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AN IMPROVEMENT IN SYNTHESES OF MERCAPTANS VIA THIOLESTERS

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In the reactions of 2-aminoethanol with trithiocarbonates(I), dithiolcarbonates(II) and xanthates(III), it was found that the reactions proceeded through the general reaction sequences as shown in Chart 1.

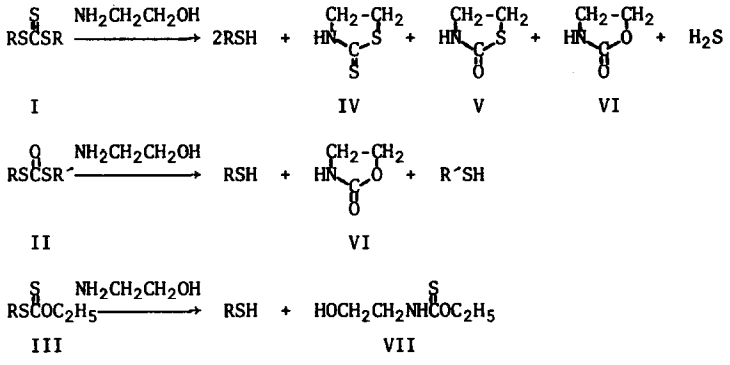


Chart 1

The formations of products in each reaction were demonstrated by following examples. A mixture of DL-trans-cyclohexene trithiocarbonate(Ia)[1] and 1 equiv. mole of 2-aminoethanol was heated at 80-120° and immediately the reaction started evolving hydrogen sulfide. After heating for a few minutes, the reaction mixture was distilled under a reduced pressure to afford DL-trans-cyclohexane-1,2-dithiol, b.p. 75-85°/5mmHg (see Table 1 (d) for identification). The remainder after distillation was chromatographed over alumina with ethyl acetate. From fractions 1, 2 and 3, there were isolated thiazolidine-2-thione(IV)[2], m.p. 98-103°, thiazolidine-2-one(V)[3], m.p. 52-54° and oxazolidine-2-one(VI)[4], m.p. 87-90°, respectively.

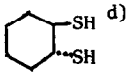
Also the reaction of ethylene dithiolcarbonate(IIa) with 2-aminoethanol was carried out analogously and the reaction mixture was distilled in vacuo. The distillate, b.p. 59-63°/30mmHg, was identical with authentic ethane-1,2-dithiol (see Table 2 (c)) and the residue was recrysta-

llized from ethanol to give VI, m.p. 88-89°.

Next, ethyl S-cyclohexyl xanthate(IIIa) was reacted with 2-aminoethanol in the way similar to the former both cases and the reaction mixture was distilled in vacuo to yield two oily substances. One, b.p. 47/18mmHg, was identified as cyclohexanethiol (see Table 3 (m) for identification) and the other, b.p. 132-133°/3.5mmHg, as ethyl N-2-hydroxyethylthionocarbamate (VII) by IR spectrum data and elemental analysis.

These findings suggested us the application of this method to the syntheses of mercaptans from thiolesters. As have been well-known, the preparations of mercaptans from thiolesters[5] are generally disadvantageous, because oxidation and sometimes polymerization[6] intervene during such operations as alkaline (basic) hydrolysis followed by acidification and isolation. In this view, the present method will be more suitable for the purpose because of the easier and less trouble operation. Trithiocarbonates(I), dithiolcarbonates(II) and xanthates(III) were treated analogously as in the case of Ia. Results are showen in Tables 1, 2 and 3 respectively.

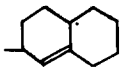
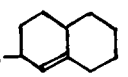
Table 1. Mercaptans from trithiocarbonates R_2CS_3

R or R-R	mercaptan	b.p. (C°)	yield(%)
CH_3-	CH_3SH a)	———	58
C_2H_5-	C_2H_5SH b)	34-37	80
CH_2- CH_2-	CH_2SH CH_2SH c)	58-63°/30mmHg	84
	 d)	75-85°/5mmHg	75

a) 2,4-dinitrophenyl methyl sulfide[7], m.p. 125-127°. b) 2,4-dinitrophenyl ethyl sulfide[7], m.p. 115°. c) by the comparison of the compound and an authentic sample [8] in IR spectra. d) bis(2,4-dinitrophenyl)derivative [9], m.p. 217°.

Ethane-1,2-dithiol which is inserted in Table 1 is commonly used for masking the carbonyl group, but the compound is not so suitable for reservation because susceptive to oxidation. Applying the present procedure, ethylene trithiocarbonate, more stable, may be reserved in place of the dithiol, because in case of need, the latter is liberated very easily from the former only by adding 2-aminoethanol and heating.

Table 2. Mercaptans from dithiolcarbonates $RS\overset{O}{\overset{\|}{C}}SR'$

R	R	mercaptan	b.p. (C°)	yield(%)
—CH_2-CH_2—		$HSCH_2$-CH_2SH c)	59-63/30mmHg	79
CH_2=CH-CH_2-	CH_3-	CH_2=CH-CH_2SH e)	68-69	60
CH_3-CH(SH)-CH=CH_2	CH_3-	CH_3-CH(SH)-CH=CH_2 f)	81-84	39
	CH_3-	 g)	———	62
cholesteryl-	CH_3-	cholestene-3-thiol h)	———	72
$(C_2H_5)_2NCH_2CH_2$-	CH_3-	$(C_2H_5)_2NCH_2CH_2SH$ i)	74/32mmHg	90

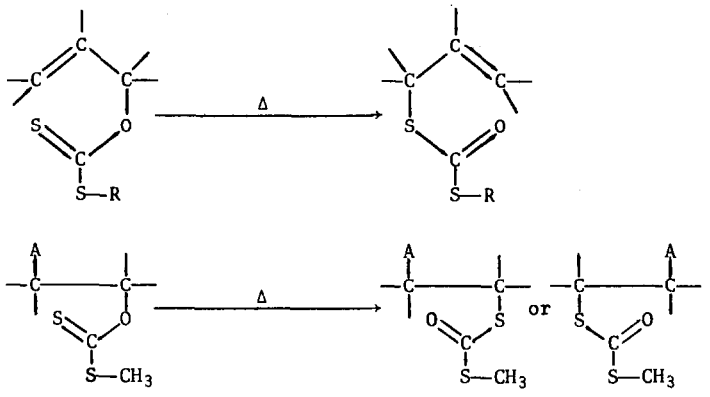
e) allyl 2,4-dinitrophenyl sulfide[10], m.p. 71.5°. f, g, h) The identifications of the products will appear in succeeding papers. i) The identification has appeared in reference[11].

Table 3. Mercaptans from xanthates $RS\overset{S}{\overset{\|}{C}}OC_2H_5$

R	mercaptan	b.p. (C°)	yield(%)
CH_3CH_2CH -	$CH_3CH_2CH_2SH$ j)	67-68	84
$CH_3(CH_2)_2CH_2$-	$CH_3(CH_2)_2CH_2SH$ k)	97-98	70
$C_6H_5CH_2$-	$C_6H_5CH_2SH$ l)	106-107/35mmHg	85
C_6H_{12}-	$C_6H_{12}SH$ m)	47/18mmHg	93
-CH_2CO_2H	$HSCH_2CO_2H$ n)	96/10mmHg	64

j) 2,4-dinitrophenyl propyl sulfide[7], m.p. 85-86°. k) butyl 2,4-dinitrophenyl sulfide[7], m.p. 66-67°. l) benzyl 2,4-dinitrophenyl sulfide[7], m.p. 129-130°. m) cyclohexyl 2,4-dinitrophenyl sulfide [10], m.p. 147-148°. n) identified by elemental analysis and comparison with an authentic sample[12] in IR spectra.

Of mercaptans listed in Table 2, non-volatile compounds(g, h) were prepared by a modified procedure which will be reported in subsequent papers. It has been reported by us[11, 13] that allylic xanthates and alkyl xanthates holding an anchimeric group on C_β rearranged to the corresponding dithiolcarbonates (see Chart 2). This rearrangement reaction adds an advantage to the



A = RS- or R_2N-

Chart 2

present procedure in supply of dithiolcarbonates as starting materials indicated in Table 2.

As have been generally known, allylic mercaptan, when prepared from allylic halide, is susceptible to oxidation and polymerization[6] during the prolonged operation for isolation and sometimes accompanies the position isomer resulted from the partial allylic shift during the procedure[14]. These faults of the method are nearly ignored in the present procedure.

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