Table VII

Isomerization of Cinnamyl Thiocyanate in Decalin at 153°

Time, hr.	RNCS, %	k_1, hr.$^{-1}$
0	7.8	...
0.5	9.2	0.030
1.25	11.2	.030
2.25	14.9	.034
3.0	18.4	.038
4.5	18	.026
8.25	29	.032
12.0	43	.040
18.0	56.4	.042

with *n*-butylamine reagent. The reactions in nitrobenzene and diphenylmethane were carried out with 0.995 *M* solutions at 153°.

The results are summarized in Tables VII and VIII. In both decalin and diphenylmethane, the reaction darkened appreciably, making end-points in the titrations difficult to observe. This factor and the sampling errors resulting from the insolubility of the substrate at room temperature probably are responsible for the erratic results from the decalin experiment.

Isomerization of Cinnamyl Thiocyanate in the Presence of Tri-*n*-butylamine.—A solution of 2.17 g. of cinnamyl thiocyanate in enough nitrobenzene to make 25.0 ml. was kept at 144° for 5.5 hr. A 5-ml. aliquot was extracted with 25 ml. of water, 10 ml. of which then required 0.91 ml. of 0.1028 *N* silver nitrate solution in a Volhard titration. This represents 9.4% of the original thiocyanate, or 16% of the amount of isothiocyanate which would have been formed in the absence of tri-*n*-butylamine, estimated from the foregoing experiment.

Table VIII

Isomerization of Cinnamyl Thiocyanate in Diphenylmethane and in Nitrobenzene at 153°

Time, hr.	Solvent: $(C_6H_5)_2CH_2$ RNCS, %	k_1, hr.$^{-1}$	$C_6H_5NO_2$ RNCS, %	k_1, hr.$^{-1}$
0	22		3.2	..
0.5	35	0.36	18	0.33
1.0	45	.35	30	.32
1.5	55	.37	42	.34
2.0	63	.37	49	.32
2.5	68	.36	52	.28
3.0	71	.33	54	.25
4.0	..	..	55	.19
5.0	78	0.25	..	..

Isomerization of 1-Naphthylmethyl Thiocyanate.—A mixture of 4.0 g. of 1-naphthylmethyl thiocyanate, 6.0 g. of nitrobenzene and 0.2 g. of anhydrous zinc chloride was heated at 50°, at which temperature it was liquid; samples withdrawn at times of 0, 6 and 20 hr. assayed 0, 51 and 62% isothiocyanate, respectively.

Ann Arbor, Mich.

[Contribution from the Research Department, Union Carbide Chemicals Co.]

The Preparation of Alkene Trithiocarbonates

By John A. Durden, Jr., Harry A. Stansbury, Jr., and William H. Catlette

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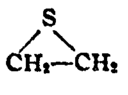
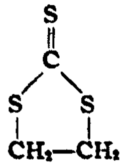
The reaction of alkylene oxides with carbon disulfide in the presence of tertiary amines under pressure has been studied. In most cases the product was the corresponding alkylene trithiocarbonate. The probable mechanism of this reaction is discussed. Several reactions of ethylene trithiocarbonate with amines have been studied.

The liquid phase reaction of ethylene oxide with carbon disulfide proceeds at 150° in the presence of amine catalyst to form 2-thio-1,3-dithiolane (II) (also known as ethylene trithiocarbonate) in 77% yield. No ethylene sulfide (I) could be isolated from the reaction mixture although the episulfide is undoubtedly a precursor of the ethylene trithiocarbonate. Infrared studies, analyses and mixed melting point determination confirmed that the product was ethylene trithiocarbonate.



I



II

Culvenor has shown that alkali xanthates react with alkylene oxides to give the corresponding trithiocarbonates in good to moderate yields.[1,2] Elkington has reported that alkylene trithiocarbonates are formed by the reaction of alkali metal xanthates with either alkylene glycols, dihalides, halohydrins or oxides.[3]

In order to determine optimum conditions for the amine-catalyzed reaction of ethylene oxide with carbon disulfide, several experiments were conducted in which one or more variables were changed. The results show that optimum yields were obtained with an initial nitrogen pressure of 34 atm. at 0°, a CS_2/oxide molar ratio of 2.5, 0.56 weight per cent. of trimethylamine and a reaction temperature of 150° for thirty minutes. When the ratio of carbon disulfide to ethylene oxide was reduced to unity, the yield of ethylene trithiocarbonate decreased considerably.

An investigation of the gases evolved from a run conducted under optimum conditions indicated the presence of carbonyl sulfide in an amount approximately equivalent to the ethylene trithiocarbonate formed and a lesser amount of carbon dioxide. When the ratio of carbon disulfide to ethylene oxide was decreased to unity, the amount of carbon dioxide in the off-gases increased at the expense of the carbonyl sulfide.

Examination of several materials as potential catalysts (Table I) showed that strongly basic tertiary amines were most active. Of these, trimethylamine was most effective. It is interesting to note that acidic substances actually inhibited the reaction. Rationalization of the catalytic activity of the materials in terms of either pK_a or structure is difficult. Perhaps the most effective

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(1) C. C. J. Culvenor, W. Davies and K. H. Pausacker, *J. Chem. Soc.*, 1050 (1946).

(2) C. C. J. Culvenor and W. Davies, *Australian J. Sci. Res., Ser. A*, 1, 236 (1948).

(3) H. D. Elkington, British Patent 496,290, May 29, 1937.

TABLE I

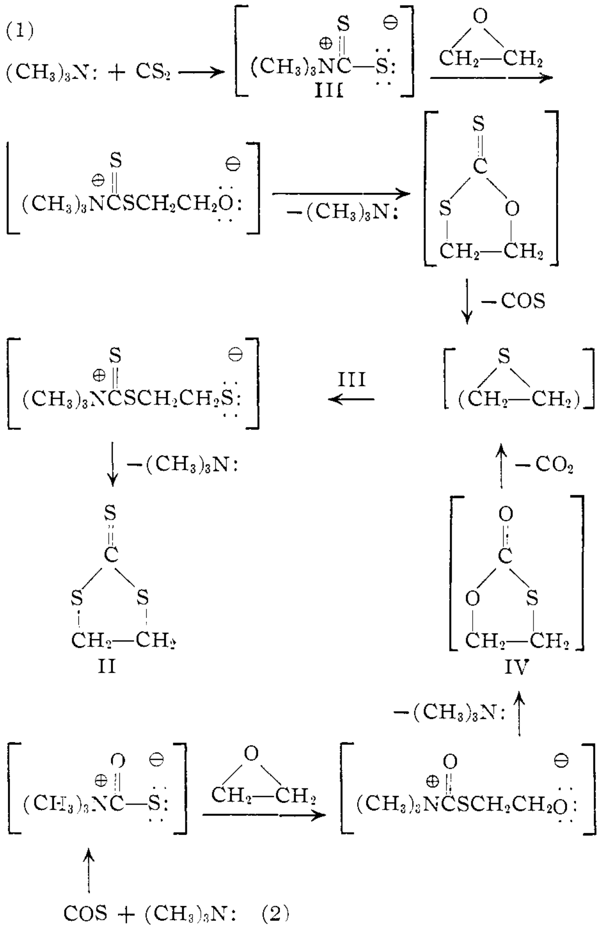
EVALUATION OF POTENTIAL CATALYSTS IN THE PREPARATION OF ETHYLENE TRITHIOCARBONATE[a]

Run	Compound	pK_a	Yield, %
1	Triethylamine	10.72	50
2	Triethylenediamine	. . .	52
3	Trimethylamine[b]	9.80	77
4	Pyridine	5.19	5
5	N-Methylmorpholine	<10.72[c]	2
6	Di-*n*-butyltin diacetate	Acid	0
7	Ammonium chloride	Acid	0

[a] Evaluation carried out in a stainless steel bomb containing 2.5 moles of carbon disulfide, one mole of ethylene oxide and 2% by weight of the desired catalyst (under an initial nitrogen pressure of 34 atm. at 0°) at 150° for 30 minutes. [b] 0.56% by weight. [c] B. A. Dombrow, "Polyurethanes," Reinhold Publishing Corp., New York, N. Y., 1957, p. 19.

catalyst, trimethylamine, combines the optimum in pK_a and steric requirements.

The following mechanism is proposed.



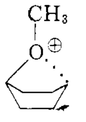
This mechanism is consistent with the observations: (1) The reaction is base-catalyzed. (2) Two moles of carbon disulfide is required for the production of one mole of ethylene trithiocarbonate. (3) Carbonyl sulfide is a by-product of the reaction along with some carbon dioxide. (4) The amount of carbonyl sulfide decreases and the amount of carbon dioxide increases as the ratio of carbon disulfide to ethylene oxide is lowered from 2.5 to 1.0.

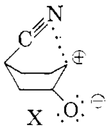
Further observations which support the above mechanism are the pyrolysis of ethylene monothiocarbonate (IV) in the presence of base to ethylene sulfide (I)[4] and the reaction of cyclohexene sulfide with potassium methyl xanthate to yield cyclohexene trithiocarbonate.[1]

Four substituted ethylene oxides each reacted with carbon disulfide to form the corresponding trithiocarbonates These experiments are summarized in Table II. It is noteworthy that Culvenor reports a 95% yield of cyclohexene trithiocarbonate using potassium hydroxide, carbon disulfide and cyclohexene oxide in methanol. By the present method only a 3.5% yield was obtained with the balance of the oxide being recovered unchanged.

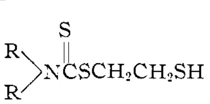
An explanation of the differences in yield observed in these two methods may be in the fact that Culvenor's work was carried out in a polar solvent which assisted in the ring opening of the expoxide while in the present work no such solvent was employed. This difference in reaction conditions was particularly noticeable in the relatively hindered cyclohexene oxide.

The enhanced yield obtained from 3,4-epoxycyclohexanecarbonitrile as compared with cyclohexene oxide may be rationalized as follows. Rate enhancement in the solvolysis of *trans*-4-methoxycyclohexyl tosylate over that of cyclohexyl tosylate has been explained on the basis of the formation of an intermediate oxonium ion (IX).[5] In a similar manner an intermediate similar to X may be operative in assisting in ring opening in this reaction.

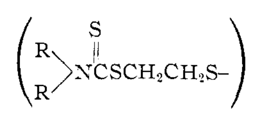

IX


X

We also wish to report the results of a few preliminary experiments on the reaction of ethylene trithiocarbonate with amines. Delaby, *et al.*,[6] have reported that ethylene trithiocarbonate reacts at room temperature with various secondary amines to yield N,N-disubstituted 2-mercaptoethyldithiocarbamates (XI). Repeating this work using morpholine and piperidine gave, as the only isolable crystalline material, products which possessed melting points similar to those reported by Delaby. Although elemental analysis could not distinguish between the reported thiol XI and the disulfide XII, molecular weight determination and infrared studies indicated that the actual product in each case was the disulfide. This is not surprising since the oxidation of mer-


$R_2NC(=S)SCH_2CH_2SH$

XI


$(R_2NC(=S)SCH_2CH_2S\text{-})_2$

XIIa, R_2N = piperidyl
b, R_2N = morpholinyl

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[4] D. D. Reynolds, THIS JOURNAL, **79**, 4951 (1957).

[5] D. S. Noyce and B. R. Thomas, *ibid.*, **79**, 755 (1957).

[6] R. Delaby, P. Piganiol and C. Warolin, *Compt. rend.*, **230**, 1671 (1950); *C. A.*, **44**, 8870[b] (1950).

TABLE II

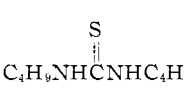
ALKYLENE TRITHIOCARBONATES

No.	Starting oxide	Product, trithiocarbonate	Wt. % $(CH_3)_3$-N:	Reaction temp., °C.	Reaction time, min.	B.p. °C. (mm.)	Yield, %	Oxide, mole	CS_2, mole
V	3,4-Epoxycyclohexanecarbonitrile	4-Cyanocyclohexene[a]	2	200	30	183–185[d]	19	1	2.5
VI	Propylene	Propylene[b]	2	200	30	126 (3.0)	36	1	2.5
VII	Cyclohexene	Cyclohexene[c]	2	200	30	165–166[d]	3.5	1	2.5
VIII	Styrene	Styrene[c]	1	150	30	83–85[d]	22	1	2.5

[a] *Anal.* Calcd. for $C_8H_9NS_3$: C, 44.65; H, 4.20; N, 6.50; S, 44.65. Found: C, 45.06; H, 4.33; N, 6.62; S, 42.88. [b] Ref. 1. [c] Ref. 2. [d] M.p., crystallized from ethyl acetate.

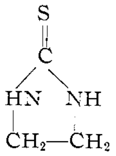
captans to disulfides proceeds readily in basic solution.

When ethylene trithiocarbonate was heated with two moles of *n*-butylamine in refluxing ethanol, 1,3-dibutylthiourea (XIII) was obtained as the only crystalline product. This was identified by mixed melting point and infrared comparison with an authentic sample. Attempts to prepare the corresponding piperidine- and morpholine-substituted thioureas gave only the disulfides XII. Thioureas do not appear to have been prepared previously by reaction of amines with ethylene trithiocarbonate.[7]



$C_4H_9NH\overset{S}{\overset{\|}{C}}NHC_4H_9$

XIII



XIV

Equimolar mixtures of ethylenediamine and ethylene trithiocarbonate reacted spontaneously and exothermically to give a white crystalline solid which was identified by analyses, infrared studies and melting point as ethylenethiourea (XIV).[8]

Experimental

Preparation of Trithiocarbonates.—The general procedure for the preparation of the trithiocarbonates is outlined. The conditions of each reaction are outlined in Table II. A mixture of oxide, carbon disulfide and amine was placed in a 3-liter stainless steel bomb at 0°, sparged with nitrogen, and nitrogen added to give 34 atm. pressure at 0°. The mixture then was heated at the appropriate temperature for the desired time with shaking. At the end of the reaction period the mixture was cooled by an air stream to room temperature and the contents of the bomb were discharged. The crude product was either crystallized or distilled.

1,10-Di-(piperidino)-1,10-dithioxo-2,5,6,9-tetrathiodecane (XIIa).—A mixture of 40.8 g. (0.3 mole) of ethylene trithiocarbonate (II) and 25.5 g. (0.3 mole) of piperidine was heated at 40° for 2.5 hours and then left at room temperature overnight. The reaction mixture had solidified the next morning. This crude product was triturated with dilute hydrochloric acid, washed with water, and then recrystallized from acetone with charcoal treatment to give 14 g. (21% yield) of a white powder, m.p. 104–105°. Infrared studies showed no –SH group to be present.

Anal. Calcd. for $C_{16}H_{28}N_2S_6$: C, 43.60; H, 6.36; N, 6.36; S, 43.64; mol. wt., 440. Found: C, 43.78; H, 6.36; N, 6.56; S, 43.99; mol. wt. (boiling point), 425 ± 5%.

1,10-Di-(4-morpholino)-1,10-dithioxo-2,5,6,9-tetrathiodecane XIIb).—The procedure was identical to that for XIIa except that morpholine was used in place of piperidine. Upon working up there was obtained 27 g. (40% yield) of off-white solid, m.p. 102–103°. No molecular weight determination or analysis was carried out on this material since it was shown by infrared studies that the material was analogous to XIIa.

1,3-Di-*n*-butylthiourea (XIII).—A mixture of 13.6 g. (0.1 mole) of ethylene trithiocarbonate and 14.6 g. (0.2 mole) of *n*-butylamine was heated at reflux in 20 ml. of ethanol for 4 hours and then left at room temperature overnight. The volume of the reaction mixture was reduced under vacuum on the steam-bath and the residue was recrystallized from ethanol to give 12 g. (32% yield) of white crystalline material, m.p. 61–62°. Mixed m.p. with known 1,3-di-*n*-butylthiourea gave no depression and direct infrared comparison showed them to be identical.

Ethylenethiourea (XIV).—Treatment of 27.2 g. (0.2 mole) of ethylene trithiocarbonate with 12 g. (0.2 mole) of ethylenediamine at room temperature resulted in an immediate exothermic reaction followed by solidification. Filtration of the reaction mixture gave 17 g. (84% yield) of white, shiny crystals, m.p. 198–200°.[5]

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(7) D. C. Schroeder, *Chem. Revs.*, **55**, 181 (1955).

(8) T. B. Johnson and C. O. Edens, THIS JOURNAL, **64**, 2706 (1942).