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Reactions of Epoxides. I. Synthesis of Trithiocarbonate by the Reaction of Epoxide with Alkali Xanthate

Seigoro Hayashi, Mitsuru Furukawa, Yoko Fujino,[1a] Toru Nakao,[1b] and Kenji Nagato

Faculty of Pharmaceutical Sciences, Kumamoto University[1a] *and Yoshitomi Seiyaku Co., Ltd.*[1b]

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Several mono and bistrithiocarbonates were synthesized by the reaction of the corresponding mono and bisepoxides with carbon disulfide in the presence of potassium hydroxide. These trithiocarbonates were successfully obtained even in the presence of a catalytic amount of potassium hydroxide. Potassium methoxide instead of potassium hydroxide as catalyst also gave trithiocarbonate in good yield.

Culvenor[2] has found that alkylene trithiocarbonate is formed by the reaction of epoxide with alkali xanthate. Durden[3] has also shown that the liquid phase reaction of ethylene oxide with carbon disulfide proceeds at 150° in the presence of amine catalyst to give ethylene trithiocarbonate in good yield. These reactions have, however, been chiefly attempted with a few simple epoxide, such as ethylene oxide, cyclohexene oxide and styrene oxide. Later no study on the reaction of epoxide with alkali xanthate has been reported in the literature, though a number of trithiocarbonates is synthesized by another synthetic route. Thus, we attempted to extend the reaction of epoxide with alkali xanthate as the general synthetic method of trithiocarbonate. This paper concerns with the synthesis of trithiocarbonate by the reaction between epoxide and carbon disulfide in the presence of alkali catalyst.

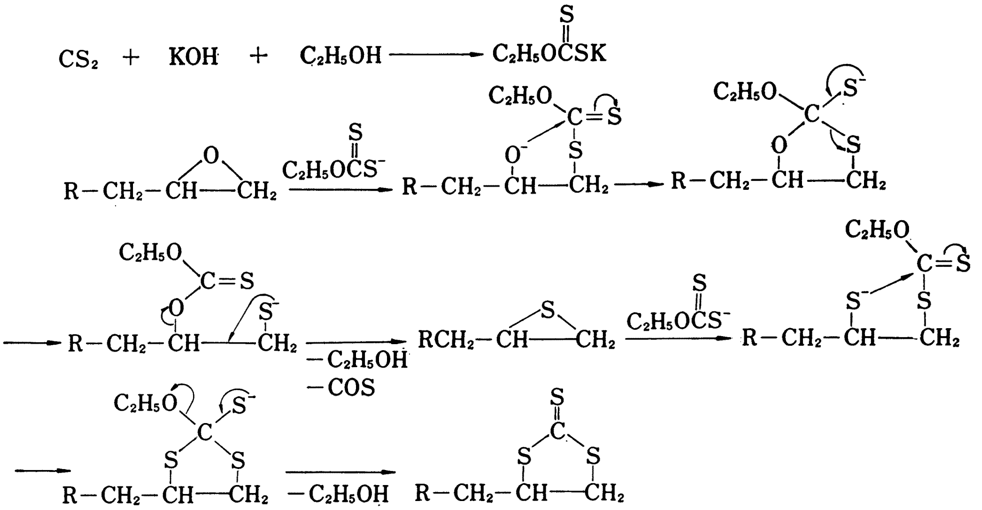

Chart 1

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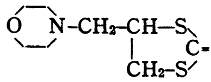
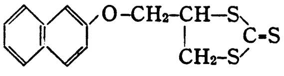
[1] Location: *a*) *Oe-moto-machi, Kumamoto*; *b*) *Yoshitomi-cho, Fukuoka.*

[2] C.C.J. Culvenor, W. Davies, and K.H. Pausacker, *J. Chem. Soc.*, **1946**, 1050.

[3] J.A. Durden, H.A. Stansbury, and W.H. Catlette, *J. Am. Chem. Soc.*, **82**, 3082 (1960).

The action of at least two moles of alkali xanthate on epoxide is necessary in this reaction, because the reaction proceeds through the formation of the intermediate, episulfide, though the intermediate can not be isolated from the reaction mixture (Chart 1). Therefore, Culvenor[2] has used two and half moles of potassium hydroxide and three moles of carbon disulfide to prepare two moles of alkali xanthate in the course of the reaction. However, in consideration of the reaction mechanism proposed by Creighton,[4] it is not necessary to use an excess of potassium hydroxide as catalyst, because potassium ethoxide is eliminated in the course of the reaction, which will behave as catalyst for the formation of alkali xanthate. In order to confirm this assumption, potassium methoxide instead of potassium hydroxide was used as catalyst in anhydrous condition and trithiocarbonate was found to obtain in about 90% yield as expected. Furthermore, variation of amounts of potassium hydroxide reacting with 3-morpholinopropylene oxide or 3-β-naphthyloxypropylene oxide and carbon disulfide in methanol was examined. Table I showed the relation between the amount of potassium hydroxide or potassium methoxide and the yield of the corresponding trithiocarbonate. In the case of the reaction of 3-β-naphthyloxypropylene oxide with potassium xanthate, the corresponding trithiocarbonate was exclusively observed to isolate from the reaction mixture and the reaction time required to isolate the crystals was also shown in Table I. Although the reaction time was prolonged by using the decreased amounts of potassium hydroxide or potassium methoxide, the yield was almost unchanged.

TABLE I. Yields of Trithiocarbonates in Variation of the Amounts of Potassium Hydroxide and Potassium Methoxide as Catalyst

Compound		KOH (mole)					KOMe (mole)				
		1.0	0.5	0.2	0.1	trace	1.0	0.5	0.2	0.1	trace
	yield (%)	88.2	85.1	78.5	74.9	over 50					
	yield (%)	92.3	92.3	93.7	86.6	over 50	96.1	92.3	—	97.1	over 50
	crystal isolation time (min)	30	60	100	100		40	50	—	155	

The reaction was most readily carried out by using one mole of potassium hydroxide or potassium methoxide with several mono and bisepoxides. Physical properties of the trithiocarbonates obtained were shown in Table II.

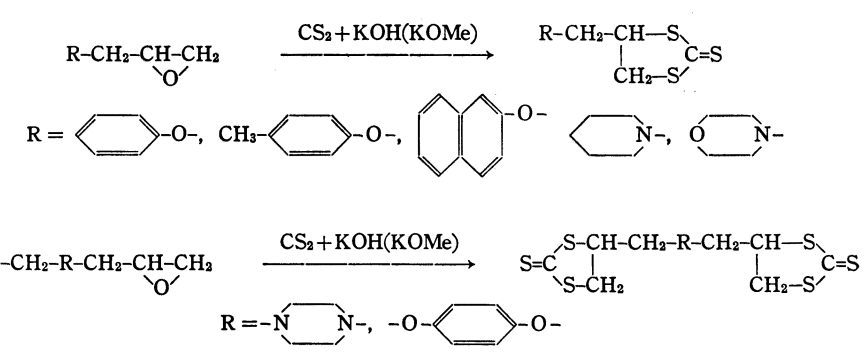


Chart 2

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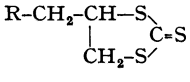
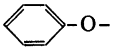
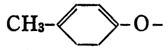
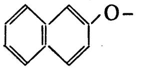
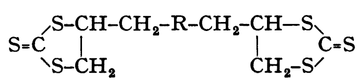
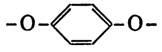
[4] A.M. Creighton and L.N. Owen, *J. Chem. Soc.*, **1960**, 1024.

Table II

No.	R	Yield (%)	mp or bp (°C)	Appearance	Recryst Solv.	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
												
I		88.8	66— 68	yellow needles	ligrion	$C_{10}H_{10}OS_3$	49.55	4.16		49.87	4.28	
II		93.0	43— 44	yellow needles	ligroin	$C_{11}H_{12}OS_3$	51.52	4.72		51.71	4.67	
III		92.3	135—136	yellow needles	toluene	$C_{14}H_{12}OS_3$	57.50	4.14		57.76	4.07	
IV		94.5	83.5	yellow prisms	toluene	$C_8H_{13}ONS_3$	40.82	5.57	5.95	40.89	5.42	6.03
V		77.2	183—187/2 mm	yellow liquid		$C_9H_{15}NS_3$	46.27	6.91	6.00	45.87	6.43	6.02
												
VI		89.1	230	yellow prisms	benzene	$C_{12}H_{18}N_2S_6$	37.66	4.74	7.32	38.14	4.84	7.47
VII		93.6	166—168	yellow prisms	benzene	$C_{14}H_{14}O_2S_6$	41.35	3.47		41.35	3.44	

It has been reported by Mecke[5] that simple trithiocarbonate exhibits the characteristic IR absorption of C=S group at 1053—1058 cm^{-1}. Jones[6] has observed that ethylene trithiocarbonate in carbon tetrachloride exhibited the strong absorption at 1074 cm^{-1}. All of the compounds obtained also exhibited strong IR absorptions in the range 1000—1100 cm^{-1}, though the precise identity of the C=S band is not certain in these case. The experimental elemental analytical values of these compounds agreed with those of the corresponding trithiocarbonates.

Table III. Infrared Absorption of Trithiocarbonate in the Range 1000—1100 cm^{-1}

Compound No.	Absorption ν_{max}^{KBr} (cm^{-1})
I	1006, 1036, 1059, 1068, 1072
II	1035, 1057, 1065, 1078
III	1015, 1022, 1037, 1055, 1070, 1083
IV	1001, 1010, 1022, 1035, 1061
V(a)	1015, 1040, 1065, 1080
VI	1009, 1050, 1060, 1085
VII	1005, 1030, 1041, 1059, 1070, 1084

a) in liquid film

Experimental

Epoxide——**a**) To a mixture of 1 mole of phenols and 2—3 moles of epichlorohydrin was added dropwise with stirring a solution of 1 mole of sodium methoxide in 300 ml of MeOH at 10—20°. The solution

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[5] R. Mecke, R. Mecke, and A. Luttringhaus, *Z. Naturforsch.*, **10b**, 367 (1955).

[6] J.I. Jones, W. Kynaston, and J. L. Hales, *J. Chem. Soc.*, **1957**, 614.

was stirred for 24 hr at 10—20°. Precipitated NaCl was filtered off and the filtrate was evaporated to remove MeOH. The residue was purified by distillation or recrystallization. 3-Phenoxypropylene oxide, bp 99°/2 mm. 3-*p*-Methylphenoxypropylene oxide, 131—132°/12 mm. 3-*β*-Naphthyloxypropylene oxide, mp 63—64°. *p*-Bis(2,3-epoxypropoxy)benzene, mp 117—119°.

b) One mole of epichlorohydrin was added dropwise with stirring to 1 mole of amines under cooling. To the mixture was added dropwise with stirring a slight excess of NaOH solution at 20—30°. The oil layer isolated was separated from aqueous layer. The aqueous layer was extracted three times with ether. Combined oil layer and ethereal extracts were dried over NaOH, evaporated to remove ether and purified by distillation or recrystallization. 3-Piperidinopropylene oxide, bp 92—94°/20 mm. 3-Morpholinopropylene oxide, bp 110—111°/30 mm. N,N-Bis(2,3-epoxypropyl)piperazine dihydrate, mp 63—64°.

Trithiocarbonate——a) To a solution of 0.03 mole of epoxides in 25 ml of CS_2 was added dropwise with stirring a solution of 0.03 mole of KOH in 50 ml of EtOH below 30°. The reaction mixture was heated with stirring for 6 hr under reflux. After removal of the solvent, the residue was poured into water. The resulting yellow precipitates were washed with H_2O, dried and recrystallized from suitable solvents. I, III, VI, and VII were prepared by this procedure. Physical data were shown in Table II.

b) To a solution of 0.03 mole of epoxides in 25 ml of CS_2 was added dropwise with stirring a solution of 0.03 mole of KOH in 50 ml of EtOH below 30°. The mixture was heated with stirring for 6 hr under reflux and then the solvent was distilled off under reduced pressure. The residue was poured into water and extracted with benzene. The extracts were dried over $NaSO_4$ and concentrated. Yellow precipitates deposited on cooling were recrystallized from benzene. II and IV were synthesized by this procedure. V was purified by distillation under reduced pressure. Physical data were shown in Table II.

c) 1-Naphthyloxypropylene 2,3-trithiocarbonate was prepared by the same procedure as (a) in 96.1% yield, using KOMe instead of KOH as catalyst.

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