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THERMAL REARRANGEMENT OF XANTHATES TO DITHIOLCARBONATES-II. MECHANISM STUDY[1]

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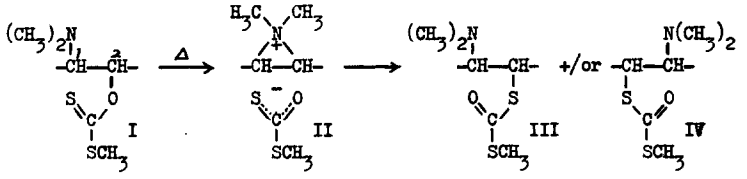
IN the first paper[2] of this series, the unusual case of the Chugaev reaction that pyrolysis causes rearrangement of xanthates to dithiolcarbonates with retention of configuration was reported. The participation of neighbouring group was found necessary for the rearrangement, because the rearrangement took place only on the treatment of compounds holding an anchimeric group adjacent to the xanthate group, such as β-dimethylaminoalkyl S-methyl xanthate (I). There are three possible pathways for the rearrangement of I; (a) through a SNi-type mechanism to afford III, (b) through 1,2-shift to afford IV and (c) through both together to afford III and IV. Pyrolysis of



DL-diastereomers of 1-phenyl-2-dimethylaminopropyl S-methyl xanthate (V) yielded the corresponding dithiolcarbonates[2] without any shift of group,

[1] Studies in Stereochemistry XXX.

[2] T. Taguchi and M. Nakao, Tetrahedron 18, 245 (1962).

$C_6H_5\overset{1}{C}H(O\overset{\overset{S}{\|}}{C}SCH_3)\overset{2}{C}H(\overset{3}{C}H_3)N(CH_3)_2$ suggesting that the rearrangement had occurred on the same carbon atom (C_1). But this aspect of the rearrangement could not be generalized, because there was the obscurity that each of other β-dimethylaminoalkyl S-methyl xanthates treated gave the corresponding dithiolcarbonate the formation of which could be attributed to any of transformations with or without shift or both[2]. The obscurity led to the present study which attempts to reveal the true feature of the rearrangement.

As materials for the study, two pairs of position isomers and an optically active diastereomer were chosen among β-dimethylaminoalkyl S-methyl xanthates. The table shows xanthates submitted to pyrolysis, which were prepared from the corresponding alcohols[3] by the general method[2]. The precursor of l-XXI, (-)trans-2-dimethylaminocyclohexanol (l-XX), was prepared by optical resolution of the corresponding racemic compound in the following way: Treatment of DL-XX with dibenzoyl-L-tartaric acid followed by recrystallization from acetone-ethanol gave l-XX hydrogen dibenzoyl-L-tartarate, yield 86 %, m.p. 104-105° (dec.), $[\alpha]_D^{28}$ - 82.5° (EtOH) (Found: C, 62.37; H, 6.24; N, 3.08. Calcd. for $C_8H_{17}NO \cdot C_{18}H_{14}O_8$: C, 62.26; H, 6.23; N, 2.79). Treatment of the salt with alkali followed by vac. distillation gave l-XX[4], b.p. 60°/5 mm, yield 80.7 %, $[\alpha]_D^{27}$ - 45.2° (EtOH) (Found: C, 67.28; H, 12.21; N, 9.52. Calcd. for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.78). Vacuum distillation of crude xanthates, VIII, IX, XV, XVI, and l-XXI, induced over-all rearrangement to dithiolcarbonates.

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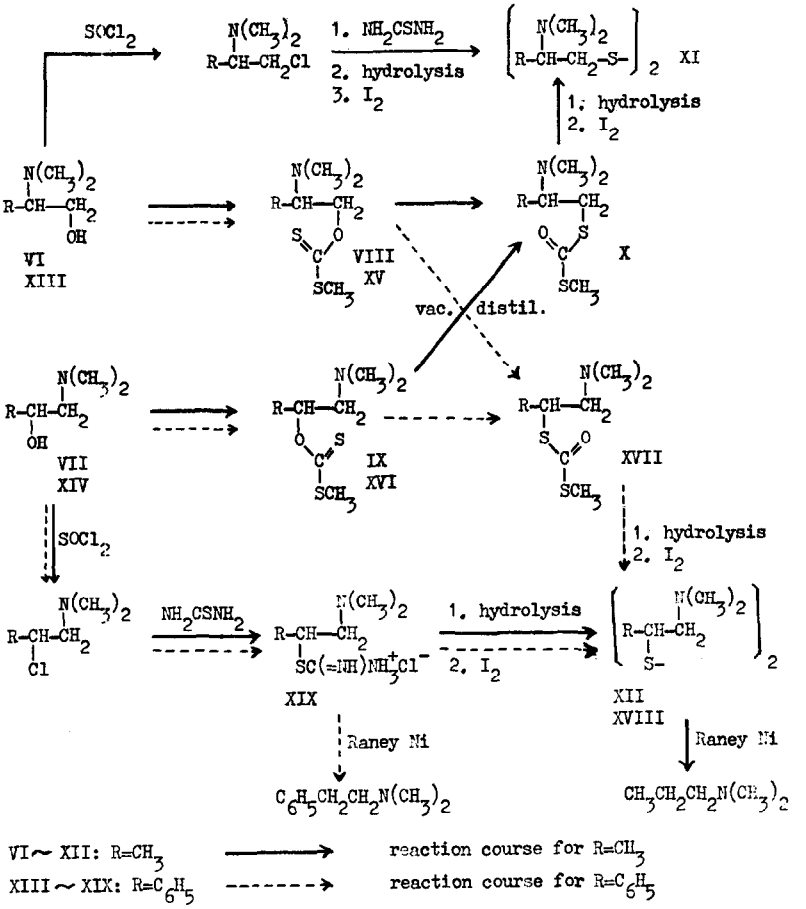
[3] VI: P. Karrer, Helv.Chim.Acta 5, 477 (1922).
VII: E.M. Schlutz and J.M. Sprague, J.Amer.Chem.Soc. 70, 48 (1948).
XIII: De Lestrange and Lévy, Bull.Sci.Pharmacol. 36, 356 (1929).
XIV: W.S. Emerson, J.Amer.Chem.Soc. 67, 516 (1945).

[4] The (+)antipode [b.p. 95°/15 mm, $[\alpha]_{579}$ + 36.5°, $[\alpha]_{546}$ + 41.2° (EtOH)] has been prepared by methylation of (+)trans-2-methylaminocyclohexanol by M. Mousseron, R. Granger, G. Combes and V.A. Pertzoff [Bull.Soc.Chim. Fr. 850 (1947)].

Table Alkyl S-methyl xanthates

Alkyl	Picrate			
	Appearance and m.p. from EtOH	Formula	Analysis Found	Calcd.
DL-2-Dimethylaminopropyl (VIII)	yellow prisms 128° (dec.)	$C_7H_{15}NOS_2 \cdot C_6H_3N_3O_7$	C,36.75 H, 4.44 N,13.20	C,36.94 H, 4.30 N,13.26
DL-2-Dimethylaminoisopropyl (IX)	yellow prisms 122° (dec.)	$C_7H_{15}NOS_2 \cdot C_6H_3N_3O_7$	C,37.29 H, 4.42 N,13.11	C,36.94 H, 4.30 N,13.26
DL-2-Phenyl-2-dimethylaminoethyl (XV)	yellow plates 115–116° (dec.)	$C_{12}H_{17}NOS_2 \cdot C_6H_3N_3O_7$	C,44.62 H, 4.22 N,11.82	C,44.63 H, 4.16 N,11.56
DL-1-Phenyl-2-dimethylaminoethyl (XVI)	yellow flakes 139° (dec.)	$C_{12}H_{17}NOS_2 \cdot C_6H_3N_3O_7$	C,44.29 H, 4.30 N,11.67	C,44.63 H, 4.16 N,11.56
(-)trans-2-Dimethylaminocyclohexyl (l-XXI)	yellow needles 151° (dec.)	$C_{10}H_{19}NOS_2 \cdot C_6H_3N_3O_7$	C,41.43 H, 4.73 N,11.97	C,41.56 H, 4.76 N,12.05

VIII and IX, a pair of position isomers, gave a same rearrangement product, DL-2-dimethylaminopropyl methyl dithiolcarbonate (X), b.p. 97-98°/2.5 mm (picrate. yellow prisms of m.p. 89-90° (Found: C, 37.16; H,4.36; N, 13.32. Calcd. for $C_7H_{15}NOS_2 \cdot C_6H_3N_3O_7$: C, 36.94; H, 4.30; N, 13.26)). The structure of X was confirmed by the fact that its oxidation product, DL(or meso)-2-dimethylaminopropyl disulfide (XI) (picrate. yellow plates of m.p. 200° (dec.) (Found: C, 38.18; H, 4.53; N, 15.98. Calcd. for $C_{10}H_{24}N_2S_2 \cdot C_{12}H_6N_6O_{14}$: C, 38.03; H, 4.35; N, 16.19)), differed from the position isomer, DL(or meso)-2-dimethylaminoisopropyl disulfide (XII) (picrate. yellow plates of m.p. 181-182° (dec.) (Found: C, 38.04; H, 4.44; N, 16.28. Calcd. for $C_{10}H_{24}N_2S_2 \cdot C_{12}H_6N_6O_{14}$: C, 38.03; H, 4.35; N, 16.19)), which was hydrogenolyzed over Raney nickel to



1-dimethylaminopropane[5], providing evidence for the structure of XII. The oxidation of X to XI was carried out by the usual method[2]. The disulfide (XII) was synthesized from the aminoalcohol (VII) through chlorination of the hydroxyl group by $SOCl_2$, followed by replacement by thiourea, hydrolysis

[5] W. Hanhart and C.K. Ingold, J.Chem.Soc. 997 (1927).

and oxidation by iodine[6]. The other pair of position isomers, XV and XVI, also gave the same pyrolysis product, DL-1-phenyl-2-dimethylaminoethyl methyl dithiolcarbonate (XVII), b.p. 144-145°/2.5 mm (picrate, yellow plates of m.p. 139-140° (dec.) (Found: C, 44.56; H, 4.20; N, 11.34. Calcd. for $C_{12}H_{17}NOS_2 \cdot C_6H_3N_3O_7$: C, 44.63; H, 4.16; N, 11.56)). The structure of XVII was confirmed by the coincidence of its oxidation product (XVIII) with the synthesized product[6], DL(or meso)-1-phenyl-2-dimethylaminoethyl disulfide (picrate, yellow prisms of m.p. 164° (Found: C, 46.63; H, 4.50; N, 13.30. Calcd. for $C_{20}H_{28}N_2S_2 \cdot C_{12}H_6N_6O_{14}$: C, 46.93; H, 4.19; N, 13.69)). The authentic disulfide was furnished with evidence for arrangement of groups by the fact that hydrogenolysis of the precursor, DL-1-phenyl-2-dimethylaminoethyl isothiuronium chloride (XIX), over Raney nickel yielded 1-phenyl-2-dimethylaminoethane[7].

Thermal treatment of l-XXI resulted in the formation of DL-trans-2-dimethylaminocyclohexyl methyl dithiolcarbonate[2] with racemization. Summarizing the examples shown, a pair of a xanthate and its position isomer rearranges to the same dithiolcarbonate which corresponds to the product without shift (III) for one and to the product with countercurrent shift (IV) for the other. On the other hand, optically active xanthate rearranges to dithiolcarbonate with racemization, the fact implying that the transformations with and without shift together take place in equal proportions. These observations lead to the conclusion that the rearrangement might proceed generally through an ion pair like II in the transition state.

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[6] This synthetic route was successfully applied to derivation of VI and XIV to XI and XVIII respectively, showing no shift of group. Thus, in general, the reaction course as a whole seems to involve no shift of group.

[7] Organic Syntheses Vol. 25, p. 89, John Wiley and Sons, Inc., New York (1945).