CXIII.—*Methoxy-derivatives of Thioxanthone.*

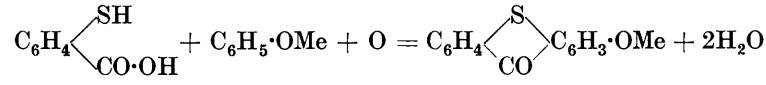
By KENNETH CHARLES ROBERTS and SAMUEL SMILES.

DURING the reduction of 1 : 4-dimethoxythioxanthone it was observed that the substance was soluble in concentrated hydrochloric acid and that the red hydrochloride formed yielded a ferrichloride and a chloroplatinate. Other methoxy-derivatives of thioxanthone then at hand did not exhibit this behaviour; hence the experiments now described were made with the purpose of determining the character of these salts and the structural conditions necessary to their formation.

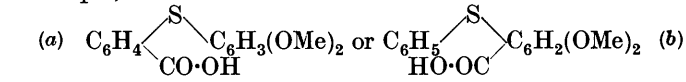
The methoxy-derivatives examined were obtained by the following methods: (1) Condensation of 2-thiolbenzoic acid with a

* The happy analogy of KFHF as a substance similarly constituted was suggested by Professor Robert Robinson in conversation.

methoxy-derivative of benzene in presence of sulphuric acid (J., 1910, **97**, 1290; 1911, **99**, 1353) :

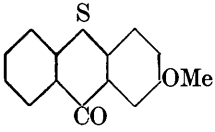


(2) Dehydration of a 2-carboxy-derivative of diphenyl sulphide, for example,

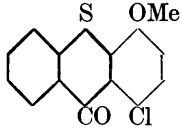


These two types of acid were obtained either (method *a*) from 2-thiolbenzoic acid and a methoxy-halogen derivative of benzene or (method *b*) from phenyl mercaptan and a 2-halogen derivative of a methoxybenzoic acid.

Monomethoxy-derivatives.—Condensation of anisole with 2-thiolbenzoic acid led to a methoxythioxanthone which was evidently the 2-derivative (I), since it was also formed from 4-iodoanisole (method 2*a*). 1-*Chloro*-4-*methoxythioxanthone* (II) was obtained from 4-chloroanisole and 2-thiolbenzoic acid (method 1). The structure assigned to this substance was inferred from the fact that



(I.)



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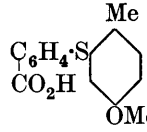

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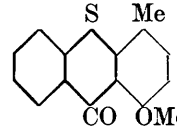
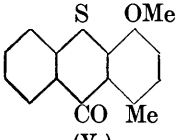


(IV.)

treatment with *p*-toluidine easily replaced the halogen by the toluidino-group (compare Ullmann and Glenck, *Ber.*, 1916, **49**, 2493, 2496). When 2-*iodo*-4-*methoxytoluene*, obtained by usual methods from 2-nitro-*p*-toluidine, was heated with sodium 2-thiolbenzoate in presence of copper acetate, 2′-*carboxy*-5-*methoxy*-2-*methyldiphenyl sulphide* (III) was obtained, and this with sulphuric acid yielded (method 2*a*) 1-*methoxy*-4-*methylthioxanthone* (IV). This substance was entirely different in chemical and physical properties from the product yielded by 4-methoxytoluene and 2-thiolbenzoic acid with sulphuric acid (method 1). Hence the latter material was 4-*methoxy*-1-*methylthioxanthone* (V).



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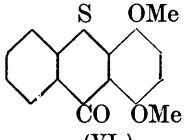

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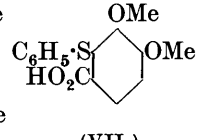
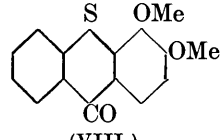


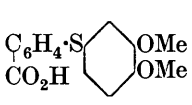
(VII.)



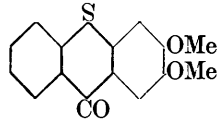
(VIII.)

Dimethoxy-derivatives.—1 : 4-Dimethoxythioxanthone (VI) was

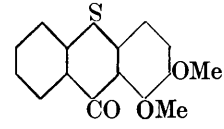
obtained (method 1) from *p*-dimethoxybenzene (Clarke and Smiles, J., 1911, **99**, 1539). When potassium 2-bromoveratrate and potassium phenyl mercaptide were heated together in presence of copper acetate, they yielded 6-carboxy-2 : 3-dimethoxydiphenyl sulphide (VII); this with sulphuric acid (method 2*b*) furnished a dimethoxythioxanthone which must therefore be regarded as the 3 : 4-*derivative* (VIII). Reaction of 4-iodoveratrole with sodium 2-thiolbenzoate gave an acid which was evidently 2′-*carboxy*-3 : 4-*dimethoxydiphenyl sulphide* (IX). Dehydration of this material might lead to either of the two dimethoxythioxanthones (X or XI). In experiment, two such derivatives were isolated as a result of this process, but one of them, later shown to be the 1 : 2-derivative (XI), was produced in only very small amount and was removed from



(IX.)



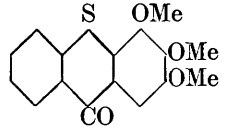
(X.)

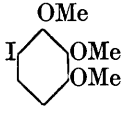


(XI.)

the mixture by means of its more soluble and stable hydrochloride. A similar mixture of these two dimethoxythioxanthones was obtained by condensation of veratrole with 2-thiolbenzoic acid (method 1). Reaction of pyrocatechol with 2-thiolbenzoic acid in sulphuric acid yielded a dihydroxythioxanthone which was easily converted by methylation in aqueous alkaline media into the dimethoxythioxanthone obtained as the chief product from the 2′-carboxy-sulphide (IX) by dehydration. The choice of structure to be assigned to this dihydroxythioxanthone therefore lies between the 2 : 3 and 1 : 2 arrangements (compare X and XI). The former alternative is indicated by the ease with which the substance is methylated and is confirmed by the fact that treatment with boroacetic anhydride did not yield a co-ordinated diacetoborate but merely gave the *diacetoxythioxanthone*. The valuable work of Dimroth (*Ber.*, 1921, **54**, 3020; *Annalen*, 1926, **446**, 97) on the use of this reagent in determining the structure of aromatic hydroxy-ketones has shown that this behaviour is incompatible with the presence of the *o*-hydroxy-group. It may be added that examination of hydroxythioxanthones has confirmed Dimroth's wider experience in other classes of similar hydroxy-ketones and that all the 1-hydroxythioxanthones examined, including 1 : 2-dihydroxy-derivatives, yield stable and characteristic diacetoborates. Hence the related dimethoxy-derivative which forms the chief product when the sulphide (IX) is dehydrated must be the 2 : 3-isomeride (X), leaving for the subordinate product the 1 : 2 structure (XI).

Trimethoxy-derivative.—Reaction of pyrogallol trimethyl ether and 2-thiolbenzoic acid (method 1) gave a trimethoxythioxanthone which had the same melting point as that recorded for the 2 : 3 : 4-derivative prepared by Ullmann and Sone (*Ber.*, 1911, **44**, 2146) from the corresponding trihydroxythioxanthone. Since there were reasons for suspecting that a small quantity of an isomeride might be present in this material, the required 2 : 3 : 4-trimethoxythioxanthone (XII) was obtained from 1-iodo-2 : 3 : 4-trimethoxy-

(XII.) 



(XIII.)

benzene (XIII) (Graebe and Suter, *Annalen*, 1905, **340**, 222) and 2-thiolbenzoic acid (method 2*a*).

Perchlorates.—Since a perchlorate of thioxanthone is obtained under anhydrous conditions (Gomberg, *Annalen*, 1910, **376**, 211), it is not surprising that most of these methoxy-derivatives yield perchlorates under less stringent conditions. Under the conditions described, perchlorates of normal composition were isolated from all except the 1-chloro-4-methoxy- (II) and 4-methoxy-1-methyl (V) thioxanthones.

Hydrochlorides.—All the methoxy-derivatives examined, except these two 4-methoxy-compounds, dissolve with varying facility in warm concentrated hydrochloric acid, those containing 1-methoxyl being exceptionally soluble compared with the others. The hydrochlorides, isolated from the cooled medium, were too readily hydrolysed to be analysed, but the corresponding chloroplatinates and ferrichlorides of 1 : 4- and 2 : 3-dimethoxythioxanthones were sufficiently stable. These salts of 1 : 4-dimethoxythioxanthone had the normal composition X_2,H_2PtCl_6 and $X,HFeCl_4$, but the 2 : 3-derivative yielded a ferrichloride, $X_2,HFeCl_4$. The formation of hydrochlorides was further examined by reaction with dry hydrogen chloride at atmospheric pressure and temperature; the results are collected in the second column of the following table. The relative stability of the salts of these derivatives was also studied with the aid of the method devised by Baeyer and Villiger (*Ber.*, 1902, **35**, 3020). This process has been used with full recognition of the errors to which it is liable (compare Ziegler and Boye, *Annalen*, 1927, **458**, 229), but with suitable precautions the chief objections to its use were overcome. Column IV of the table gives the volumes (c.c.) of alcohol which were required for decomposition of the halochromic salts formed from equimolecular proportions of the thioxanthone derivatives under standard conditions. Quantitative

accuracy is not claimed for these data; they are recorded as illustrating the approximate stability of the salts of the various derivatives compared with that formed from thioxanthone itself.

I. Derivative.	II. Mols. HCl absorbed.	III. Colour of salts.	IV. C.c. alcohol required.
Thioxanthone	None.	—	7
1-Chloro-4-methoxy-	None.	—	6·5
4-Methoxy-1-methyl-	None.	—	7
2-Methoxy-	HCl absorbed; product unstable.	Orange.	10
3 : 4-Dimethoxy-	HCl absorbed; product unstable.	Orange.	12
2 : 3 : 4-Trimethoxy-	*ca.* 1·5; unstable.	Orange.	10
2 : 3-Dimethoxy-	2HCl.	Orange.	14
1 : 2-Dimethoxy-	Not examined.	Crimson.	26
1 : 4-Dimethoxy-	2HCl.	Crimson.	28
1-Methoxy-4-methyl-	3HCl.	Deep red.	30
1 : 4-Dimethyl-	None.	—	7–8
1 : 4-Dimethoxy-dioxide	None.	—	4–5
2 : 3-Dimethoxy-dioxide	None.	—	0

The results obtained by these two methods (columns II and IV) are in qualitative agreement. The stability of the salts of these methoxy-derivatives evidently does not primarily depend on the number of methoxy-groups present, but is more readily influenced by their position. The 4-methoxy-group does not favourably influence the basic character of the thioxanthone nucleus, in fact in certain cases the group in question may have an adverse effect; this appears on comparing the behaviour of the 2 : 3-, 2 : 3 : 4-, and 3 : 4-derivatives. Also it is clear that the salts of 1-methoxythioxanthones have exceptional physical properties and are more stable than those formed by other methoxy-derivatives. On comparing the 3 : 4- and 1 : 4-isomerides, the enhanced effect of 1-methoxyl in comparison with 3-methoxyl becomes apparent; and the contrast between 1-methoxy-4-methylthioxanthone and its epimeride is even more striking. Another interesting feature is the inert character of the sulphones derived from the 1 : 4- and 3 : 4-dimethoxythioxanthones. Before a discussion of the structure of these salts and of the remarkable influence of the 1-methoxyl can be profitably undertaken, further evidence is desirable; this is being collected and will be given in a future communication.

EXPERIMENTAL.

2-Carboxy-derivatives of Diphenyl Sulphide (2*a* and 2*b*).—*2′-Carboxy-4-methoxydiphenyl sulphide*, $MeO{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H$. Amyl alcohol (17 c.c.), containing 2-thiolbenzoic acid (4·9 g.), 4-iodoanisole (7·5 g.), potassium carbonate (4·5 g.), and a little copper acetate, was boiled for 16 hours. After addition of aqueous alkali hydroxide the alcohol was removed by a current of steam, and the filtered

solution mixed with an excess of dilute hydrochloric acid. The required *acid*, which was precipitated (90% yield), separated from acetic acid in needles, m. p. 232° (Found : C, 64·1 ; H, 4·5. $C_{14}H_{12}O_3S$ requires C, 64·6 ; H, 4·6%).

2'-Carboxy-5-methoxy-2-methyldiphenyl sulphide (III). The reduction of 2-nitro-4-methoxytoluene was effected by tin and hydrochloric acid under the usual conditions or by the method described by West (J., 1925, **127**, 494), but the latter gave poor yields. The product obtained by the former method was purified by a current of steam in order to separate a small quantity of a less volatile base (m. p. 112°) containing halogen. This material (compare Beilstein and Kuhlberg, *Annalen*, 1870, **156**, 85) was evidently *chloro-4-methoxy-o-toluidine* (Found : C, 55·8 ; H, 5·6 ; *M*, 175. $C_8H_{10}ONCl$ requires C, 56·0 ; H, 5·8% ; *M*, 171·5) and appeared to be identical with the substance (m. p. 111°) encountered in this process by Limpach (*Ber.*, 1889, **22**, 791) and described by him as 4-methoxy-*o*-toluidine.

When the diazotised 4-methoxy-*o*-toluidine was treated with potassium iodide under the usual conditions, *2-iodo-4-methoxytoluene* was obtained in good yield. Purified by distillation under atmospheric pressure, it was a pale yellow liquid, b. p. 252—253° (Found : C, 38·7 ; H, 3·5. C_8H_9OI requires C, 38·7 ; H, 3·6%).

Amyl alcohol (17 c.c.), mixed with 2-iodo-4-methoxytoluene (7·9 g.), 2-thiolbenzoic acid (4·9 g.), dry potassium carbonate (4·5 g.), and a little copper acetate, was boiled (16 hours). The usual treatment (*vide supra*) then gave the crude product (75% yield), which was purified from acetic acid. The *substance* (III) formed colourless needles, m. p. 176—177° (Found : C, 65·7 ; H, 5·0. $C_{15}H_{14}O_3S$ requires C, 65·7 ; H, 5·1%).

2'-Carboxy-3 : 4-dimethoxydiphenyl sulphide (IX). 4-Iodoveratrole, obtained from 4-aminoveratrole by the usual method, was condensed with 2-thiolbenzoic acid in boiling amyl alcohol in presence of carbonate and copper acetate. The required *derivative* of diphenyl sulphide separated from acetic acid in plates, m. p. 212—213° (Found : C, 62·2 ; H, 4·9. $C_{15}H_{14}O_4S$ requires C, 62·1 ; H, 4·8%).

Derivatives of Thioxanthone.—The perchlorates described were obtained by addition of perchloric acid to a benzene solution of the methoxy-derivative concerned which had been saturated with hydrogen chloride, and the precipitated salts were analysed after the usual treatment. The formation and composition of hydrochlorides was examined by submitting the methoxy-derivatives to the action of hydrogen chloride until constant weight had been attained. The approximate relative stabilities of the salts of these thioxanthone derivatives, as indicated by column IV of the table

(p. 867), were studied by the following method. A solution of the sulphate was obtained by adding a mixture (2 c.c.) of sulphuric and acetic acids (1 : 2 by vol.) to a solution of 0·00025 mol. of the thioxanthone in acetic acid (5 c.c.). Alcohol was then added until decomposition of the salt was complete, the end-point being indicated by comparison with solutions of similar dilution without sulphuric acid. In cases where the presence of sulphuric acid caused a permanent change in the colour, titration was continued until the colour was the same as that of a solution of similar composition and " permanent " tint.

2-Methoxythioxanthone (I) was obtained from 2'-carboxy-4-methoxydiphenyl sulphide by treatment (1 hour) with sulphuric acid at 15°. The product, isolated by addition of ice, separated from chloroform in bright yellow needles, m. p. 129°; it was identical with the methoxythioxanthone obtained from anisole and 2-thiolbenzoic acid (J., 1910, **97**, 1296). 2-Hydroxythioxanthone (J., 1928, 3158) was formed in both these methods if solution in sulphuric acid was prolonged. The orange *perchlorate* was isolated in the manner described (Found : $HClO_4$, 29·1. $C_{14}H_{10}O_2S,HClO_4$ requires $HClO_4$, 29·3%). This thioxanthone was slightly soluble in hot concentrated hydrochloric acid and absorbed dry hydrogen chloride, but the product of the latter process was too unstable to permit quantitative examination.

1-*Chloro*-4-*methoxythioxanthone* (II). A mixture of 2-thiolbenzoic acid (6 g.), sulphuric acid (150 c.c.), and 4-chloroanisole (16 g.) was stirred (1½ hours). After isolation by addition of ice and treatment with alkali to remove acids and phenols, the *product* (8 g.) crystallised from acetone in pale yellow needles, m. p. 196° (Found : C, 60·7; H, 3·4; Cl, 12·5. $C_{14}H_9O_2ClS$ requires C, 60·7; H, 3·3; Cl, 12·8%). The substance did not yield a perchlorate or hydrochloride by the methods described. When a solution in *p*-toluidine containing potassium acetate and a little copper acetate was boiled (15 mins.), the halogen was replaced by the *p*-toluidino-group (compare Ullmann and Glenck, *loc. cit.*). 1-p-*Toluidino*-4-*methoxythioxanthone* separated from alcohol in red needles, m. p. 133°, which yielded a yellow hydrochloride (Found : C, 72·6; H, 5·2. $C_{21}H_{17}O_2NS$ requires C, 72·6; H, 4·9%).

4-*Methoxy*-1-*methylthioxanthone* (V). Condensation of 4-methoxytoluene and 2-thiolbenzoic acid was effected as described in the case of 1-chloro-4-methoxythioxanthone. The *substance* separated from alcohol in pale yellow needles, m. p. 162°, was insoluble in warm concentrated hydrochloric acid, and did not yield a perchlorate under the conditions described (Found : C, 70·0; H, 4·8. $C_{15}H_{12}O_2S$ requires C, 70·3; H, 4·7%).

1-*Methoxy*-4-*methylthioxanthone* (IV). A solution of 2′-carboxy-3-methoxy-6-methyldiphenyl sulphide (III) in ten times its weight of cooled sulphuric acid was stirred (1 hour). After addition of ice a red sulphate separated, but with excess of water this was hydrolysed, yielding (50%) the required *thioxanthone*. This separated from hot alcohol in bright yellow needles, m. p. 128° (Found : C, 70·2; H, 4·7. $C_{15}H_{12}O_2S$ requires C, 70·3; H, 4·7%). The substance was soluble in warm hydrochloric acid and absorbed dry hydrogen chloride, forming a red *hydrochloride* (Found : HCl, 29·9. $C_{15}H_{12}O_2S$,3HCl requires HCl, 29·9%). The crimson *perchlorate* was relatively stable, being slowly hydrolysed by cold water (Found : $HClO_4$, 28·2. $C_{15}H_{12}O_2S$,$HClO_4$ requires $HClO_4$, 28·1%).

1 : 4-Dimethoxythioxanthone (VI) prepared by the method of Clarke and Smiles (*loc. cit.*) was readily soluble in concentrated hydrochloric acid; the hydrochloride separated in crimson needles from the cooled solution. With the dry reagent a *dihydrochloride* was formed (Found : HCl, 21·2. $C_{15}H_{12}O_3S$,2HCl requires HCl, 21·1%). The *chloroplatinate* was obtained as sparingly soluble, deep red needles by adding chloroplatinic acid to a solution of the hydrochloride in alcohol [Found : Pt, 20·3. $(C_{15}H_{12}O_3S)_2$,H_2PtCl_6 requires Pt, 20·4%]. The *ferrichloride* separated in red needles when a solution of the hydrochloride in acetic acid was mixed with ferric chloride in the same solvent (Found : Fe, 11·6. $C_{15}H_{12}O_3S$,$HFeCl_4$ requires Fe, 11·9%). The crimson *perchlorate* was obtained in the usual manner (Found : $HClO_4$, 26·8. $C_{15}H_{12}O_3S$,$HClO_4$ requires $HClO_4$, 27·0%).

3 : 4-*Dimethoxythioxanthone* (VIII). 2-Bromoveratric acid (3·4 g.), thiophenol (1·8 g.), potassium carbonate (1·8 g.), and a little copper acetate were kept in boiling amyl alcohol (3½ hours). The required acid (VII) was isolated by the usual method (*vide supra*) in the crystalline state; it was converted by solution in sulphuric acid (1 hour; 15°) into the required *thioxanthone*. This was isolated in the usual manner; it separated from hot alcohol in pale yellow needles, m. p. 185° (Found : C, 66·0; H, 4·5. $C_{15}H_{12}O_3S$ requires C, 66·2; H, 4·4%). The orange *perchlorate* was obtained in the usual way (Found : $HClO_4$, 26·9. $C_{15}H_{12}O_3S$,$HClO_4$ requires $HClO_4$, 27·0%), but the hydrochloride, evidently formed by reaction with dry hydrogen chloride, was too unstable for examination. This dimethoxythioxanthone was very slightly soluble in warm hydrochloric acid.

2 : 3-*Dihydroxythioxanthone* (compare X). Pyrocatechol (3 g.) was gradually added to cooled stirred sulphuric acid (40 c.c.) which contained 2-thiolbenzoic acid (2 g.). The solid which separated after addition of ice was collected and dissolved in aqueous alkali

hydroxide; the required substance was liberated from this solution by carbonic acid. It separated from acetic acid or alcohol in orange needles which firmly retained these solvents; it was brought to analysis as the *diacetyl* derivative, pale yellow needles, m. p. 191°, from alcohol (Found: C, 61·9; H, 3·8. $C_{17}H_{12}O_5S$ requires C, 62·2; H, 3·6%). Oxidation of the hydroxythioxanthone yielded the dioxide (J., 1928, 3159), and aqueous alkaline methylation furnished the dimethoxy-derivative, m. p. 172°. The substance gave a yellow solution in boiling acetic anhydride which contained boroacetic anhydride (compare Dimroth, *loc. cit.*): when this was cooled, the diacetyl derivative separated in the crystalline state; it was identified with a sample prepared by another method. The formation of a boroacetate was not observed. In contrast with this behaviour, that of 1 : 4-dihydroxythioxanthone is described. With the reagent in question, this substance furnished a crimson boroacetate which was decomposed by boiling water, yielding 1-*hydroxy*-4-*acetoxythioxanthone*, which formed yellow needles, m. p. 171°, from alcohol (Found: C, 62·8; H, 3·6. $C_{15}H_{10}O_4S$ requires C, 62·9; H, 3·5%). For comparison, 1 : 4-*diacetoxythioxanthone* was prepared in the usual manner; it formed yellow needles, m. p. 168°, from alcohol (Found: C, 61·7; H, 3·6. $C_{17}H_{12}O_5S$ requires C, 62·2; H, 3·6%). A mixture of this with the monoacetyl derivative melted indistinctly below 150°.

2 : 3-*Dimethoxythioxanthone* (X). 2′-Carboxy-3 : 4-dimethoxydiphenyl sulphide (IX) was converted into the thioxanthone by solution in sulphuric acid. The product, isolated in the usual way, contained two substances, one of which was present in only small quantity and gave a more soluble, crimson hydrochloride. The material was triturated with concentrated hydrochloric acid, the deep red filtrate being set aside. The sparingly soluble, yellow hydrochloride was treated with this reagent until the red salt was removed. The residue was then decomposed with water and the liberated *thioxanthone*, purified from alcohol, was obtained in pale yellow needles, m. p. 172° (Found: C, 65·9; H, 4·4. $C_{15}H_{12}O_3S$ requires C, 66·2; H, 4·4%). The substance was sparingly soluble in concentrated hydrochloric acid. The orange *hydrochloride* was obtained by reaction with hydrogen chloride (Found: HCl, 21·2. $C_{15}H_{12}O_3S,2HCl$ requires HCl, 21·2%). When a solution of ferric chloride in acetic acid was added to a solution of the thioxanthone in this medium which had been saturated with hydrogen chloride, the *ferrichloride* separated in orange needles [Found: Fe, 7·4. $(C_{15}H_{12}O_3S)_2,HFeCl_4$ requires Fe, 7·5%]. Under conditions which provided a large excess of ferric chloride, a chocolate-brown *ferrichloride* separated in plates (Found: Fe, 11·9. $C_{15}H_{12}O_3S,HFeCl_4$

requires Fe, 11·9%). This dimethoxythioxanthone was also prepared by (1) aqueous alkaline methylation of the dihydroxythioxanthone obtained from pyrocatechol and 2-thiolbenzoic acid in sulphuric acid and (2) condensation of veratrole with 2-thiolbenzoic acid in the same medium. The latter method was the more convenient (yield, 30%), but the product contained a small quantity of the 1 : 2-dimethoxy-derivative, which was removed by treatment with hydrochloric acid.

1 : 2-*Dimethoxythioxanthone* (XI) was contained in the red solution of the more soluble hydrochloride removed during purification of the 2 : 3-derivative as described in the previous paragraph. The thioxanthone was recovered from this by treatment with water, the process of fractionating the hydrochloride being repeated; finally the thioxanthone was obtained in yellow needles, m. p. 143—144°, from acetic acid (Found: C, 66·6; H, 4·7. $C_{15}H_{12}O_3S$ requires C, 66·2; H, 4·4%). The substance gave a crimson hydrochloride and perchlorate.

2 : 3 : 4-*Trimethoxythioxanthone* (XII). A mixture of 2-thiolbenzoic acid (3 g.), 1 : 2 : 3-trimethoxybenzene (4 g.), and sulphuric acid (60 c.c.) was warmed until a clear solution was obtained. The product, isolated after the usual treatment, separated from alcohol in pale yellow needles, m. p. 150° (Ullmann and Sone record m. p. 153—154° for the methylation product of 2 : 3 : 4-trihydroxythioxanthone). Since this mode of preparation does not exclude the presence of the 1 : 2 : 3-isomeride as an impurity, the material required for further examination was prepared from 1-iodo-2 : 3 : 4-trimethoxybenzene (Graebe and Suter, *loc. cit.*) and 2-thiolbenzoic acid in presence of alkali carbonate and copper acetate by the usual method. The carboxylic acid obtained was dissolved in warm sulphuric acid (15 mins.), from which ice precipitated the 2 : 3 : 4-trimethoxythioxanthone. After purification this had m. p. 150° and was identical with the material obtained by the other method (Found: C, 63·8; H, 4·8. Calc.: C, 63·6; H, 4·6%). The substance was sparingly soluble in warm hydrochloric acid, and the orange *salt* prepared with the dry reagent was unstable, losing hydrogen chloride during manipulation (Found: HCl, 16·5. $C_{16}H_{14}O_4S,2HCl$ requires HCl, 19·5%). The orange *perchlorate* had the normal composition (Found: $HClO_4$, 25·0. $C_{16}H_{14}O_4S,HClO_4$ requires $HClO_4$, 24·9%).

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