O. N. Nuretdinova and B. A. Arbuzov

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The reactions of O,O-diethyl dithiophosphate with epichlorohydrin in toluene and of O,O-diethyl thiophosphate with thioepichlorohydrin in benzene, in the presence of an equimolar amount of triethylamine, give, based on the data of the IR spectra, identical products, although there is some difference in the constants of these compounds



Apparently, identical products can be obtained in these reactions if the triethylammonium salt of the diethyl dithiophosphate reacts with epichlorohydrin in the same manner as does potassium thiocyanate, with the formation of thioepichlorohydrin and the triethylammonium salt of diethyl thiophosphate

$$\underbrace{\text{ClCH}_2-\text{CH}-\text{CH}_2+(\text{C}_2\text{H}_5\text{O})_2}_{\text{O}} \underbrace{\text{PSH}}_{\text{S}} \xrightarrow{\text{ClCH}_2-\text{CH}-\text{CH}_2+(\text{C}_2\text{H}_5\text{O})_2\text{POH}}_{\text{S}} \underbrace{\|}_{\text{S}}$$

The alkali metal salts and ammonium salts of O,O-dialkyl thiophosphates and O,O-dialkyl dithiophosphates are good thioepoxidation agents. Acting on epoxide compounds in the same manner as potassium thiocyanate or thiourea, they convert them to thioepoxy compounds. Thus, the heating of propylene oxide or phenyl glycidyl ether in water at 60-70° with an equimolar amount of either potassium diethyl thiophosphate or potassium diethyl dithiophosphate gave propylene thioxide or phenyl thioglycidyl ether. The constants of the obtained compounds are given in Table 1

$$\begin{array}{c} \operatorname{RCH}_2\operatorname{CH}-\operatorname{CH}_2+(\operatorname{C}_2\operatorname{H}_5)_2\operatorname{PSK} \to \operatorname{RCH}_2\operatorname{CH}-\operatorname{CH}_2+(\operatorname{C}_2\operatorname{H}_5\operatorname{O})_2\operatorname{POK} \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

We also ran a series of reactions of potassium O,O-dialkyl dithiophosphates with the esters and ester-amides of  $\beta$ , $\gamma$ -epoxypropylphosphinic acid, which were obtained by us according to the scheme

$$\begin{array}{c} \mathbf{R}'\mathbf{O} & \mathbf{R}'' \\ \mathbf{R}'' - \mathbf{P} + \mathbf{C}\mathbf{H}_2 - \mathbf{C}\mathbf{H} - \mathbf{C}\mathbf{H}_2\mathbf{B}\mathbf{r} \rightarrow & \mathbf{P}\mathbf{C}\mathbf{H}_2\mathbf{C}\mathbf{H} - \mathbf{C}\mathbf{H}_2 + \mathbf{R}'\mathbf{B}\mathbf{r} \\ \mathbf{R}''' & \mathbf{O} & \mathbf{R}''' & \mathbf{O} & \mathbf{O} \end{array}$$

R	Bp, °C (p, mm of Hg)	$d_4^{20}$	$n_D^{20}$	C, %	Н, %	EpoxidesS,* %	Yield,%
н	7274 (760)	0,9425	1,4758			$\frac{43,03}{43,24}$	40
$C_6H_5$	81 (0,2)	1,1375	1,5700	$\frac{65,12}{65,05}$	$\frac{6,14}{\overline{6,02}}$	$\frac{17,80}{19,20}$	50

TABLE 1

\* The upper figures are the found values and the lower figures are the calculated values.

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TABLE 2

R'	R"	R'''	Bp, °C (p, mm of Hg)	$d_{4}^{20}$	$n_D^{20}$	C*, %	н*, %	P*, %	Yield, %
CH3	CH3O	CH3O	123—125,5 (11)	1,2420	1,4475	$\frac{35,88}{36,14}$	$\frac{6,48}{6,62}$	$\frac{18,62}{18,67}$	24
C₂H₅	$C_2H_5O$	$(C_2H_5)_2N$	92 (0,3)	1,0802	1,4582	$\frac{48,94}{48,86}$	$\frac{8,94}{9,04}$	$\frac{13,86}{14,02}$	38

\* The upper figures are the found values and the lower figures are the calculated values.

TABLE 3

R'	R'''	Bp, °C (p, mm of Hg)	$d_4^{20}$	$n_D^{20}$	C*, %	H*, %	P*, %	Thioepo- xide S*, %	Yield, %
CH₃	CH3	69—70 (0,2)	1,2640	1,4950	$\frac{32,66}{32,96}$	6,00 6,00	17,25 17,03	$\frac{17,15}{17,58}$	25
$C_2H_5$	C <sub>2</sub> H <sub>5</sub>	93 (0,3)	1,1574	1,4790	40,09 40,00	$\frac{7,30}{7,14}$	$\frac{14,60}{14,76}$	15,43 15,23	54
C3H7	C <sub>2</sub> H <sub>5</sub>	99 (0,3)	1,1012	1,4751	$\frac{45,92}{45,37}$	8,19 8,00	$\frac{13,05}{13,02}$	13,60 13,44	40

• The upper figures are the found values and the lower figures are the calculated values.

In Table 2 are given those epoxy compounds whose constants are not given in [1, 2].

The thioepoxidation of the dialkyl esters of  $\beta$ , $\gamma$ -epoxypropylphosphinic acid goes when equimolar amounts of the starting components are heated in propanol at 60-80°.

In Table 3 are given the constants of the O,O-dialkyl esters of  $\beta$ , $\gamma$ -thioepoxypropylphosphinic acid.

The thioepoxidation of the ester-amides of  $\beta$ , $\gamma$ -epoxypropylphosphinic acid with the salts of phosphorus thioacids gave either polymeric materials or compounds that lent themselves with difficulty to purification in a yield not exceeding 10%. Thus, from 4 g of the ethyl ester of diethylamido- $\beta$ , $\gamma$ -epoxypropylphosphinic acid was isolated ~0.3 g of the thioepoxy compound with bp 78-94° (0.5 mm);  $d_4^{20}$  1.1097;  $n_D^{20}$  1.4840. Found: Sthioepoxy 11%. C<sub>9</sub>H<sub>20</sub>NO<sub>2</sub>PS. Calculated: Sthioepoxy 13.50%. From the butyl ester of diethylamido- $\beta$ , $\gamma$ -epoxypropylphosphinic acid was obtained in 8% yield a compound with bp 116-118° (0.2 mm);  $d_4^{20}$  1.1016;  $n_D^{20}$  1.4780. Found: N 4.10; P 11.97; Sthioepoxy 10%. C<sub>11</sub>H<sub>24</sub>NO<sub>2</sub>PS. Calculated: N 5.28; P 11.69; Sthioepoxy 12.07%. The reaction of potassium diethyl dithiophosphate with the diethyl ester of  $\alpha$ -methylepoxyvinyl-phosphinic acid gave a compound in which the thioepoxide sulfur cannot be determined by titration

$$\begin{array}{c} O \\ (C_2H_5O)_2PC-CH_2 + (C_2H_5O)_2PSK \rightarrow (C_2H_5O)_2PC-CH_2 \\ \parallel & \parallel \\ O & CH_3 \\ \end{array}$$

It is known that thioepoxides, in contrast to thietane derivatives, react easily with certain trivalent phosphorus compounds [3]. The diethyl ester of  $\alpha$ -methylthioepoxyvinylphosphinic acid reacts exothermally (the temperature rises from 24 to 74°) with hexaethyltriamidophosphite according to the scheme:



The possibility of forming thioepoxy compounds from olefin oxides and salts of phosphorus thioacids was shown in [4].

Since the dialkyl thiophosphates or the dialkyl dithiophosphates of the alkali metals react with epichlorohydrin in the same manner as does potassium thiocyanate, with the formation of thioepichlorohydrin, then O,O-diethyl glycidyl dithiophosphate (the obtained compound does not react with thiourea in methanol) is not obtained when equimolar amounts of epichlorohydrin and potassium diethyl dithiophosphate are reacted. The thioepichlorohydrin formed in the first step immediately reacts with the still unconsumed salt of the dithio acid, and after this is consumed – with the obtained salt of the monothio acid. Since these reactions are run in aqueous solution, then the formation of a mixture of isomers is possible, which cannot be separated by distillation. The formation of a mixture of isomers when the dialkyl dithiophosphate of the alkali metals are reacted with thioepichlorohydrin in aqueous solution was shown by us previously [5]



The possibility of forming this mixture is also corroborated by the elemental analysis: for  $C_7H_{15}O_2PS_3$  calculated: C 32.55; H 5.81; P 12.00%; for  $C_7H_{15}O_3PS_2 - C$  34.71; H 6.18; P 12.81%; for the reaction product of epichlorohydrin with potassium diethyl dithiophosphate in water (1:1 ratio of the reactants), found: C 33.98; H 6.00; P 12.25; S<sub>thioepoxy</sub> 6.8%. If 2 moles of potassium diethyl dithiophosphate is taken for reaction, then in the second step the thioepichlorohydrin will react more rapidly with the second mole of the dialkyl dithiophosphate to give a mixture of O,O-diethyl thioglycidyl dithiophosphate and O,O-diethyl 3-thietanyl dithiophosphate



Since the thioepoxide derivative in this mixture can be titrated with iodine, then titration of the substance, obtained as described in [6] from 2 moles of potassium diethyl dithiophosphate and 1 mole of epichlorohydrin in aqueous solution, gives a value of approximately 7-8% of thioepoxide sulfur.

The formation of thioepichlorohydrin in the first step of the reaction of epichlorohydrin with the salts of phosphorus thioacids was proved by its isolation in small amount of the reaction mixture. Thus, the heating of the triethylammonium salt of diethyl dithiophosphate with epichlorohydrin at 50-60° for 30 min resulted in the isolation of a small amount of thioepichlorohydrin as a mixture with epichlorohydrin: bp  $30-33^{\circ}$  (10 mm);  $d_4^{20}$  1.220;  $n_D^{20}$  1.5180. Found: Sthioepoxy 21%; Cl 35.65%. Allyl chloride with  $n_D^{20}$  1.4170 was isolated when this mixture was reacted with hexaethyltriamidophosphite

$$ClCH_{2}CH-CH_{2} + [(C_{2}H_{5})_{2}N]_{3}P \rightarrow CH_{2} = CH-CH_{2}Cl + [(C_{2}H_{5})_{2}N]_{3}PS$$

We are of the opinion that when equimolar amounts of potassium thioacetate and epichlorohydrin are reacted the first reaction to take place is also thioepoxidation of the ring, which, entering into reaction with the formed potassium acetate, gives thietanol acetate as the result of isomerization

$$CH_{2}-CH-CH_{2}Cl+CH_{3}CSK \rightarrow ClCH_{2}CH-CH_{2}+CH_{3}COOK \rightarrow CH_{3}COOCH S+KCl$$

The IR spectra of this compound are identical with those of the 3-thietanyl acetate obtained by countersynthesis [7]. In addition, the compound obtained in this reaction fails to react with thiourea in methanol. In [8] the theory was expressed that alkali metal xanthates react with olefin oxides to give the thioepoxy compound, from which the trithiocarbonate is formed in the next step. But the authors of [8] isolated only the end reaction products, i.e., the trithiocarbonates. From the reaction of potassium ethyl xanthate with propylene oxide in water we were able to isolate propylene sulfide in low yield, and consequently corroborate the theory expressed in [8].

$$\begin{array}{c} C_2H_5OCSK + CH_3 - CH - CH_2 \rightarrow CH_3 - CH - CH_2 + C_2H_5OCOK \\ \parallel \\ S \\ 0 \\ \end{array}$$

## É X P E R I M E N T A L

Reaction of Thioepichlorohydrin with the Triethylammonium Salt of O,O-Diethyl Thiophosphate. From 13.8 g of diethyl phosphate, 3.2 g of S, and 10.1 g of  $(C_2H_5)_3N$  in benzene was obtained the triethylammonium salt, to which, with heating at 60° and stirring, was added 10 g of thioepichlorohydrin. The reaction mixture was heated at benzene reflux for 30 min. Then the  $(C_2H_5)_3N$ ·HCl was filtered, while the benzene solution was fractionally distilled. We obtained 11.7 g (50%) of O,O-diethyl thioglycidyl thiophosphate with bp 116-118° (0.3 mm);  $d_4^{20}$  1.2198;  $n_D^{20}$  1.5140. Found: Sthioepoxy 13.24; P 12.67%.  $C_7H_{15}O_3PS_2$ . Calculated: P 12.81; Sthioepoxy 13.22%.

When a mixture of 9.3 g of O,O-diethyl dithiophosphate, 5 g of  $(C_2H_5)_3N$ , and 4.5 g of epichlorohydrin was heated in refluxing toluene we obtained 5 g of diethyl thioglycidyl thiophosphate with bp 111-113° (0.2 mm);  $d_4^{20}$  1.2280;  $n_D^{20}$  5180. Found: P 13.05; Sthioepoxy 13.32%.  $C_7H_{15}O_3PS_2$ . Calculated: P 12.81; Sthioepoxy 13.22%.

Preparation of Dimethyl Ester of  $\beta$ , $\gamma$ -Epoxypropylphosphinic Acid. In a two-necked flask, fitted with a reflux condenser and a dropping funnel, was placed 20 g of epibromohydrin and it was heated up to 120-130°. To the flask contents was added 16.5 g of trimethyl phosphite in drops. After adding all of the trimethyl phosphite the reaction mass was heated at 130° for approximately 40 min, and then it was fractionally distilled. The constants of the obtained ester are given in Table 2.

Synthesis of Ethyl Ester of Diethylamido- $\beta,\gamma$ -epoxypropylphosphinic Acid. To 13 g of epibromohydrin, contained in an Arbuzov flask and heated to 130°, was slowly added 13.2 g of the diethyl ester of diethylamidophosphorous acid. Here the bath temperature was not allowed to exceed 140°. When about half of the calculated amount of ethyl bromide had distilled off, the residue in the flask was distilled. The constants of the obtained product are given in Table 2. All of the other esters and ester-amides of  $\beta,\gamma$ -epoxypropylphosphinic acid were obtained in a similar manner.

Preparation of Dimethyl Ester of  $\beta$ , $\gamma$ -Thioepoxypropylphosphinic Acid. A mixture of 4.5 g of the dimethyl ester of  $\beta$ , $\gamma$ -epoxypropylphosphinic acid and 5 g of anhydrous dimethyl dithiophosphate in 15 ml of propanol was heated at 70-80° for 1 h. The reaction mixture was cooled, ether was added, and the ether solution was washed twice with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and distilled. The constants of the obtained ester are given in Table 3. The other dialkyl esters of  $\beta$ , $\gamma$ -thioepoxypropylphosphinic acid were obtained in a similar manner (see Table 3).

Preparation of Diethyl Ester of α-Methylthioepoxyvinylphosphinic Acid. Using the same method as in the preceding, from 9.5 g of the diethyl ester of α-methylepoxyvinylphosphinic acid and 11 g of potassium diethyl dithiophosphate was obtained 5 g of the diethyl ester of α-methylthioepoxyvinylphosphinic acid with bp 74-76° (0.3 mm);  $d_4^{20}$  1.1449;  $n_D^{20}$  1.4690. Found: C 39.90; H 7.17; P 14.42; S 14.70%. C<sub>7</sub>H<sub>15</sub>O<sub>3</sub>PS. Calculated: C 40.00; H 7.14; P 14.76; S 15.23%. When 2.1 g of the obtained compound was mixed with 2.45 g of hexaethyltriamidophosphite the temperature of the reaction mass rose to 74°. After additional heating at 100-120° for 10 min and fractional distillation of the reaction mass we obtained: 1) the diethyl ester of α-methylvinylphosphinic acid with bp 79-80° (10 mm);  $d_4^{20}$  1.0258;  $n_D^{20}$  1.4320 in an amount of 1.2 g. Found: C 46.66; H 8.58; P 17.38%.  $C_7H_{15}O_3P$ . Calculated: C 47.19; H 8.42; P 17.41%; 2) 2.7 g of hexaethyltriamidothiophosphate with bp 105-107° (0.3 mm);  $n_D^{20}$  1.5000.

Reaction of Potassium Thioacetate with Epichlorohydrin. To a solution of 36 g of potassium thioacetate in 50 ml of water was added 29 g of epichlorohydrin. The mixture was heated at 60-70° for 1 h, extracted with CHCl<sub>3</sub>, dried over CaCl<sub>2</sub>, and fractionally distilled. We obtained 7.6 g of 3-thietanyl acetate with bp 44-46° (0.3 mm);  $d_4^{20}$  1.1776;  $n_D^{20}$  1.4940. Found: C 44.90; H 6.12%. C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>S. Calculated: C 45.40; H 6.06%.

Reaction of Propylene Oxide with Potassium Xanthate. In a three-necked flask, fitted with a stirrer, dropping funnel and a reflux condenser, was placed a solution of 16 g of potassium ethyl xanthate in 50 ml of water, and the solution was heated up to 60°. To the stirred solution was then added 10 g of propylene oxide, keeping the temperature below 60°. When all of the oxide had been added at 60° the heating was stopped, the reflux condenser was replaced by a descending condenser, and the bath temperature was raised to 90-100°. We distilled off about 2.5 g of crude propylene sulfide, which on redistillation boiled at 73-75° (760 mm);  $d_4^{20}$  0.9376;  $n_2^{D}$  1.4730. Found: Sthioepoxy 42.1%. C<sub>3</sub>H<sub>6</sub>S. Calculated: Sthioepoxy 43.24%.

Reaction of Epichlorohydrin with Potassium O,O-Diethyl Dithiophosphate. Ratio of Reactants 1:2. The heating of a mixture of 6 g of epichlorohydrin and 30 g of potassium diethyl dithiophosphate in 50 ml of water at 60-70°, and subsequent treatment of the reaction mixture as described in [6], gave 11 g of a mixture of O,O-diethyl thioglycidyl dithiophosphate and O,O-diethyl 3-thietanyl dithiophosphate with bp 111-113° (0.2 mm);  $d_4^{20}$  1.2230;  $n_D^{20}$  1.5521. Found: C 33.07; H 5.94; P 12.09; Sthioepoxy 7.7%.  $C_7H_{15}O_2PS_3$ . Calculated: C 32.55; H 5.81; P 12.00; Sthioepoxy 12.40%.

Ratio of Reactants 1:1. From a solution of 18 g of potassium diethyl dithiophosphate in 50 ml of water and 7.4 g of epichlorohydrin was obtained by a similar procedure 7 g of a mixture with bp 111-114° (0.1 mm);  $d_4^{20}$  1.2300;  $n_D^{20}$  1.5339, the composition and elemental analysis of which was mentioned above.

Synthesis of Propylene Sulfide and Phenyl Thioglycidyl Ether. The heating of an aqueous solution of equimolar amounts of propylene oxide or phenyl glycidyl ether at 60-80° with either potassium diethyl thiophosphate or potassium diethyl dithiophosphate respectively gave propylene sulfide and phenyl thio-glycidyl ether, the constants of which are given in Table 1.

## CONCLUSIONS

1. When the alkali metal salts or the ammonium salts of O,O-dialkyl thiophosphates or O,O-dialkyl dithiophosphates are reacted with epoxy compounds the latter undergo thioepoxidation.

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