Tetrahedron, 1962, Vol. 18, pp. 245 to 255. Pergamon Press Ltd. Printed in Northern Ireland

THERMAL REARRANGEMENT OF XANTHATES TO DITHIOLCARBONATES—I*

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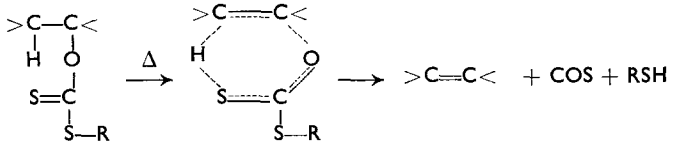
(*Received* 29 *July* 1961)

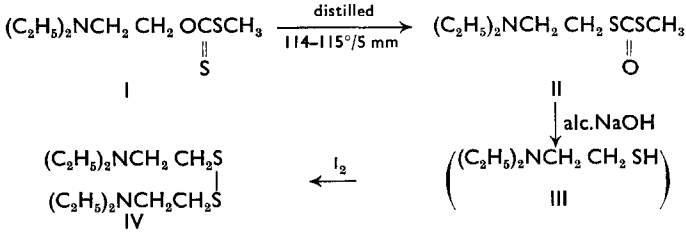
Abstract—During the pyrolysis of β-dialkylaminoalkyl S-methyl xanthates, DL-*trans*-2-dimethylaminocyclohexyl S-methyl xanthate was rearranged without elimination to the corresponding dithiolcarbonate while the *cis* isomer suffered over-all elimination. It has been suggested that the dimethylamino group attached to the carbon carrying the xanthate group induces the rearrangement. Other examples studied support this mechanism. 2-Benzamidoethyl S-methyl and DL-*trans*-2-benzamidocyclohexyl S-methyl xanthates have been converted to the corresponding oxazoline derivatives.

IN the Chugaev reaction,[1] xanthate esters produce olefins on pyrolysis if a β-hydrogen is in the *cis* position to the xanthate function. It has been accepted,[2-5] that this reaction requires the cyclic coplanarity which favours *cis* elimination through the following transition state.



transition state

In connection with the thermal behaviour of DL-2-dimethylaminocyclohexyl iodides,[6] pyrolyses of 2-dialkylaminoalkyl S-methyl xanthates were investigated. Distillation of 2-diethylaminoethyl S-methyl xanthate (I) under reduced pressure (114–115°/5 mm) yields 2-diethylaminoethyl methyl dithiolcarbonate (II) without any elimination. Hydrolysis of II in alcoholic sodium hydroxide followed by oxidation



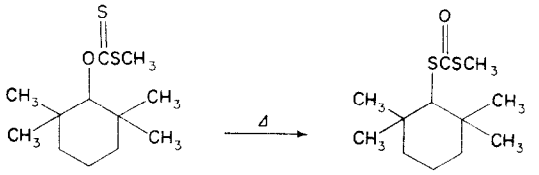
with iodine yields 2-diethylaminoethyl disulphide (IV) via 2-diethylaminoethane thiol

* Studies in Stereochemistry. XXVIII. Part XXVII, Yakugaku Zasshi, in press.

[1] L. Tschugaeff, *Ber. Dtsch. Chem. Ges.* **32**, 3332 (1899).
[2] D. S. Tarbell and D. P. Harnish, *Chem. Revs.* **49**, 56 (1951).
[3] C. H. DePuy and R. W. King, *Chem. Revs.* **60**, 431 (1960).
[4] M. S. Newman, *Steric Effects in Organic Chemistry* p. 304. John Wiley, New York (1956).
[5] D. H. R. Barton, A. J. Head and R. T. Williams, *J. Chem. Soc.* 453 (1952).
[6] T. Taguchi and M. Eto, *J. Amer. Chem. Soc.* **80**, 4075 (1958).

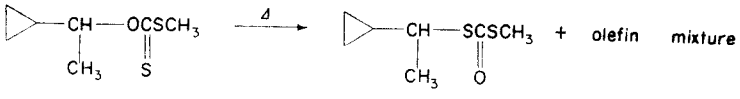
(III). This together with the infra-red spectrum, λ_{max} 6·03 and 11·48 μ, supports the structure assigned to II.

Further examples of this rearrangement may be classified according to the following two general cases: (a) xanthates carrying no β-hydrogen available for the elimination and (b) as a side reaction accompanying the normal formation of olefin. In case (a), several examples have been reported by Laakso;[7] for example, 2,2,6,6-tetramethylcyclohexyl S-methyl xanthate (V) was converted to the corresponding dithiolcarbonate (VI).



V VI

In case (b), McAlpine[8] obtained from the pyrolyses of menthyl and bornyl S-methyl xanthates etc, the corresponding olefins and in addition stable compounds considered to be dithiolcarbonates but not identified. Also, in the pyrolysis of 1-cyclopropylethyl S-methyl xanthate (VII), Overberger, *et al.*[9] obtained the corresponding dithiolcarbonate (VIII) in addition to an olefin mixture. It has, however, not yet been demonstrated that a compound with a β-hydrogen in *cis* position to the xanthate group may be converted thermally to the dithiolcarbonate without olefin formation.



VII VIII

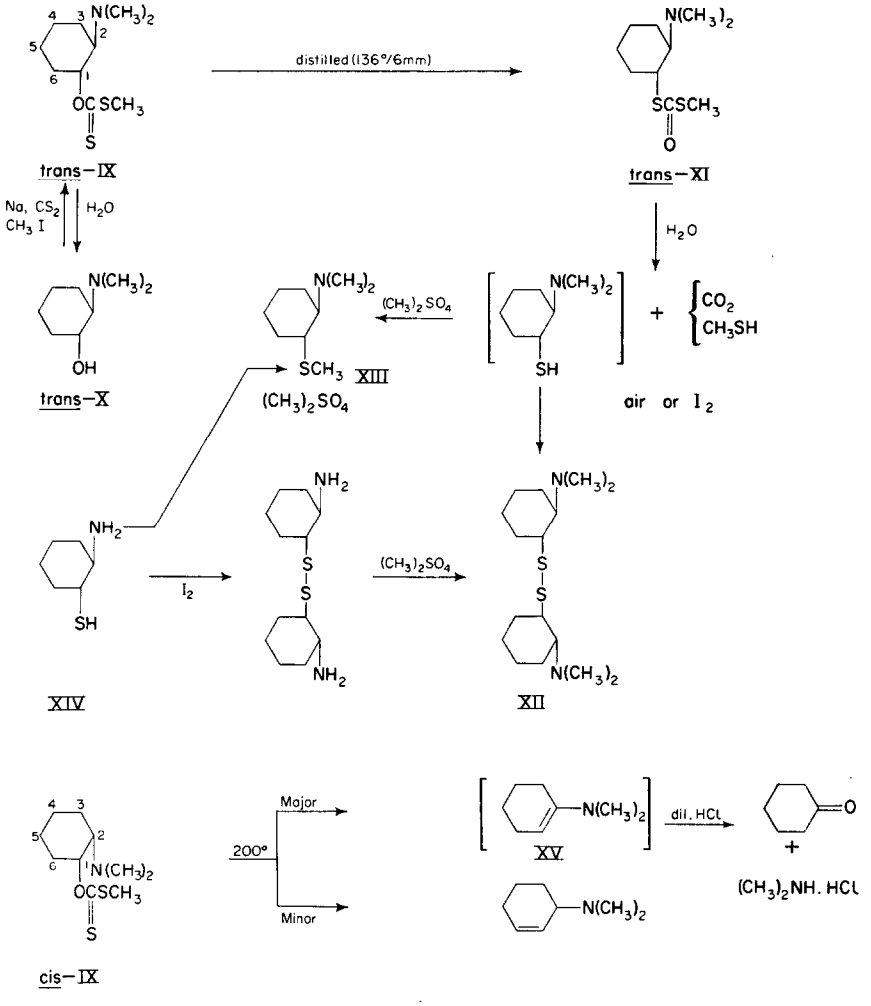
DL-*trans*-2-Dimethylaminocyclohexyl S-methyl xanthate (*trans*-IX) and the *cis* isomer (*cis*-IX) were prepared from the corresponding DL-2-dimethylaminocyclohexanols,[10–12] and their behaviour on heating investigated.

The *trans* xanthate (*trans*-IX) is converted without elimination to DL-*trans*-2-dimethylaminocyclohexyl methyl dithiolcarbonate (XI) by distillation at 136°/6 mm. The configuration of the product (XI) was established in the following way. The *trans*-IX shows the characteristic absorption bands of the xanthate at 8·15 and 9·47 μ and hydrolyses to the alcohol (*trans*-X), whereas the product (XI) shows the bands characteristic for the dithiolcarbonate at 6·08 and 11·59 μ and hydrolyses to a mixture of DL-*trans*-2-dimethylaminocyclohexane thiol and its autoxidation product, DL-*trans*-2-dimethylaminocyclohexyl disulphide (XII). This mixture may be converted by methylation with dimethyl sulphate to DL-*trans*-2-dimethylaminocyclohexyl methyl sulphide (XIII) and unchanged XII. Since XII and XIII may also be obtained from

[7] P. V. Laakso, *Suomen Kemi* **13B**, 8 (1940); *Chem. Abstr.* **34**, 5059 (1940); *Suomen Kemi* **16B**, 19 (1943); *Chem. Abstr.* **40**, 4687 (1946).
[8] I. M. McAlpine, *J. Chem. Soc.* 1114 (1931); *Ibid* 906 (1932).
[9] C. G. Overberger and A. E. Borchert, *J. Amer. Chem. Soc.* **82**, 4896 (1960).
[10] C. S. Winstein, *J. Amer. Chem. Soc.* **64**, 2792 (1942).
[11] M. Mousseron, J. Jullien and Y. Jolchine, *Bull. Soc. Chim. Fr.* 757 (1952).
[12] H. D. Baldridge, Jr., W. J. McCarville and S. L. Friess, *J. Amer. Chem. Soc.* **77**, 739 (1955).

DL-*trans*-2-aminocyclohexane thiol[13] by methylation, oxidation with iodine[14] and further methylation, the configuration of XII, XIII and the dithiolcarbonate (XI) has been established.

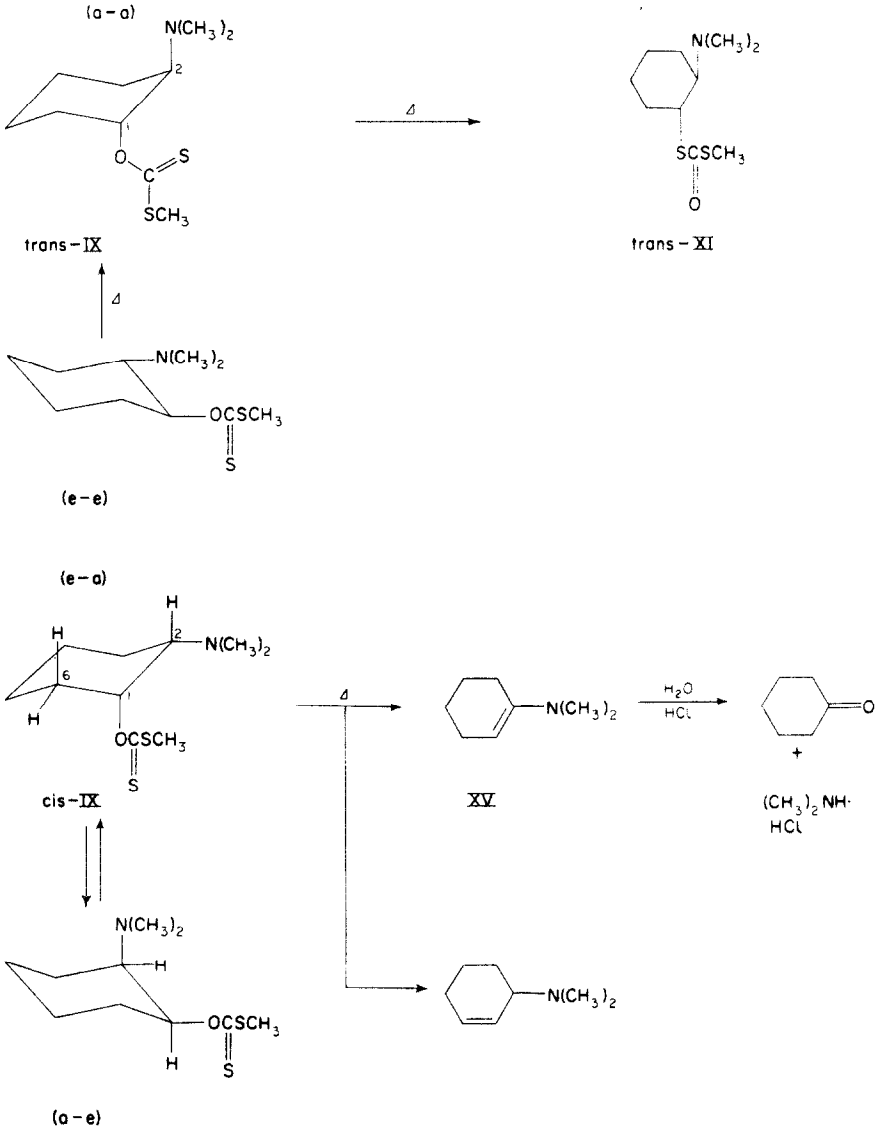
On the other hand, the *cis* xanthate (*cis*-IX) is unchanged by distillation under reduced pressure, b.p. 135–147°/5 mm, but is decomposed by heating at 200° with



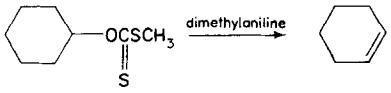
evolution of carbonyl sulphide and methyl mercaptan. The residue on treatment with dilute hydrochloric acid, gives cyclohexanone, a small amount of 3-dimethylamino-cyclohexene and dimethylamine hydrochloride. Thus, the *trans*- and *cis*-xanthates do not undergo the Chugaev reaction or *cis*-elimination, although each has a β-hydrogen *cis*-oriented to the xanthate function. This may be attributed to the dimethylamino group and the conformation of the compounds. The diaxial form of the *trans*-IX in which the two substituents are coplanar, the dimethylamino group at C_1 assists the

[13] T. Taguchi and M. Kojima, *J. Amer. Chem. Soc.* **78**, 1464 (1956).
[14] F. Winternitz, M. Mousseron and R. Dennilauer, *Bull. Soc. Chim. Fr.* 1228 (1956).

release of C_1—O bond and simultaneously the attack of the thion-S in the xanthate group at C_1; thus favouring the rearrangement without elimination to the dithiolcarbonate (XI). In the *cis*-IX, the dimethylamino and the xanthate groups are in *e-a* or *a-e* relationship. In the *e-a* form, H_2 and the xanthate group being in the antiparallel coplanarity, the basic property of the dimethylamino group facilitates the

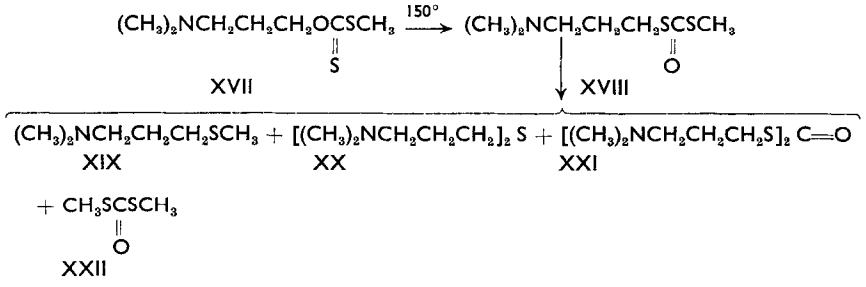


trans elimination of H_2 and the xanthate ion to produce cyclohexanone via XV. The formation of 3-dimethylaminocyclohexene, may occur by *trans* elimination catalysed by the basic group. Since cyclohexyl S-methyl xanthate (XVI) on heating in dimethylaniline produces cyclohexene without any rearrangement, the participation of the dimethylamino group in the rearrangement of *trans*-IX is confirmed.



XVI

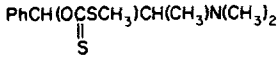
3-Dimethylaminopropyl S-methyl xanthate (XVII) was distilled unchanged at 97°/3 mm, but on heating at 150°, XVII rearranges to 3-dimethylaminopropyl methyl dithiolcarbonate (XVIII), which is subsequently decomposed to 3-dimethylaminopropyl methyl sulphide (XIX), 3-dimethylaminopropyl sulphide (XX), 3-dimethylaminopropyl dithiolcarbonate (XXI) and methyl dithiolcarbonate (XXII).



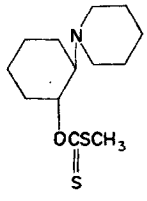
The structures of the dithiolcarbonates, XVIII and XXI, were established as described above and the remaining products, XIX, XX, and XXII, were confirmed by syntheses.

In order to determine the effect of nitrogen containing groups on the rearrangement, the following xanthates were investigated. DL-diastereoisomers of 1-phenyl-2-dimethylaminopropyl S-methyl xanthate (XXIII), DL-*trans*-2-(1′-piperidyl)-cyclohexyl S-methyl xanthate (XXIV), DL-*trans*-2-benzamidocyclohexyl S-methyl xanthate (XXV) and 2-benzamidoethyl S-methyl xanthate (XXVI).

The *threo*-XXIII, the *erythro*-XXIII and XXIV give the corresponding dithiolcarbonates (*threo*-XXVII, *erythro*-XXVII and XXVIII) by a rearrangement analogous with that of *trans*-IX. The structures were confirmed by I.R. spectra or by hydrolyses followed by methylation, the methods being analogous with the case of *trans*-IX. Further, DL-*threo*-1-phenyl-2-dimethylaminopropyl methyl sulphide derived from the *threo*-XXVII was proved identical with the product from the reaction of DL-*threo*-1-phenyl-2-dimethylaminopropyl chloride and sodium thiosulphate after hydrolysis and methylation.



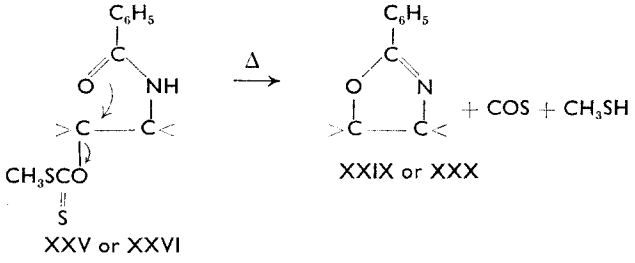
XXIII



XXIV

On the other hand, under similar conditions the benzamido xanthates, XXV and XXVI, result in the corresponding oxazoline derivatives (XXIX and XXX) with inversion and evolution of carbonyl sulphide and methyl mercaptan. These results for

the benzamido derivatives indicate a stabilization of reaction at the stage of the oxazoline formation before the rearrangement.



XXV or XXVI XXIX or XXX

As it seems probable that neighbouring groups may be a motive force in the rearrangement, the following compounds with other groups which can participate, were examined; S-methyl xanthates of allyl alcohol, *trans*-cinnamyl alcohol, DL-*trans*-2-methylthiocyclohexanol, glycolic acid, DL-*trans*-2-methoxycyclohexanol, DL-*trans*-2-methylsulphonylcyclohexanol, DL-*trans*-2-benzoyloxycyclohexanol and DL-*trans*-2-p-toluenesulphonmethylamidocyclohexanol. Of these xanthates, only the first three rearranged but details will appear in subsequent papers.

EXPERIMENTAL[15]

DL-*cis*-2-*Dimethylaminocyclohexanol* (cis-X).[11] To 0·57 g DL-*cis*-2-aminocyclohexanol dissolved in 14·5 g 80% aqueous formic acid, 12·9 g 37% aqueous formaldehyde was added and the mixture heated gradually. After vigorous evolution of CO_2 the solution was refluxed for 10 hr, cooled, conc HCl added and evaporated to dryness leaving the hydrochloride of *cis* X. The recrystallization from ethanol–ethyl acetate gave colourless leaflets, m.p. 177–178° (0·6 g). The hydrochloride was treated with aqueous sodium hydroxide, extracted with ether, dried (K_2CO_3) and evaporated to dryness. The residue was distilled, b.p. 100°/32 mm, m.p. 43–44°, and converted to the picrate, yellow pillars from ethanol, m.p. 163–165°. (Found; C, 53·22; H, 10·04; N, 8·09. Calc. for $C_8H_{17}NO{\cdot}HCl$: C, 53·42; H, 9·54; N, 7·80%).

DL-*trans*-2-(1′-*Piperidyl*)-*cyclohexanol*. This was prepared from *meso*-*cis*-cyclohexene oxide and piperidine by the procedure of Kusner,[16] b.p. 146–148°/30 mm, yield 90%. *Picrate*: m.p. 135–138°. *Hydrochloride*: m.p. 266–268° (dec). (Found: C, 60·08; H, 10·01; N, 6·32. Calc. for $C_{11}H_{21}NO{\cdot}HCl$: C, 60·00; H, 10·02; N, 6·38%).

DL-*trans*-2-*Dimethylaminocyclohexyl methyl sulphide* (XIII). DL-*trans*-2-Aminocyclohexane thiol (XIV; 2·5 g) was treated with dimethyl sulphate (1·9 g) in aqueous sodium hydroxide at 40–50° for 5 hr. The mixture was extracted with ether, dried (K_2CO_3) and evaporated to dryness. Distillation gave 2·1 g of XIII, b.p. 115°/35 mm. *Picrate*: yellow plates, m.p. 133–135° from ethanol. (Found: C, 44·15; H, 5·78; N, 13·72. Calc. for $C_9H_{19}NS{\cdot}C_6H_3N_3O_7$: C, 44·54; H, 5·48; N, 13·85%).

DL-*trans*-2-*Dimethylaminocyclohexyl disulphide* (XII). DL-*trans*-2-Aminocyclohexyl disulphide (0·65 g) was methylated by adaptation of the method used for XIII (yield 0·66 g). The picrate recrystallized as yellow needles from aqueous methanol, m.p. 202–205° (dec). (Found: C, 43·22; H, 5·17; N, 14·41. Calc. for $C_{16}H_{32}N_2S_2{\cdot}C_{12}H_6N_6O_{14}$: C, 43·29; H, 5·19; N, 14·46%).

3-*Dimethylaminopropyl chloride*. This was prepared from 3-dimethylaminopropanol and thionyl-chloride by the procedure of Gilman and Shirley,[17] b.p. 47°/32 mm. *Picrate*: yellow plates from ethanol, m.p. 109–110°. (Found: C, 37·85; H, 4·41; N, 15·53. Calc. for $C_5H_{12}NCl{\cdot}C_6H_3N_3O_7$: C, 37·66; H, 4·28; N, 15·98%).

3-*Dimethylaminopropyl methyl sulphide* (XIX). Compound XIX was prepared from 3-dimethyl-aminopropyl chloride and sodium methylmercaptide by the procedure of Kirchner, *et al.*[18] The

[15] All m.ps and b.ps are uncorrected.
[16] T. S. Kusner, *Ukrain. Khem. Zhur.* **7**, *Wiss. Abt.* 179 (1932).
[17] H. Gilman and D. A. Shirley, *J. Amer. Chem. Soc.* **66**, 888 (1944).
[18] F. K. Kirchner, A. E. Soria and C. J. Cavallito, *J. Amer. Chem. Soc.* 77, 4599 (1955).

picrate, yellow needles or prisms m.p. 74° crystallized from ethanol. (Found: C, 39·78; H, 4·98; N, 15·54. Calc. for $C_6H_{15}NS{\cdot}C_6H_3N_3O_7$: C, 39·78; H, 4·97; N, 15·47%).

3-*Dimethylaminopropyl sulphide* (XX). This was prepared from 3-dimethylaminopropyl chloride and sodium sulphide nonahydrate in ethanol in accordance with the method of McAllan, *et al.*[19] The *picrate*, yellow scales m.p. 146° (Found: C, 39·88; H, 4·56; N, 16·88. Calc. for $C_{10}H_{24}N_2S{\cdot}C_{12}H_6N_6O_{14}$: C, 39·82; H, 4·82; N, 17·07%).

3-*Dimethylaminopropyl disulphide* (XXXIII). This was prepared from 3-dimethylaminopropyl chloride hydrochloride and thiourea by the procedure of Clinton, *et al.*[20] The *picrate*, yellow prisms m.p. 147–149° crystallized from acetone–ethanol. (Found: C, 38·42; H, 4·53; N, 16·09. Calc. for $C_{10}H_{24}N_2S_2{\cdot}C_{12}H_6N_6O_{14}$: C, 38·03; H, 4·35; N, 16·13%).

Methyl dithiolcarbonate (XXII). Ammonium dithiocarbamate (11 g) was refluxed with methyl iodide (28·4 g) in acetone with formation of colourless plates of methyl dithiolimide hydroiodide and ammonium iodide. The precipitate (16·5 g) was collected and hydrolysed in water for 1 hr at 100°. The mixture was extracted with ether, dried (Na_2SO_4) and evaporated to dryness, b.p. 70°/25 mm, yield 4·7 g λ_{max} 5·70 (w), 6·05 (s) and 11·65 μ(s). (Found: C, 29·77; H, 5·13. Calc. for $C_3H_6OS_2$: C, 29·48; H, 4·94%).

DL-*threo*-1-*Phenyl*-2-*dimethylaminopropyl methyl sulphide* (*threo*-XXXI) *and* DL-*threo*-1-*phenyl*-2-*dimethylaminopropyl disulphide* (*threo*-XXXII). DL-*threo*-1-Phenyl-2-dimethylaminopropyl chloride hydrochloride[21] (9·35 g) and sodium thiosulphate pentahydrate (12·4 g) was refluxed in 215 ml 50% ethanol for 5 hr. During evaporation under red press, the Bunte salt precipitated (yield 7·8 g). A solution of the Bunte salt (2 g) in 20 ml ethanol and conc HCl was refluxed for 2 hr, and then condensed *in vacuo*. A sample of the residue was methylated with dimethyl sulphate and aqueous sodium hydroxide in the usual way. The product gave two picrates which were separated by solubility difference in warm ethanol. The more soluble recrystallized from ethanol, yellow plates (*threo*-XXXI) m.p. 170–171°. (Found: C, 49·57; H, 5·28; N, 13·02. Calc. for $C_{12}H_{19}NS{\cdot}C_6H_3N_3O_7$: C, 49·31; H, 5·06; N, 12·78%). The insoluble picrate m.p. 200° (dec) was identical with *threo*-XXXII described below. The remainder was treated with iodine in aqueous sodium hydroxide to cause precipitation and recrystallized from acetone as colourless prisms, m.p. 172°. (Found: C, 68·10; H, 8·33; N, 7·61. $C_{22}H_{32}N_2S_2$ requires: C, 67·99; H, 8·30; N, 7·21%). *Picrate*: m.p. 200° (dec).

General method for preparation of alkyl S-*methyl xanthates*

To a suspension of 1 mole powdered sodium in anhydrous ether[22] 1 mole alkanol (ROH, Table 1) was added and refluxed with stirring. After the sodium had reacted, 1·2 mole carbon disulphide was added with ice cooling, stirred for 1–2 hr at room temp and then 1 mole methyl iodide added with stirring. After agitation for about 30 hr, the mixture was filtered, washed with water, dried (Na_2SO_4) and the solvent removed leaving the xanthate (Table 1) and the corresponding alkanol (ROH) was regenerated by hydrolysis. The distillation of I, *trans*-IX and XXIV should be avoided, as they are converted to the corresponding dithiolcarbonates (see the following item).

DL-*threo*-1-*Phenyl*-2-*dimethylaminopropyl methyl dithiolcarbonate* (*threo*-XXVII). The preparation of DL-*threo*-1- phenyl-2-dimethylaminopropyl S-methyl xanthate (*threo*-XXIII) was attempted from DL-*threo*-1-phenyl-2-dimethylaminopropanol (5·8 g) according to the general method for the preparation of xanthates. The oily substance was produced and gradually crystallized after several days. But after washing with pet ether, the crystals, m.p. 56–60°, already showed the characteristic band (I.R.) due to the dithiolcarbonate function. Distillation, b.p. 160–162°/2·5 mm followed by recrystallization from pet ether gave colourless plates of m.p. 60–61°, yield 3·7 g. Infra-red absorption: 5·77 (w), 6·09 (s) and 11·55 μ(s). (Found: C, 57·84; H, 7·04; N, 5·00. $C_{13}H_{19}NOS_2$ requires: C, 57·97; H, 7·05; N, 5·20%). *Picrate*: yellow plates (ethanol), m.p. 142–143·5°.

DL-*erythro*-1-*Phenyl*-2-*dimethylaminopropyl methyl dithiolcarbonate* (*erythro*-XXVII). *Erythro*-XXVII was prepared from DL-*erythro*-1-phenyl-2-dimethylaminopropanol (6·3 g) as in the case of *threo*-XXVII (yield 6·1 g). Recrystallization from pet ether gave colourless plates, m.p. 83–84·5°. Infra-red absorption: 5·72 (w), 6·07 (s), and 11·51 μ(s). (Found: C, 58·22; H, 7·10; N, 4·94, $C_{13}H_{19}NOS_2$ requires: C, 57·97; H, 7·05; N, 5·20%).

[19] D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler, *J. Amer. Chem. Soc.* **73**, 3627 (1951).
[20] O. Clinton, U. J. Salvador, S. C. Laskowski and C. M. Suter, *J. Amer. Chem. Soc.* **70**, 950 (1948).
[21] T. Taguchi, T. Tomoeda and T. Koga, *Pharm. Bull. Tokyo* **5**, 189 (1957).
[22] Solvent is replaced by benzene and toluene for the preparation of XXV and XXVI respectively.

TABLE 1. ALKYL S-METHYL XANTHATE, ROC═S(SCH_3)

R	Yield% (crude prod)	I.R. μ	Appearance, m.p. and b.p.	Analyses		
				Formula	Found	Calcd.
2-Diethylaminoethyl (I)	72·2	8·17(s) 9·36(s)	*Picrate*: yellow cubes, m.p. 81–82° (acetone–ether)	$C_8H_{17}NOS_2 \cdot C_6H_3N_3O_7$	C, 38·46 H, 4·85 N, 12·56	C, 38·51 H, 4·58 N, 12·84
DL-*trans*-2-Dimethylamino-cyclohexyl (*trans*-IX)	88·0	8·15(s) 9·47(s)	*Picrate*: yellow needles, m.p. 141–143° (dec) (ethanol) *Methiodide*: colourless plates, m.p. 155–156° (dec) (acetone–ether)	$C_{10}H_{19}NOS_2 \cdot C_6H_3N_3O_7$	C, 41·81 H, 5·00 N, 12·05	C, 41·56 H, 4·76 N, 12·11
DL-*cis*-2-Dimethylamino-cyclohexyl (*cis*-IX)	23·1	8·22(s) 9·47(s)	*Picrate*: yellow needles, m.p. 122–126° (ethanol) b.p. 135–137°/5 mm	$C_{10}H_{19}NOS_2 \cdot C_6H_3N_3O_7$	C, 41·75 H, 4·99 N, 12·24	C, 41·56 H, 4·76 N, 12·11
Cyclohexyl (XVI)	97·8	8·25(s) 9·47(s)	b.p. 117°/5 mm	$C_8H_{14}OS_2$	C, 51·01 H, 7·60	C, 50·48 H, 7·41
3-Dimethylaminopropyl (XVII)	49·6	8·22(s) 9·45(s)	b.p. 97°/3 mm, *Picrate*: yellow needles, m.p. 133–135° (ethanol) *Methiodide*: colourless plates, m.p. 125° (dec) (acetone–ether)	$C_7H_{15}NOS_2 \cdot C_6H_3N_3O_7$	C, 37·03 H, 4·33 N, 13·29	C, 36·96 H, 4·26 N, 13·29
DL-*trans*-2-(1′-piperidyl)-cyclohexyl (XXIV)	90·1	—	*Picrate*: yellow needles, m.p. 150–152° (dec) (methanol) *Hydrochloride*: colourless needles, m.p. 147–148° (dec) (acetone)	$C_{13}H_{23}NOS_2 \cdot C_6H_3N_3O_7$	C, 45·48 H, 5·23 N, 11·16	C, 45·42 H, 5·18 N, 11·15
2-Benzamidoethyl (XXV)	16·1	—	colourless needles m.p. 62–65° (ether)	$C_{11}H_{13}NO_2S_2$	C, 51·56 H, 5·55 N, 5·74	C, 51·74 H, 5·13 N, 5·48
DL-*trans*-2-Benzamidocyclo-hexyl (XXVI)	40·8	—	colourless needles, m.p. 160° (dec) (ethyl acetate)	$C_{15}H_{19}NO_2S_2$	C, 58·62 H, 6·24 N, 4·51	C, 58·22 H, 6·19 N, 4·53

Pyrolysis of 3-*Dimethylaminopropyl* S-*methyl xanthate* (XVII)

Formation of XVIII, XIX, XX, XXI, and XXII. XVII (1·7 g) was heated at 150° for 30 min with evolution of carbonyl sulphide. The pyrolysis product was submitted to fractional distillation, yielding (a) 400 mg, b.p. 70°/30 mm; (b) 600 mg, b.p. 96°/2 mm and (c) 250 mg, b.p. 135–136°/2 mm. Fraction (a) was extracted with a mixture of ether and 10% HCl. The residue (180 mg) from the ether layer was identical with methyl dithiolcarbonate (XXII) in the I.R. spectrum and hydrolysis of it in alcoholic potassium hydroxide gave methylmercaptan and potassium carbonate. The hydrochloric acid layer was concentrated *in vacuo* to leave 300 mg of hygroscopic crystals, m.p. 60–75°. *Methiodide*: colourless plates (acetone–ether), m.p. 198–200° (dec). *Picrate*: yellow needles (ethanol), m.p. 74–75° alone and on admixture with an authentic sample of XIX.

Fraction (b) dissolved in 10% HCl was evaporated to dryness, extracted with hot acetone and filtered. The filtrate was evaporated to dryness to leave 640 mg XVIII, m.p. 85–115°. The picrate recrystallized from ethanol as yellow prisms, m.p. 96°. (Found: C, 37·26; H, 4·55; N, 13·29. $C_7H_{15}NOS_2 \cdot C_6H_3N_3O_7$ requires: C, 36·96; H, 4·26; N, 13·29%). Infra-red absorption: 5·70 (w), 6·06 (s), and 11·53 μ(s). The residue from the acetone extraction (above mentioned) 150 mg was recrystallized from ethanol–acetone, m.p. 160–170°. The mother liquor was set aside for the subsequent treatment and the crystals were converted to the picrate, m.p. 117–132° (200 mg). Recrystallization from acetone–methanol gave two picrates, m.p. 151–154° (50 mg) and 124–140° (60 mg). The former picrate was not characterized but the latter was identified as XX-picrate by a mixed m.p. determination. The mother liquor (ethanol–acetone solution) was evaporated to dryness and converted to the picrate, m.p. 126–146° (110 mg) which showed no depression on admixture with a sample of XX.

Fraction (c) with hydrochloric acid yielded the *hydrochloride* of XXI, m.p. 205–208° (dec) 160 mg. Infra-red absorption: 5·72 (w), 6·08 (s) and 11·34 μ(s). The *picrate:* yellow prisms m.p. 159–162° from ethanol–acetone. (Found: C, 38·33; H, 4·37; N, 15·30. $C_{11}H_{24}N_2OS_2 \cdot C_{12}H_6N_6O_{14}$ requires: C, 38·22; H, 4·18; N, 15·51%).

Hydrolyses of dithiolcarbonates followed by methylation or oxidation

(a) *Formation of* 2-*diethylaminoethyl disulphide* (IV). A solution of 700 mg 2-dimethylaminoethyl methyl dithiolcarbonate (II) in 5 ml of 1 N-ethanolic sodium hydroxide was refluxed for 1 hr, precipitated sodium carbonate filtered off and ethanolic hydrochloric acid added to evolve methyl mercaptan and carbon dioxide. After evaporation to dryness under red press, the residue was oxidized with iodine until the nitroprusside test for thiol group was negative. *Picrate*: yellow needles m.p. 148–150° from methanol. (Found: C, 40·01; H, 5·02; N, 15·60. $C_{12}H_{28}N_2S_2 \cdot C_{12}H_6N_6O_{14}$ requires: C, 39·85; H, 4·75; N, 15·50%).

(b) *Formation of* DL-*trans*-2-*dimethylaminocyclohexyl disulphide* (XII) *and* DL-*trans*-2-*dimethylaminocyclohexyl methyl sulphide* (XIII). Hydrolysis of *trans*-XI (2 g) was worked up in the atmosphere of nitrogen as for II. The hydrolysed product (1·96 g) was methylated with dimethylsulphate in aqueous sodium hydroxide. The mixture was extracted with ether, washed with water, dried (Na_2SO_4) and evaporated to dryness. The residue was converted to the picrate, 0·45 g, which, after fractional recrystallization from ethanol yielded a small quantity of yellow needles, m.p. 200–208° (dec) identical with an authentic sample of XII·picrate. The concentration of the mother liquor and recrystallization from ethanol gave yellow plates (0·31 g), m.p. 132–134° identical with an authentic sample of XIII·picrate.

(c) *Formation of* DL-*trans*-2-(1′-*piperidyl*)*cyclohexyl disulphide*. Hydrolysis of XVIII (1 g) as in the treatment of II gave 0·67 g of the corresponding thiol hydrochloride, m.p. 195° (dec), which was oxidized with iodine. *Hydrochloride*: colourless needles (ethanol–ethyl acetate), m.p. 252° (dec). (Found: C, 55·67; H, 9·02; N, 6·13. $C_{22}H_{40}N_2S_2 \cdot 2HCl$ requires: C, 56·26; H, 9·02; N, 5·97%).

(d) *Formation of* DL-*threo*-1-*phenyl*-2-*dimethylaminopropyl methyl sulphide* (*threo*-XXXI) *and* DL-*threo*-1-*phenyl*-2 *dimethylaminopropyl disulphide* (*threo*-XXXII). The hydrolysis of the *threo*-XXII followed by methylation or oxidation was carried out as described under (a) and (b) to yield *threo*-XXXI or *threo*-XXXII. The *picrate* of *threo*-XXXI, yellow prisms from ethanol, m.p. 170–171° was identical with an authentic sample. *Threo*-XXXII, colourless plates from acetone, m.p. 172° was also identical with an authentic sample.

(e) *Formation of* DL-*erythro*-1-*phenyl*-2-*dimethylaminopropyl methyl sulphide* (*erythro*-XXXI). *Erythro*-XXXI was obtained on treatment of the *erythro*-XXII as in (b) and (d). The *picrate*, yellow

General method for the formation of alkyl methyl dithiolcarbonates

The dithiolcarbonates were produced by rearrangement during vacuum distillation of the corresponding xanthates. (Table 2)

TABLE 2. ALKYL METHYL DITHIOLCARBONATE RSC(=O)(SCH$_3$)

R	B.p. or re-arrangement temperature	Yield %	I.R. μ	Appearance and m.p.	Analyses		
					Formula	Found	Calcd.
2-Diethylaminoethyl (II)	114–115°/5 mm	85·5	5·71(w) 6·03(s) 11·55(s)	*Picrate*: yellow prisms, m.p. 103–104° (methanol)	$C_8H_{17}NOS_2 \cdot C_6H_3N_3O_7$	C, 38·38 H, 4·53 N, 12·55	C, 38·51 H, 4·58 N, 12·84
DL-*trans*-2-Dimethyl-aminocyclohexyl (*trans*-XI)	136°/6 mm	84·1	5·73(w) 6·08(s) 11·59(s)	*Picrate*: yellow plates, m.p. 167–168° (dec) (ethanol)	$C_{10}H_{19}NOS_2 \cdot C_6H_3N_3O_7$	C, 41·81 H, 5·00 N, 12·05	C, 41·56 H, 4·76 N, 12·11
DL-*trans*-2-(1′-Piperidyl)-cyclohexyl (XXVIII)	162°/5 mm m.p. 59–61°	81·5	5·71(w) 6·05(s) 11·55(s)	*Picrate*: yellow plates, m.p. 136–137° (ethanol) *Hydrochloride*: colourless plates, m.p. 177° (dec) (acetone)	$C_{13}H_{23}NOS_2 \cdot C_6H_3N_3O_7$	C, 45·37 H, 5·22 N, 11·09	C, 45·42 H, 5·18 N, 11·15

plates m.p. 146–148° from methanol. (Found: C, 49·33; H, 5·23; N, 12·39. $C_{12}H_{19}NS{\cdot}C_6H_3N_3O_7$ requires: C, 49·31; H, 5·06; N, 12·78%).

(f) *Formation of 3-dimethylaminopropyl disulphide.* (i) XVIII was hydrolysed and then oxidized as in (a) to yield XXXIII and methyl mercaptan. The *picrate*, m.p. 147–149° was identical with an authentic sample. (ii) Hydrolysis of XXI followed by oxidation with iodine as in (a) yielded XXXIII. The *picrate*, 147–148° was identical with an authentic sample. Methyl mercaptan was not detected in the course of hydrolysis.

Heating of cyclohexyl S-*methyl xanthate* (XVI) *in dimethylaniline*

A solution of 7 g XVI in 14 g dimethylaniline was refluxed in a flask with an air condenser for 30 min, evolving methyl mercaptan and carbonyl sulphide which were absorbed in alcoholic sodium hydroxide. The former product was characterized by conversion to 2,4-dinitrophenyl methyl sulphide, golden yellow plates m.p. 124–126°, and the latter was confirmed by a qualitative test of its hydrolysis products, carbon dioxide and hydrogen sulphide. The reaction product was distilled at 80–82°, yielding 2·1 g identical with cyclohexene in the I.R. spectrum.

Pyrolysis of DL-*cis-2-dimethylaminocyclohexyl* S-*methyl xanthate* (*cis*-IX)

The *cis*-IX (0·6 g) was heated at 200° and the evolved gas absorbed in alcoholic potassium hydroxide. After filtration of potassium carbonate, 2,4-dinitrochlorobenzene was added to the alcoholic solution yielding golden yellow plates of 2,4-dinitrophenyl methyl sulphide, m.p. and a mixed m.p. with an authentic sample 124–126°. The pyrolysis residue was treated with 2 ml 10% HCl, set aside for 3½ hr, extracted with ether and evaporated to dryness. The residue was distilled with ethanol several times and the distillate collected. The 2,4-dinitrophenyl hydrazone was prepared from the alcoholic distillate and recrystallized from ethanol, 510 mg of orange yellow plates, m.p. 155–156° identical with an authentic sample of the cyclohexanone derivative. The hydrochloric acid solution was evaporated *in vacuo* and the residue recrystallized from ethanol–ethylacetate. The hydrochloride was changed to the picrate, m.p. 130–147° (40 mg) identical with an authentic sample of the dimethylamine derivative. To the mother liquor from the recrystallization of the hydrochloride an aqueous solution of sodium picrate was added to give two picrates, the first oily and the second a solid precipitate. Several recrystallizations of the latter gave yellow prisms, m.p. 170–173° (dec) identical with an authentic sample of the 3-dimethylaminocyclohexene derivative. After addition of methanol, the oily picrate crystallized and recrystallization from ethanol gave yellow prisms, m.p. 118–125°, identical with the picrate of the starting material (*cis*-IX).

Pyrolysis of 2-benzamidoethyl S-*methyl xanthate* (XXVI)

Compound XXVI (530 mg) was heated at 100–110° until the methyl mercaptan and carbonyl sulphide were evolved. The oily residue was converted to the picrate, yellow needles, 450 mg, m.p. 177° (dec) without recrystallization and identical with the 2-phenyloxazoline derivative.[23]

If 2-phenyloxazoline picrate was recrystallized from methanol, it was converted to the picrate of 2-aminoethyl benzoate, m.p. 188–190° (dec). (Found: C, 46·28; H, 3·79; N, 14·23. Calc. for $C_9H_{11}NO_2{\cdot}C_6H_3N_3O_7$: C, 45·94; H, 3·58; N, 14·21%).

Pyrolysis of DL-*trans-2-benzamidocyclohexyl* S-*methyl xanthate* (XXVII)

Compound XXVII (1 g) was heated at 160–165° and after cooling, the residue solidified to a wax-like substance, b.p. 126–127°/8 mm, 500 mg and m.p. 45–46° identical with an authentic sample of DL-*cis*-2-phenyl-4,5-cyclohexano-oxazoline.

Acknowledgements—The authors are deeply grateful to the Yoshitomi Seiyaku Co., Ltd. for supplying some raw material. They are also indebted to the Microanalytical Section of this Institute for micro-analyses and also for infra-red spectral measurements. Part of expenses of this study was defrayed by the Grant-in-Aid for Institutional Research from the Ministry of Education which is gratefully acknowledged.

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