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It is known that during the reaction of sodium phenate and thioepichlorohydrin the formation of two forms of product A and B is possible [1]



The yields of these products depend on the solvent. Thus, in an aprotic solvent, for exampe in glycol dimethyl ether, 44.5% A and 5.7% B are obtained; in water 47.5% B and 10% A are obtained. Therefore, both in the first but particularly in the second case the isomerization of the three-membered thiirane ring to the four-membered thietene ring takes place. The possibility of the isomerization of the thiirane ring under the influence of certain reagents is disregarded by some authors and has led them to an erroneous interpretation of the structure of the compounds obtained. Thus, Étlis [2] gives the preparation of thioglycidol from thioepichlorohydrin and anhydrous potassium acetate and the subsequent hydrolysis of the obtained, in his opinion, thioglycidyl acetate with alkali according to the scheme

It should be noted that the constants obtained by Étlis for thioglycidol are close to the constants of 3-thietanol [2-6] (Table 1). Also 3-thietanol was obtained in [6] from thioepichlorohydrin according to the scheme



In order to clarify the true structure of thioglycidol [2] we prepared thioglycidol according to method [7] by the pyrolysis of  $C_{2}H_{5}OCSCH_{2}CHOHCH_{2}OH$  and it had the following constants: bp 46-47° (0.4 mm);  $n_{D}^{20}$  1.5292;

 $d_4^{20}$  1.1869. As is evident the constants we obtained for thioglycidol prepared by method [7] are different from the constants of "thioglycidol" prepared in [2]. Therefore, on treating thioepichlorohydrin with alkali isomerization of the thiirane ring to a thietane ring takes place. Étlis assumed that thioglycidyl acetate is

Compound	bp, °C (p, mm Hg)	$n_D^{20}$	d420
"Thioglycido1"[2] 3-Thetano1 [3] The same [4] " [5] " [6]	$ \begin{array}{c} 75-76 (6) \\ 57 (1,3) \\ 51-52 (0,9) \\ - \\ 86 (16) \end{array} $	1,5415 1,5433 1,5408  1,5393	1,2170 1,2130 1,2129

obtained on treating thioepichlorohydrin with potassium acetate (scheme 1). Other authors [6] give this selfsame method for the preparation of 3-thietanyl acetate. It can therefore be assumed that thioglycidyl acetate is formed in the first stage, this then under the influence of alkali is transformed into 3-thietanol. Or else 3-thietanyl acetate is formed in the first stage by the reaction of thioepichlorohydrin with potassium acetate and subsequently hydrolyzed to 3-thietanol.

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$$S \underbrace{CH_2}_{CH_2} CHOH \xrightarrow{CH_2COOK} S \underbrace{CH_2}_{CH_2} \underbrace{H_2}_{O}$$
(b)

$$\underbrace{CH_2-CH-CH_2CI-\frac{CH_2COOK}{CH_3COOH}}_{S} S \underbrace{CH_2-CHOCCH_3}_{O}$$
(c)

The constants of the compounds obtained were as follows: a) bp 70-71° (10 mm);  $n_D^{20}$  1.4940;  $d_4^{20}$  1.1712; b) mp 72° (10 mm);  $n_D^{20}$  1.4901; c) bp 69-71° (10 mm);  $n_D^{20}$  1.4940;  $d_4^{20}$  1.1707. The IR spectra of these compounds were identical. Analyses showed that dioepoxide sulfur was absent from the compound obtained from thioepichlorohydrin and potassium acetate. We carried out the thioepoxide sulfur analysis according to [1]. Therefore, 3-thietanyl acetate is formed by the reaction of thioepichlorohydrin and potassium acetate.

A method of preparing thioglycidyl esters of acrylic acids by the reaction of the acid chlorides of acrylic acids with thioepichlorohydrin was proposed in [8]. As we have shown with the data for methacrylic acid, for example, in this case also the acrylates of thietanol are formed. "Thioglycidyl methacrylate" prepared by us by the method of Étlis had bp  $59-62^{\circ}$  (0.1 mm);  $n_{\rm D}^{20}$  1.5079;  $d_4^{20}$  1.1338. 3-Thietanyl methacrylate prepared by the following scheme



had bp  $81.5-83^{\circ}$  (10 mm);  $n_D^{20}$  1.5089;  $d_4^{20}$  1.1330. The IR spectra of these compounds were identical. Thioepoxide sulfur was absent.

We prepared thioglycidyl methacrylate in the following manner

$$\begin{array}{c} CH_2 - CH - CH_2OH + CH_2 = C - C \\ \searrow \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_2 - CH - CH_2OC - C = CH_2 \\ & & & & & \\ O \\ CH_3 \\ CH_3$$

$$\begin{array}{c} CH_2 - CH - CH_2OC - C = CH_2 \xrightarrow{CS(NH_2)_2} CH_2 - CH - CH_2OC - C = CH_2 \\ \searrow & || & | \\ S & O & CH_3 \\ \end{array}$$
 (e)

The constants of the products obtained were: d) bp 90° (20 mm);  $n_D^{20}$  1.4970;  $d_4^{20}$  1.1030; e) bp 59-61° (0.4 mm);  $n_D^{20}$  1.4950;  $d_4^{20}$  1.1004. For product (e), found 18.1% thioepoxide sulfur, calculated for  $C_7H_{10}O_2S$  sulfur 20.2%.

## EXPERIMENTAL

Preparation of Thioglycidol. The method in [7] was used for the preparation of thioglycidol. The thioglycidol obtained by us had bp 46-47° (0.4 mm);  $n_D^{20}$  1.5292;  $d_4^{20}$  1.1869. Found %: thioepoxide S 33.65, 34.1.  $C_3H_6OS$ . Calculated %: S 35.55

<u>Preparation of 3-Thietanol</u>. The constants of 3-thietanol obtained from thioepichlorohydrin and  $K_2CO_3$  in aqueous alcohol solution bp 86° (16 mm);  $n_D^{20}$  1.5395 agreed with the literature [6]. Thioepox-ide sulfur was not present in 3-thietanol.

<u>Preparation of 3-Thietanyl Acetate.</u> 3-Thietanyl acetate was prepared by three methods: 1) from thioepichlorohydrin and potassium acetate according to [2]; 2) from 3-thietanol and acetic anhydride according to [6]; 3) from 3-thietanol and acetyl chloride by the method described below. To 9 g of 3-thietanol in 150 ml of ethyl ether 10.2 g of triethylamine was added with cooling from -8 to  $-5^{\circ}$  C, then at the same temperature 7.8 g of acetyl chloride in 50 ml of ethyl ether was added dropwise with stirring. The reaction mixture was stirred for a further 15 min with cooling to  $-5^{\circ}$  after the addition of all the acetyl chloride, then the cooling was stopped, the triethylamine hydrochloride was filtered off, the ether was distilled off at room temperature under 10 mm vacuum, and the residue in quantity 12.5 g was distilled. The yield of 3-thietanyl acetate was 9 g with bp 70-71° (10 mm);  $n_D^{20}$  1.4940;  $d_4^{20}$  1.1712. The IR spectra of the 3-thietanyl acetate prepared by the three different methods were identical.

<u>Preparation of Thioglycidyl Acetate.</u> Glycidyl acetate was prepared from glycidol and acetyl chloride by the method described above for the preparation of 3-thietanyl acetate from 3-thietanol and acetyl chloride. To 12 g of glycidyl acetate  $(n_D^{26} 1.4210)$  dissolved in 30 ml of methanol was added 8 g of thiourea and the reaction mixture was stirred at room temperature until the thiourea was completely dissolved. Then 100 ml of ether and 50 ml of water were added to the reaction flask and the contents of the flask were vigorously stirred, the ether layer was separated, it was dried over CaCl<sub>2</sub> and distilled. The yield was 8 g of thioglycidyl acetate with bp 71° (12 mm);  $n_D^{20} 1.4822$ ;  $d_4^{20} 1.1444$ . Found %: thioepoxide S 23.6.  $C_5H_6OS_2$ . Calculated %: S 24.2.

<u>Preparation of 3-Thietanyl Methacrylate</u> 1) 3-Thietanyl methacrylate was prepared exactly according to the method in [8]. The authors of [8] did not give constants for the compounds obtained. We obtained 3-thietanyl methacrylate with bp 59-62° (0.1 mm);  $n_D^{20}$  1.5079;  $d_4^{20}$  1.1338. Thioepoxide sulfur was absent.

2) 3-Thietanyl methacrylate was obtained from 7 g of 3-thietanol, 6.9 g of methacryloyl chloride, and 7 g of triethylamine by the method used for the preparation of 3-thietanyl acetate. 3-Thietanyl methacrylate was obtained with bp 81.5-83° (10 mm);  $n_D^{20}$  1.5089;  $d_4^{20}$  1.1330. The IR spectra of the samples of 3-thietanyl methacrylate obtained by these methods were identical.

<u>Preparation of Thioglycidyl Methacrylate</u>. 1) From 5.6 g of methacryloyl chloride, 5 g of thioglycidol, and 5.6 g of triethylamine in ether solution with cooling to  $-18^{\circ}$  we obtained  $\sim 2$  g of thioglycidyl methacrylate with bp 90° (20 mm);  $n_D^{20}$  1.4970;  $d_4^{20}$  1.1030. There was considerable amount of polymer in the residue.

2) From 7 g of glycidyl methacrylate  $(n_D^{20} 1.4510)$  and 4 g of thiourea in 20 ml of methanol by the method used for the preparation of thioglycidyl acetate 2.3 g of thioglycidyl methacrylate was obtained with bp 59-61° (0.4 mm);  $n_D^{20} 1.4950$ ;  $d_4^{20} 1.1004$ . Found %: thioepoxide S 18.1.  $C_7H_{10}O_2S$ . Calculated %: S 20.2.

## CONCLUSIONS

Compounds having the 3-thietanyl radical and not the thioglycidyl radical are obtained during the reaction of thioepichlorohydrin with potassium carbonate, potassium acetate, and the acid chlorides of acrylic acids.

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