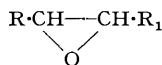


232. Reactions of Ethylene Oxides. Part I. Preparation of Ethylene Sulphides and Trithiocarbonates.

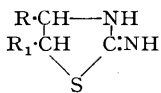
By C. C. J. CULVENOR, W. DAVIES, and K. H. PAUSACKER.

Some simple ethylene oxides are converted into the corresponding ethylene sulphides by the action of thiourea, thiocyanates, and thiocarbanilide. Control of the experimental conditions diminishes the amount of high-molecular material sometimes formed, which, however, is the exclusive product from glycidol and styrene oxide. The characteristic sparingly soluble yellow trithiocarbonates are obtained from some simple ethylene oxides and sulphides by the action of xanthates. *cyclo*Hexene oxide with sodium trithiocarbonate, and *cyclohexene sulphide* with this and higher thiocarbonates, Na_2CS_n ($n = 3-6$), yield *cyclohexene trithiocarbonate*, whereas this product, mixed with a white compound, m. p. 155.5° , is obtained from *cyclohexene oxide* and the perthiocarbonates.

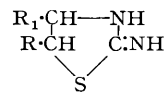
BODFORSS (*Ber.*, 1918, 51, 212) showed that 1-benzoyl-2-*m*-nitrophenylethylene oxide (I; $\text{R} = \text{Bz}$, $\text{R}_1 = m\text{-C}_6\text{H}_4\text{NO}_2$) reacted with thiourea to form 2-imino-4-benzoyl-5-*m*-nitrophenylthiazolidine (II) or the isomeric 2-imino-5-benzoyl-4-*m*-nitrophenylthiazolidine (III); thiocarbanilide behaved similarly. Olin and Dains (*J.*



(I.)



(II.)



(III.)

Amer. Chem. Soc., 1930, 52, 3322) found that ethylene oxide and thiocarbanilide gave *NN'*-diphenyl-2-hydroxyethylisothiourea, $\text{CH}_2(\text{OH})\cdot\text{CH}_2\cdot\text{S}\cdot\text{C}(\text{NPh})\text{:NHPh}$, and thiourea apparently gave the unstable 2-hydroxyethylthiourea. On the other hand, it was claimed by Dachlauer and Jackel (D.R.-P. 636,708) that ethylene oxide and thiourea or potassium thiocyanate gave good yields of ethylene sulphide, and that glycidol, epichlorohydrin, and propylene oxide behaved similarly. The few aliphatic ethylene sulphides described in the literature had usually been prepared by the action of sodium sulphide on 1:2-dithiocyanates or halogeno-thiocyanates (Delépine and Jaffeux, *Compt. rend.*, 1921, 172, 158).

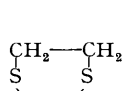
The present work shows that the course of the reaction with thiourea partly depends on the structure of the ethylene oxide used. The ethyl ester of dimethylglycidic acid and benzylideneacetone oxide yield derivatives

containing both nitrogen and sulphur. Simpler oxido-compounds behave differently, and the monomeric sulphides of ethylene, propylene, chloropropylene, *isobutylene* and *cyclohexene* are obtained in good yield from the corresponding oxides. The use of *cyclohexene* oxide in a series of comparative experiments shows that ammonium or potassium thiocyanate tends to cause polymerisation and to give lower yields of the monomeric sulphide than does thiourea. With thiocarbanilide, the reaction is very sluggish. It should be noted that, despite the above patent, the monomeric sulphide from glycidol has not been obtained from any of the above reagents, and the b. p. of *3-chloropropylene sulphide* is 79—81°/114 mm. or 138—139°/760 mm., and not 94—96°/6 mm. It is evident that the use of the reagents requires careful control; *e.g.*, Engle (*J. Amer. Chem. Soc.*, 1898, 20, 676) claims that the only substance isolated in the reaction between epichlorohydrin and potassium thiocyanate is epithiocyanohydrin.

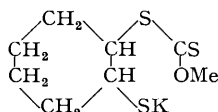
Potassium selenocyanate and *cyclohexene* oxide yield *cyclohexene* and selenium, and not *cyclohexene* selenide.

The action of at least 2 mols. of metallic xanthates on ethylene oxide gives a 97% yield of ethylene trithiocarbonate (IV), which is also produced by the same reagent with ethylene chlorohydrin and with ethylenedithiol. Similarly, *cyclohexene trithiocarbonate* (VI) is formed from *cyclohexene* oxide, 2-chloro*cyclohexanol*, and *cyclohexene sulphide*, and *tetramethylethylene trithiocarbonate* (in small yield) is likewise formed from the oxide. Experiments so far show that there always is a reaction between xanthate and a compound with an undoubted ethylene oxide structure, but in some cases, *e.g.*, epichlorohydrin and glycidol, the products are polymeric.

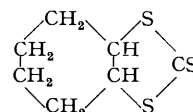
Variation of the amounts of potassium hydroxide reacting with methyl-alcoholic solutions of *cyclohexene* oxide and sulphide containing excess of carbon disulphide indicates that the oxide is first converted by the xanthate into the sulphide, which then very rapidly reacts with more xanthate to form the intermediate (V), which loses potassium methoxide (available for further xanthate formation) to form (VI). The use of 0.1 mol. of potassium hydroxide with the sulphide gives a yield of over 80% of (VI), which is also slowly formed through the agency of the alkali in the glass of the vessel in which the operation is carried out. It is noteworthy that, whilst all attempts to make styrene sulphide give merely high-molecular material, styrene oxide with xanthate gives *styrene trithiocarbonate* in 77% yield.



(IV.)



(V.)



(VI.)

The action of the salts of thiocarbonic acids on ethylene oxides has been chiefly carried out with *cyclohexene* oxide, though in this case polymers are sometimes formed. *cyclohexene* oxide and Na_2CS_3 give (VI) in 39% yield, whereas Na_2CS_4 , Na_2CS_5 , and Na_2CS_6 produce a mixture of (VI) and colourless crystals. The above four salts and *cyclohexene* sulphide give (VI) alone.

These colourless crystals crystallise well from benzene and melt at 155.5°. Upon standing in the air the m. p. may fall to 132° although it is unaltered if the substance is kept in a vacuum desiccator over phosphoric oxide. Both sublimation in a high vacuum and heating in a water-oven raise the m. p. of the low-melting forms. This apparent hydrate formation is being further investigated.

EXPERIMENTAL.

Preparation of Ethylene Sulphides.—The reaction between ethylene oxides and some of the thio-reagents can be very vigorous, and the low temperatures mentioned can usually be maintained only by efficient external cooling. Some aliphatic sulphides are unstable in the presence of acid or alkali solutions, and any sudden rise of temperature during the reaction results in formation of little monomeric sulphide and much insoluble non-volatile material. The table indicates variations in yields of ethylene sulphides with various reagents and conditions. As the reaction proceeds, the pH of the

Oxide.	Reagent.	Conditions.	Yield, %.	Residue, %.
<i>cyclohexene</i> oxide (5 g.)	Thiourea (5 g.)	32 hrs. at 15°	40	—
		1.5 hrs. at 60°	58	15.5
		3 hrs. at 60°	55	24
	KCNS (7.5 g.)	24 hrs. at 15°	43.5	—
		1 hr. at 60°	61	—
		2 hrs. at 60°	42	—
NH_4CNS (7 g.)	3 hrs. at 60°	—	100	
	1.5 hrs. at 60°	60	—	
	3 hrs. at 60°	43	55	
Epichlorohydrin (11.6 g.) *	Thiourea (10.5 g.)	1 hr. at 0° and then at 20° for 3 hrs.	67	—
		6 hrs.	47	16
		3 hrs.	38	30
		3 hrs.	38	30
<i>iso</i> Butylene oxide (5 g.) †	Thiourea (6 g.)	Time (hrs.) at 20°		
		3.25	39	—
		17.5	57	—
		30	51	13

* In 35 ml. of methyl alcohol. When water is used instead of methyl alcohol, lower yields are obtained.

† Very small yields of sulphide obtained when water is used instead of methyl alcohol. This sulphide is extracted with ether.

medium and the yield of polymeric residual compound usually increase. The following details of the process for the formation of *cyclohexene sulphide* apply essentially to the other reactions in the table. *cycloHexene oxide* (5 g.) and methyl alcohol (20 ml.) are treated with the reagent shown in the table, the product poured into water (150 ml.) and the mixture extracted with chloroform. *cycloHexene sulphide* has b. p. 67—68°/16 mm., n_D^{20} 1.5309 (Found: S, 28.0. $C_6H_{10}S$ requires S, 28.05%). Refluxing *cyclohexene oxide* (6 g.) and thiocarbonyl (11.7 g.) in ethyl alcohol (25 ml.) gives in 2 hours a 15%, and in 13 hours a 37%, yield of the sulphide. The sulphides described have slightly unpleasant odours.

3-Chloropropylene sulphide has b. p. 79—81°/114 mm., 138—139°/760 mm., n_D^{20} 1.5280 (Found: S, 29.8; Cl, 32.9. C_3H_5ClS requires S, 29.5; Cl, 32.7%). It is slowly decomposed by cold brine, forming a white insoluble solid. *isobutylene sulphide* has b. p. 87°/760 mm., n_D^{20} 1.4661 (Found: S, 36.7. C_4H_8S requires S, 36.4%).

Propylene sulphide is obtained in 61% yield when propylene oxide (5 g.), thiourea (7 g.), ice (10 g.), and water (15 ml.) are stirred at 0° for 0.5 hour, and at 20° for a further 3 hours; it has b. p. 75—76°, n_D^{15} 1.4780. Delépine and Jaffeur (*loc. cit.*) record b. p. 75—77°, n_D^{15} 1.473.

cycloHexene Trithiocarbonate (VI).—*cycloHexene oxide* reacts immediately in the cold with alkali xanthates in alcohol but is unaffected by carbon disulphide alone over a period of two months. A solution of potassium hydroxide (3.50 g., 2½ mols.) in methyl alcohol (15 ml.) containing carbon disulphide (5.7 g., 3 mols.), is treated at room temperature with *cyclohexene oxide* (2.45 g., 1 mol.), the mixture kept overnight, water (100 ml.) added, and the product heated on the water-bath until carbon disulphide is removed. *cycloHexene trithiocarbonate* (thick yellow crystals, 87% yield), moderately soluble in cold benzene, sparingly soluble in cold alcohol, has m. p. 169° (Found: S, 50.1. $C_7H_{10}S_3$ requires S, 50.5%). Lower yields are given by less than 2 mols. of carbon disulphide with alcoholic alkali. Similarly, a 95% yield of the trithiocarbonate is rapidly obtained from *cyclohexene sulphide*, and a 43% yield from 2-chloro*cyclohexanol*. Lower yields are obtained when water is used instead of methyl alcohol.

Ethylene Trithiocarbonate.—Ethylene oxide (2.2 g., 1 mol.), with carbon disulphide (11.4 g., 3 mols.), potassium hydroxide (7.0 g., 2½ mols.), and methyl alcohol (25 ml.), requires efficient cooling to prevent loss and gives a 97% yield of ethylene trithiocarbonate, yellow crystals from benzene—light petroleum, m. p. 36—37° (Found: S, 71.0. Calc. for $C_2H_2S_3$: S, 70.6%); it was identified by mixed m. p. with the compound obtained (78% yield) after Husemann (*Annalen*, 1862, 123, 83) by the action of ethylene dibromide on sodium trithiocarbonate. Ethylene trithiocarbonate is obtained in 83% yield by allowing ethylenedithiol (2.0 g.) to stand for 5 days with methyl alcohol (15 ml.) containing carbon disulphide (2.5 g.) and potassium hydroxide (1.5 g.), or in 42% yield by allowing ethylene chlorohydrin (2.0 g.) to stand for 3 days with methyl alcohol (15 ml.) containing carbon disulphide (5.7 g.) and potassium hydroxide (3.15 g.).

Styrene Trithiocarbonate.—*Styrene trithiocarbonate* is obtained in 77% yield when styrene oxide (2 g., 1 mol.), potassium hydroxide (2.2 g., 2.25 mols.), and carbon disulphide (3.2 g., 2.5 mols.) in methyl alcohol react at room temperature for 24 hours; yellow needles, m. p. 87—88°, very soluble in benzene, much less soluble in alcohol (Found: S, 45.2. $C_8H_8S_3$ requires S, 45.3%).

Tetramethylethylene Trithiocarbonate.—Tetramethylethylene oxide (2 g.), carbon disulphide (3.8 g.), potassium hydroxide (2.6 g.), and methyl alcohol (15 ml.), after three weeks at 36° and then addition of water, give the *trithiocarbonate* as yellow crystals from alcohol (yield 0.2 g.), m. p. 156° (Found: S, 49.8. $C_7H_{12}S_3$ requires S, 50.0%).

Action of Sodium Thiocarbonates on cycloHexene Oxide and Sulphide.—The alcoholic solution of sodium trithiocarbonate is made by admixture of the hydrated sulphide and carbon disulphide with alcohol. Fresh solutions of the perthiocarbonates, using appropriate proportions of sulphur, are made and used as exemplified in the following account of the action of Na_2CS_4 on *cyclohexene oxide*. Water (9 ml.), sulphur (1 g., 1¼ mols.), and sodium sulphide nonahydrate (7.5 g., 1¼ mols.) are heated until the sulphur dissolves, then cooled, methyl alcohol (35 ml.) and carbon disulphide (2.9 g., 1½ mols.) added, and shaking is continued until the last dissolves. *cycloHexene oxide* (2.45 g., 1 mol.) is then added, and the mixture kept at room temperature for 3 weeks. It is then treated with water (200 ml.), and cooled; the light yellow precipitate (2.6 g.) is collected and crystallised from benzene, and the more soluble *cyclohexene trithiocarbonate* separated from the less soluble colourless crystals (1.1 g.), m. p. 154.5—155.5°. Na_2CS_5 and Na_2CS_6 give a similar mixture. *cycloHexene oxide* with 1¼ and 2½ mols. of the trithiocarbonate give a 39% yield of *cyclohexene trithiocarbonate*, which compound is also formed from *cyclohexene sulphide* and Na_2CS_3 , Na_2CS_4 , Na_2CS_5 , and Na_2CS_6 .