177. *The Chemistry of Xanthic Acid Derivatives. Part II. The Thermal Decomposition of Disulphurdicarbothionic Esters.*

By Gerald Bulmer and Frederick G. Mann.

The dialkyl and various dibenzyl disulphurdicarbothionates,* $(RO\cdot CS\cdot S\cdot)_2$, can usually be readily prepared by the action of chloramine-T or sodium tetrathionate on the corresponding alkali xanthate, $RO\cdot CS\cdot SNa$. The diethyl and dimethyl esters distil unchanged when heated at 0·1 mm. pressure, but at *ca.* 17 mm. pressure undergo thermal decomposition to the corresponding xanthate, $RO\cdot CS\cdot SR$. The dibenzyl ester, and *di*-p-*methyl* and *di*-p-*chloro* analogues, however, when heated at 0·1 mm. undergo decomposition to the corresponding disulphides,

---

* These esters were formerly known as " dixanthides " : the above systematic name was first used by Cambron and Whitby (*loc. cit.*) at the suggestion of the late Editor (Dr. Clarence Smith). Compounds of formula $(RO\cdot CS\cdot)_2S$ are named sulphurdicarbothionates (cf. Part III).

whilst at 18 mm. or higher pressures they furnish the corresponding stilbenes : the corresponding xanthates are apparently never formed. It is shown that the formation of the stilbenes in these reactions is almost certainly independent of that of the disulphides, although the latter may also furnish the stilbenes under suitable conditions.

ALTHOUGH diethyl disulphurdicarbothionate, $(EtO{\cdot}CS{\cdot}S{\cdot})_2$, and its simple homologues have been known for over a century, little precise knowledge is available concerning the behaviour of such compounds on heating. Since esters of this type form one of the products of the action of arylsulphonyl chlorides on metallic xanthates and frequently undergo thermal decomposition during the further course of this action (see Part IV), it was essential that their behaviour on heating should be separately studied. As a necessary preliminary, methods for their preparation have been re-examined.

Oxidation of alkali salts of the alkylxanthic acids, $2RO{\cdot}CS{\cdot}SK \longrightarrow (RO{\cdot}CS{\cdot}S{\cdot})_2$, forms the standard method for the preparation of the dialkyl disulphurdicarbothionates. Zeise (*Schw. J.*, 1822, **36**, 36; *Berz. J.*, 1824, **3**, 82; 1837, **16**, 306; *Ann. Phys.*, 1835, **35**, 489) originally used iodine and also copper sulphate for this purpose : more recently Cambron and Whitby (*Canad. J. Res.*, 1930, **2**, 144), in an extensive investigation of this reaction, have shown that sodium tetrathionate, cyanogen bromide, nitrous acid, chloramine-T, nitrosyl chloride and benzenesulphonyl chloride could be used as oxidising agents. Although Cambron and Whitby claim that sodium tetrathionate and cyanogen bromide give very pure products, we find that chloramine-T is the most convenient oxidising agent for obtaining the pure diethyl, dimethyl, dibenzyl and *di*-p-*methylbenzyl* esters in high yield; for the preparation of the *di*-p-*chlorobenzyl* ester, however, sodium tetrathionate was markedly superior to chloramine-T. The use of benzenesulphonyl chloride (see Part IV) is limited to low temperatures and is unsatisfactory.

It should be noted that the above conversion of metallic xanthates to the disulphurdicarbothionic esters can be accomplished by electrolysis (Schall, *Z. Elektrochem.*, 1895, **2**, 475), and can be reversed by alkali metals (Drechsel, *Z. Chem.*, 1865, 583).

Desains (*Ann. Chim. Phys.*, 1847, **20**, 507; *Annalen*, 1847, **64**, 328) claimed that di-*iso*amyl disulphurdicarbothionate decomposed on heating to give *O*-*iso*amyl *S*-*iso*amyl xanthate, and Debus (*Annalen*, 1850, **75**, 123) that the diethyl ester similarly decomposed, to furnish *O*-ethyl *S*-ethyl xanthate, *OO'*-diethyl thiocarbonate, carbon disulphide and sulphur; the identity of the liquid esters obtained in these and other similar early investigations was, however, not decisively proved. At reduced pressure diethyl disulphurdicarbothionate distils unchanged (Boehringer and Sohne, U.S.P., 1,626,558).

Tschugaeff (*Ber.*, 1899, **32**, 3332; *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 116) prepared several terpenoid esters such as dimenthyl disulphurdicarbothionate and showed, for example, that the latter on heating afforded menthene, menthol, carbon disulphide, carbonyl sulphide and sulphur. McAlpine (J., 1932, 912) has investigated the thermal decomposition of Tschugaeff's dimenthyl ester and of the corresponding dibornyl ester, when heated alone at various pressures, and when dissolved in certain solvents. She confirmed Tschugaeff's results, and showed that the dibornyl ester similarly gave bornylene (with some camphene) and borneol. Both esters when heated in ethylene dibromide solution gave some evidence of partial conversion to a " stable form," differing from the parent form only in thermal stability, and ultimately giving the same decomposition products.

We find that pure diethyl disulphurdicarbothionate distils unchanged at 0·05 mm. pressure, but at 18 mm., decomposes to produce *O*-ethyl *S*-ethyl xanthate; the identity of the latter has now been proved by the fact that with phenylhydrazine it furnished *N*-phenylamino-*O*-ethyl-thiourethane and with chloramine-T it gave ethyl *p*-toluenesulphonimidosulphine-*p*-toluenesulphonylimine (see Part I). The pure dimethyl ester behaved precisely similarly when heated under both these conditions. In neither case could we detect as a product of thermal decomposition either the dialkyl thiocarbonate, as Debus claimed, or the corresponding alcohol, as Tschugaeff and McAlpine found in their terpenoid homologues.

Both the above pure diethyl and dimethyl esters, after distillation at 0·05 mm. pressure, decomposed as described above when heated subsequently at 18 mm.; no indication of a " stable form " arising during the distillation at the lower pressure, similar to that observed with certain xanthates and dithiocarbonates (see Part I), was obtained.

The effect of heat on dibenzyl disulphurdicarbothionate and its *p*-substituted analogues is entirely different from that on the simple dialkyl esters. The dibenzyl ester itself when heated at 0·1 mm. decomposed to form dibenzyl disulphide in 82% yield, but at 19 mm. and at 760 mm. it gave stilbene in 88% and 85% yield respectively. The di-*p*-methylbenzyl ester similarly gave di-*p*-methylbenzyl disulphide (80%) at the lowest pressure, and 4 : 4'-dimethylstilbene (84 and 81%) at the intermediate and higher pressures : the di-*p*-chlorobenzyl ester at 0·5 mm. gave, however, a mixture of di-*p*-chlorobenzyl disulphide and 4 : 4'-dichlorostilbene, but solely the stilbene (84 and 81%) at 19 mm. and 760 mm. The nature of these products proves that the thermal decomposition of the disulphurdicarbothionates does not proceed *via* the intermediate formation of the corresponding xanthates, which give entirely different products; for example, *O*-*p*-methylbenzyl *S*-*p*-methylbenzyl xanthate and its *p*-chloro-analogue are converted solely to the corresponding dithiocarbonates when heated at either 0·1 or 18 mm. pressure (cf. Part I).

Since, however, dibenzyl disulphide when heated at atmospheric pressure gives stilbene (Fromm and Achert, *Ber.*, 1903, **36**, 539), it might appear that the initial stage in the decomposition of the above dibenzyl disulphurdicarbothionates is always the formation of the corresponding disulphide, $(RCH_2{\cdot}O{\cdot}CS{\cdot}S{\cdot})_2 \longrightarrow (RCH_2{\cdot}S{\cdot})_2 + 2COS$, and this disulphide then either distils unchanged at the lowest pressure, or undergoes further decomposition at the higher pressures to the corresponding stilbenes. Evidence on two points, however, shows that formation of the disulphides and the stilbenes occurs by independent reactions determined by the conditions, and the stilbenes are almost certainly direct decomposition products of the esters. First, we find that dibenzyl, di-*p*-methylbenzyl and di-*p*-chlorobenzyl disulphides distil unchanged at 18 mm. pressure, whereas the disulphurdicarbothionates give stilbenes at this pressure. Secondly, Fromm and Achert (*loc. cit.*) showed that the formation of stilbene by the thermal decomposition of dibenzyl disulphide at atmospheric pressure, was accompanied by that of toluene, 2 : 3 : 4 : 5-tetraphenylthiophen, αβγδ-tetraphenylbutane and sulphur. We have confirmed that dibenzyl, di-*p*-methylbenzyl and di-*p*-chlorobenzyl disulphides when heated at atmospheric pressure yield a mixture of products, from which we have isolated the corresponding stilbenes in only *ca.* 40% yield. On the contrary, the corresponding disulphurdicarbothionates when heated at this pressure give a distillate consisting of the almost pure stilbenes in *ca.* 80% yield; in this decomposition, therefore, the intermediate formation of the disulphides could not have occurred.

EXPERIMENTAL.

The solvents used for recrystallisation are named in parenthesis after the compounds concerned. The ligroin used throughout had b. p. 40—60°. The specified weights of chloramine-T refer to the trihydrate.

Diethyl Disulphurdicarbothionate.—(A) *Preparation.* An aqueous solution (250 c.c.) of freshly prepared potassium ethyl xanthate (64 g.) was slowly added with vigorous shaking to a cold solution of chloramine-T (43·8 g., 1 mol.) in water (250 c.c.), and the mixture then set aside for 2 hours. The colourless crystalline ester which had separated was collected and was almost pure; 47 g. (97%), m. p. 31—32·5°, raised to 32—32·5° by one crystallisation (alcohol) (Found : C, 29·6; H, 4·0; S, 52·8. Calc. for $C_6H_{10}O_2S_4$: C, 29·7; H, 4·15; S, 52·95%). This preparation is based on that of Cambron and Whitby (*loc. cit.*).

(B) *Effect of heat.* (i) *At* 0·05 *mm. pressure.* The ester distilled without decomposition, b. p. 107—109°, and readily crystallised on cooling, m. p. 31·5—32·5° (alone and mixed) (Found : C, 29·8; H, 4·15%). (ii) *At* 15 *mm. pressure.* The ester decomposed, and a yellow oil, b. p. 78—84°, distilled. This, on fractionation, gave pure colourless *O*-ethyl *S*-ethyl xanthate, b. p. 81—82°/20 mm. (Found : C, 39·9; H, 6·65; S, 42·8; *M*, cryoscopic in 1·701% ethylene dibromide solution, 154. Calc. for $C_5H_{10}O_2S_2$: C, 39·95; H, 6·7; S, 42·7%; *M*, 150). This xanthate was further identified by the action of phenylhydrazine and of chloramine-T (for experimental details, see Part I, p. 674). The former gave *N*-phenylamino-*O*-ethylthiourethane (alcohol), m. p. 72—74° (alone and mixed) (Found : C, 55·15; H, 6·2; N, 14·35; S, 16·3. Calc. for $C_9H_{10}ON_2S_2$: C, 55·05; H, 6·15; N, 14·3; S, 16·35%) and ethanthiol; the latter reagent afforded ethyl *p*-toluenesulphonimidosulphine-*p*-toluenesulphonylimine (alcohol), m. p. 186—187° (alone and mixed) (Found : C, 48·1; H, 5·15; N, 7·15; S, 23·9. Calc. for $C_{16}H_{20}O_4N_2S_3$: C, 47·95; H, 5·05; N, 7·0; S, 24·0%).

Dimethyl Disulphurdicarbothionate.—(A) *Preparation.* This ester was prepared precisely as the diethyl compound and was recrystallised by chilling in ice-salt an alcoholic solution previously saturated at room temperature; colourless crystals, m. p. 23—23·5° (Found : C, 22·35; H, 2·75; S, 59·7. Calc. for $C_4H_6O_2S_4$: C, 22·3; H, 2·8; S, 59·85%). Cambron and Whitby (*loc. cit.*) give m. p. 23—23·5°.

(B) *Effect of heat.* (i) *At* 0·1 *mm. pressure.* The ester distilled unchanged, b. p. 90—94°, and then had m. p. 23—23·5° (alone and mixed). (ii) *At* 19 *mm. pressure.* The ester decomposed, but the only volatile product that condensed was *O*-methyl *S*-methyl xanthate, b. p. (on refractionation) 62—63°/19 mm. (Found : C, 29·35; H, 5·3; S, 52·5. Calc. for $C_3H_6OS_2$: C, 29·5; H, 4·95; S, 52·45%). This was identified by (a) phenylhydrazine, giving methanethiol and *N*-phenylamino-*O*-methylthiourethane (alcohol), m. p. 110—111° (alone and mixed) (Found : C, 53·0; H, 6·7. Calc. for $C_8H_{10}ON_2S$: C, 52·7; H, 5·55%), and (b) chloramine-T, giving methyl *p*-toluenesulphonimidosulphine-*p*-toluenesulphonylimine (alcohol), m. p. 190·5—192° (alone and mixed).

Unless otherwise stated, the weight of all the following disulphurdicarbothionates used in the thermal decomposition experiments was 6 g. : the use of larger quantities would undoubtedly have given higher yields of the distilled product, owing to proportionately smaller mechanical losses.

Dibenzyl Disulphurdicarbothionate.—(A) *Preparation.* This ester was prepared in 92% yield as for the diethyl homologue : colourless needles (alcohol), m. p. 56·5° (Found : C, 52·45; H, 3·9; S, 34·95. Calc. for $C_{16}H_{14}O_2S_4$: C, 52·4; H, 3·85; S, 35·0%).

(B) *Effect of heat.* (i) *At* 0·1 *mm. pressure.* The ester decomposed, giving a colourless distillate, b. p. 182—189° which rapidly crystallised and, when washed once with ligroin, afforded dibenzyl disulphide (3·3 g., 82%), m. p. 69—70·5° (alone and mixed), raised to 70—71° by one crystallisation (ligroin) (Found : C, 68·3; H, 5·7. Calc. for $C_{14}H_{14}S_2$: C, 68·2; H, 5·75%). (ii) *At* 19 *mm. pressure.* The ester again decomposed, giving a colourless distillate, b. p. 177—182°, which on cooling immediately solidified, m. p. 120—121·5°; on recrystallisation (alcohol), it was identified as stilbene (2·6 g., 88%), m. p. 124° (alone and mixed) (Found : C, 93·35; H, 6·7. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%). (iii) *At atmospheric pressure.* Decomposition of the ester again afforded a colourless distillate of stilbene (2·5 g., 85%), b. p. 310—314°, which immediately solidified on cooling : m. p. 120—121° (alone and mixed).

*Di-*p*-methylbenzyl Disulphurdicarbothionate.*—(A) *Preparation.* Prepared as the diethyl ester, using solutions of sodium *p*-methylbenzyl xanthate (30 g., 1 mol.) and chloramine-T (38·8 g., 1 mol.), each in water (200 c.c.). The mixture was set aside in an ice-chest overnight, and the colourless crystals of the *di-*p*-methylbenzyl* ester collected (24·5 g., 91%), m. p. 71—72° (alcohol) (Found : C, 54·6; H, 4·5; S, 32·7. $C_{18}H_{18}O_2S_4$ requires C, 54·75; H, 4·6; S, 32·5%).

(B) *Effect of heat.* (i) *At* 0·1 *mm. pressure.* The ester decomposed, giving a colourless distillate, b. p. 195—200°, of di-*p*-methylbenzyl disulphide, which rapidly crystallised when cooled; m. p. 64—64·5° after washing with chilled ligroin, raised to 65° by recrystallisation (ligroin) (Found : C, 70·2; H, 6·6; S, 23·1. Calc. for $C_{16}H_{18}S_2$: C, 70·0; H, 6·6; S, 23·4%); 3·3 g., 80%. (ii) *At* 18 *mm. pressure.* Decomposition furnished a colourless distillate, b. p. 210—215°, of 4 : 4′-dimethylstilbene, which rapidly crystallised; m. p. 178—179° (alone and mixed) : 2·8 g., 87%. (iii) *At atmospheric pressure.* The colourless distillate, b. p. 305—308°, of 4 : 4′-dimethylstilbene crystallised immediately on cooling; m. p. 178—179·5° (alone and mixed), raised to 179—180° by recrystallisation (alcohol) : 2·7 g., 84%.

*Di-*p*-chlorobenzyl Disulphurdicarbothionate.*—(A) *Preparation.* (i) When an aqueous solution (200 c.c.) of sodium *p*-chlorobenzyl xanthate (40 g.) was slowly added to a similar solution (250 c.c.) of chloramine-T (47·4 g., 1 mol.) with vigorous shaking, and the mixture set aside in an ice-chest overnight, the *di-*p*-chlorobenzyl* ester separated as colourless crystals contaminated with a pale yellow oil. The collected crystals (24 g., 66%) had m. p. 87—89°, raised to 90·5—91° by recrystallisation (alcohol) (Found : C, 43·9; H, 2·6; Cl, 16·45; S, 29·7. $C_{16}H_{12}O_2Cl_2S_4$ requires C, 44·1; H, 2·8; Cl, 16·3; S, 29·45%). (ii) When this preparation was repeated, the aqueous solution (50 c.c.) of the sodium xanthate (24 g.) being now added to an aqueous solution (50 c.c.) of sodium tetrathionate (13·5 g., 0·5 mol.), the crystalline ester separated without oily contamination; m. p. 88—90°, raised by recrystallisation to 90·5—91° (alone and mixed): 18 g., 83%.

(B) *Effect of heat.* (i) *At* 0·5 *mm. pressure.* The ester (9 g.) decomposed giving a colourless liquid distillate, b. p. 198—212°, which, when diluted with chilled ligroin, deposited crystals of 4 : 4′-dichlorostilbene (1·5 g., 29%), m. p. 170—172·5°, raised to 172·5—173° (alone and mixed) by recrystallisation (alcohol). The ligroin extract, evaporated to dryness, gave a residue of di-*p*-chlorobenzyl disulphide (3·2 g., 49%), m. p. 56—58·5° raised to 59° (alone and mixed) by recrystallisation (ligroin) (Found: C, 53·15; H, 3·8; S, 20·1. Calc. for $C_{14}H_{12}Cl_2S_2$: C, 53·3; H, 3·85; S, 20·35%). (ii) *At* 19 *mm. pressure.* The ester decomposed and the colourless distillate, b. p. 220—226°, of 4 : 4′-dichlorostilbene immediately solidified on cooling (2·9 g., 84%), m. p. 171—172·5°, raised to 172·5—173° (alone and mixed) by recrystallisation (alcohol). (iii) *At atmospheric pressure.* The result was precisely as in (ii), the distillate having b. p. 326—330°, m. p. 171·5—172·5° (alone and mixed) (2·8 g., 81%).

Dibenzyl Disulphide.—(i) This compound boiled unchanged at 210—216°/18 mm., and the crude distillate after solidification had m. p. 68·5—70° (alone and mixed). (ii) When heated at atmospheric pressure the disulphide (5 g.) decomposed giving a distillate which on cooling furnished colourless crystals mixed with a colourless oil. This mixture, when carefully extracted with chilled ligroin, gave a residue of stilbene, m. p. 119—120·5° (alone and mixed): 1·5 g., 41%.

*Di-*p*-methylbenzyl Disulphide.*—(i) This boiled unchanged at 225—232°/18 mm., the crude distillate having m. p. 64—64·5° (alone and mixed). (ii) The disulphide (5 g.), heated at atmospheric pressure, behaved precisely as the previous disulphide. Extraction of the crude distillate with ligroin gave 4 : 4′-dimethylstilbene, m. p. 178—179·5° (alone and mixed): 1·6 g., 42%.

*Di-*p*-chlorobenzyl Disulphide.*—(i) This had b. p. 234—240°/18 mm., and the crude distillate then had m. p. 58—59° (alone and mixed). (ii) The disulphide (5 g.), heated at atmospheric pressure, also behaved precisely as the two previous disulphides. Extraction of the crude semi-solid distillate with ligroin gave a residue of 4 : 4′-dichlorostilbene, m. p. 171—172·5° (alone and mixed): 1·5 g., 38%.

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

The University Chemical Laboratory, Cambridge.

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