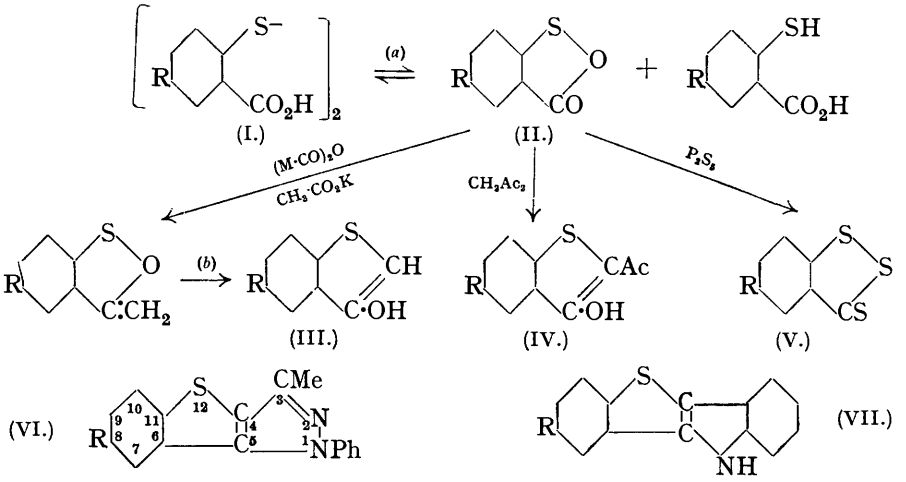
## 41. *The Dismutation of Some Disulphides. Part IV.*

By F. S. Fowkes and E. W. McClelland.

It is shown that chlorine in the para-position to sulphur decreases the tendency of a 2 : 2′-dithiobenzoic acid to undergo dismutation. In consequence 5 : 5′-dichloro-2 : 2′-dithiobenzoic acid reacts less readily than the non-chlorinated disulphide with acetylacetone in sulphuric acid but yields similar products, *viz.*, hydroxythionaphthens. The effect of chlorine as a substituent on the reactivity of these hydroxythionaphthens has been investigated. 2 : 2′-Dithiobenzoic acid undergoes dismutation in neutral media.

It has been suggested (Part II; D'Silva and McClelland, J., 1932, 2883) that the formation of thionaphthens in the reaction of 2 : 2′-dithiobenzoic acid with acetic anhydride and potassium acetate is dependent on the dismutation (*a*) of the disulphide and reaction of the sulphenic anhydride (II), followed by the intramolecular rearrangement (*b*).




5 : 5′-Dichloro-2 : 2′-dithiobenzoic acid (I; R = Cl) reacts with acetic anhydride and potassium acetate to give 5-*chloro*-3-*hydroxy*-2-*acetyl*-1-*thionaphthen* (IV; R = Cl) and 5-*chloro*-3-*acetoxy*-1-*thionaphthen* (III; R = Cl, OAc instead of OH). The dichlorodisulphide reacts less readily than the non-chlorinated disulphide, for 2 : 2′-dithiobenzoic acid (I; R = H) yields the thionaphthens when heated with the reactants at 120—125° for 2 hours, whereas 5 : 5′-dichloro-2 : 2′-dithiobenzoic acid requires heating at 130° for 4 hours with the reactants, little or no reaction taking place under the milder conditions effective for the non-chlorinated disulphide. It is evident that chlorine in the para-position to sulphur depresses the tendency of the disulphide to dismutation.

2 : 2′-Dithiobenzoic acid reacts with acetylacetone in sulphuric acid to give 3-hydroxy-2-acetyl-1-thionaphthen (Smiles and McClelland, J., 1921, **119**, 1810). The formation of the hydroxythionaphthen was attributed to condensation of the acetylacetone with the sulphenic acid formed by fission of 2 : 2′-dithiobenzoic acid in sulphuric acid. It seems probable that condensations of this type may be dependent on dismutation of the disulphide and that the sulphenic anhydride (II) and not the sulphenic acid may be the reactive intermediate.

5 : 5′-Dichloro-2 : 2′-dithiobenzoic acid also reacts with acetylacetone in presence of sulphuric acid to give 5-chloro-3-hydroxy-2-acetyl-1-thionaphthen (IV; R = Cl). The reaction proceeds less readily than with 2 : 2′-dithiobenzoic acid, thus supporting the conclusion that chlorine in the para-position to sulphur decreases the tendency to dismutation. The effect of chlorine in decreasing the tendency to dismutation suggests that chlorine in the para-position to sulphur partly neutralises the tendency of a carbonyl group in the ortho-position to sulphur to promote a positive charge on the sulphur atom, thereby rendering the sulphur atom in a chloro-compound less positive in character than in a corresponding unsubstituted compound. This would have the effect of decreasing the stability of the S–O link in the dismutation product (II) and therefore decrease the tendency to dismutation.

Comparison of the chlorohydroxythionaphthens with the unsubstituted hydroxythionaphthens shows that chlorine substitution has no marked effect on their reactivity; *e.g.*, 5-chloro-3-hydroxy-2-acetyl-1-thionaphthen readily gives the *chlorothionaphthenopyrazole* (VI; R = Cl) and 5-chloro-3-hydroxy-1-thionaphthen yields the *chlorothionaphthindole* (VII; R = Cl), with the same facility as the corresponding unsubstituted hydroxythionaphthens (compare Barry and McClelland, J., 1935, 471; McClelland and D'Silva, J., 1932, 227). Chlorine, however, does exert some effect on the heterocyclic nucleus, since

the chloro-compounds are not so readily oxidised to the thioindigotin as the unsubstituted compounds. It has been recorded (Smiles and Cohen, J., 1930, 411) that the 1 : 1-dioxide of 3-hydroxy-2-acetyl-1-thionaphthen cannot be obtained by direct oxidation with hydrogen peroxide owing to the formation of thioindigotin, and this has been confirmed. In contrast 5-chloro-3-hydroxy-2-acetyl-1-thionaphthen (IV; R = Cl) is oxidised with hydrogen peroxide under mild conditions to the 1 : 1-*dioxide* (IV; R = Cl, $SO_2$ instead of S). Similarly 5-chloro-3-acetoxy-1-thionaphthen (III; R = Cl, OAc instead of OH) is oxidised to the 1 : 1-*dioxide* (III; R = Cl, $SO_2$ instead of S, OAc instead of OH); more vigorous oxidation yields the deacetylated 1 : 1-*dioxide*, which gives a *hydrazone* resistant to indolisation (compare McClelland and D'Silva, J., 1932, 227). The *acetyl* derivative of 5-chloro-3-hydroxy-2-acetyl-1-thionaphthen appears to be more resistant to hydrolysis than the *acetyl* derivative of the corresponding non-chlorinated compound.

2 : 2′-Dithiobenzoic acid reacts with phosphorus pentasulphide in xylene to give 2 : 3-dithiosulphindene (V; R = H), which might be expected to result from the action of phosphorus pentasulphide on the sulphenic anhydride (II). The formation of 2 : 3-dithiosulphindene from 2 : 2′-dithiobenzoic acid supports the dismutation hypothesis, and suggests that 2 : 2′-dithiobenzoic acid undergoes dismutation in neutral as well as in acid media.

## Experimental.

*Reaction of 5 : 5′-Dichloro-2 : 2′-dithiobenzoic Acid with Acetic Anhydride and Potassium Acetate.*—The acid (Hart, McClelland, and Fowkes, J., 1938, 2114) (1 g.) together with potassium acetate (1·25 g.) and acetic anhydride (12 c.c.) was heated at 130° for 4 hours. The mixture was poured into water, heated at 100° and distilled in steam. The distillate was extracted with ether, and the ethereal extract washed with 2N-sodium hydroxide. Acidification of the alkaline washings precipitated 5-chloro-3-hydroxy-2-acetyl-1-thionaphthen (0·05 g.). Evaporation of the ethereal extract gave 5-*chloro*-3-*acetoxy*-1-*thionaphthen* (0·2 g.), m. p. 67° (Found: C, 53·0; H, 3·2; S, 14·2. $C_{10}H_7O_2ClS$ requires C, 53·1; H, 3·1; S, 14·2%), which on hydrolysis gave 5-chloro-3-hydroxy-1-thionaphthen. The residue from the steam-distillation was unchanged starting material. At 125° little reaction resulted in 2 hours.

5-*Chloro*-3-*hydroxy*-2-*acetyl*-1-*thionaphthen.*—Acetylacetone (0·56 c.c.) was added portionwise during 1 hour to a well-stirred suspension of 5 : 5′-dichloro-2 : 2′-dithiobenzoic acid (1 g.) in concentrated sulphuric acid (8 c.c.) kept at 50—55°. The mixture was kept for 40 minutes at 50—55°, then poured on ice, and the solid material collected, washed with water, and extracted with 2N-sodium hydroxide. The alkaline extract was filtered and acidified. The precipitate crystallised from alcohol (charcoal) in yellow plates (0·75 g.), m. p. 166° (Found: C, 52·8; H, 2·9; S, 14·1. $C_{10}H_7O_2ClS$ requires C, 53·0; H, 3·1; S, 14·2%). 5-*Chloro*-3-*hydroxy*-2-*acetyl*-1-*thionaphthen* gives an olive-green coloration with alcoholic ferric chloride and is oxidised by warm alkaline potassium ferricyanide to the corresponding thioindigotin.

5-Chloro-3-hydroxy-2-acetyl-1-thionaphthen (1 g.) was refluxed in toluene (20 c.c.) containing acetic anhydride (4 c.c.) and a trace of pyridine for 6 hours. The *acetyl* derivative crystallised in colourless needles, m. p. 132°, on addition of light petroleum to the cooled solution (Found: C, 53·4; H, 3·1. $C_{12}H_9O_3ClS$ requires C, 53·6; H, 3·3%). It gave no coloration with alcoholic ferric chloride and was deacetylated to 5-chloro-3-hydroxy-2-acetyl-1-thionaphthen by refluxing with 2N-sulphuric acid for 1¼ hours. 3-*Acetoxy*-2-*acetyl*-1-*thionaphthen*, prepared in a similar way, had m. p. 127° (Found: C, 61·6; H, 4·1. $C_{12}H_{10}O_3S$ requires C, 61·5; H, 4·1%), and was deacetylated to 3-hydroxy-2-acetyl-1-thionaphthen in 30 minutes under similar conditions.

8-*Chloro*-1-*phenyl*-3-*methyl*-4 : 5-*thionaphthenopyrazole.*—A solution of 5-chloro-3-hydroxy-2-acetyl-1-thionaphthen (1 g.) and phenylhydrazine (1·45 g.) in benzene was refluxed for 3 hours. The *hydrazone*, which separated overnight, crystallised from benzene in yellow prisms, m. p. 162° (Found: C, 60·5; H, 4·2. $C_{16}H_{13}ON_2ClS$ requires C, 60·7; H, 4·1%). A solution of the hydrazone (0·1 g.) in alcohol containing a drop of concentrated sulphuric acid was refluxed for 30 minutes. The solution was diluted with water and the material, precipitated on cooling, was collected and washed with alkali and acid. It crystallised from alcohol in colourless needles, m. p. 135°(Found: C, 64·2; H, 4·1. $C_{16}H_{11}N_2ClS$ requires C, 64·3; H, 3·7%).

5-*Chloro*-3-*hydroxy*-2-*acetyl*-1-*thionaphthen* 1 : 1-*Dioxide.*—Finely ground 5-chloro-3-hydroxy-2-acetyl-1-thionaphthen (0·5 g.) was suspended in acetic acid (5 c.c.) and hydrogen peroxide (0·6 c.c., 90—100 vol.) was added to the mixture, which was left for 3 days. The required

material, together with a small amount of the thioindigotin, separated. It crystallised from benzene–petroleum (charcoal) in colourless plates, m. p. 265° (Found: C, 46·7; H, 2·8. $C_{10}H_7O_4ClS$ requires C, 46·4; H, 2·7%).

10-*Chlorothionaphthindole.*—A solution of 5-chloro-3-hydroxy-1-thionaphthen (0·5 g.) and phenylhydrazine (0·3 g.) in acetic acid was heated at 100° for 35 minutes. The product which separated was washed with a little alcohol; it crystallised from acetic acid in colourless plates, m. p. 222° (Found: C, 65·05; H, 3·4. $C_{14}H_8NClS$ requires C, 65·25; H, 3·1%). It gave a blue coloration with isatin in sulphuric acid. It was also obtained in a similar way from 5-chloro-3-acetoxy-1-thionaphthen.

5-*Chloro*-3-*acetoxy*-1-*thionaphthen* 1 : 1-*Dioxide.*—Hydrogen peroxide (0·5 c.c., 90—100 vol.) was added to a suspension of 5-chloro-3-acetoxy-1-thionaphthen (0·3 g.) in acetic acid (2 c.c.), and the mixture kept for 4½ days with frequent shaking. The product (0·15 g.), which separated, crystallised from benzene–petroleum (charcoal) in colourless prisms, m. p. 164° (Found: C, 46·7; H, 2·8. $C_{10}H_7O_4ClS$ requires C, 46·4; H, 2·7%).

5-*Chloro*-3-*hydroxy*-1-*thionaphthen* 1 : 1-*Dioxide.*—A solution of 5-chloro-3-acetoxy-1-thionaphthen (1 g.) in acetic acid (12 c.c.) and hydrogen peroxide (6 c.c., 90—100 vol.) was heated at 100° for 1 hour, and water added. The material (0·5 g.), which separated on cooling, crystallised from benzene–petroleum in colourless needles, m. p. 194° (Found: C, 44·2; H, 2·3. $C_8H_5O_3ClS$ requires C, 44·3; H, 2·3%). 5-*Chloro*-3-*hydroxy*-1-*thionaphthen* 1 : 1-*dioxide phenylhydrazone*, obtained by heating the above material (1 mol.) in glacial acetic acid with phenylhydrazine (3 mols.), crystallised from acetic acid in yellow needles, m. p. 290—292° (Found: C, 54·6; N, 3·7. $C_{14}H_{11}O_2N_2ClS$ requires C, 54·8; H, 3·6%). The hydrazone resisted attempts to indolise it.

*Reaction of* 2 : 2′-*Dithiobenzoic Acid with Phosphorus Pentasulphide.*—2 : 2′-Dithiobenzoic acid (30 g.) in xylene (1 l.) and phosphorus pentasulphide (30 g.) were refluxed with stirring for 6 hours. After filtration the xylene was removed in steam and the residual oily material was heated at 100° for some time to remove traces of water and xylene. 2 : 3-Dithiosulphindene was obtained from the product by crystallisation from alcohol. Yield, 75%.

The authors are indebted to the Department of Scientific and Industrial Research for a grant to one of them (F. S. F.).

KING'S COLLEGE, LONDON. [*Received, March* 13*th*, 1941.]