

118. *Extrusion of Sulphur. Part VII.*¹

By J. D. LOUDON, L. B. YOUNG, and (in part) A. A. ROBERTSON.

By thermal decomposition the octahydrothianthren (II) yields the octahydrodibenzothiophen (IV) while the hexahydro-3-phenyl-1,4,5-benzothiadiazepine (VII) yields the tetrahydro-3-phenylcinnoline (VIII). Both starting materials are indirectly prepared from 2-mercaptocyclohexanone.

THE interaction of 2-chlorocyclohexanone and sodium hydrogen sulphide was recently shown^{2,3} to yield the diol (I) as principal product instead of the earlier reported mixture of di-2-oxocyclohexyl sulphide and disulphide.⁴ We had independently reached the same conclusion and now record two applications of the diol to the study of sulphur extrusion.

Acid-catalysed dehydration of the diol affords a compound for which analysis, dehydrogenation to thianthren, and an ultraviolet absorption spectrum closely resembling that of 2,5-dimethyl-1,4-dithiin (III; R = Me) justify the octahydrothianthren structure (II). This compound as a tetra-alkylated 1,4-dithiin is of interest in relation to work by Parham and his colleagues⁵ who have shown that 2,5-diphenyl-1,4-dithiin (III; R = Ph) yields 2,4-diphenylthiophen when heated at 180° or when oxidised by hydrogen peroxide in acetic acid, whereas the parent 1,4-dithiin (III; R = H) and its benzo-derivative are thermally much more stable, do not afford thiophens, and on oxidation yield the corresponding bis-sulphones. 2,5-Dimethyl-1,4-dithiin (III; R = Me) is intermediate in its behaviour,⁶ being oxidised to the bis-sulphone but affording a small amount of 2,4-dimethylthiophen when heated at 200°. The dithiin (II) yielded the bis-sulphone on oxidation; it was largely unchanged by 8 hours' refluxing in ethylene glycol (b. p. 200°) but it gave the octahydrodibenzothiophen (IV; yield, 80%) when heated in diethyl phthalate (b. p. 295°) in the presence of copper bronze. Broadly, therefore, it seems to resemble 2,5-dimethyl-1,4-dithiin in its behaviour.

¹ Part VI, *J.*, 1963, 5496.

² Asinger, Thiel, and Kaltwasser, *Annalen*, 1957, **606**, 67; Asinger, Thiel, Usbeck, Grobe, Grundman, and Trankner, *ibid.*, 1960, **634**, 144.

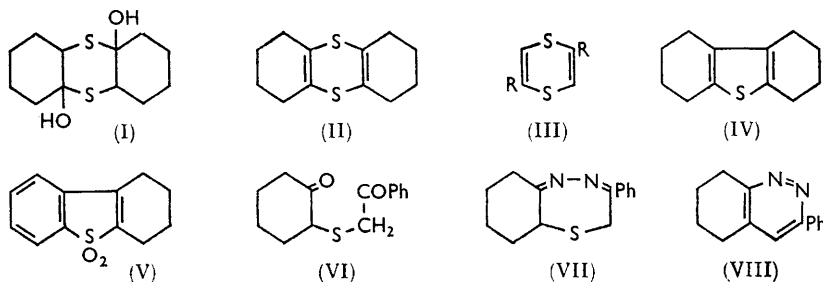
³ Milligan and Swan, *J.*, 1961, 5552.

⁴ Backer, Strating, and Huisman, *Rec. Trav. chim.*, 1941, **60**, 387.

⁵ Cf. Parham, in "Organic Sulphur Compounds," ed. Kharasch, Pergamon, London, 1961, p. 248.

⁶ Parham, Mayo, and Gradsby, *J. Amer. Chem. Soc.*, 1959, **81**, 5993.

The octahydrodibenzothiophen (IV), alternatively prepared ⁷ from 2-cyclohex-1'-enyl-cyclohexanone in reaction with sulphur, is a low-melting solid. For closer characterisation, it was oxidised with hydrogen peroxide in acetic acid whereby it formed the sulphone



(V) (ν_{SO_2} 1290 and 1146 cm^{-1}) with partial dehydrogenation (M (mass spectrum), 220; $\nu_{\text{aromatics}}$ 1592, 1580, 772, and 731 cm^{-1}). Reduction of this sulphone with lithium aluminium hydride gave 1,2,3,4-tetrahydrodibenzothiophen which was identified as its picrate and trinitrobenzene derivatives ⁸ and was re-oxidised to the sulphone (V) by hydrogen peroxide. It is noteworthy that the tetrahydrosulphone (V) resisted dehydrogenation by chloranil under conditions which rapidly convert the octahydrodibenzothiophen (IV) into dibenzothiophen; moreover, similar resistance was observed in the bis-sulphone corresponding to the 1,4-dithiain (II), whereas dehydrogenation of the 1,4-dithiain itself readily yields thianthren. Probably, therefore, in the conversion of the octahydrodibenzothiophen (IV) into the tetrahydrodibenzothiophen sulphone (V), dehydrogenation precedes oxidation of sulphur to the sulphone level which appears to be reached more easily with benzo[*b*]thiophen than with thiophen derivatives.

In an alkaline medium the diol (I) provides the anion of 2-mercaptocyclohexanone and hence, by reaction with phenacyl bromide, furnished the diketo-sulphide (VI). This reacted with hydrazine hydrate, affording the dihydrothiadiazepine (VII), a variant of the class of compound investigated in Part VI.¹ The new thiadiazepine was too sensitive towards oxidation to give useful results from this line of inquiry;¹ on the other hand it was smoothly decomposed by heat, affording the cinnoline derivative (VIII), and thus further illustrating the potentialities of this type of ring contraction.

EXPERIMENTAL

Perhydro-4a,9a-dihydroxythianthren (I).—(a) A solution of sodium hydrogen sulphide, prepared ⁹ from sodium sulphide (64 g.), sodium hydrogen carbonate (22.4 g.), and methanol (160 ml.) was slowly stirred at 0° into a solution of 2-chlorocyclohexanone (8.7 g.) in methanol (50 ml.). The mixture was stirred for 30 min., then water (300 ml.) was added and the diol (5–6 g.) was collected and washed with water.

(b) A cold solution of hydrated sodium sulphide (20 g.) in dimethylformamide (200 ml.) was added at 0° to another of 2-chlorocyclohexanone (10 g.) in the same solvent (15 ml.), with stirring which was then continued for 1 hr. at 18°. Dilution with water gave the diol (6 g.), m. p. 151° (from ethanol) [Found: C, 55.4; H, 7.35%; M (mass spectrum), 260. Calc. for $\text{C}_{12}\text{H}_{20}\text{O}_2\text{S}_2$: C, 55.35; H, 7.75%; M , 260].

1,2,3,4,6,7,8,9-Octahydrothianthren (II).—A solution of the diol (1 g.) and toluene-*p*-sulphonic acid (0.2 g.) in benzene (30 ml.) was heated under reflux for 2 hr. before being cooled, diluted with ether, and washed with aqueous sodium hydroxide. The thianthren (0.8 g.), recovered from the dried solution, formed plates, m. p. 97° (from ethanol) ^{2,3} λ_{max} (ethanol) 254 and 265 μ .

⁷ Cooper, J., 1955, 1386.

⁸ Cagniant and Cagniant, *Bull. Soc. chim. France*, 1952, 19, 336.

⁹ Hodgson and Ward, J., 1948, 242.

(ϵ 4385 and 3162) (Found: C, 64.2; H, 7.1. Calc. for $C_{12}H_{16}S_2$: C, 64.25; H, 7.2%). Oxidation with hydrogen peroxide in acetic acid at 70° (12 hr.) gave the bis-sulphone,⁶ m. p. 262° (from ethanol), ν_{SO_2} 1320 and 1142 cm^{-1} (Nujol) (Found: C, 50.3; H, 5.7. Calc. for $C_{12}H_{16}O_4S_2$: C, 50.0; H, 5.6%). Dehydrogenation of the octahydro-compound (II) (0.5 g.) by chloranil (2.5 g.) in boiling phenetole (25 ml.) (3 hr.) gave thianthren which was identified by comparison of m. p. (153°) and i.r. spectrum with those of an authentic sample.

1,2,3,4,6,7,8,9-Octahydrodibenzothiophen (IV).—A solution of the octahydrothianthren (II) (0.5 g.) in diethyl phthalate (3 ml.) was heated under reflux for 20 min. with copper bronze (0.5 g.) in suspension. After dilution with benzene, filtration, and partial concentration, the resultant solution was chromatographed on alumina (Woelm, neutral grade I). Elution with light petroleum (b. p. 60–80°) gave as first fraction the octahydrodibenzothiophen (235 mg.), m. p. 30–31° (from ethanol); its i.r. spectrum was identical with that of an authentic sample.⁷ Subsequent fractions, after hydrolysis of contaminating diethyl phthalate, gave more (140 mg.) of the thiophen. Dehydrogenation to dibenzothiophen was effected by chloranil in boiling phenetole.

80% recovery of the octahydrothianthren (II) followed from 8 hours' refluxing with copper bronze in ethylene glycol.

1,2,3,4-Tetrahydrodibenzothiophen-SS-dioxide (V).—To a solution of octahydrodibenzothiophen (1 g.) in acetic acid (10 ml.) at 95°, hydrogen peroxide (4 ml.; 30%) was added during 15 min. and heating was continued for a further 15 min. Dilution with water then gave the sulphone (0.75 g.), m. p. 184–185° (from ethanol) (Found: C, 65.65; H, 5.45. $C_{12}H_{12}O_2S$ requires C, 65.45; H, 5.5%).

1,2,3,4-Tetrahydrodibenzothiophen.—A mixture of the preceding sulphone (0.49 g.), lithium aluminium hydride (0.32 g.), and anhydrous ether (120 ml.) was heated under reflux (2 hr.) before being cooled, treated with ethyl acetate, and then with dil. sulphuric acid. The ethereal layer, combined with ethereal extracts of the aqueous layer, was washed, dried, and evaporated, giving the thiophen as a colourless oil which showed no sulphonyl absorption in the i.r. region. The oil was characterised as the picrate,⁸ m. p. 105°, and as the trinitrobenzene complex,⁸ m. p. 137°; when oxidised by hydrogen peroxide in acetic acid it gave the sulphone, m. p. and mixed m. p. 185°.

2-(Phenacylthio)cyclohexanone (VI) [with A. A. ROBERTSON].—4N-Potassium hydroxide (2 ml.) was added, with vigorous stirring at 18°, to a solution of the diol (I) (10 g.) and phenacyl bromide (16 g.) in dimethylformamide (400 ml.). Stirring was continued for 30 min. and then for a further 30 min. at 95°. After dilution with water, the product slowly crystallised, m. p. 68–69° (from ethanol), $\nu_{C=O}$ 1690 and 1666 cm^{-1} (KCl disc) (Found: C, 67.4; H, 6.7. $C_{14}H_{16}O_2S$ requires C, 67.6; H, 6.5%).

2,6,7,8,9,9a-Hexahydro-3-phenyl-1,4,5-benzothiadiazepine (VII), m. p. 116–117° (from ethanol, was prepared by adding an excess of hydrazine hydrate to a hot solution of the sulphide (VI) (5 g.) in acetic acid, shaking the mixture for a few minutes, and then diluting with water (Found: C, 69.1; H, 6.8; N, 11.6. $C_{14}H_{16}N_2S$ requires C, 68.8; H, 6.6; N, 11.5%).

5,6,7,8-Tetrahydro-3-phenylcinnoline (VIII).—The thiadiazepine (VII) (0.4 g.) was added to boiling ethylene glycol (12 ml.), heating being continued for 15 min. while hydrogen sulphide was evolved. The solution was cooled, diluted with water, and extracted with chloroform (charcoal). The recovered yellow oil was converted into the picrate, m. p. 169–172° (lit.,¹⁰ m. p. 174–175°) (Found: C, 54.9; H, 4.4; N, 15.8. Calc. for $C_{20}H_{17}N_3O_7$: C, 54.7; H, 4.0; N, 15.9%). A solution of the picrate in chloroform was chromatographed on alumina affording the cinnoline (VIII) (0.15 g.), m. p. 87–88° [from light petroleum (b. p. 60–80°)] (lit.,¹⁰ 86–87.5°) (Found: C, 79.9; H, 6.4; N, 13.1. Calc. for $C_{14}H_{14}N_2$: C, 80.0; H, 6.7; N, 13.3%).

The authors thank the D.S.I.R. for an award to one of them (L. B. Y.), and Mr. J. M. L. Cameron and his staff for microanalyses.

THE UNIVERSITY, GLASGOW W.2.

[Received, July 8th, 1963.]

¹⁰ Baumgarten, Cregar, and Villars, *J. Amer. Chem. Soc.*, 1958, **80**, 6609.