentrated and cooled, the *sodium* salt of the required acid separated in flocculent aggregates, and was purified from hot water (Found : Na, 9.0. $C_{20}H_{12}O_6S_4Na_2$ requires Na, 8.8%).

1 : 1'-*Dithiodinaphthalene-8 : 8'-disulphonic Acid* (II).—The dried sodium sulphonate thus obtained was triturated (10 g.) with phosphorus pentachloride (20 g.). The mixture was kept for 6 hours, the crude sulphonic chloride being then isolated in the usual manner. The use of larger quantities of material and higher temperatures gave less favourable results. The crude acid chloride was treated for 10 minutes with a boiling aqueous solution of an equal weight of sodium sulphite. When the cooled and clear solution (charcoal) was mixed with sulphuric acid, the required *sulphinic acid* separated in needles, which when purified from alcohol had m. p. 144° (Found : C, 53.7; H, 3.0. $C_{20}H_{14}O_4S_4$ requires C, 53.8; H, 3.1%).

1 : 8-*Dithiolnaphthalene*.—Zinc dust (4.5 g.) was gradually added

to the warm mixture of the sulphinic acid (1 g.) with alcohol (15 c.c.) and concentrated hydrochloric acid (15 c.c.). After the reaction had been maintained for 2 hours, the required mercaptan separated from the cooled liquid in colourless plates; these had m. p. 113—114° and were readily soluble in common organic solvents, but attempts further to purify the substance were abandoned owing to the ease with which it is converted into the disulphide. The substance was characterised as the dimethylthiol which was obtained by treatment with methyl sulphate in presence of aqueous alkali. 1:8-Dimethyldithiolnaphthalene formed colourless plates, m. p. 84°, from acetic acid (Found: C, 65·3; H, 5·5. $C_{12}H_{12}S_2$ requires C, 65·4; H, 5·4%).

When alcoholic solutions of the dithiol and nickel acetate are mixed, a characteristic *nickel* derivative is precipitated in the crystalline state. This brownish-purple substance (Found: Ni, 23·5. $C_{10}H_6S_2Ni$ requires Ni, 23·7%) is slightly soluble in chloroform; it appears to contain the co-ordinated metal but its constitution has not been examined.

2-Phenyl-*peri-naphtha*-1:3-dithiane (IV).—1:1'-Dithiodinaphthalene-8:8'-disulphinic acid was reduced with zinc dust and alcohol into which dry hydrogen chloride was passed. When reduction was complete, the requisite amount of benzaldehyde was added to the solution, which was then saturated with hydrogen chloride. After being kept for 12 hours, the solution was mixed with water and the required material then separated in the crystalline state. It was purified from aqueous alcohol and formed needles, m. p. 116° (Found: C, 73·1; H, 4·7. $C_{17}H_{12}S_2$ requires C, 72·85; H, 4·3%).

Naphthylene 1:8-Disulphide (III).—This is readily obtained by spontaneous oxidation of the dithiol in presence of atmospheric oxygen. It was prepared by passing air through a solution of the dithiol in ammonia. The precipitated material was purified from alcohol and formed orange plates, m. p. 116° (Found: C, 62·8; H, 4·3; *M*, 191. $C_{10}H_6S_2$ requires C, 63·1; H, 3·1%; *M*, 190). In the preparation of this disulphide, the use of ferric chloride should be avoided owing to the formation of complex iron derivatives of the mercaptan which contaminate the product. Oxidation of the disulphide readily ensues in presence of hydrogen peroxide in acetic acid; a study of the process has shown that it proceeds beyond the thiolulphonate and that successive oxidation products are generally formed simultaneously. The separation of these was not satisfactorily accomplished with the amount of material available.