CCVII.—*Derivatives of 3-Oxy(1)thionaphthen.*

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THE experiments described in the following pages are the outcome of a previous investigation of the reactions of aromatic mercaptans in sulphuric acid solution. In this medium oxidation of the mercaptan takes place, disulphides being formed; the properties of the solution indicate that the disulphide is in equilibrium with the mercaptan and sulphenic acid :

The presence of the sulphenic acid has been inferred from the reactions of these solutions. By the addition of other compounds which contain hydrogen available for removal in the form of water, various types of sulphides have been isolated from them :

In the case of 2-thiolbenzoic acid and the corresponding disulphide it has been shown that aromatic compounds yield the thioxanthenes and that aliphatic compounds containing the ketomethylene group furnish derivatives of 3-oxy(1)thionaphthen; for example, malonic acid or ethyl acetoacetate (T., 1912, **101**, 572) yielded this substance :

In simple cases such as these the groups $\text{R}\cdot\text{CO}\cdot$ were found to be eliminated during the condensation, in fact in only one case, that of benzoylacetone, from which 2-benzoyl-3-oxy(1)thionaphthen was obtained, did the product contain the ketonic group of the original substance. The study of this type of reaction was interrupted and a somewhat incomplete account of the results was published (Smiles and Ghosh, T., 1915, **107**, 1378). The experiments which are now described were carried out primarily with the object of obtaining further evidence that derivatives of 3-oxy(1)thionaphthen with substituents in position 2 are formed in the earlier stages of the reaction. This evidence has been obtained in two ways : either by employing milder conditions of reaction which permit these substitution products to escape decomposition, or by choosing material which furnishes characteristic derivatives of greater stability.

In previous experiments with the condensation of 2-thiolbenzoic acid and acetylacetone the formation of 3-oxy(1)thionaphthen was recorded (Smiles and Ghosh, *loc. cit.*). By repeating the process at lower temperatures 2-acetyl-3-oxy(1)thionaphthen (I) has now been obtained in good yield, but the diacetyl derivative (II), which is no doubt the primary product, could not be isolated. In the case of ethyl acetoacetate it has been shown (T., 1912, **101**, 572; 1915, **107**, 1379) that with 2-thiolbenzoic acid and sulphuric acid at 90° "thioindigo," small amounts of oxythionaphthen, and the methylcoumarin (III) are formed. Further experiments carried out at lower temperatures have yielded none of these, but instead gave a product which from its general properties appears without

doubt to be the acid (IV). This substance proved too unstable for isolation in a state fit for analysis; oxythionaphthen, in place of the 2-acetyl derivative as expected, being formed from it by hydrolysis with alkaline or acid media or even by mere recrystallisation.

According to the work of von Pechmann (*Ber.*, 1884, **17**, 932), the solution of malic acid in sulphuric acid may be used for generating malonic semialdehyde in the production of coumarins from phenols. This solution also undergoes reaction with 2-thiolbenzoic acid, yielding the 3-oxy(1)thionaphthen-2-aldehyde (V). The aldehyde acid would appear to be formed in the first stage of the process before loss of carbon dioxide takes place; but the amount

of the aldehyde met with is quite small, the chief product being the red dyestuff (VI) which is formed from it by the action of sulphuric acid (Friedländer, *Ber.*, 1911, **44**, 3100).

The reaction of 2-thiolbenzoic acid with acetonedicarboxylic acid or with citric acid in sulphuric acid solution has also been studied. The presence of two methylene groups in acetonedicarboxylic acid suggests the possibility that this might unite with one or two molecules of the mercaptan according to the proportions of the reagents present, yielding after loss of carbon dioxide the following substances (VII or VIII) :

3-Oxy(1)thionaphthen yields the methylcoumarin (III) on treatment with ethyl acetoacetate in presence of sulphuric acid and, bearing in mind the stability of this coumarin, it must be expected that if a product of type VII were formed, it should be converted by loss of water to the oxycoumarin (IX). This substance has been obtained from the reaction of acetonedicarboxylic acid with 2-thiolbenzoic acid, in fact it appears to be the sole product; a

substance derived from type VIII has not been isolated even when excess of the mercaptan was taken.

The structure assigned to this product has been proved by the isolation of the thionaphthen nucleus with the acetyl group derived from the oxycoumarin complex, and by the fact that the substance possesses the characteristic properties of benzotetronic acid (X), or 4-oxycoumarin, which it closely resembles. By distillation with a current of steam the compound yields, with loss of carbon dioxide and absorption of the elements of water, 2-acetyl-3-oxy(1)thionaphthen (I). The constitution of the latter substance is determined by (1) the synthesis from acetylacetone as described in a foregoing paragraph, (2) the conversion to "thioindigo" by alkaline ferricyanide, and (3) the formation of a phenylhydrazone. Moreover, the coumarin derivative is soluble in aqueous sodium carbonate solution; it yields a nitroso-derivative, and on treatment with formaldehyde furnishes the corresponding methylene-bisthionaphthaoxycoumarin. These properties are in close accord with those assigned to benzotetronic acid by Anschutz (*Annalen*, 1909, **367**, 169; 1911, **379**, 333), who recorded the formation of the nitroso- and bismethylene derivatives and the hydrolysis by alkali hydroxide with formation of 2-hydroxyacetophenone :

From the experiments which have now been made on this subject, it is clear that the reaction between 2-thiolbenzoic acid and substances containing the ketomethylene group is of fairly wide application. In all the cases examined the formation of derivatives of 3-oxy(1)thionaphthen has been shown, and from the evidence collected there is little doubt that the 2-derivatives of this substance are the primary products, which, under certain conditions, such as high temperature, may suffer decomposition, yielding the parent oxythionaphthen.

EXPERIMENTAL.

1. *Ethyl Acetoacetate and 2-Thiolbenzoic Acid* (compare T., 1912, **101**, 572).—Twelve grams of ethyl acetoacetate were slowly added to a mixture of 10 grams of 2-thiolbenzoic acid and 120 grams of concentrated sulphuric acid. The solution was continually shaken during the addition of the ester, and the temperature was maintained at 28—30°. The reaction progressed with evolution of sulphur dioxide and solution of the dithiobenzoic acid; it was complete in

about thirty-five minutes. The mixture was then poured over crushed ice and the yellow solid was collected and washed with water. The filtrate contained a small quantity of oxythionaphthen. The solid material proved to be very unstable, being easily resolved into oxythionaphthen; it was obtained in the crystalline state, but still impure, by the slow addition of water to the solution in alcohol. It is soluble in aqueous sodium carbonate, and when heated it decomposes rapidly with effervescence. When treated with a current of steam in presence of a little dilute sulphuric acid, the substance yielded 2-oxy(1)thionaphthen and a considerable quantity of "thioindigo." From 10 grams of thiolbenzoic acid 5 grams of oxythionaphthen were isolated. Hydrolysis may also be effected by dilute aqueous ammonia. The methylcoumarin isolated in previous experiments was not observed in the product formed under these conditions.

2. *2-Acetyl-3-oxy(1)thionaphthen* (formula I).—This substance was prepared from the thionaphthacoumarin derivative described in a subsequent paragraph, and by the action of acetylacetone on 2-thiolbenzoic acid.

(a) The crude thionaphthoxycoumarin obtained from the interaction of citric acid and 2-thiolbenzoic acid was treated with a current of steam in presence of a little dilute sulphuric acid. The first portion of the distillate contained oxythionaphthen which had been formed during the preparation of the coumarin derivative by the action of hot concentrated sulphuric acid on that substance. The solid which separated from the subsequent distillate was collected and recrystallised from aqueous alcohol; 2-acetyl-3-oxy(1)thionaphthen was thus obtained in pale yellow needles which melted at 81° . The substance is very soluble in most organic media and sparingly so in water (Found: C = 62.1; H = 4.2; S = 16.9; $M = 186$. $C_{10}H_8O_2S$ requires C = 62.45; H = 4.19; S = 16.69 per cent.; $M = 192$). The addition of ferric chloride to the alcoholic solution produces a green colour. With hot concentrated sulphuric acid "thioindigo" is slowly formed and the same substance is readily obtained by the addition of potassium ferri-cyanide to the alkaline solution.

The *phenylhydrazone* of 2-acetyl-3-oxy(1)thionaphthen was prepared by boiling an alcoholic solution of the components for three hours. The crude product was recrystallised by the addition of water to the alcoholic solution; the pure substance formed slender, reddish-brown needles which melted at 131° (Found: N = 10.0. $C_{16}H_{14}ON_2S$ requires N = 9.9 per cent.). The scarlet sodium salt of this hydrazone is sparingly soluble in water.

(b) Five grams of 2-thiolbenzoic acid were suspended in 50 c.c.

of concentrated sulphuric acid; 3.3 grams of acetylacetone were then gradually added to the mixture, which was kept at 40° for three-quarters of an hour. The solid material obtained by pouring this mixture over crushed ice was washed with water and then treated with a current of steam. The volatile product, after recrystallisation from aqueous alcohol, was identical with that obtained in the foregoing preparation; samples of the phenylhydrazone prepared from the two sources also were identical.

3. 3-Oxy(1)thionaphthen-2-aldehyde (formula V).—A mixture of 10 grams of 2-thiolbenzoic acid and 100 c.c. of concentrated sulphuric acid was heated rapidly to 90°; 15 grams of finely powdered malic acid were then added in the course of fifteen minutes, the contents of the vessel being constantly shaken. After remaining at 90° for another period of fifteen minutes, the mixture was rapidly cooled and then poured over ice. The solid material was collected and thoroughly washed with water; then the aqueous filtrates were shaken with ether, and the solid remaining after this solvent had been evaporated was treated with a current of steam. After recrystallisation, the volatile product melted at 107° (Found: S = 18.1. Calc., S = 18.0 per cent.). It reduced an ammoniacal solution of silver oxide, imparted a green colour to an alcoholic solution of ferric chloride, and with dilute sulphuric acid readily yielded the red dyestuff (formula VI). In all these properties the substance entirely agrees with the 3-oxy(1)thionaphthen-2-aldehyde previously prepared by Friedländer (*loc. cit.*) from "2-thionaphthen-3-indole-indigotin" (3'-indoxyl-2-thionaphthen-3-one) with sodium ethoxide. The phenylhydrazone was prepared (Found: N = 10.4. Calc., N = 10.4 per cent.), it melted at 136–137°; Friedländer gives 137° as the melting point of this substance. The yields of the aldehyde in this process are very poor, but this is not surprising, since in presence of mineral acids it is readily converted (Friedländer, *loc. cit.*) to the red condensation product. This substance forms the chief product of the reaction now described; it was obtained from the solid material by extraction with a hot dilute solution of sodium hydroxide.

4. (1)Thionaphtha-4-oxycoumarin (formula IX).—A mixture of 5 grams of 2-thiolbenzoic acid and 12 grams of acetonedicarboxylic acid was added to 50 c.c. of concentrated sulphuric acid. The reaction which set in immediately was completed by keeping the solution at 40–50° for one and a half hours. When the evolution of sulphur dioxide had ceased, the mixture was poured over ice, and the precipitated solid was collected and washed until free from acid. It was then recrystallised from aqueous alcohol, when (1)thionaphtha-4-oxycoumarin was obtained in faintly yellow

needles which melted and decomposed at about 275° (Found: C = 60.1; H = 2.9; S = 14.7. $C_{11}H_8O_3S$ requires C = 60.51; H = 2.77; S = 14.7 per cent.). The substance is insoluble in water and soluble in aqueous sodium hydroxide or carbonate. The action of sodium nitrite yields a yellow nitroso-derivative. The same material is readily prepared by substituting 15 grams of citric acid for the acetonedicarboxylic acid mentioned in the foregoing preparation; at the same time the amount of sulphuric acid should be increased to 80 c.c., but the temperature quoted should not be exceeded, otherwise oxythionaphthen is formed by decomposition of the coumarin derivative. The formation of 2-acetyl-3-oxy(1)thionaphthen from this substance by treatment with steam is described in a foregoing paragraph.

Methylene bis-(1)thionaphtha-4-oxycoumarin was prepared by the action of formaldehyde upon this coumarin derivative. The substance was easily obtained in the pure condition by adding the calculated quantity of 40 per cent. aqueous formaldehyde to a solution of the naphthacoumarin in alcohol. The mixture was then set aside in a stoppered flask, when the desired substance was gradually precipitated in the crystalline state. The material was collected and the adherent components were removed by boiling alcohol (Found: C = 61.3; H = 3.0; S = 14.3. $C_{23}H_{12}O_6S_2$ requires C = 61.57; H = 2.69; S = 14.3 per cent.). The substance is insoluble in water and most organic media; it dissolves in hot nitrobenzene, from which it separates in small, yellow needles; these melt and decompose at about 300° .

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