

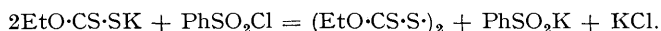
**179.** *The Chemistry of Xanthic Acid Derivatives. Part IV. The Interaction of Sulphonyl Chlorides and Potassium Ethyl Xanthate.*

By GERALD BULMER and FREDERICK G. MANN.

Potassium ethyl xanthate reacts with benzene-, *p*-toluene- and naphthalene-2-sulphonyl chlorides to form the corresponding potassium sulphonate, the disulphone  $\text{RSO}_2\cdot\text{SO}_2\text{R}$ , and diethyl disulphurdicarbothionate,  $(\text{EtO}\cdot\text{CS}\cdot\text{S})_2$ . In the reaction with other sulphonyl chlorides, the production of the disulphone may be partly or wholly replaced by that of the thiolicsulphonate  $\text{RSO}_2\cdot\text{SR}$ , the disulphide  $\text{RS}\cdot\text{SR}$ , or the corresponding sulphinic acid. Evidence is adduced that the initial reaction in all cases is the formation of the unstable, highly reactive sulphonyl xanthate,  $\text{EtO}\cdot\text{CS}\cdot\text{S}\cdot\text{SO}_2\cdot\text{R}$ : the mechanism by which the above products arise from this xanthate is discussed.

Many alkali xanthates (and hence carbon disulphide itself) can be readily identified by conversion to the corresponding palladium xanthates  $[(\text{RO}\cdot\text{CS}\cdot\text{S})_2\text{Pd}]$ , which are non-ionic compounds usually having characteristic m. p.s.

It has been claimed by Richter (*Ber.*, 1916, **49**, 1026) that potassium ethyl xanthate reacts with benzenesulphonyl chloride in carbon disulphide solution to form *O*-ethyl *S*-benzenesulphonyl xanthate,  $\text{EtO}\cdot\text{CS}\cdot\text{S}\cdot\text{SO}_2\text{Ph}$ : the identification of this compound, however, rested solely on the analysis of the liquid which remained after the removal of the solvent from the filtered reaction solution, for this liquid was too unstable to be distilled or otherwise purified. Cambron and Whitby (*Canad. J. Res.*, 1930, **2**, 147) have stated, however, that potassium xanthate reacts with benzenesulphonyl chloride in ethereal solution at  $-10^\circ$  thus :

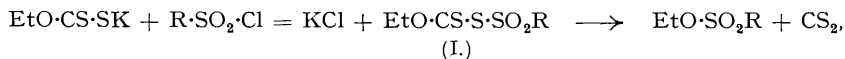


They isolated the diethyl disulphurdicarbothionate in 47.5% yield, but had no experimental evidence for the formation of the potassium sulphinat or, apparently, of any other product.

We find that potassium xanthate, when added in equimolecular quantity to benzenesulphonyl chloride dissolved in either carbon disulphide or ether at  $0^\circ$ , reacted to form potassium benzenesulphonate, diphenyl disulphone,  $\text{PhSO}_2\cdot\text{SO}_2\text{Ph}$ , and diethyl disulphurdicarbothionate. The use of two molecular proportions of the xanthate gave the same products, half the xanthate remaining unchanged. When potassium xanthate was added to one molecular proportion of benzenesulphonyl chloride without a solvent, a vigorous reaction with heat evolution occurred in spite of external cooling, and the products were now the potassium sulphonate, the disulphone, and *O*-ethyl *S*-ethyl xanthate,  $\text{EtO}\cdot\text{CS}\cdot\text{SEt}$ ; the latter is known, however, to be formed very readily by the thermal decomposition of the disulphurdicarbothionate (see Part II, p. 675), and its origin in this

experiment is beyond doubt. Similar results, with one significant addition, have been obtained with *p*-toluenesulphonyl chloride. Potassium xanthate reacted with one molecular proportion of this chloride, dissolved in carbon disulphide or ether, to form potassium *p*-toluenesulphonate, di-*p*-tolyl-disulphone, and the disulphurdicarbothionate. When, however, the xanthate was added to the chilled chloride in the absence of a solvent, the vigorous reaction produced the potassium sulphonate, the disulphone, *O*-ethyl *S*-ethyl xanthate, and ethyl *p*-toluenesulphonate.

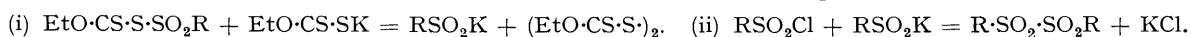
Two alternative series of reactions, (A) and (B), will account for the above formation of the disulphones and of diethyl disulphurdicarbothionate. Both are based on the initial formation of the unstable and highly reactive *O*-ethyl *S*-arylsulphonyl xanthate (I), identical in type with the benzenesulphonyl derivative



claimed by Richter (*loc. cit.*). Although we have no direct evidence of this intermediate compound, we consider that the isolation of ethyl *p*-toluenesulphonate affords strong confirmation of its formation, since it could dissociate to give the ethyl sulphonate and carbon disulphide, a reaction precisely parallel to the known dissociation of carboxylic xanthates,  $\text{EtO}\cdot\text{CS}\cdot\text{S}\cdot\text{COR}$ , to ethyl carboxylates and carbon disulphide (cf. Part III). This direct dissociation of the sulphonyl xanthate must be regarded as exceptional under our experimental conditions, however, as we have detected it only in the *p*-toluene series.

By mechanism (A) the disulphones and the disulphurdicarbothionate arise by direct dismutation of this sulphonyl xanthate:  $2\text{EtO}\cdot\text{CS}\cdot\text{S}\cdot\text{SO}_2\text{R} = \text{R}\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{R} + (\text{EtO}\cdot\text{CS}\cdot\text{S})_2$ .

By mechanism (B), however, the sulphonyl xanthate reacts immediately on formation with unchanged potassium xanthate to give the potassium sulphinat and the disulphurdicarbothionate (reaction i), and the sulphinat then reacts with unchanged sulphonyl chloride to form the disulphone (reaction ii).



There is considerable experimental support for reactions of type (i) and (ii). Otto *et al.* (*Ber.*, 1876, **9**, 1636; 1878, **11**, 2070) showed that sulphonyl chlorides reacted with thiols to give, not the expected thiolic-sulphonates, but sulphinic acids and disulphides:  $\text{RSO}_2\text{Cl} + 2\text{R}'\text{SH} = \text{RSO}_2\text{H} + \text{R}'\text{S}\cdot\text{SR}' + \text{HCl}$ . Saunders (*Biochem. J.*, 1933, **27**, 397) showed that the sodium derivatives of thiols gave the same reaction. Gibson, Miller and Smiles (*J.*, 1925, **127**, 1821) showed that Otto's reaction, although usually rapid and complete, consisted actually of two consecutive reactions (*a*) and (*b*), which, formulated for the potassium thiols, were: (*a*)  $\text{RSO}_2\text{Cl} + \text{R}'\text{SK} = \text{KCl} + \text{RSO}_2\cdot\text{SR}'$ ; (*b*)  $\text{RSO}_2\cdot\text{SR}' + \text{R}'\text{SK} = \text{RSO}_2\text{K} + \text{R}'\text{SSR}'$ . They determined the conditions under which reaction (*a*) proceeded but reaction (*b*) was almost entirely suppressed, so that thiolic-sulphonates,  $\text{RSO}_2\cdot\text{SR}'$ , could actually be prepared from these reagents. Potassium ethyl xanthate is also a potassium thiol, and if  $\text{R}' = \text{EtO}\cdot\text{CS}\cdot$ , equation (*a*) represents the initial formation of our sulphonyl xanthate (I), and equation (*b*) becomes identical with reaction (i) above. Reaction (ii) represents one of the standard methods of disulphone formation and has received experimental confirmation (Kohler and MacDonald, *Amer. Chem. J.*, 1899, **22**, 219; Hinsberg, *Ber.*, 1916, **49**, 2593).

Mechanism B is thus more complex than A, and clearly demands high reactivity of the intermediate sulphonyl xanthate. Nevertheless, although the results obtained with benzene- and *p*-toluene-sulphonyl chlorides can be explained by mechanism A, those obtained with other sulphonyl chlorides, particularly when (in the absence of a solvent) the vigorous reaction caused a marked rise in temperature, afford strong evidence that mechanism B may partly or wholly replace mechanism A. The products obtained from these sulphonyl chlorides will be described first and the probable mechanism of their formation discussed subsequently. Unless otherwise stated, the reaction of these chlorides with potassium xanthate has been investigated only in the absence of a solvent, and in such case the *O*-ethyl *S*-ethyl xanthate isolated undoubtedly arose as a thermal decomposition product of the disulphurdicarbothionate formed in the initial vigorous reactions.

Naphthalene-2-sulphonyl chloride reacted "normally" with potassium xanthate, affording *di*-2-naphthyl disulphone,  $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{C}_{10}\text{H}_7$ , potassium naphthalene-2-sulphonate, and *O*-ethyl *S*-ethyl xanthate. Naphthalene-1-sulphonyl chloride reacted very vigorously, with the formation of naphthalene, naphthalene-1-thiol, the potassium sulphonate and *O*-ethyl *S*-ethyl xanthate. The reaction of this sulphonyl chloride appears to be unique, however, since no other chloride investigated afforded a hydrocarbon or a thiol.

The reaction of *p*-chlorobenzenesulphonyl chloride with potassium xanthate was of particular interest, as it afforded a link between the "normal" sulphonyl chlorides which gave the disulphones, and those which gave solely reduction products. This sulphonyl chloride gave the usual vigorous reaction with the xanthate, but the product now consisted of potassium *p*-chlorobenzenesulphonate, *di*-*p*-chlorophenyl disulphone *O*-ethyl *S*-ethyl xanthate and also *p*-chlorophenyl *p*-chlorobenzene thiolic-sulphonate (or *di*-*p*-chlorophenyl sulphide-sulphone),  $\text{ClC}_6\text{H}_4\cdot\text{S}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Cl}$ . The identity of this compound, which Otto (*Annalen*, 1868, **145**, 323) originally prepared by heating *p*-chlorobenzenesulphonic acid with water at 130–140°, was confirmed synthetically by the interaction of *p*-chlorobenzenesulphonyl iodide and silver *p*-chlorophenyl sulphide (cf. Gibson, Miller, and Smiles, *loc. cit.*):  $\text{ClC}_6\text{H}_4\cdot\text{SO}_2\text{I} + \text{ClC}_6\text{H}_4\cdot\text{SAg} \longrightarrow \text{ClC}_6\text{H}_4\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_4\text{Cl}$ . No other sulphonyl chloride investigated gave both the disulphone and the thiol-sulphonate.

*p*-Nitrobenzenesulphonyl chloride reacted with potassium xanthate to form both *p*-nitrobenzenesulphonic acid and its potassium salt, *O*-ethyl *S*-ethyl xanthate, and *p*-nitrophenyl *p*-nitrobenzene thiolic-sulphonate,

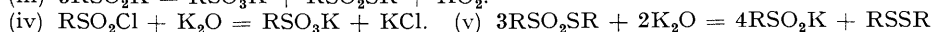
$\text{NO}_2\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{SC}_6\text{H}_4\text{NO}_2$ : the last compound had the same m. p. as that synthesised by Zincke and Lenhardt (*Annalen*, 1913, **400**, 15) by the interaction of silver *p*-nitrobenzenesulphinate,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Ag}$ , and *p*-nitrophenyl chlorosulphide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SCl}$ . The production of the free acid in this and (subsequent) experiments is noteworthy.

*p*-Acetamidobenzenesulphonyl chloride reacted only sluggishly with potassium xanthate, producing *p*-acetamidophenyl *p*-acetamidobenzene thiolicsulphonate,  $\text{AcNH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ . This compound was identified (a) by alkaline hydrolysis, which furnished *p*-aminobenzenesulphonic acid and di-*p*-acetamidophenyl disulphide, a reaction which is discussed later; (b) synthetically, by the interaction of *p*-acetamidobenzenesulphonyl iodide,  $\text{AcNH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{I}$ , and silver *p*-acetamidophenyl sulphide,  $\text{AcNH}\cdot\text{C}_6\text{H}_4\cdot\text{SAg}$ . The production of this thiolicsulphonate was undoubtedly accompanied by that of *p*-acetamidobenzenesulphonic acid or its potassium salt; these were not isolated, but cold aqueous extraction of the crude product furnished sulphanilic acid, to which the free acetamido-acid and its salts are known to be very readily hydrolysed. [It is significant that Hinsberg (*Ber.*, 1906, **39**, 2430) claimed to have isolated di-*p*-acetamidophenyl disulphoxide,  $\text{AcNHC}_6\text{H}_4\cdot\text{SO}\cdot\text{SO}\cdot\text{C}_6\text{H}_4\text{NHAc}$ , in two distinct forms. Although in the past there has been much confusion between disulphoxides and the isomeric thiolicsulphonates, Hinsberg's two compounds are quite distinct from our authentic thiolicsulphonate, and are apparently the true disulphoxides, representing possibly the *dl*- and the *meso*-forms of this compound.]

A nitro-group, present in the *meta* position to the sulphonyl chloride group, appears to influence the reaction profoundly. *m*-Nitrobenzenesulphonyl chloride reacted very vigorously with potassium xanthate, forming *m*-nitrobenzenesulphonic acid, its potassium salt, and *O*-ethyl *S*-ethyl xanthate: no indication of the formation of any compounds of the disulphone or thiolicsulphonate type could be detected. 4-Nitrotoluene-2-sulphonyl chloride also reacted vigorously, but produced 4-nitrotoluene-2-sulphonic acid (II) in addition to potassium 4-nitrotoluenesulphonate and the ethyl xanthate. Since this was the only sulphonyl chloride which furnished a free sulphonic acid, the initial reaction was investigated in a solvent at low temperature. The only products isolated, however, by the interaction of potassium xanthate (1 or 2 molecular proportions) and the sulphonyl chloride in carbon disulphide or ethereal solution at 0° were the above potassium sulphonate and diethyl disulphurdicarbthionate. It is clear, therefore, that the sulphonic acid (II) must arise only in supplementary reactions occurring at higher temperatures in the absence of a solvent.

Aliphatic sulphonyl chlorides appeared to react quite differently from the aromatic analogues. For example, methanesulphonyl chloride reacted with potassium methyl xanthate to form potassium methane-sulphonate, dimethyl disulphide and dimethyl disulphurdicarbthionate (identified as its decomposition product, *O*-ethyl *S*-methyl xanthate); ethanesulphonyl chloride reacted similarly with potassium ethyl xanthate to produce potassium ethanesulphonate, carbon disulphide, diethyl disulphide, diethyl disulphurdicarbthionate and *O*-ethyl *S*-ethyl xanthate. This formation of a disulphide was never observed in the reactions of the aromatic sulphonyl chlorides.

The above production of sulphonic acid derivatives, of thiolicsulphonates and of disulphides cannot be satisfactorily explained by Mechanism A; these compounds are, however, those whose formation might be anticipated as the result of side-reactions occurring during the course of Mechanism B. It is known that many aromatic sulphonic acids decompose at room temperature, even in the absence of air, to form the corresponding sulphonic acids and thiolicsulphonates, a reaction which is accelerated by hydrogen chloride (Pauly and Otto, *Ber.*, 1877, **10**, 2182; 1878, **11**, 2070). Salts of sulphonic acids give the same reaction: thus Hälssig (*J. pr. Chem.*, 1897, **56**, 213) has shown that ammonium *p*-toluenesulphinate in hot benzene decomposes thus:  $3\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{NH}_4 = \text{C}_7\text{H}_7\cdot\text{SO}_2\text{NH}_4 + \text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{SC}_7\text{H}_7 + 2\text{NH}_3 + \text{H}_2\text{O}$ . It is clear therefore that in the course of Mechanism B, the occurrence of reaction (i) might be followed by other reactions which would compete with (and in favourable circumstances completely replace) reaction (ii). Thus the potassium sulphinate formed in (i) might undergo the normal decomposition to sulphonate and thiolicsulphonate shown in reaction (iii), provided other reagents were available to react immediately with the potassium oxide formed. Clearly any unchanged sulphonyl chloride would then react with the oxide to give the potassium sulphonate and chloride (reaction iv). Furthermore, the thiolicsulphonate esters are known to undergo very ready alkaline



hydrolysis to alkali sulphinates and the organic disulphides (Pauly and Otto, *Ber.*, 1877, **10**, 2181; 1878, **11**, 2073; Otto and Rössing, *Ber.*, 1886, **19**, 1235), and a precisely similar reaction (v) might well occur between the potassium oxide and the thiolicsulphonate formed in reaction (iii). It must be emphasised that the occurrence of reaction (iii) as an independent process is not claimed: it is suggested solely that reaction (iii) might occur in strict conjunction with one or both of reactions (iv) and (v).

We consider that reactions (ii), (iii), (iv), and (v), following reaction (i) and mutually competing to an extent determined by the individual sulphonyl chloride and the local conditions employed, furnish the most probable explanation of our main results. Thus in the *p*-chlorobenzene series, reactions (ii) and (iii) occur simultaneously, and the disulphone and thiolicsulphonate are thus both formed: in the *p*-nitrobenzene series, reaction (iii) apparently completely displaces reaction (ii), and the thiolicsulphonate is therefore formed to the exclusion of the disulphone. Furthermore, although comparatively little is known of the properties of aliphatic sulphonic

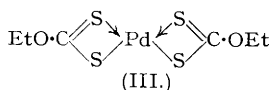
acids and thiolcsulphonates, these compounds are much less stable than their aromatic analogues; therefore in the methyl and ethyl series, it would be expected that reactions (iii) and (v) would occur particularly readily and, since the potassium sulphinate formed in reaction (v) would continue this cycle of reactions, the disulphide alone would ultimately remain—a deduction precisely in accordance with experimental facts. The reactions of the aliphatic sulphonyl chlorides do actually, therefore, fall into line with those of their aromatic analogues.

Certain difficulties still remain. It will be seen that although the reactions constituting Mechanism B readily explain the consistent formation of the potassium sulphonates in all our experiments, yet these potassium salts can only be formed in conjunction with the thiolcsulphonates, or, if the latter undergo complete hydrolysis, with the disulphides. Yet with benzene-, *p*-toluene- and naphthalene-2-sulphonyl chlorides, where Mechanisms A and B may have occurred simultaneously, and with the *m*-nitrobenzenesulphonyl chloride, where there was no evidence of Mechanism A, the production of the thiolcsulphonates or disulphides could not be detected. There is some evidence that *m*-nitrobenzenesulphonyl chloride shows other abnormal reactions (Limpricht, *Annalen*, 1894, 278, 239), but the difficulty concerning the previous three sulphonyl chlorides remains.

The production of naphthalene during the reaction of naphthalene-1-sulphonyl chloride and potassium xanthate has probably, however, no particular significance, as naphthalene-1-sulphonic acid and its derivatives are known readily to furnish the hydrocarbon in several reactions (cf. Kimberly, *Annalen*, 1860, 114, 133; Merz, *Z. fur. Chem.*, 1868, 399; Friedlander and Lucht, *Ber.*, 1893, 26, 3020).

It is noteworthy that our preparation of the  $\alpha$ -disulphones by the xanthate reaction forms the fifth known method of preparation, the previous methods being (a) by the interaction of sulphonyl chlorides and metallic sulphinates (Kohler and MacDonald, *loc. cit.*), (b) by the permanganate oxidation of sulphinic acids (Hilditch, *J.*, 1908, 93, 1524), (c) by the hydrogen peroxide oxidation of thiolcsulphonates (Gilman, Smith and Parker, *J. Amer. Chem. Soc.*, 1925, 47, 851), and (d) by the action of alkali metals on sulphonyl chlorides (Pearl, Evans, and Dehn, *ibid.*, 1938, 60, 2478).

In the course of this work we have had occasion to identify small quantities of carbon disulphide. For this purpose, the latter has been converted to potassium ethyl xanthate, which has then been added in approximately correct proportions to an aqueous solution of potassium chloropalladite,  $K_2[PdCl_4]$ . The precipitated *palladium bisethylxanthate* forms orange-red crystals, m. p. 152°, soluble in many organic solvents. It is therefore a derivative of 4-covalent palladium of formal structure (III), although it would clearly exist as a resonance hydrid. Other xanthates give similar palladium derivatives of characteristic m. p., and these compounds can be used therefore for the rapid identification of carbon disulphide or (more usefully) the alkali salts of many xanthic acids.



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#### EXPERIMENTAL.

The solvents used for recrystallisation are named in parenthesis after the compounds concerned. In addition to the analytical data quoted, the identity of every sample of *O*-ethyl *S*-ethyl xanthate isolated was further confirmed by conversion through the action of phenylhydrazine to *O*-ethyl-*N*-phenylamino-thiourethane. All the various potassium sulphonates isolated by aqueous extraction were necessarily initially contaminated with potassium chloride, which was eliminated by the subsequent alcoholic recrystallisation.

*Benzenesulphonyl Chloride.*—(i) Dry powdered potassium ethyl xanthate (8.8 g.) was slowly added to a solution of freshly distilled benzenesulphonyl chloride (8.8 g., 0.91 mol.) in dry ether (400 c.c.) which was maintained at 0° and continuously shaken. The complete mixture was then shaken at 0° for a further 30 minutes, and finally set aside at room temperature for 6 hours. Filtration now gave a colourless solid, which when extracted with cold water left a small insoluble residue of diphenyldisulphone (alcohol), m. p. 192.5° (alone and mixed) (Found: C, 51.1; H, 3.4; S, 22.6. Calc. for  $C_{12}H_{10}O_4S_2$ : C, 51.0; H, 3.55; S, 22.7%). Hilditch (*loc. cit.*) gives m. p. 193–194°. The aqueous extract was evaporated to dryness, and repeated recrystallisation of the residue (alcohol) eliminated both potassium chloride and unchanged xanthate, furnishing potassium benzenesulphonate (Found: C, 36.8; H, 2.7; S, 16.5. Calc. for  $C_6H_5O_3SK$ : C, 36.7; H, 2.55; S, 16.35%).

Evaporation of the ethereal filtrate at room temperature gave a yellow oil from which a small second crop of the disulphone separated. This was collected, m. p. 192–192.5° (alone and mixed), and the filtrate, when confined in a vacuum, slowly deposited crystals of diethyl disulphurdicarbothionate; these, when collected and washed with alcohol, were pure, m. p. 31–32° (alone and mixed), raised to 31.5–32.5° by recrystallisation (alcohol) (Found: C, 29.6; H, 4.05; S, 52.9. Calc. for  $C_6H_{10}O_2S_4$ : C, 29.7; H, 4.15; S, 52.95%). The filtrate gave no further crystals but, on distillation at 0.1 mm. pressure, gave solely a second crop of the thionate, b. p. 115–121°, which rapidly solidified on cooling, and when once washed with chilled ligroin had m. p. 31.5–32° (alone and mixed) (Found: C, 29.65; H, 4.1; S, 53.0%).

The same products were obtained when the ether in the above experiment was replaced by carbon disulphide (400 c.c.), and when the experiment was repeated in each solvent using only half of the above benzenesulphonyl chloride. The products in all experiments were identified by analysis and/or mixed m. p. determinations. No evidence for the existence of a sulphonyl-xanthate of type (I) could be detected at any stage in these experiments.

(ii) The potassium xanthate (8 g.) was now added rapidly to vigorously stirred benzenesulphonyl chloride (8.8 g.) chilled in ice-water, no solvent being used. A reaction rapidly occurred, with the evolution of heat and of malodorous fumes. The grey pasty product when cold was extracted with cold ether and then with boiling benzene. The final colourless residue which contained potassium chloride, after repeated crystallisation (alcohol) furnished potassium benzenesulphonate (Found: C, 36.9; H, 2.75; S, 16.55%). The benzene extract was evaporated to dryness and the residue, after recrystallisation (alcohol), gave diphenyl disulphone m. p. 193° (alone and mixed) (Found: C, 51.15; H, 3.45; S, 22.8%). The ethereal extract was evaporated at reduced pressure, giving a yellow oil which on cooling deposited a small second crop of the disulphone which, when collected and crystallised (benzene, alcohol), had m. p. 193° (alone and mixed). The oily filtrate from this crop when fractionated at 13 mm. gave solely *O*-ethyl *S*-ethyl xanthate, b. p. 76°/13 mm. (Found: C, 40.05; H, 6.55; S, 42.65. Calc. for  $C_5H_{10}OS_2$ : C, 39.95; H, 6.7; S, 42.7%).

*p*-Toluenesulphonyl Chloride.—(i) Potassium xanthate (9.6 g.) was slowly added to a solution of freshly recrystallised *p*-toluenesulphonyl chloride (10.4 g., 0.91 mol.) in dry ether (350 c.c.), which was chilled in ice-water and vigorously

shaken meanwhile. Filtration gave a colourless solid which was extracted with cold water. The residue furnished di-*p*-tolyl disulphone (alcohol), m. p. 223.5°, with incipient decomp. at 220° (Found: C, 54.2; H, 4.75; S, 20.75. Calc. for  $C_{14}H_{14}O_4S_2$ : C, 54.15; H, 4.55; S, 20.65%). The aqueous extract on evaporation gave a mixed residue from which crystallisation (alcohol) ultimately gave potassium *p*-toluenesulphonate (Found: C, 40.0; H, 3.45; S, 15.35. Calc. for  $C_7H_7O_3SK$ : C, 39.95; H, 3.35; S, 15.25%). Hilditch (*loc. cit.*) gives m. p. 221° (decomp.), and Kohler and MacDonald (*loc. cit.*) give m. p. 212° (decomp.) for the disulphone: the m. p. is however markedly affected by the rate of heating.

The ethereal filtrate, on evaporation at reduced pressure below 15°, gave a colourless oil from which a small crop of the disulphone separated; this was collected and crystallised (alcohol), m. p. 223° with incipient decomp. at 219° (Found: C, 54.15; H, 4.55%). The oily filtrate, after prolonged confinement in a vacuum, gave an initial crop of diethyl disulphurdicarbothionate, m. p. 31–32° (Found: C, 29.6; H, 4.0%), and the residue, on distillation at 0.1 mm. gave a second crop, b. p. 114–120°, m. p. 31.5–32° (mixed and unmixed) (Found: C, 29.8; H, 4.0; S, 53.05%).

The same results were obtained in carbon disulphide (350 c.c.), and when half the above sulphonyl chloride was used in each solvent.

(ii) When potassium xanthate (6 g.) and powdered *p*-toluenesulphonyl chloride were rapidly and thoroughly mixed, a vigorous reaction occurred with evolution of heat and gaseous products having a foul odour. The product when cold was extracted first with ether and then with cold water. The insoluble residue on crystallisation (alcohol) furnished the disulphone, m. p. as above (Found: C, 54.2; H, 4.6%). The aqueous extract was evaporated; and the residue, after repeated crystallisation (alcohol), afforded potassium *p*-toluenesulphonate (Found: C, 39.9; H, 3.45; S, 15.4%). The ethereal extract was evaporated and the oily residue, on fractional distillation, gave ultimately two pure fractions (a) *O*-ethyl *S*-ethyl xanthate, b. p. 77–78°/14 mm. (Found: C, 40.15; H, 6.6; S, 42.75%), (b) ethyl *p*-toluenesulphonate, b. p. 125–128°/0.15 mm., m. p. 31.5–32° alone and mixed, after crystallisation (ligroin) (Found: C, 53.9; H, 6.25; S, 15.95. Calc. for  $C_9H_{12}O_3S$ : C, 53.95; H, 6.05; S, 16.0%).

*Naphthalene-2-sulphonyl Chloride*.—An intimate powdered mixture of the sulphonyl chloride (9 g.) and potassium xanthate (6.4 g., 1 mol.) was heated with stirring at 100°; when the usual vigorous reaction, which rapidly occurred, had subsided the product was heated for 1 hour at 100°, and then cooled and extracted with ether and then with cold water. The insoluble residue from these extractions consisted of *di-2-naphthyl*disulphone still contaminated with potassium naphthalene-2-sulphonate; the disulphone, best purified by crystallisation in turn from acetic acid and from alcohol with intermediate washing with boiling water, formed colourless crystals, m. p. 218° (decomp.) when rapidly heated (Found: C, 63.0; H, 3.9; S, 16.6; *M*, ebullioscopic in 0.609, 0.901, and 1.221% benzene solution, 407, 405, 402.  $C_{20}H_{14}O_4S_2$  requires C, 62.8; H, 3.7; S, 16.8%; *M*, 382).

The ethereal extract was evaporated, and the residue fractionally distilled; only *O*-ethyl *S*-ethyl xanthate, b. p. 78–79°/16 mm., was obtained (Found: C, 39.8; H, 6.65; S, 42.6%). The aqueous extract was evaporated to dryness, and the residue, twice crystallised (alcohol), furnished potassium naphthalene-2-sulphonate (Found: C, 48.8; H, 3.05; S, 13.15. Calc. for  $C_{10}H_7O_3SK$ : C, 48.75; H, 2.85; S, 13.0%).

*Naphthalene-1-sulphonyl Chloride*.—When the finely powdered chloride (8.5 g.) and the xanthate (6 g., 1 mol.) were rapidly mixed, an immediate and very vigorous reaction occurred; the pasty product was stirred until the reaction was complete and then, when cold, extracted with ether. The residue, repeatedly recrystallised (alcohol), furnished potassium naphthalene-1-sulphonate (Found: C, 48.55; H, 3.05; S, 13.2. Calc. for  $C_{10}H_7O_3SK$ : C, 48.75; H, 2.85; S, 13.0%).

The ethereal extract was evaporated, and the residual oil, when distilled at 18 mm., gave 3 crude fractions: (a) b. p. 60–85°, (b) b. p. 85–100°, (c) b. p. 100–150°, and a black tarry residue. Fraction (a), refractionated, gave *O*-ethyl *S*-ethyl xanthate, b. p. 78–80°/17 mm. (Found: C, 40.15; H, 6.95; S, 42.8%). Fraction (b) readily solidified on cooling and, recrystallised (alcohol), afforded naphthalene, m. p. 80–80.5° (alone and mixed) (Found: C, 93.85; H, 6.3. Calc. for  $C_{10}H_8$ : C, 93.7; H, 6.3%). Fraction (c), refractionated, gave naphthyl-1-thiol, b. p. 143–147°/14 mm. (Found: C, 74.8; H, 5.2; S, 20.2. Calc. for  $C_{10}H_8S$ : C, 74.95; H, 5.05; S, 20.0%). The identity of this thiol was confirmed by two methods. (i) A portion was gently warmed with concentrated nitric acid for 10 minutes, and the mixture then cooled and diluted with water. The precipitated yellow solid, recrystallised (benzene), gave 4:4'-dinitro-1:1'-dinaphthyl disulphide, m. p. 193.5° (Found: C, 59.0; H, 3.05; N, 6.85; S, 15.95. Calc. for  $C_{10}H_{12}O_4N_2S_2$ : C, 58.8; H, 2.95; N, 6.85; S, 15.7%). The m. p. was unaffected by admixture with a sample prepared by Hodgson and Leigh's method (*J.*, 1937, 1352) and kindly supplied by Dr. H. H. Hodgson. (ii) An alcoholic solution of another portion, when oxidised with iodine (1 atom) furnished 1:1'-dinaphthyl disulphide (alcohol), m. p. 88.5–89° (Found: C, 75.45; H, 4.5; S, 20.0. Calc. for  $C_{20}H_{14}S_2$ : C, 75.4; H, 4.45; S, 20.15%). This disulphide, when gently warmed with nitric acid, gave the above dinitro-disulphide (benzene), m. p. 192–192.5° (alone and mixed) (Found: C, 58.75; H, 3.1; N, 6.9; S, 16.0%).

*p*-Chlorobenzenesulphonyl Chloride.—A mixture of the chloride (21 g.) and the xanthate (16 g., 1 mol.) when ground together, gave a vigorous reaction. The cold product was extracted with ether and then with water. The residue when recrystallised (benzene) gave colourless crystals of *di-p-chlorophenyl* disulphone, m. p. 214° (Found: C, 41.3; H, 2.25; Cl, 19.85; S, 18.05.  $C_{12}H_8O_4Cl_2S_2$  requires C, 41.0; H, 2.3; Cl, 20.2; S, 18.25%). Evaporation of the solvent from the ethereal extract left a mixture of a yellow oil and colourless crystals. The latter, when collected and repeatedly crystallised (alcohol), gave *p*-chlorophenyl *p*-chlorobenzenethiolsulphonate, m. p. 137–138° (Found: C, 45.35; H, 2.8; Cl, 22.1; S, 20.2. Calc. for  $C_{12}H_8O_3Cl_2S_2$ : C, 45.1; H, 2.5; Cl, 22.2; S, 20.1%); Otto (*loc. cit.*) gives m. p. 136–138°. The yellow oil, on fractional distillation, gave solely *O*-ethyl *S*-ethyl xanthate, b. p. 78–79°/19 mm. (Found: C, 40.1; H, 6.9; S, 42.6%). The residue from evaporation of the aqueous extract, repeatedly crystallised (alcohol), gave colourless crystals of potassium *p*-chlorobenzenesulphonate (Found: C, 31.0; H, 1.5; Cl, 15.35; S, 14.0. Calc. for  $C_6H_4O_3ClSK$ : C, 31.2; H, 1.4; Cl, 15.4; S, 13.9%).

*Synthesis of p-Chlorophenyl p-Chlorobenzenethiolsulphonate*.—(a) *p*-Chlorobenzenesulphonyl iodide. A mixture of *p*-chlorobenzenesulphonyl chloride (17.9 g.), ether (75 c.c.), water (1–2 c.c.) and zinc dust (15 g.) was refluxed for 2 hours. The precipitated zinc sulphinate was collected, washed with water, and heated with a solution of anhydrous sodium carbonate (15 g.) in water (75 c.c.) for 1 hour, filtered and cooled. To the solution of the sodium sulphinate obtained, an alcoholic solution of iodine (67.2 g.) was slowly added with stirring. The crystalline *sulphonyl iodide* which separated was collected, washed, dried and recrystallised (petrol): m. p. 74–75° (Found: C, 23.65; H, 1.25; S, 10.8.  $C_6H_4O_2ClIS$  requires C, 23.8; H, 1.35; S, 10.6%). These preparations of the sodium sulphinate and the sulphonyl iodide are based on the methods of Ullmann and Pasdermadjian (*Ber.*, 1901, **34**, 1151) and Otto and Troger (*Ber.*, 1891, **24**, 478) respectively.

(b) *Silver p-chlorophenyl sulphide*. The preparation of the thiol was adapted from Decker and Fellenberg's method (*Annalen*, 1907, **356**, 326), a mixture of the sulphonyl chloride (11.3 g.), iron filings (74 g.) and acetic acid (30 g.) being heated at 100° whilst 15% aqueous hydrochloric acid (100 c.c.) was slowly added. After 5 hours' heating, the mixture was distilled in steam, and the thiol, which crystallised in the distillate, was collected and recrystallised (alcohol): m. p. 53.5–54°. Otto (*Annalen*, 1867, **143**, 109), using zinc for this reduction, records m. p. 53–54°. An alcoholic solution of silver nitrate (3.4 g.) was added to one of the thiol (2.9 g., 1 mol.) containing also sodium acetate (1.6 g., 1 mol.).

The precipitated silver *p*-chlorophenyl sulphide was collected, washed, and thoroughly dried (cf. Gibson and Smiles, *loc. cit.*).

(c) *The thioic sulphonate.* The silver sulphide (2.5 g., 1.1 mol.) was slowly added to a vigorously shaken solution of the sulphonyl iodide (3 g., 1 mol.) in dry ether. After 30 minutes' shaking, the silver iodide was collected and the filtrate treated with aqueous sodium carbonate and sulphite to remove free iodine. The ether was removed under reduced pressure, and the residue, thrice recrystallised (alcohol), furnished the pure thioic sulphonate, m. p. 137—138°, unchanged by admixture with that obtained from the xanthate reaction (Found: C, 45.0; H, 2.8; Cl, 22.1; S, 20.05%).

*p*-Nitrobenzenesulphonyl Chloride.—The powdered sulphonyl chloride (22.2 g.) and potassium xanthate (16 g., 1 mol.), when ground together, gave the usual vigorous reaction. The cold pulverised product was extracted in turn with ether and cold water. The insoluble residue, thrice recrystallised (alcohol), gave *p*-nitrophenyl *p*-nitrobenzenethioic sulphonate, m. p. 180—180.5° (Found: C, 42.5; H, 2.3; N, 7.95; S, 18.6. Calc. for  $C_{12}H_8O_6N_2S_2$ : C, 42.35; H, 2.35; N, 8.25; S, 18.85%). Zincke and Leuhardt (*loc. cit.*) give m. p. 180—181°. The aqueous extract was evaporated, and the residue, repeatedly recrystallised (alcohol), furnished colourless crystals of potassium *p*-nitrobenzenesulphonate (Found: C, 30.0; H, 1.7; N, 5.85; S, 13.5. Calc. for  $C_6H_4O_3NSK$ : C, 29.85; H, 1.65; N, 5.8; S, 13.3%). Evaporation of the ethereal extract left a colourless solid mixed with a yellow oil. The solid, collected by filtration and thrice recrystallised (cyclohexane), gave *p*-nitrobenzenesulphonic acid, colourless crystals, m. p. 94.5—95° (Found: C, 35.2; H, 2.7. Calc. for  $C_6H_5O_3NS$ : C, 35.45; H, 2.5%). The yellow oil, on fractional distillation, afforded *O*-ethyl *S*-ethyl xanthate, b. p. 77—78°/16 mm. (Found: C, 39.8; H, 6.6; S, 42.6%).

*p*-Acetamidobenzenesulphonyl Chloride.—The sulphonyl chloride (2.9 g.) and potassium xanthate (2 g., 1 mol.), each freshly prepared and carefully dried, were ground thoroughly together, transferred to a boiling-tube closed with a calcium chloride tube, and heated in a boiling water-bath for 4 hours during which reaction slowly occurred, the mixture becoming pale yellow and emitting malodorous fumes. (Neglect of the above conditions or the use of larger quantities always caused the mixture to form a charred mass from which no definite product could be isolated.) The cold powdered product was extracted with water and the insoluble residue thrice crystallised (acetic acid) and finally heated at 137°/18 mm. for 6 hours to remove traces of solvent; *p*-acetamidophenyl *p*-acetamidobenzenethioic sulphonate was thus obtained as colourless crystals, m. p. 210—211° (decomp.) (Found: C, 52.8; H, 4.4; N, 7.8; S, 17.4.  $C_{16}H_{16}O_4N_2S_2$  requires C, 52.7; H, 4.45; N, 7.7; S, 17.6%). The aqueous extract was evaporated to dryness and the residue crystallised 4 times (water); the sulphanic acid obtained was then dehydrated at 137°/18 mm. (Found: C, 41.8; H, 4.0; N, 8.1; S, 18.4. Calc. for  $C_6H_7O_3NS$ : C, 41.6; H, 4.1; N, 8.1; S, 18.5%).

*Hydrolysis of the Thioic Sulphonate.*—A mixture of the powdered thioic sulphonate (1 g.) and a solution of sodium hydroxide (1 g.) in alcohol (50 c.c.) was refluxed for 5 hours, the thioic sulphonate slowly dissolving and being replaced by a grey solid. The boiling mixture was then filtered. The grey solid was dissolved in water and the solution made just acid with hydrochloric acid and evaporated to dryness. The residue, thrice crystallised (water), furnished *p*-amino-benzenesulphonic acid, colourless crystals which decomposed on being heated without melting (Found: C, 45.9; H, 4.35; N, 8.75; S, 20.35.  $C_6H_7O_2NS$  requires C, 45.8; H, 4.5; N, 8.9; S, 20.4%). The alcoholic filtrate, concentrated and poured into much water, deposited a solid which when collected and thrice crystallised (dilute acetic acid), furnished di-*p*-acetamidophenyl disulphide, m. p. 184—185° (alone and mixed) (Found: C, 57.9; H, 4.9; N, 8.5; S, 19.2. Calc. for  $C_{16}H_{16}O_2N_2S_2$ : C, 57.8; H, 4.85; N, 8.45; S, 19.3%).

*Synthesis of the Thioic Sulphonate.*—(a) *p*-Acetamidobenzenesulphonyl iodide was prepared precisely as the *p*-chloro-analogue above, using *p*-acetamidobenzenesulphonyl chloride (19.8 g.): colourless crystals (ligroin) m. p. 170—171° (Found: C, 29.7; H, 2.6; N, 4.45.  $C_8H_8O_3NIS$  requires C, 29.55; H, 2.5; N, 4.3%). (b) *Silver p*-acetamidophenyl sulphide. *p*-Acetamidophenylthiol was prepared from the corresponding disulphide by Hinsberg's method (*Ber.*, 1906, **39**, 2427), and recrystallised from dilute acetic acid. The thiol (3 g.) was converted to its silver salt precisely as the above *p*-chloro-analogue.

Interaction of the sulphonyl iodide (2.8 g.) and the silver sulphide (2.6 g., 1.1 mol.), as previously described, afforded the thioic sulphonate, colourless crystals (acetic acid), m. p. 210—211°, unchanged by admixture with that formed in the xanthate reaction (Found: C, 52.5; H, 4.6; N, 7.6; S, 17.7%).

*m*-Nitrobenzenesulphonyl Chloride.—A rapid and vigorous reaction occurred when the powdered sulphonyl chloride (16.6 g.) and potassium xanthate (12 g., 1 mol.) were quickly mixed in a vessel immersed in ice-water, much heat and malodorous vapour being evolved. The mixture became molten, and was stirred until the reaction appeared complete. The cold product was then thoroughly extracted with ether. The insoluble residue, after recrystallisation (methanol), furnished colourless crystals of potassium *m*-nitrobenzenesulphonate (Found: C, 30.0; H, 1.75; N, 5.9; S, 13.45. Calc. for  $C_6H_4O_3NSK$ : C, 29.85; H, 1.65; N, 5.8; S, 13.3%). Evaporation of the ether extract left an oil containing much solid matter. The latter, collected and recrystallised (cyclohexane), afforded *m*-nitrobenzenesulphonic acid, m. p. 53.5—56° (alone and mixed) (Found: C, 35.45; H, 2.45; N, 6.95; S, 15.7. Calc. for  $C_6H_5O_3NS$ : C, 35.45; H, 2.5; N, 6.9; S, 15.8%). The oil, on attempted fractionation at 15 mm., underwent violent decomposition, but ultimately the only distillate obtained was *O*-ethyl *S*-ethyl xanthate, b. p. 77—78.5°/15 mm. (Found: C, 39.95; H, 6.8; S, 42.8%).

*4*-Nitrotoluene-2-sulphonyl Chloride.—(A) *Without a solvent.* This experiment, using the sulphonyl chloride (11.8 g.) and the xanthate (8 g., 1 mol.) without external cooling, was precisely similar to previous ones. The insoluble residue from the ether extraction, after recrystallisation (alcohol), furnished colourless crystals of potassium 4-nitrotoluene-2-sulphonate (Found: C, 33.0; H, 2.45; N, 5.65; S, 12.6. Calc. for  $C_7H_6O_3NSK$ : C, 32.95; H, 2.35; N, 5.5; S, 12.55%). The ethereal extract on evaporation gave an oil containing considerable solid material; the latter, collected and recrystallised (water), gave 4-nitrotoluene-2-sulphonic acid (II), colourless crystals readily soluble in water, m. p. 122—122.5° (Found: C, 41.9; H, 3.45; N, 7.0; S, 15.9.  $C_7H_7O_4NS$  requires C, 41.8; H, 3.5; N, 6.95; S, 15.95%). One portion of the yellow oil was heated at 0.15 mm. pressure; much decomposition occurred and diethyl disulphurdicarbothionate distilled over; it had b. p. 114—116° and readily solidified, m. p. 31.5—32° (alone and mixed) (Found: C, 29.75; H, 4.2%). A second portion of the oil, heated at 25 mm., underwent violent decomposition; ultimately, fractionation gave only *O*-ethyl *S*-ethyl xanthate, b. p. 77—78°/15 mm. (Found: C, 40.0; H, 6.75; S, 42.7%).

(B) *In solution.* A slight excess of powdered potassium xanthate (8 g.) was slowly added to a solution of the sulphonyl chloride (10.7 g., 0.91 mol.) in ether (400 c.c.) which was chilled in ice-water and vigorously shaken meanwhile. The mixture was shaken for a further 30 minutes and then set aside for 6 hours. The colourless solid was separated and, after repeated crystallisation (alcohol), furnished potassium 4-nitrotoluene-2-sulphonate (Found: C, 33.05; H, 2.4; N, 5.7; S, 12.7%). Evaporation under reduced pressure of the ethereal extract left a residual yellow oil which completely solidified, and when washed with cold alcohol afforded the disulphurdicarbothionate, colourless crystals, m. p. 31.5—32° (alone and mixed) (Found: C, 29.6; H, 4.0%).

The above experiment was repeated in ether using 2 mols. of xanthate, and in carbon disulphide (400 c.c.) using both 1 and 2 mols. of xanthate; the same products were obtained as in the first experiment, except that in the 2nd and 4th experiments the excess of xanthate remained unchanged. No indication of the formation of a stable *O*-ethyl *S*-4-nitrotoluene xanthate, or of the above sulphonic acid, could be detected.

In all these experiments, particular care was taken to ensure the purity of the reactants.

When equimolecular quantities of potassium xanthate and anthraquinone-1-sulphonyl chloride were heated together at 180° for 10 hours, the chloride was recovered unchanged; when the heating was maintained at 250° for 2 hours the only product isolated was the potassium sulphionate. Similar results were obtained with anthraquinone-2-sulphonyl chloride.

*Methanesulphonyl Chloride.*—Powdered potassium methyl xanthate (14.6 g.) was added to the freshly distilled sulphonyl chloride (11.5 g., 1 mol.) which was vigorously stirred and chilled in ice-water. After the vigorous and immediate reaction had subsided the cold product was extracted with ether. The residue, four times crystallised (alcohol), afforded potassium methanesulphonate (Found: C, 9.0; H, 2.1; S, 29.3. Calc. for  $\text{CH}_3\text{O}_3\text{SK}$ : C, 8.95; H, 2.25; S, 29.15%). The ethereal extract was evaporated, and the residual oily residue then gave the main fractions: (a) b. p. 29–36°/20 mm., (b) b. p. 60–68°/20 mm. Fraction (a) was repeatedly refractionated at atmospheric pressure and pure dimethyl disulphide, b. p. 116–118°, obtained (Found: C, 25.7; H, 6.3; S, 68.0. Calc. for  $\text{C}_2\text{H}_6\text{S}_2$ : C, 25.5; H, 6.4; S, 68.1%). Its identity was confirmed by treatment with aqueous chloramine-T, which furnished methyl *p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine, colourless crystals (alcohol), m. p. 190–192° (alone and mixed). Fraction (b), refractionated at 18 mm., ultimately gave *O*-methyl *S*-methyl xanthate, b. p. 59–60°/18 mm. (Found: C, 29.1; H, 5.2; S, 52.5. Calc. for  $\text{C}_2\text{H}_6\text{OS}_2$ : C, 29.5; H, 4.95; S, 52.45%). Its identity was confirmed by boiling with alcoholic phenylhydrazine, which afforded *O*-methyl-*N*-phenylamino-thiourethane (alcohol), m. p. 110–111° (alone and mixed).

*Ethanesulphonyl Chloride.*—This was performed precisely as with the methane analogue, using potassium ethyl xanthate (10 g.) and the pure sulphonyl chloride (8 g., 1 mol.), a vigorous reaction again ensuing. The residue from the ether extraction, repeatedly recrystallised (alcohol), gave potassium ethanesulphonate (Found: C, 16.2; H, 3.5; S, 21.55. Calc. for  $\text{C}_2\text{H}_5\text{O}_3\text{SK}$ : C, 16.2; H, 3.4; S, 21.65%). The solvent was evaporated from the ethereal extract, and the residual yellow oil, when fractionated at 0.05 mm., gave 4 crude fractions: (a) b. p. below room temperature; the fraction being collected in a liquid-air trap; (b) b. p. 39–50°; (c) b. p. 50–57°; (d) 115–120°.

Fraction (a) had b. p. 46–49°/760 mm. Its identity as carbon disulphide was proved by adding it to alcoholic potassium hydroxide solution, and then collecting the precipitated xanthate, which was washed and dried. A concentrated aqueous solution of this xanthate (0.6 g.) was added with shaking to a similar solution of potassium chloropalladite (0.6 g., 0.5 mol.). The brownish-green precipitate was collected, washed with water and alcohol, and when recrystallised (alcohol) gave orange-red crystals of *palladium bisethylxanthate* (III), m. p. 152° (alone and mixed) (Found: C, 20.7; H, 3.0; Pd, 30.7.  $\text{C}_6\text{H}_{10}\text{O}_2\text{S}_4\text{Pd}$  requires C, 20.65; H, 2.9; Pd, 30.6%). It is essential for this preparation that the xanthate should be added to the palladite and not *vice versa*. Fraction (b), on refractionation gave ultimately *O*-ethyl *S*-ethyl xanthate, b. p. 46.5°/0.05 mm. (Found: C, 40.0; H, 6.7; S, 42.85%). Fraction (c), after repeated fractionation, gave diethyl disulphide, b. p. 52–54°/0.1 mm. (Found: C, 39.1; H, 8.2; S, 52.6; *M*, cryscopic in 1.676% ethylene dibromide solution, 128. Calc. for  $\text{C}_4\text{H}_{10}\text{S}_2$ : C, 39.25; H, 8.25; S, 52.5%; *M*, 122). Its identity was confirmed by the action of cold aqueous chloramine-T (6 mols.), which furnished ethyl *p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine, m. p. 187–188° (alone and mixed) (Found: C, 48.1; H, 4.95; N, 6.85; S, 24.05. Calc. for  $\text{C}_{16}\text{H}_{20}\text{O}_4\text{N}_2\text{S}_8$ : C, 47.95; H, 5.05; N, 7.0; S, 24.0%). Fraction (d) on refractionation gave a yellow oil, b. p. 114–117°/0.04 mm., which rapidly solidified, and when recrystallised (alcohol) gave diethyl disulphurdicarbothionate, m. p. 32–32.5° (alone and mixed) (Found: C, 29.6; H, 4.1; S, 52.85%).

The following palladium derivatives of other xanthic acids were prepared to illustrate their value for characterisation purposes. *Palladium bismethylxanthate* (as III). A concentrated aqueous solution of potassium methyl xanthate (1.4 g.) was slowly added with shaking to a similar solution of potassium palladochloride (1.6 g., 0.5 mol.). The *xanthate*, collected and recrystallised (alcohol), formed orange-red plates which decomposed on heating above *ca.* 140° (Found: C, 15.1; H, 2.2.  $\text{C}_4\text{H}_6\text{O}_2\text{S}_4\text{Pd}$  requires C, 15.3; H, 1.9%). The *bis-n-propylxanthate*, similarly prepared and recrystallised, also formed orange-red plates, m. p. 126–127° (Found: C, 25.8; H, 3.9.  $\text{C}_8\text{H}_{14}\text{O}_2\text{S}_4\text{Pd}$  requires C, 26.05; H, 3.7%). The *bis-benzylxanthate*, similarly prepared from sodium benzyl xanthate (0.4 g.) and the palladochloride (0.32 g., 0.5 mol.) formed orange crystals (alcohol), m. p. 134–135° (decomp.) (Found: C, 40.65; H, 3.25; S, 27.4; Pd, 22.95.  $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}_4\text{Pd}$  requires C, 40.6; H, 3.0; S, 27.1; Pd, 22.55%). Similar compounds could not be prepared from sodium *p*-chloro- or *p*-methyl-benzyl xanthate and sodium or ammonium chloropalladite.

The fact that the first (*i.e.*, the methyl) member of this series of metallic derivatives decomposes on heating whilst the others have sharp m. p.s which fall as the alkyl series is ascended is not unexpected; similar properties are shown by other homologous series of palladium compounds (Mann and Purdie, *J.*, 1935, 1549; 1936, 873). It is probable that platinum also forms a similar series of non-ionic xanthates, as Ramberg (*Z. anorg. Chem.*, 1906, 50, 439) has described the platinum analogue of (III) as yellow crystals, m. p. 129–130°, soluble in benzene.

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