176. *The Chemistry of Xanthic Acid Derivatives. Part I. The Preparation and Comparative Properties of Isomeric Xanthates and Dithiocarbonates.*

By Gerald Bulmer and Frederick G. Mann.

The preparation and properties of several series of isomeric compounds consisting of two xanthates and one dithiocarbonate, of structure $RO{\cdot}CS{\cdot}SR'$, $R'O{\cdot}CS{\cdot}SR$ and $RS{\cdot}CO{\cdot}SR'$ respectively, have been studied. The action of phenylhydrazine differentiates decisively between the three isomerides, for the two xanthates furnish different thiourethanes, and the dithiocarbonate is unaffected. When R is a benzyl and R′ a *p*-substituted benzyl group, thermal decomposition of all three isomerides gives dibenzyl disulphide and a *p*-substituted stilbene; when R and R′ are different *p*-substituted benzyl groups, such decomposition affords two *p*-substituted stilbenes. When R and R′ are identical *p*-substituted benzyl groups, the dithiocarbonate apparently exists as a " parent " and a " stable form," into the latter of which the xanthate passes on heating.

The simpler alkyl xanthates and dithiocarbonates also show the above differentiation with phenylhydrazine, but differ from the benzyl analogues in that, with chloramine-T, they both furnish di-sulphonamido-derivatives of type (XXIV), which have previously been obtained by the action of chloroamine-T on thiols and disulphides. Evidence is adduced for the mechanism of the conversion of the thiols and disulphides to the di-sulphonamido-derivatives.

In order to interpret results obtained in other aspects of the chemistry of xanthic acid derivatives (see Parts II and III), we found it necessary to extend and to systematise current knowledge concerning the isomeric compounds $RO{\cdot}CS{\cdot}SR'$, $R'O{\cdot}CS{\cdot}SR$, $RS{\cdot}CO{\cdot}SR'$, the first two being esters of xanthic acids and the last an ester of *sym.* dithiocarbonic acid; in particular, we wished to know (*a*) the conditions under which such compounds were stable, or underwent interconversion or underwent thermal decomposition, (*b*) the nature of the thermal decomposition products and their relation to the structure of the parent compounds and (*c*) other reactions which might serve to identify the parent compounds.

The results of a considerable amount of uncorrelated work on these aspects of xanthic acid chemistry have been recorded; the salient points of the most important investigations are therefore briefly summarised. Although Debus (*Annalen*, 1850, **75**, 127) showed that *O*-ethyl *S*-ethyl xanthate, $EtO{\cdot}CS{\cdot}SEt$, could be readily prepared by the interaction of potassium xanthate and ethyl iodide, apparently only three pairs of isomeric xanthates having two unlike alkyl groups have hitherto been prepared; the members of each pair were liquids having very similar physical properties, and a chemical proof of the non-identity of the two members has been obtained for only one such pair. Thus Mylius (*Ber.*, 1872, **5**, 972) prepared *O*-methyl *S*-*n*-propyl xanthate, and Scala (*Gazzetta*, 1887, **17**, 81) prepared *O*-*n*-propyl *S*-methyl xanthate. Salomon (*J. pr. Chem.*, 1874, **8**, 114), using Debus's reaction, prepared *O*-methyl *S*-ethyl xanthate and *O*-ethyl *S*-methyl xanthate, and showed that the former reacted with ammonia to form *O*-methylthiourethane and ethanethiol, $MeO{\cdot}CS{\cdot}SEt + NH_3 = MeO{\cdot}CS{\cdot}NH_2 + EtSH$, whereas the second xanthate simarly afforded *O*-ethyl-thiourethane and methanethiol. Tschugaeff (*Ber.*, 1898, **31**, 1775), using optically active amyl alcohol, prepared the isomeric *O*-ethyl *S*-amyl and *O*-amyl *S*-ethyl xanthates, which possessed markedly different optical rotations.

sym.-Dithiocarbonates have been prepared by the action of phosgene on the sodium alkyl sulphides (Salomon, *J. pr. Chem.*, 1872, **6**, 444), and by the acid hydrolysis of alkyl thiocyanates (Schmitt and Glutz, *Ber.*, 1868, **1**, 166). Apparently, only one such ester containing two unlike alkyl groups has been recorded: Schone (*J. pr. Chem.*, 1885, **32**, 244) prepared *S*-methyl *S*′-*iso*amyl dithiocarbonate by the interaction of sodium methyl sulphide and *iso*-amyl chloro-thioformate, $Me_2CH(CH_2)_2{\cdot}S{\cdot}CO{\cdot}Cl$. It has been claimed (Schmitt and Glutz, *loc. cit.*; Debus, *loc. cit.*) that *sym.*-dialkyl thiocarbonates can be distinguished from the isomeric xanthates by the fact that heating with water at 160° causes the reactions (Ai) and (Aii) respectively, whilst alcoholic ammonia causes reactions (Bi) and (Bii) respectively.

$$2RSNa + COCl_2 = (RS)_2CO + 2NaCl; \qquad 2RSCN + 3H_2O = (RS)_2CO + CO_2 + 2NH_3$$

$$\text{(Ai)}\ (EtS)_2CO + H_2O = 2EtSH + CO_2; \quad \text{(Aii)}\ 2EtO{\cdot}CS{\cdot}SEt + 2H_2O = 2EtOH + 2EtSH + CO_2 + CS_2$$

$$\text{(Bi)}\ (EtS)_2CO + NH_3 = (NH_2)_2CO + 2EtSH; \quad \text{(Bii)}\ EtO{\cdot}CS{\cdot}SEt + NH_3 = EtO{\cdot}CS{\cdot}NH_2 + EtSH$$

The thermal decomposition of xanthate esters presents several points of special interest. Tschugaeff (*Ber.*, 1899, **32**, 3332; 1900, **33**, 735; *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1116; 1904, **36**, 988) first prepared unsaturated terpenoid hydrocarbons by the destructive distillation of suitable xanthates: for example, *O*-menthyl *S*-methyl xanthate afforded menthene, methanethiol and carbonyl sulphide, whilst the corresponding bornyl derivative decomposed similarly with the production of bornylene. Parallel results with *O*-fenchyl derivatives were obtained by Nametkin and Seliwanoff (*J. Russ. Phys. Chem. Soc.*, 1917, **49**, 417) and by Qvist (*Annalen*, 1918, **417**, 278), and with various *O*-*cyclo*hexyl derivatives by Nametkin and Brussov (*Ber.*, 1923, **56**, 1807), Kursanov (*J. Russ. Phys. Chem. Soc.*, 1928, **60**, 92) and Alexandrovitsch (*J. Gen. Chem. Russ.*, 1923, **3**, 38): for example, the latter showed that *O*-*cyclo*hexylmethyl *S*-methyl xanthate on destructive distillation afforded methylene-*cyclo*hexane, $(CH_2)_5{:}C{:}CH_2$. In all the above compounds, the group attached to the oxygen atom in the original xanthate could break off (with loss of hydrogen) as a stable unsaturated hydrocarbon: Nametkin and Kursanov (*J. pr. Chem.*, 1926, **112**, 164; *J. Russ. Phys. Chem. Soc.*, 1926, **57**, 390) investigated the thermal decomposition of *O*-benzyl *S*-methyl xanthate, where such a reaction cannot occur, and showed that this xanthate afforded stilbene:

$$2PhCH_2{\cdot}O{\cdot}CS{\cdot}SMe = PhCH{:}CHPh + 2MeSH + 2COS.$$

Kursanov (*ibid.*, 1928, **60**, 921) showed that *O*-benzhydryl *S*-methyl xanthate similarly afforded tetraphenyl ethylene, $Ph_2C{:}CPh_2$. We show later that this formation of stilbenes is characteristic of certain types of *p*-substituted benzyl xanthates and dithiocarbonates.

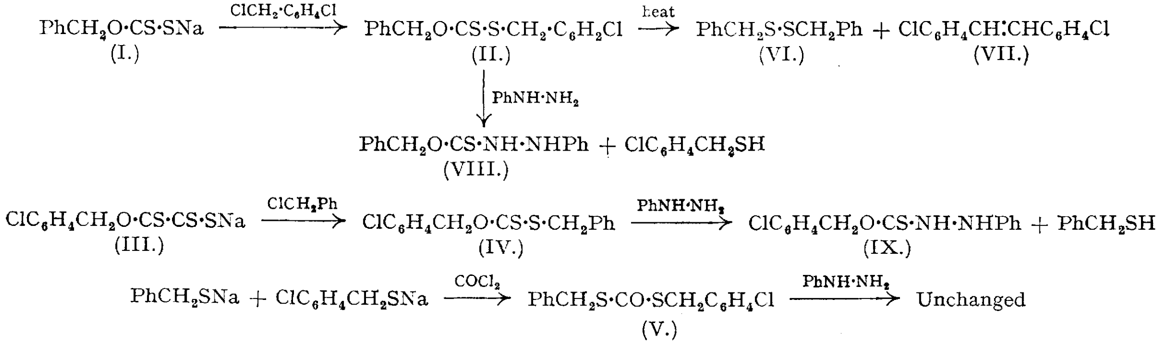
McAlpine (J., 1931, 1114; 1932, 906) reinvestigated the work of Tschugaeff (*loc. cit.*) on the thermal decomposition of *O*-menthyl (and *O*-bornyl) *S*-methyl xanthate and of several similar compounds. She found that although these esters, when heated alone at atmospheric or reduced pressure, or in certain solvents, usually decomposed as Tschugaeff described, yet each ester when heated in various alcohols or in ethylene dibromide, was converted to a " stable form " which had the same composition, molecular weight and melting point (alone and mixed) as the parent ester, but possessed much greater thermal stability; consequently, thermal decomposition of the " stable form " required a much higher temperature than that of the parent form, but gave the same decomposition products. Some of the esters were converted into their " stable form " even by distillation under reduced pressure. The tendency to " stable form " production was increased by replacement of the *S*-methyl group by higher alkyl groups, and decreased by replacement of this group by the *S*-benzyl group. The true nature of McAlpine's " stable forms " is still uncertain; we have encountered similar " stable forms " of various *sym.*-dithiocarbonates (see later), but McAlpine's evidence shows clearly that her " stable forms " were still xanthates and not the isomeric dithiocarbonates.

Laakso (*Suomen Kem.*, 1940, **133**, 8) has recently described the effect of heat on many xanthates, RO·CS·SR′, where R represented the fenchyl, pivalyl, and also various methylated *cyclo*-hexyl groups, and R′ the methyl, ethyl, *n*- and *iso*-propyl groups. Many of these compounds on heating were converted to the isomeric dithiocarbonates; decisive evidence for this isomerisation was adduced by Laakso, who, however, refers to the dithiocarbonates as " stable forms " of the xanthates.

We have consequently made a detailed investigation of the formation and reactions of various benzyl xanthates and dithiocarbonates, and also of their simpler alkyl homologues; the benzyl compounds are more conveniently described first, however, as these compounds and their significant derivatives are all well defined crystalline compounds having sharp m. p.'s, whereas the lower alkyl analogues are often liquid.

The reactions of the dibenzyl xanthates and dithiocarbonates indicate that these compounds apparently fall into three distinct classes according as whether (*a*) one benzyl group is substituted in the *p*-position, (*b*) both benzyl groups are thus substituted, but these substituents are unlike, (*c*) both benzyl groups carry identical *p*-substituents.

In class (*a*), we have found that sodium benzyl xanthate (I) reacts readily with *p*-chlorobenzyl chloride, affording O-*benzyl* S-p-*chlorobenzyl xanthate* (II), m. p. 63·5°, whereas sodium *p*-chlorobenzyl xanthate (III) with benzyl chloride gave O-p-*chlorobenzyl* S-*benzyl xanthate* (IV), m. p. 49°. When, however, a chilled ethereal solution of phosgene was treated with sodium derivatives of benzyl- and *p*-chlorobenzyl-thiols in correct proportions, the isomeric S-*benzyl* S′-p-*chlorobenzyl dithiocarbonate* (V), m. p. 67·5°, was obtained. All three isomeric compounds, (II), (IV), and (V), when heated at 18 mm. gave the same products, namely, dibenzyl disulphide (VI) and 4 : 4′-dichlorostilbene (VII); the compounds (II) and (V) underwent this decomposition even at 0·5 mm., but the xanthate (IV) distilled unchanged at this low pressure.



$$\begin{tikzcd}
\underset{\text{(I.)}}{PhCH_2O{\cdot}CS{\cdot}SNa} \arrow[r, "ClCH_2{\cdot}C_6H_4Cl"] & \underset{\text{(II.)}}{PhCH_2O{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}C_6H_2Cl} \arrow[r, "heat"] \arrow[d, "PhNH{\cdot}NH_2"] & \underset{\text{(VI.)}}{PhCH_2S{\cdot}SCH_2Ph} + \underset{\text{(VII.)}}{ClC_6H_4CH{:}CHC_6H_4Cl} \\
 & \underset{\text{(VIII.)}}{PhCH_2O{\cdot}CS{\cdot}NH{\cdot}NHPh} + ClC_6H_4CH_2SH &
\end{tikzcd}$$

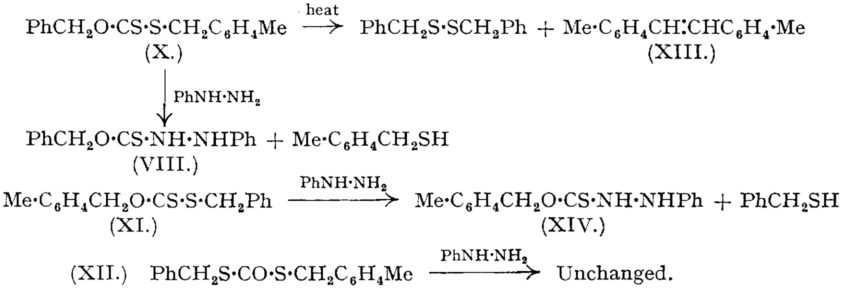
$$\underset{\text{(III.)}}{ClC_6H_4CH_2O{\cdot}CS{\cdot}CS{\cdot}SNa} \xrightarrow{ClCH_2Ph} \underset{\text{(IV.)}}{ClC_6H_4CH_2O{\cdot}CS{\cdot}S{\cdot}CH_2Ph} \xrightarrow{PhNH{\cdot}NH_2} \underset{\text{(IX.)}}{ClC_6H_4CH_2O{\cdot}CS{\cdot}NH{\cdot}NHPh} + PhCH_2SH$$

$$PhCH_2SNa + ClC_6H_4CH_2SNa \xrightarrow{COCl_2} \underset{\text{(V.)}}{PhCH_2S{\cdot}CO{\cdot}SCH_2C_6H_4Cl} \xrightarrow{PhNH{\cdot}NH_2} \text{Unchanged}$$

The identity of the three isomeric esters is clearly shown by their synthesis: it was however proved independently by their behaviour towards phenylhydrazine. The xanthate (II), when boiled in alcoholic solution with an excess of phenylhydrazine, afforded the crystalline O-*benzyl*-N-*phenylamino-thiourethane* (VIII) and *p*-chlorobenzyl thiol; the isomeric xanthate (IV) similarly afforded O-p-*chlorobenzyl*-N-*phenylamino-thiourethane* (IX) and benzyl thiol: the dithiocarbonate (V), even when refluxed with alcoholic phenylhydrazine for many hours, was unchanged. This reaction of phenylhydrazine with xanthic esters was discovered by Wheeler and Barnes (*Amer. Chem. J.*, 1900, **24**, 60), using *O*-ethyl *S*-ethyl xanthate; their work, which is discussed later, placed the structure of the resulting thiourethane beyond doubt. Our results now show that phenylhydrazine is a decisive reagent for the identification of the members of any isomeric triad consisting of two xanthates and one dithiocarbonate; several other confirmatory examples are quoted later.

The above results appear to be general in type for xanthates and dithiocarbonates of class (*a*), *i.e.*, those having one unsubstituted benzyl group. For example, we have prepared, by precisely similar reactions to those described above, another isomeric triad, namely, O-*benzyl* S-p-*methylbenzyl xanthate* (X), m. p. 62·5—

63°, O-p-*methylbenzyl* S-*benzyl xanthate* (XI), m. p. 39—39·5°, and S-*benzyl* S′-p-*methylbenzyl dithiocarbonate* (XII), m. p. 65°.



$$\underset{\text{(X.)}}{PhCH_2O{\cdot}CS{\cdot}S{\cdot}CH_2C_6H_4Me} \xrightarrow{\text{heat}} PhCH_2S{\cdot}SCH_2Ph + \underset{\text{(XIII.)}}{Me{\cdot}C_6H_4CH{:}CHC_6H_4{\cdot}Me}$$

$$\Big\downarrow {\scriptstyle PhNH\cdot NH_2}$$

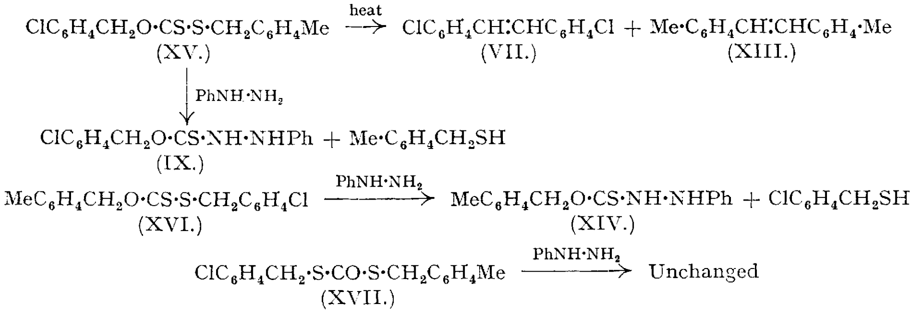
$$\underset{\text{(VIII.)}}{PhCH_2O{\cdot}CS{\cdot}NH{\cdot}NHPh} + Me{\cdot}C_6H_4CH_2SH$$

$$\underset{\text{(XI.)}}{Me{\cdot}C_6H_4CH_2O{\cdot}CS{\cdot}S{\cdot}CH_2Ph} \xrightarrow{PhNH\cdot NH_2} \underset{\text{(XIV.)}}{Me{\cdot}C_6H_4CH_2O{\cdot}CS{\cdot}NH{\cdot}NHPh} + PhCH_2SH$$

$$\text{(XII.)}\quad PhCH_2S{\cdot}CO{\cdot}S{\cdot}CH_2C_6H_4Me \xrightarrow{PhNH\cdot NH_2} \text{Unchanged.}$$

All these compounds when heated at 18 mm. gave dibenzyl disulphide and 4 : 4′-dimethylstilbene (XIII); the compounds (X) and (XII) gave this decomposition when heated even at 0·1 mm., but the compound (XI) distilled unchanged at this lower pressure. The xanthate (X), treated with phenylhydrazine as before, gave the thiourethane (VIII) and *p*-methylbenzylthiol; the xanthate (XI), similarly treated, afforded O-p-*methylbenzyl*-N-*phenylamino-thiourethane* (XIV) and benzylthiol; the isomeric dithiocarbonate (XII) was unaffected by boiling alcoholic phenylhydrazine.

Compounds in class (*b*), *i.e.*, those in which the two benzyl groups carry dissimilar *p*-substituents, differ in two respects from those in class (*a*); the three members show no apparent difference in thermal stability, and the products of thermal decomposition in all cases consist of two substituted stilbenes. No disulphides could be detected in the products of this decomposition. To illustrate these points, we have prepared, by similar methods to those above, O-p-*chlorobenzyl* S-p-*methylbenzyl xanthate* (XV), m. p. 57—58°, O-p-*methylbenzyl* S-p-*chlorobenzyl xanthate* (XVI), m. p. 46·5—47°, and S-p-*chlorobenzyl* S′-p-*methylbenzyl dithiocarbonate* (XVII), m. p. 73°. All these compounds, when heated at 0·5 mm. or at 18 mm., decomposed smoothly with the formation of 4 : 4′-dichlorostilbene (VII) and 4 : 4′-dimethylstilbene (XIII). The xanthate (XV) with phenylhydrazine afforded the *p*-chloro-thiourethane (IX) and *p*-methylbenzylthiol; the xanthate (XVI) gave similarly the *p*-methyl-thiourethane (XIV) and *p*-chlorobenzylthiol; the dithiocarbonate (XVII) was unaffected.



$$\underset{\text{(XV.)}}{ClC_6H_4CH_2O{\cdot}CS{\cdot}S{\cdot}CH_2C_6H_4Me} \xrightarrow{\text{heat}} \underset{\text{(VII.)}}{ClC_6H_4CH{:}CHC_6H_4Cl} + \underset{\text{(XIII.)}}{Me{\cdot}C_6H_4CH{:}CHC_6H_4{\cdot}Me}$$

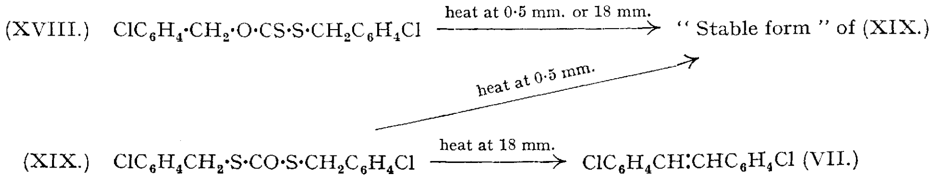
$$\Big\downarrow {\scriptstyle PhNH\cdot NH_2}$$

$$\underset{\text{(IX.)}}{ClC_6H_4CH_2O{\cdot}CS{\cdot}NH{\cdot}NHPh} + Me{\cdot}C_6H_4CH_2SH$$

$$\underset{\text{(XVI.)}}{MeC_6H_4CH_2O{\cdot}CS{\cdot}S{\cdot}CH_2C_6H_4Cl} \xrightarrow{PhNH\cdot NH_2} \underset{\text{(XIV.)}}{MeC_6H_4CH_2O{\cdot}CS{\cdot}NH{\cdot}NHPh} + ClC_6H_4CH_2SH$$

$$\underset{\text{(XVII.)}}{ClC_6H_4CH_2{\cdot}S{\cdot}CO{\cdot}S{\cdot}CH_2C_6H_4Me} \xrightarrow{PhNH\cdot NH_2} \text{Unchanged}$$

Entirely different factors enter into the thermal stability of members of class (*c*), in which each benzyl group carries the same *p*-substituent, and in which there are therefore only two isomeric members of each series. By the interaction of sodium *p*-chlorobenzyl xanthate and *p*-chlorobenzyl chloride, we have prepared O-p-*chlorobenzyl* S-p-*chlorobenzyl xanthate* (XVIII), m. p. 75·5—76°. The action of phosgene on an alcoholic solution of sodium *p*-chlorobenzyl sulphide furnished the isomeric SS′-*bis*-p-*chlorobenzyl dithiocarbonate* (XIX), m. p. 78—78·5°; this form of the compound (XIX) will be referred to as the parent form. When this dithiocarbonate (XIX) was heated at 18 mm., it decomposed, affording 4 : 4′-dichlorostilbene (VII), but when heated at 0·5 mm., it distilled without decomposition but with conversion to its " stable form "; the latter had the same composition, molecular weight, and m. p. as the parent form, but possessed much higher thermal stability. It could now be distilled unchanged at 18 mm., no indication of decomposition to the chloro-stilbene being detectable. When the isomeric xanthate (XVIII) was heated at either 18 mm. or 0·5 mm., it underwent smooth conversion to the " stable form " of (XIX) which constituted the only component in the distillate. It should be emphasised that no doubt existed concerning the chemical identity of the xanthate (XVIII) and the dithiocarbonate (XIX); the former reacted with phenylhydrazine producing the *p*-chloro-thiourethane (IX) and



$$\text{(XVIII.)}\quad ClC_6H_4{\cdot}CH_2{\cdot}O{\cdot}CS{\cdot}S{\cdot}CH_2C_6H_4Cl \xrightarrow{\text{heat at 0·5 mm. or 18 mm.}} \text{`` Stable form '' of (XIX.)}$$

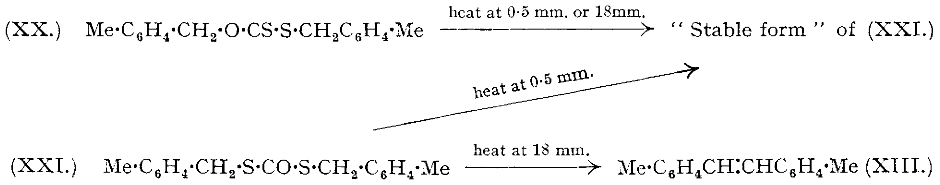
$$\nearrow {\scriptstyle \text{heat at 0·5 mm.}}$$

$$\text{(XIX.)}\quad ClC_6H_4CH_2{\cdot}S{\cdot}CO{\cdot}S{\cdot}CH_2C_6H_4Cl \xrightarrow{\text{heat at 18 mm.}} ClC_6H_4CH{:}CHC_6H_4Cl\ \text{(VII.)}$$

p-chlorobenzylthiol, whereas the dithiocarbonate (XIX) in the parent or the " stable form " was unaffected by this reagent.

The plausible explanation of this remarkable thermal behaviour of the dithiocarbonate (XIX) is that the parent form of this compound possessed traces of impurity, undetectable by ordinary analytical methods, which catalysed its thermal decomposition to the stilbene, and, when this (presumably non-volatile) impurity was removed by distillation (at 0·5 mm.) of the dithiocarbonate, the latter then possessed its true thermal stability. Three factors, however, make this explanation improbable. (i) We have recrystallised samples of the parent form of the dithiocarbonate (XIX) repeatedly from alcohol, acetic acid and ligroin. Each sample was unaffected in m. p. or in thermal behaviour by this treatment, *i.e.*, each sample at 18 mm. still gave the stilbene and at 0·5 mm. the " stable form." It is exceedingly unlikely that traces of an impurity would still remain after such crystallisation from both polar and non-polar solvents. (ii) The conversion of the xanthate (XVIII) to the dithiocarbonate (XIX) is a reaction apparently unknown in benzyl derivatives of classes (*a*) and (*b*), and indicates that a novel and fundamental factor, rather than a mere impurity, determines the reactions of members of class (*c*). (iii) Other examples of the production of " stable forms " of dithiocarbonates have been detected, and it is unlikely that a similar and unstabilising impurity should be present in all such compounds.

To illustrate the last point, we have prepared O-p-*methylbenzyl* S-p-*methylbenzyl xanthate* (XX), m. p. 68·5—69°, and SS′-*bis*-p-*methylbenzyl dithiocarbonate* (XXI), m. p. 72—72·5°. The latter compound on heating at 18 mm. gave 4 : 4′-dimethylstilbene (XIII) but at 0·5 mm. gave a distillate of the " stable form " of (XXI), which could now be distilled undecomposed at 18 mm. The isomeric xanthate (XX) when heated at 0·5 mm. or 18 mm. gave a distillate of the pure " stable form " of (XXI). As before, repeated crystallisation of the " parent form " of (XXI) from alcohol, acetic acid or ligroin left this form unchanged in properties.

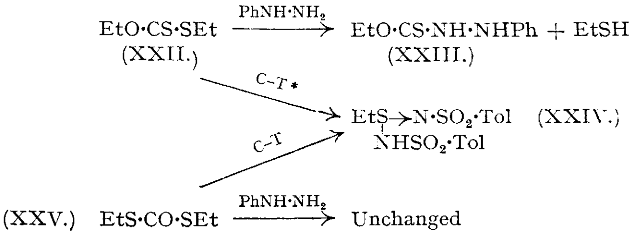


The fundamental difference between the parent and the stable forms of our dithiocarbonates (and of McAlpine's xanthates) still remains uncertain and warrants further investigation.

One unique case should be mentioned which does not fall into any of the above classes, *i.e.*, when neither benzyl group carries a substituent. We have treated sodium benzyl xanthate with benzyl chloride in order to obtain *O*-benzyl *S*-benzyl xanthate, $PhCH_2O{\cdot}CS{\cdot}SCH_2Ph$, but the only product isolated was dibenzyl disulphide, and the xanthate is apparently too unstable for normal preparation. This is not surprising; the ready formation of the disulphide which was characteristic of compounds of class (*a*) having one unsubstituted benzyl group is now so accentuated that it has become a spontaneous reaction under our preparative conditions. By the action of phosgene on alcoholic sodium benzyl sulphide we have, however, prepared SS′-*dibenzyl dithiocarbonate*, $(PhCH_2S)_2CO$. This compound is a liquid which when heated at 18 mm. readily decomposed with the formation of dibenzyl disulphide; when heated at 0·5 mm., however, it distilled apparently as a " stable form," which could then be distilled unchanged also at 18 mm. In view of the liquid nature of this compound, however, the essential difference between the parent and the stable forms is not so clearly defined as in the highly crystalline compounds (XIX) and (XXI).

We have treated several of the above xanthates and dithiocarbonates with an excess of chloramine-T (sodio-toluene-*p*-sulphonchloroamide) in boiling alcoholic solution. Although a reaction occurred in every case, with the formation of sodium chloride and *p*-toluenesulphonamide, no other decisive product was isolated. In this respect, these xanthates and dithiocarbonates differ strikingly from their simpler alkyl analogues described below.

The simple dialkyl xanthates and *sym.*-dithiocarbonates show interesting similarities and differences compared with the benzyl analogues previously described. We have prepared *O*-ethyl *S*-ethyl xanthate (XXII) by Debus's method; it is a colourless liquid which distils unchanged at 78°/18 mm., and which reacts with phenylhydrazine to give *O*-ethyl-*N*-phenylamino-thiourethane (XXIII) and ethanethiol as Wheeler and Barnes (*loc. cit.*) have described. When treated with an excess of chloramine-T it is converted to ethyl *p*-toluene-

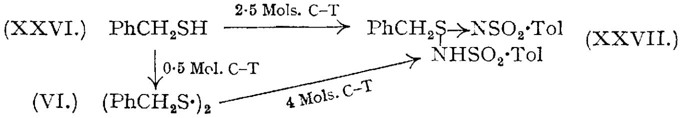


* Abbreviation for chloramine-T.

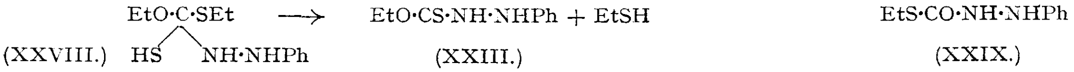
sulphonimidosulphine-*p*-toluenesulphonylimine (XXIV, where Tol = *p*-tolyl); the yield of the latter never exceeded one molecular equivalent, however, and it is clear that only the ethyl group joined to sulphur in the xanthate (XXII) enters the compound (XXIV). By the action of phosgene on sodium ethyl sulphide, we have prepared *SS'*-diethyl dithiocarbonate (XXV), a colourless liquid of b. p. 85—87°/19 mm., which, as expected, was unaffected by phenylhydrazine; when treated with an excess of chloramine-T, it also gave the di-sulphonamido-compound (XXIV). In view of the symmetrical structure of the dithiocarbonate (XXV), however, it is remarkable that the compound (XXIV) was never formed in more than one molecular equivalent. The reason for this identical behaviour of dialkyl xanthates and dithiocarbonates with chloramine-T is obscure; it is possible, however, that the initial action in each case is hydrolysis of the ester giving equimolecular quantities of ethanethiol, ethanol and carbonyl sulphide, and the first of these products then furnishes the di-sulphonamido-compound of type (XXIV).

We have obtained precisely similar results to those described above, using the *dimethyl* analogue of (XXII). It is clear, therefore, that isomeric dialkyl xanthates and dithiocarbonates can be differentiated by their behaviour towards phenylhydrazine; furthermore, that the structure of an *as*.-dialkyl xanthate, RO·CS·SR', can be determined by its reaction with phenylhydrazine, and readily confirmed by that with chloramine-T.

Clarke, Kenyon, and Phillips (J., 1930, 1225) first obtained the disulphonamido-compound (XXIV) by the action of chloramine-T on ethanethiol and on sodium ethylthiolactate; Alexander and McCombie (*J.*, **1932**, 2087) prepared it similarly from diethyl disulphide. Its present production from the compounds (XXII) and (XXV) led us to re-examine these earlier reactions. We find that benzylthiol (XXVI), when treated with 0·5 mol. of chloramine-T, is oxidised to dibenzyl disulphide (VI), but with 2·5 mols. is converted to *benzyl* p-*toluenesulphonimidosulphine*-p-*toluenesulphonylimine* (XXVII). The disulphide (VI) when treated with an excess (4 mols.) of this reagent also furnishes the compound (XXVII). We have obtained precisely similar results using *p*-methylbenzylthiol. It is consequently almost certain that the action of an excess of chloramine-T on a thiol is first to oxidise the latter to the disulphide, which then in turn is converted to the di-sulphonamido-compound of type (XXVII). It is significant that Clarke, Kenyon, and Phillips (*loc. cit.*) found that the production of the phenyl analogue of (XXVII) by the action of 2 mols. of chloramine-T on phenylthiol was always accompanied by the formation of some diphenyl disulphide.



The structure of the compound (XXIII) obtained by Wheeler and Barnes (*loc. cit.*) by the interaction of *O*-ethyl *S*-ethyl xanthate (XXII) and phenylhydrazine—and hence of the homologous compounds, (VIII), (IX) and (XIV), now similarly obtained—requires discussion. Wheeler and Barnes considered that the xanthate (XXII) reacted first by direct addition to give the product (XXVIII), which then lost ethanethiol to give the *O*-ethyl-*N*-phenylamino-thiourethane (XXIII), m. p. 72—74°. They considered that the structure of the latter compound was confirmed by the fact that it differed from the isomeric compound (XXIX), m. p. 112°, which Busch and Stern (*J. pr. Chem.*, 1899, **60**, 242) had obtained by the action of ethyl iodide on potassium phenylhydrazino-thioformate, PhNH·NH·CO·SK. Although it is now clear that the latter reaction would not necessarily produce an *S*-ethyl derivative, Wheeler and Barnes' conclusions were supported by the fact that their compound (XXIII) when treated with ethyl iodide readily furnished Busch and Stern's compound (XXIX).



This reaction was interpreted as the addition of ethyl iodide to the :CS group in (XXIII) to give the compound, EtO·CI(SEt)NH·NHPh, followed by loss of the iodine in combination with the ethyl group originally linked to the oxygen atom. This mechanism was confirmed by the fact that the ethyl compound (XXIII), treated with methyl iodide or benzyl chloride, similarly furnished the *S*-methyl or *S*-benzyl analogue of (XXIX). This conversion, RO·CS·NR'R'' ⟶ RS·CO·NR'R'', where R' and R'' were hydrogen, alkyl, arylamino or even acyl groups, under the influence of alkyl halides, was investigated in detail and placed beyond reasonable doubt (see also Wheeler and Barnes, *Amer. Chem. J.*, 1899, **22**, 141; Wheeler and Johnson, *ibid.*, 1900, **24**, 189; Wheeler and Dustin, *ibid.*, 1900, **24**, 424). We have therefore adopted the structure (as XXIII) for the similar compounds which we have isolated in the present investigation.

EXPERIMENTAL.

The names of solvents used for recrystallisation are stated in parenthesis after the compounds concerned. The ligroin used throughout had b. p. 60—80° unless otherwise stated. The expression " m. p. (alone and mixed) " refers to the m. p. of the substance alone and when mixed with authentic sample of the compound specified. All molecular-weight determinations were cryoscopic, the concentrations recorded being g. solute/100 g. solvent. All the xanthates and dithiocarbonates, having one or two *para* substituted benzyl groups, separated from solution in colourless, odourless crystals. The trihydrated chloramine-T was used throughout. The various thiols used were prepared from the corresponding chlorides or bromides by the method of Mann and Purdie (J., 1935, 1557).

Preparation of Metallic Xanthates.—Potassium ethyl xanthate. A solution of potassium hydroxide (100 g.) in hot alcohol (300 c.c., 2·9 mols.) was chilled in ice-water, and carbon disulphide (110 c.c., 1 mol.) added in small quantities with vigorous stirring so that the temperature did not rise above 30°. The crystalline xanthate (230 g., 80%) which separated was collected, washed thoroughly with ether, and stored in a vacuum over sodium hydroxide. It was used within a few days of preparation. Potassium methyl xanthate was prepared similarly.

Sodium benzyl xanthate (I). Sodium wire (23 g.) was added to benzyl alcohol (311 c.c., 3 mols.) and, when the initial reaction moderated, the mixture was gently boiled until all the sodium had reacted. The solution was chilled, and carbon disulphide (60 c.c., 1 mol.) added precisely as before; yield of the pale yellow, odourless xanthate, 130 g. (63%).

Sodium p-*chlorobenzyl xanthate* (III). "Powdered" sodium was prepared by vigorously shaking molten sodium (6·9 g.) with boiling xylene. *p*-Chlorobenzyl alcohol (51·3 g., 1·2 mols.) was added to the cold mixture, which was then maintained at 75—80° with occasional shaking for 5 hours, by which time the sodium had been entirely converted into sodium *p*-chlorobenzyloxide. The cold mixture was then treated with carbon disulphide (17·5 c.c., 1 mol.) as described above, the precipitated *xanthate* being ultimately collected (Found: C, 39·7; H, 2·7; Cl, 14·6; S, 26·6. $C_8H_6OClS_2Na$ requires C, 39·9; H, 2·5; Cl, 14·75; S, 26·45%). *Sodium* p-*methylbenzyl xanthate* was similarly prepared (Found: C, 48·9; H, 4·0; S, 29·35. $C_9H_9OS_2Na$ requires C, 49·05; H, 4·1; S, 29·1%).

O-*Benzyl* S-p-*Chlorobenzyl Xanthate* (II).—A mixture of dry powdered sodium benzyl xanthate (7·7 g.) and *p*-chlorobenzyl chloride (6 g., 1 mol.) was heated on a boiling water-bath for 2 hours with occasional stirring. The cold pasty yellowish-grey mass was then shaken with a mixture of equal volumes of water and ether. The ethereal layer was separated, dried (sodium sulphate), and the ether removed under reduced pressure. The residue of crystals containing a small quantity of oil was washed with ice-cold ligroin to remove the oil, and the solid residue of the *xanthate* then collected and recrystallised from petrol; needles, m. p. 63·5° (Found: C, 58·45; H, 4·2; Cl, 11·5; S, 20·65; *M*, in 1·187% ethylene dibromide solution, 311. $C_{15}H_{13}OClS_2$ requires C, 58·3; H, 4·25; Cl, 11·5; S, 20·75%; *M*, 309).

(A) *Effect of heat.* (a) *At* 0·1 *mm. pressure.* The xanthate decomposed and a colourless liquid, b. p. 190—199°, distilled. This distillate when cooled to 0° partly solidified, and the liquid portion was then extracted with ligroin (b. p. 40—60°). The residual crystals afforded 4 : 4′-dichloro-stilbene (VII) (alcohol), m. p. 172—173° (alone and mixed), (Found: C, 67·5; H, 4·1; Cl, 28·4. Calc. for $C_{14}H_{10}Cl_2$: C, 67·45; H, 4·05; Cl, 28·5%). The ligroin extract, when allowed to evaporate, ultimately deposited a crystalline residue of dibenzyl disulphide (VI) (ligroin), m. p. 70—71° (alone and mixed) (Found: C, 68·15; H, 5·7; S, 26·05. Calc. for $C_{14}H_{14}S_2$: C, 68·2; H, 5·75; S, 26·05%). It was confirmed that the disulphide was a direct product of the reaction, and did not arise by subsequent oxidation of benzylthiol. (b) *At* 18 *mm. pressure.* Decomposition again occurred, giving a liquid, b. p. 230—242°, which was separated as before into the previous components, identified by m. p. and analysis.

(B) *Action of phenylhydrazine.* A solution of the xanthate (3·1 g.) and phenylhydrazine (1·1 g., 1 mol.) in alcohol (50 c.c.) was refluxed for 6 hours, and the alcohol then evaporated. The residual oil when chilled at 0° underwent partial solidification, and the liquid component was then extracted with cold ligroin (b. p. 40—60°). The insoluble residue furnished O-*benzyl*-N-*phenylamino-thiourethane* (VIII), needles (alcohol), m. p. 136° (Found: C, 65·0; H, 5·4; N, 11·0; S, 12·5. $C_{14}H_{14}ON_2S$ requires C, 65·05; H, 5·45; N, 10·85; S, 12·4%). The ligroin extract, on spontaneous evaporation, gave an oily residue of *p*-chlorobenzylthiol; this was identified by treating a portion (0·4 g.) in alcoholic solution with iodine (0·3 g., 1 atom) and then with 10% aqueous sodium hydroxide solution (1 c.c., 1 mol. NaOH). After 30 minutes, the alcohol was evaporated and the residual solid (which had rapidly crystallised) furnished 4 : 4′-dichlorodibenzyl disulphide (ligroin), m. p. 59° (alone and mixed) (Found: C, 53·35; H, 3·8; Cl, 22·45. Calc. for $C_{14}H_{12}Cl_2S_2$: C, 53·3; H, 3·85; Cl, 22·5%).

O-p-*Chlorobenzyl* S-*Benzyl Xanthate* (IV).—This was prepared precisely as (II), using sodium *p*-chlorobenzyl xanthate (8·1 g.) and benzyl chloride (4·2 g., 1 mol.); needles (ligroin, b. p. 40—60°), m. p. 49°, depressed by admixture with (II) (Found: C, 58·4; H, 4·45; Cl, 11·6; S, 20·6; *M*, in 1·256% ethylene dibromide, 304. $C_{15}H_{13}OClS_2$ requires C, 58·3; H, 4·25; Cl, 11·5; S, 20·75%, *M*, 309).

(A) *Effect of heat.* (a) *At* 0·15 *mm. pressure.* The xanthate distilled unchanged as a colourless oil, b. p. 186—191°, which readily solidified, and when recrystallised from ligroin (b. p. 40—60°) had m. p. 49° unchanged by admixture with above sample (Found: C, 58·9; H, 4·4; Cl, 11·3; S, 20·9%). (b) *At* 16 *mm. pressure.* The xanthate decomposed, and a colourless oil, b. p. 225—240°, distilled and partly solidified when chilled. Treatment as previously described separated it into 4 : 4′-dichlorostilbene (VII), m. p. 172—173° (alone and mixed) (Found: C, 67·5; H, 3·95; Cl, 28·55%), and dibenzyl disulphide (VI), m. p. 70—71° (alone and mixed) (Found: C, 68·1; H, 5·8; S, 26·1%). Precisely the same decomposition occurred when the xanthate which had previously been distilled at 0·15 mm. was now heated at 16 mm.; hence, there was no evidence of a "stable form" being produced by the distillation.

(B) *Action of phenylhydrazine.* This was performed precisely as with the previous xanthate. The semi-solid residue after evaporation of the alcohol was again extracted with ligroin (b. p. 40—60°). The solid residue afforded colourless crystals of O-p-*chlorobenzyl*-N-*phenylamino-thiourethane* (IX) (alcohol), m. p. 173° (Found: C, 57·55; H, 4·5; N, 9·65; Cl, 12·2; S, 10·9. $C_{14}H_{13}ON_2ClS$ requires C, 57·4; H, 4·45; N, 9·6; Cl, 12·1; S, 10·95%). The ligroin extract on evaporation left oily benzylthiol, which was similarly identified by oxidation with iodine to dibenzyl disulphide (Found: C, 68·1; H, 5·7%), m. p. 70—71° (alone and mixed). The xanthate (IV) after distillation at 0·15 mm. gave precisely the same results with phenylhydrazine.

S-*Benzyl* S′-p-*Chlorobenzyl Dithiocarbonate* (V).—Sodium benzyl sulphide (29·2 g.) was added to a solution of phosgene (19·8 g., 1 mol.) in ether (300 c.c.) at 0°, the mixture vigorously shaken for 30 minutes, sodium *p*-chlorobenzyl sulphide (36·1 g., 1 mol.) then added and the shaking maintained for a further 30 minutes. After removal of the sodium chloride, the ether was evaporated under reduced pressure; the residual solid afforded the *dithiocarbonate* (V) (ligroin), m. p. 67·5° (Found: C, 58·25; H, 4·3; Cl, 11·6; S, 20·6; *M*, in 1·119% ethylene dibromide solution, 320. $C_{15}H_{13}OClS_2$ requires C, 58·3; H, 4·25; Cl, 11·5; S, 20·75%; *M*, 309). The m. p. was considerably depressed by admixture with (II), (IV), and (XIX) respectively.

(A) *Effect of heat.* (a) *At* 0·15 *mm. pressure.* The dithiocarbonate decomposed, and a colourless oil distilled at 192—203° and solidified on cooling. This was separated, as previously described, into 4 : 4′-dichlorostilbene (VII), m. p. 172·5—173° (alone and mixed) (Found: C, 67·35; H, 4·05; Cl, 28·5%), and dibenzyl disulphide (VI), m. p. 70—71° (alone and mixed) (Found: C, 68·05; H, 5·8; S, 26·0%). (b) *At* 17 *mm. pressure.* Decomposition again occurred, and the oil, which distilled at 228—239°, was again separated into the stilbene (VII) and the disulphide (VI), each being identified by mixed m. p. and analysis.

(B) *Phenylhydrazine.* A solution of the dithiocarbonate (1·5 g.) and phenylhydrazine (0·5 g., 1 mol.) in alcohol (50 c.c.) was refluxed for 6 hours. After evaporation of the solvent, crystals of the unchanged dithiocarbonate (V) separated in the residue; these, when washed with a small quantity of chilled alcohol, were pure, m. p. 66·5—67° (alone and mixed) (Found: C, 58·4; H, 4·3%): 1·4 g. (93%). The experiment was repeated using phenylhydrazine (2 mols.) but the unchanged (V) was again recovered in 90% yield.

Similar experiments showed that no reaction could be detected between phenylhydrazine and the other dithiocarbonates subsequently described, and therefore no further details are given of such experiments.

O-*Benzyl* S-p-*Methylbenzyl Xanthate* (X).—This *xanthate* was prepared precisely as (II), using sodium benzyl xanthate

(8·2 g.) and *p*-methylbenzyl bromide (7·4 g., 1 mol.); needles (ligroin), m. p. 62·5—63° (Found: C, 66·6; H, 5·8; S, 22·25; *M*, in 1·788% ethylene dibromide, 274. $C_{16}H_{16}OS_2$ requires C, 66·6; H, 5·6; S, 22·25%; *M*, 288).

(A) *Effect of heat.* (a) *At* 0·1 *mm. pressure.* The xanthate decomposed and a colourless liquid distilled at 186—187°, and partly solidified on cooling. Extraction with cold petrol (b. p. 40—60°), as previously described, left a residue of 4 : 4′-dimethylstilbene (XIII) (alcohol), m. p. 179—180° (alone and mixed) (Found: C, 92·15; H, 7·55. Calc. for $C_{16}H_{16}$: C, 92·25; H, 7·75%), whilst evaporation of the petrol extract afforded dibenzyl disulphide (VI) (ligroin), m. p. 70—71° (alone and mixed) (Found: C, 68·1; H, 5·85; S, 26·1%). (b) *At* 16 *mm. pressure.* Decomposition occurred and an oil distilled at 215—228°; this was again separated into the stilbene (XIII) and the disulphide (VI), each being identified by mixed m. p. and analyses.

(B) *Phenylhydrazine.* The xanthate (1·6 g.) and phenylhydrazine (0·6 g., 1 mol.) were boiled together in alcohol for 6 hours. The solution, treated as previously described for the xanthate (II), afforded the thiourethane (VIII), m. p. 136° (alone and mixed) (Found: C, 65·05; H, 5·5; N, 10·8; S, 12·5%), and *p*-methylbenzylthiol. The latter was identified by oxidation with iodine to 4 : 4′-dimethyldibenzyl disulphide (ligroin), m. p. 64° (alone and mixed) (Found: C, 70·1; H, 6·65; S, 23·3. Calc. for $C_{16}H_{18}S_2$: C, 70·0; H, 6·6; S, 23·4%).

O-p-*Methylbenzyl* S-*Benzyl Xanthate* (XI).—This *xanthate* was prepared from sodium *p*-methylbenzyl xanthate (11 g.) and benzyl chloride (6·3 g., 1 mol.); needles, which were recrystallised by chilling to *ca.* − 20° a solution in ligroin (b. p. 40—60°) previously saturated at room temperature; m. p. 39—39·5° (Found: C, 66·7; H, 5·6; S, 22·2; *M*, in 1·924% ethylene dibromide solution, 280. $C_{16}H_{16}OS_2$ requires C, 66·6; H, 5·6; S, 22·25%; *M*, 288). A mixture of this xanthate with (X) was liquid at room temperature.

(A) *Effect of heat.* (a) *At* 0·1 *mm. pressure.* The xanthate distilled without decomposition as a colourless oil, b. p. 174—178°, which readily crystallised: m. p. 39° (alone and mixed) after one crystallisation from ligroin (Found: C, 66·65; H, 5·7; S, 22·3%). (b) *At* 20 *mm. pressure.* The xanthate decomposed, and the colourless distillate, which boiled at 220—233° and rapidly solidified on cooling, was separated as before into 4 : 4′-dimethylstilbene (XIII), m. p. 179—180° (alone and mixed) (Found: C, 92·1; H, 7·7%) and dibenzyl disulphide (VI), m. p. 70—71° (alone and mixed) (Found: C, 68·3; H, 5·8%). The same results were obtained when the xanthate which had been distilled at 0·1 mm. was then heated at 20 mm. pressure.

(B) *Phenylhydrazine.* A solution of the xanthate (XI) (1·6 g.) and phenylhydrazine (0·6 g., 1 mol.) in alcohol (50 c.c.) was refluxed for 6 hours. The product, worked up as previously described, afforded O-p-*methylbenzyl*-N-*phenylaminothiourethane* (XIV), colourless crystals (alcohol), m. p. 179° (Found: C, 76·35; H, 4·15; N, 7·3; S, 8·1. $C_{15}H_{16}ON_2S$ requires C, 76·5; H, 4·1; N, 7·15; S, 8·15%), and benzylthiol, which was identified by oxidation to the disulphide, m. p. 70—71° (alone and mixed) (Found: C, 68·15; H, 5·75%). Identical results were obtained when a sample of the xanthate (XI) which had been distilled at 0·1 mm. was used.

S-*Benzyl* S′-p-*Methylbenzyl Dithiocarbonate* (XII).—This compound was prepared precisely as (V), adding sodium benzyl sulphide (36·5 g.) and sodium *p*-methylbenzyl sulphide (40 g., 1 mol.) in turn to a solution of phosgene (24·7 g., 1 mol.) in ether (300 c.c.): needles (ligroin), m. p. 65° (Found: C, 66·5; H, 5·5; S, 22·3; *M*, in 1·23% ethylene dibromide solution, 294. $C_{16}H_{16}OS_2$ requires C, 66·6; H, 5·6; S, 22·25%; *M*, 288). The m. p. was considerably depressed by admixture with (X), (XI), and (XXI) respectively.

(A) *Effect of heat.* (a) *At* 0·2 *mm. pressure.* The compound decomposed and the distillate, b. p. 189—204°, readily solidified on cooling. It was separated into 4 : 4′-dimethylstilbene (XIII), m. p. 179—180° (alone and mixed) (Found: C, 92·25; H, 7·75%), and dibenzyl disulphide (VI), m. p. 70—71° (alone and mixed) (Found: C, 68·3; H, 5·7%). (b) *At* 17 *mm. pressure.* Precisely the same results were obtained as in (a) except the distillate now had b. p. 217—231°.

O-p-*Chlorobenzyl* S-p-*Methylbenzyl Xanthate* (XV).—This *xanthate* was prepared from sodium *p*-chlorobenzyl xanthate (4 g.) and *p*-methylbenzyl bromide (3·1 g., 1 mol.): needles (ligroin), m. p. 57—58° (Found: C, 59·35; H, 4·6; Cl, 10·95; S, 19·65; *M*, in 1·670% ethylene dibromide solution, 315. $C_{16}H_{15}OClS_2$ requires C, 59·5; H, 4·7; Cl, 11·0; S, 19·85%; *M*, 323).

(A) *Effect of heat.* (a) *At* 0·1 *mm. pressure.* The xanthate decomposed, and two colourless fractions, b. p. 187—191° and 198—201°, were collected; both readily solidified on cooling and were then repeatedly crystallised from alcohol. The first thus afforded 4 : 4′-dimethylstilbene (XIII), m. p. 179—180° (alone and mixed) (Found: C, 92·25; H, 7·75%), and the second furnished 4 : 4′-dichlorostilbene (VII), m. p. 172·5—173° (alone and mixed) (Found: C, 67·45; H, 4·0; Cl, 28·6%). (b) *At* 17 *mm. pressure.* The two fractions now had b. p. 207—212° and 219—223°, and afforded as before the stilbenes (XIII), m. p. 179—180° (Found: C, 92·15; H, 7·85%), and (VII), m. p. 172·5—173° (Found: C, 67·4; H, 3·95%).

(B) *Phenylhydrazine.* Interaction of the xanthate (XV) (1·8 g.) and phenylhydrazine (0·6 g., 1 mol.), as previously described, afforded the chloro-thiourethane (IX), m. p. 173° (alone and mixed) (Found: C, 57·5; H, 4·5; N, 9·5; Cl, 12·0%), and *p*-methylbenzylthiol, identified by oxidation to the disulphide (ligroin), m. p. 64° (alone and mixed) (Found: C, 70·05; H, 6·65; S, 23·3%).

O-p-*Methylbenzyl* S-p-*Chlorobenzyl Xanthate* (XVI).—This *xanthate* was prepared from sodium *p*-methylbenzyl xanthate (5·5 g.) and *p*-chlorobenzyl chloride (4 g., 1 mol.); needles (ligroin, b. p. 40—60°), m. p. 46·5—47°, depressed by admixture with (XV) (Found: C, 59·45; H, 4·65; Cl, 11·15; S, 19·7; *M*, cryoscopic in 1·793% ethylene dibromide solution, 316. $C_{16}H_{15}OClS_2$ requires C, 59·5; H, 4·7; Cl, 11·0; S, 19·85%; *M*, 323).

(A) *Effect of heat.* (a) *At* 0·15 *mm. pressure.* Decomposition gave two fractions, m. p. 189—194° and 200—204°, which, as described above, afforded respectively the stilbenes (XIII), m. p. 179—180° (alone and mixed) (Found: C, 92·3; H, 7·7%) and (VII), m. p. 172·5—173° (alone and mixed) (Found: C, 67·45; H, 4·0; Cl, 28·6%). (b) *At* 16 *mm. pressure.* The two fractions, b. p. 206—210° and 217—222°, again furnished the stilbenes (XIII) and (VII) respectively, identified by m. p. and analysis.

(B) *Phenylhydrazine.* The reaction of the xanthate (XVI) (1·8 g.) and phenylhydrazine (0·6 g., 1 mol.), as previously described, afforded the *p*-methyl-thiourethane (XIV), m. p. 179° (alone and mixed) (Found: C, 76·55; H, 4·1; N, 7·1; S, 8·2%) and *p*-chlorobenzylthiol, identified by oxidation to the disulphide (ligroin), m. p. 59° (alone and mixed) (Found: C, 53·2; H, 5·9; Cl, 22·4%).

S-p-*Chlorobenzyl* S′-p-*Methylbenzyl Dithiocarbonate* (XVII).—This *compound* was prepared by the addition of sodium *p*-chlorobenzyl sulphide (36·1 g.) and sodium *p*-methylbenzyl sulphide (32 g., 1 mol.) in turn to a solution of phosgene (19·8 g., 1 mol.) in chilled ether (300 c.c.); needles (ligroin), m. p. 73° (Found: C, 59·55; H, 4·75; Cl, 11·1; S, 20·0; *M*, in 1·397% ethylene dibromide solution, 317. $C_{16}H_{15}OClS_2$ requires C, 59·5; H, 4·7; Cl, 11·0; S, 19·85%; *M*, 323). The m. p. was depressed by admixture with (XV), (XVI), (XIX), and (XXI) respectively.

(A) *Effect of heat.* The decomposition both at 0·05 mm. and at 19 mm. was precisely similar to that obtained with the xanthates (XV) and (XVI), the stilbenes (XIII) and (VII) being identified in each case by m. p.s and analysis.

In the following description of benzyl derivatives of class (*c*), the dithiocarbonates are for convenience described before the isomeric xanthates.

SS′-*Bis*-p-*chlorobenzyl Dithiocarbonate* (XIX).—*p*-Chlorobenzylthiol (41·4 g.) was added to sodium ethoxide solution prepared from sodium (6 g., 1 atom) and alcohol (300 c.c.), and phosgene then passed through the mixture for 4 hours.

The sodium chloride was collected and the alcohol evaporated at reduced pressure. The residual solid furnished the *dithiocarbonate* (XIX) (ligroin), needles, m. p. 78—78·5° (Found: C, 52·35; H, 3·6; Cl, 20·75; S, 18·85; *M*, in 1·273% ethylene dibromide solution, 337. $C_{15}H_{12}OCl_2S_2$ requires C, 52·45; H, 3·5; Cl, 20·65; S, 18·7%; *M*, 343).

(A) *Effect of heat.* (a) *At* 0·1 *mm. pressure. Production of the "stable form."* The dithiocarbonate distilled without decomposition as a colourless oil, b. p. 185—188°, which crystallised on cooling, and then had m. p. 78—78·5°, alone and when mixed with the undistilled material (Found: C, 52·5; H, 3·6; Cl, 20·8; S, 18·75%; *M*, in 1·240% ethylene dibromide solution, 340). This distillate was now the "stable form" (see below). (b) *At* 18 *mm. pressure.* (i) *The undistilled ester.* The pure recrystallised but undistilled ester (XIX) on heating decomposed, giving a colourless oily distillate, b. p. 220—225°, of 4 : 4′-dichlorostilbene (VII) which immediately solidified on cooling, and then had m. p. 171·5—172·5°, raised to 172·5—173° by one recrystallisation (alcohol) (Found: C, 67·65; H, 3·9; Cl, 28·35%).

(ii) *The distilled ester* ("*stable form*"). The ester which had been distilled as described in (*a*) now distilled at 18 mm. without decomposition, b. p. 220—226°, and readily solidified on cooling, m. p. 78—78·5° (alone and mixed) (Found: C, 52·55; H, 3·55; Cl, 20·7; S, 18·8%).

One sample of the undistilled dithiocarbonate (XIX) was recrystallised four times from alcohol, and another sample four times from glacial acetic acid; each sample still retained its original m. p., and when heated at 18 mm. decomposed to the stilbene (VII), but when heated at 0·1 mm. distilled without decomposition as the "stable form." Neither the parent nor the stable form of (XIX) was affected by boiling even with an excess of alcoholic phenylhydrazine.

O-p-*Chlorobenzyl* S-p-*Chlorobenzyl Xanthate* (XVIII).—This *xanthate* was prepared by the interaction of sodium *p*-chlorobenzyl xanthate (12 g.) and *p*-chlorobenzyl chloride (8 g., 1 mol.): needles (ligroin), m. p. 75·5—76°, depressed by admixture with (XIX) (Found: C, 52·55; H, 3·65; Cl, 20·55; S, 18·5; *M*, in 1·569% ethylene dibromide solution, 343. $C_{15}H_{12}OCl_2S_2$ requires C, 52·45; H, 3·5; Cl, 20·65; S, 18·7%; *M*, 343).

(A) *Effect of heat.* (a) *At* 0·3 *mm. pressure.* No decomposition was apparent, but a colourless distillate, b. p. 190—194°, was obtained which readily crystallised on cooling; these crystals, when washed once with ligroin (b. p. 40—60°) were the almost pure dithiocarbonate (XIX); they had m. p. 77—78°, unchanged by admixture with (XIX), but depressed to 49—58° by admixture with (XVIII). One crystallisation from petrol gave the pure dithiocarbonate (XIX), needles, m. p. 78—78·5° (Found: C, 52·25; H, 3·35; Cl, 20·5; S, 18·75%; *M*, in 1·340% ethylene dibromide solution, 351). (b) *At* 16 *mm. pressure.* The results were identical with those in (a), except that the distillate had b. p. 218—222°; the solidified distillate had m. p. 76·5—78°, unchanged by admixture with (XIX), considerably depressed by admixture with (XVIII), and raised to 78·5° by one recrystallisation (ligroin) (Found: C, 52·3; H, 3·4; Cl, 20·6; S, 18·85%). The product obtained in both (a) and (b) was the "stable form" of (XIX), and was distilled again unchanged at 221—226°/19 mm. (Found: C, 52·25; H, 3·35%).

(B) *Phenylhydrazine.* The xanthate (XVIII) (1·6 g.), treated with phenylhydrazine (0·5 g., 1 mol.) under the previous conditions afforded the *p*-chlorobenzyl-thiourethane (IX), m. p. 173° (alone and mixed) (Found: C, 57·3; H, 4·35; N, 9·5; Cl, 12·2; S, 11·05%), and *p*-chlorobenzylthiol, identified by oxidation to the disulphide, m. p. 59° (alone and mixed) (Found: C, 53·2; H, 3·9; Cl, 22·6%).

SS′-*Bis*-p-*methylbenzyl Dithiocarbonate* (XXI).—This *compound* was prepared precisely similarly to (XIX), using *p*-methylbenzylthiol (42 g.) and sodium (7 g., 1 atom): needles (petrol), m. p. 72—72·5° (Found: C, 67·45; H, 5·9; S, 21·3; *M*, in 1·525% ethylene dibromide solution, 294. $C_{17}H_{18}OS_2$ requires C, 67·5; H, 6·0; S, 21·2%; *M*, 302).

(A) *Effect of heat.* (a) *At* 0·15 *mm. pressure.* The ester distilled without decomposition, b.p. 180—185°, and then rapidly crystallised as the "stable form," m. p. 72—72·5°, alone and mixed with the parent form (Found: C, 67·65; H, 6·1; S, 21·05%; *M*, in 1·335% ethylene dibromide solution, 294). (b) *At* 20 *mm. pressure.* (i) *The undistilled ester.* This ester decomposed giving a colourless distillate, b. p. 210—217°, of 4 : 4′-dimethylstilbene (XIII), which readily solidified, m. p. 176·5—178°, raised to 179—180° by one recrystallisation (alcohol) (Found: C, 92·3; H, 7·75%). (ii) *The distilled ester* ("*stable form*"). This form distilled unchanged, b. p. 214—220°, and then readily crystallised, m. p. 72—72·5°, alone and mixed with the parent form (Found: C, 67·5; H, 6·05; S, 21·1%).

One sample of the parent ester (XXI) was again crystallised four times from alcohol, and another four times from acetic acid; both samples retained their m. p. unchanged and their identity as the parent form. Both forms of the ester were unaffected by boiling phenylhydrazine.

O-p-*Methylbenzyl* S-p-*Methylbenzyl Xanthate* (XX).—This *xanthate* was prepared from sodium *p*-methylbenzyl xanthate (11 g.) and *p*-methylbenzyl bromide (9·2 g., 1 mol.): needles, m. p. 68·5—69°, depressed on admixture with (XXI) (Found: C, 67·35; H, 5·9; S, 21·35; *M*, in 1·465% ethylene dibromide solution, 308. $C_{17}H_{18}OS_2$ requires C, 67·5; H, 6·0; S, 21·2%; *M*, 302).

(A) *Effect of heat.* (a) *At* 0·3 *mm. pressure.* A colourless distillate, b. p. 186—192°, of the "stable form" of (XXI) was obtained; this readily crystallised and, after washing with ligroin (b. p. 40—60°), had m. p. 70·5—71·5°, unchanged by admixture with (XII) but depressed by (XX) and, after one recrystallisation (ligroin), had m. p. 72—27·5° (alone and mixed) (Found: C, 67·35; H, 6·1; S. 21·25%; *M*, in 1·303% ethylene dibromide, 301). (b) *At* 17 *mm. pressure.* The colourless distillate now had b. p. 211—219°, but the results were otherwise essentially identical with those in (a). To confirm the identity of the "stable form" of (XXI) thus obtained it was redistilled, b. p. 210—215°/16 mm.; this second distillation left the m. p. unchanged (72—72·5°).

(B) *Phenylhydrazine.* The usual treatment with phenylhydrazine furnished the *p*-methyl-thiourethane (XIV), m. p. 179° (Found: C, 76·5; H, 4·0; N, 7·25; S, 8·2%) and *p*-methylbenzylthiol, identified by oxidation as the disulphide, m. p. 64° (alone and mixed) (Found: C, 70·1; H, 6·5; S, 23·55%).

SS′-*Dibenzyl Dithiocarbonate.*—This ester was prepared as (XIX), using benzylthiol (52·5 g.) and sodium (10 g., 1 atom); after distillation of the alcohol, the colourless oily residual *ester* was apparently pure after remaining several days under reduced pressure (Found: C, 65·7; H, 5·2; S, 23·55; *M*, in 1·393% ethylene dibromide solution, 281. $C_{15}H_{14}OS_2$ requires C, 65·65; H, 5·15; S, 23·4%; *M*, 274).

(A) *Effect of heat.* (a) *At* 0·1 *mm. pressure.* The ester distilled, b. p. 166—172°, apparently as a "stable form" (Found: C, 65·45; H, 5·1; S, 23·4%; *M*, in 1·115% ethylene dibromide solution, 286). (b) *At* 17 *mm. pressure.* (i) *The undistilled ester.* The ester decomposed, and a colourless liquid, b. p. 227—234°, distilled and solidified; washing with ligroin afforded dibenzyl disulphide, m. p. 70—71° (alone and mixed) (Found: C, 68·1; H, 5·9; S, 26·1%). (ii) *The distilled ester* ("*stable form*"). The form distilled unchanged, b. p. 202—206° (Found: C, 65·6; H, 5·15; S, 23·3%). Neither form of the ester reacted with boiling alcoholic phenylhydrazine.

Attempts to prepare *O*-benzyl *S*-benzyl xanthate failed. When, for example, a mixture of sodium benzyl xanthate (5 g.) and benzyl chloride (3·1 g., 1 mol.) was heated for four hours and the product worked up as for (II) the ethereal extract furnished solely dibenzyl disulphide, identified by m. p. and analysis.

O-*Ethyl* S-p-*Nitrobenzyl Xanthate.*—This was readily prepared by the interaction of potassium ethyl xanthate (4 g.) and *p*-nitrobenzyl bromide (5·4 g., 1 mol.): needles (ligroin), m. p. 63—63·5° (Found: C, 46·55; H, 4·35; N, 5·5; S, 24·9. $C_{10}H_{11}O_3NS_2$ requires C, 46·65; H, 4·3; N, 5·45; S, 24·95%). It distilled undecomposed, b. p. 115—118°/0·05 mm.

The isomeric xanthate could not be prepared, as the sodium derivative of *p*-nitrobenzyl alcohol exists as the scarlet (*aci*) form.

The xanthates (II), (IV), (XVIII), and (XX), and the dithiocarbonates (XIX), (XXI), and the *SS'*-dibenzyl member were treated in boiling alcoholic solution with chloramine-T (1, 2, 4 and 6 mols. in each case) : no crystalline product other than sodium chloride and *p*-toluenesulphonamide could be isolated, and the ester appeared therefore to be undergoing extensive disruption. The esters were unaffected by cold aqueous or alcoholic chloramine-T.

O-*Ethyl* S-*Ethyl Xanthate* (XXII).—This ester was prepared by heating a mixture of potassium ethyl xanthate (80 g.) and ethyl bromide (65·4 g., 1·2 mols.) at 50° for 4 hours. The filtered product was dried (sodium sulphate) and fractionally distilled under reduced pressure: the xanthate was obtained in almost theoretical amount as a colourless liquid, b. p. 78°/18 mm. (Found : C, 40·25; H, 7·45. Calc. for $C_5H_{10}OS_2$: C, 39·95; H, 6·7%).

(A) *Phenylhydrazine.* A mixture of the xanthate (2·8 g.) and phenylhydrazine (2 g., 1 mol.) in alcohol (50 c.c.) was refluxed for 6 hours, and gave a strong odour of ethanethiol; the solution furnished the thiourethane (XXIII) (alcohol), m. p. 72—24° (Found : C, 55·1; H, 6·1; N, 14·4; S, 16·4. Calc. for $C_9H_{12}ON_2S$; C, 55·05; H, 6·15; N, 14·3; S, 16·35%).

(B) *Chloramine-T.* A mixture of the xanthate (2·2 g.) and chloramine-T (16·6 g., 4 mols.) dissolved in water (100 c.c.) was shaken for 2 hours. The sulphonylimine (XXIV) (5·3 g., 0·9 mol.) which had separated was collected; after crystallisation from alcohol it had m. p. 186—187·5° (alone and mixed) (Found : C, 48·0; H, 5·0; N, 7·05; S, 23·85. Calc. for $C_{16}H_{20}O_4N_2S_3$: C, 47·95; H, 5·05; N, 7·0; S, 24·0%). Clark, Kenyon, and Phillips (*loc. cit.*) give m. p. 189°.

SS'-*Diethyl Dithiocarbonate* (XXV).—Phosgene was passed for 6 hours through alcohol (500 c.c.) to which sodium (11·5 g.) and ethanethiol (31 g., 1 mol.) had previously been added in turn. The alcohol was evaporated and the residue, on fractional distillation, gave the ester (XXV) as a colourless liquid, b. p. 85—87°/19 mm. (Found : C, 40·05; H, 6·6; S, 42·5. Calc. for $C_5H_{10}OS_2$: C, 39·95; H, 6·7; S, 42·7%) It was unaffected by boiling with phenylhydrazine. The ester reacted with chloramine-T precisely as the xanthate (XXII) in (B) above: the yields of the sulphonylimine (XXIV), using 2, 4, and 8 mols. of chloramine-T were 0·45, 0·9, and 0·9 mols. respectively. No other products, except sodium chloride and *p*-toluene sulphonamide, could be detected.

O-*Methyl* S-*Methyl Xanthate.*—This *ester* was prepared in almost theoretical yield similarly to (XXII) using potassium methyl xanthate (36·5 g.) and methyl iodide (42·6 g., 1 mol.) : colourless liquid, b. p. 65°/20 mm., 89°/64 mm. (Found : C, 30·0; H, 4·8. $C_3H_6OS_2$ requires C, 29·5; H, 4·95%).

(A) *Phenylhydrazine.* The reaction of this ester (2·5 g.) with phenylhydrazine afforded O-*methyl*-N-*phenylaminothiourethane* in colourless needles (alcohol), m. p. 110—111° (Found : C, 52·9; H, 5·4; N, 15·1; S, 17·4. $C_8H_{10}ON_2S$ requires C, 52·7; H, 5·55; N, 15·4; S, 17·6%).

(B) *Chloramine-T.* The ester (2 g.), shaken for 2 hours with a solution of chloramine-T (15·6 g., 4 mols.) in water (50 c.c.) deposited *methyl* p-*toluenesulphonimidosulphine*-p-*toluenesulphonylimine* (as XXIV), (4·6 g., 0·9 mol.), m. p. 186—189°, raised to 190·5—192° by crystallisation from alcohol (Found : C, 46·4; H, 4·6; N, 7·4; S, 24·95. $C_{15}H_{18}O_4N_2S_3$ requires C, 46·6; H, 4·7; N, 7·25; S, 24·9%). The use of chloramine-T (2 mols.) gave the same product in the same yield.

Reaction of Chloramine-T with Thiols and Disulphides.—(A) *Benzyl series.* (i) Alcoholic solutions of benzylthiol (XXVI) (2·5 g.) and chloramine-T (2·8 g., 0·5 mol.) were mixed (causing precipitation of sodium chloride), refluxed for 1 hour, filtered and evaporated to dryness. The solid residue was extracted with hot water to remove *p*-toluenesulphonamide; the molten insoluble portion, which readily solidified on cooling, consisted solely of dibenzyl disulphide (VI) (2·2 g., 0·45 mol.), m. p. 68—69·5°, raised to 70—71° by one recrystallisation (ligroin). The use of chloramine-T (14 g., 2·5 mols.), however, in this experiment afforded *benzyl* p-*toluenesulphonimidosulphine*-p-*toluenesulphonylimine* (XXVII), colourless crystals (alcohol), m. p. 171—171·5° (Found : C, 54·8; H, 5·1; N, 6·2; S, 21·1. $C_{21}H_{22}O_4N_2S_3$ requires C, 54·5; H, 4·8; N, 6·05; S, 20·8%). (ii) Experiment (i) was repeated, using alcoholic solutions of dibenzyl disulphide (VI) (2 g.) and chloramine-T (9·3 g., 4 mols.); the product, worked up as before, furnished the di-sulphonamido-compound (XXVII) (alcohol), m. p. 171—171·5° (alone and mixed).

(B) p-*Methylbenzyl series.* (i) Experiment (A) (i) above was repeated, using *p*-methylbenzylthiol (2 g.) and chloramine-T (2 g., 0·5 mol.); the extracted product was bis-*p*-methylbenzyl disulphide (as VI) (1·7 g., 0·43 mol.), m. p. 63—64·5°, raised to 65° (alone and mixed) by recrystallisation (ligroin). The use of chloramine-T (10·2 g., 2·5 mols.) afforded, however, p-*methylbenzyl* p-*toluenesulphonimidosulphine*-p-*toluenesulphonylimine* (as XXVII) (alcohol), m. p. 160° (Found : C, 55·2; H, 5·0; N, 6·2; S, 20·2. $C_{22}H_{24}O_4N_2S_3$ requires C, 55·4; H, 5·1; N, 5·9; S, 20·2%). (ii) Experiment A (ii) was repeated, using alcoholic solutions of bis-*p*-methylbenzyl disulphide (as VI) (2 g.) and chloramine-T (8·3 g., 4 mols.); the product, isolated as before, gave the above di-sulphonamido-compound (as XXVII) (alcohol), m. p. 160° (alone and mixed).

(C) *Methyl series.* An authentic sample of dimethyl disulphide, prepared by the iodine oxidation of methanethiol in the presence of very dilute sodium hydroxide, was obtained, after fractional distillation, as a colourless liquid, b. p. 117—118° (Found : C, 25·4; H, 6·4; S, 68·1. Calc. for $C_2H_6S_2$: C, 25·5; H, 6·4; S, 68·1%). A mixture of this disulphide (1 g.) and a cold aqueous solution of chloramine-T (12·1 g., 4 mols.) was shaken for 2 hours, and the white solid deposited, when collected and crystallised (alcohol), afforded methyl *p*-toluenesulphonimidosulphine-*p*-toluenesulphonylimine (as XXIV), m. p. 191—192° (alone and mixed).

We gratefully acknowledge grants from the Department of Scientific and Industrial Research and from Imperial Chemical Industries, Ltd.

THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, July* 12*th*, 1945.]