ADDITION OF SOME α-HALOGENO ETHERS TO α-THIOOXIDES OF ALKENES

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From the literature it is well known that compounds with the general formula $p\text{-}ClC_6H_4OCH_2R$, where R is an aryloxy or arylmercaptoxy group, have insecticidal and acaricidal activity [1]. Some of the ethers of methylene glycol that have been prepared [2] with various groups in the β-position from the oxygen bridge have biological activity.

In the present work we carried out the addition of some α-halogeno ethers to the thiooxides of ethylene and propylene. This reaction of α-halogeno ethers, as a result of which it also is possible to obtain biologically active compounds, had not yet been studied. When α-halogeno ethers add to the thiooxide of ethylene at −10 to −15° in the presence of $HgCl_2$, products of the following structure are obtained

$$\underset{\diagdown\ \diagup}{CH_2-CH_2} + ClCH_2OR \xrightarrow{HgCl_2} ClCH_2CH_2SCH_2OR$$

The reaction with the propylene thiooxide may follow two routes:

$$\underset{\diagdown S \diagup}{CH_2-CH-CH_3} + ClCH_2OR \rightarrow \begin{cases} \rightarrow ClCH_2\overset{CH_3}{\overset{|}{C}}HSCH_2OR \\ \rightarrow CH_3CHClCH_2SCH_2OR \end{cases}$$

For evidence of the structure of the products obtained, we determined the IR spectra of the dehydrochlorinated product from 5 (see Table 2). As a result of dehydrochlorination three compounds might be obtained

$$1)\ CH_2=\overset{CH_3}{\overset{|}{C}}-SCH-OC_2H_5 \quad (CH_3 \text{ on } SCH)$$

$$2)\ CH_2=CH-CH_2SCH-OC_2H_5 \quad (CH_3 \text{ on } SCH)$$

$$3)\ CH_3-CH=CH-S-CH-OC_2H_5 \quad (CH_3 \text{ on } CH) \Bigg\}$$

The first compound may be obtained if the reaction goes by the first route, and the second and third compounds may be obtained by the second route. In the IR spectrum of the dehydrochlorinated product there was a band at 1620 cm^{-1} in the region for double bonds. In the region of the valence vibrations of olefinic C—H bonds a peak stood out at a frequency of 3019 cm^{-1}, and in the region of characteristic extraplanar deformation vibrations of olefinic C—H bonds a band was observed with a frequency of 937 cm^{-1}. The IR spectral data indicate the formation of product 3, i.e., the second route of reaction and the formation of compounds of the following structure $CH_3CHClCH_2SCH_2OR$ The constants of the products of addition of α-halogeno ethers to the thiooxides of ethylene and propylene are given in Tables 1 and 2.

Most of the compounds obtained cause long-lasting burns on the skin.

TABLE 1. Addition of α-Halogeno Ethers to Ethylene Thiooxide

Expt. No.	α-Halogeno ether added	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	Cl, % found	Cl, % calculated	Yield, %
1	$ClCH_2OCH_2CH_2Cl$	79—82 (1)	1,5120	1,2734	44,53	44,67	37,50	37,52	46,5
2	$ClCH_2OCH_2CH=CH_2$	83—85 (9)	1,4962	1,1097	43,87	43,95	20,95	21,28	35
3	$ClCH_2OC_6H_{11}$	102—104 (1)	1,5056	1,1021	56,22	56,07	16,65	16,99	78
4	$C_2H_5OCHClCH_3$	75—76 (9)	1,4781	1,0700	44,61	44,42	20,85	21,01	70
5	$ClCH_2OCH_2CH_2OCOCH_3$ *	92—94 (1)	1,4823	1,1861	51,12	50,69	15,85	16,65	40

*Constants given after four distillations of product.

TABLE 2. Addition of α-Halogeno Ethers to Propylene Thiooxide

Expt. No.	α-Halogeno ether added	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	Cl, % found	Cl, % calculated	Yield, %
1	$ClCH_2OCH_2CH_2Cl$	81 (1)	1,5046	1,2205	49,32	49,28	35,15	34,92	23
2	$ClCH_2OCH_2CH=CH_2$*	100—102 (13)	1,4920	1,0826	48,39	48,57	20,15	19,66	31,5
3	$ClCH_2OCH_2CH_2OCOCH_3$	98—101 (1)	1,4740	1,1506	55,36	55,31	15,45	15,64	31
4	$ClCH_2OC_6H_{11}$	102—106 (1)	1,4976	1,0702	60,95	60,69	15,35	15,92	49
5	$C_2H_5OCHClCH_3$	79—82 (13)	1,4722	1,0380	49,27	49,04	19,30	19,41	78

*Constants for products 3, 4, 5 given after first distillation, and for product 2 after three distillations.

EXPERIMENTAL

In a three-necked flask equipped with a mechanical stirrer, dropping funnel, and calcium chloride tube, and kept in a cooling mixture at − 15 to − 10° were placed 40 g of cyclohexyl chloromethyl ether and 1 g of $HgCl_2$. Over the course of 45 minutes 17 g of ethylene sulfide was dropped into the contents of the flask, after which the reaction mixture was stirred for 1½ hours longer. Then the cooling was discontinued and the contents of the flask were allowed to stand over night at room temperature. The next day 100 ml of ether was added to the contents of the flask and the ether layer was washed three times with water and dried with Na_2SO_4. The ether was distilled off and the residue was subjected to vacuum distillation. The yield was 44 g of a compound whose constants are given in Table 1 under No. 3. Four other products of the addition of α-halogeno ethers to ethylene sulfide were prepared in a similar manner (see Table 1).

The addition of α-chloro ethers to propylene thiooxide was carried out in the same apparatus. The physical constants of the products obtained are given in Table 2.

SUMMARY

Products of the addition of allyl chloromethyl ether, β-chloroethyl methyl ether, β-acetoxyethyl chloromethyl ether, cyclohexyl chloromethyl ether, and α-chloroethyl ethyl ether to the thiooxides of ethylene and propylene have been prepared.

LITERATURE CITED

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