SYNTHESIS OF SOME THIOGLYCIDYL ESTERS OF MONOBASIC CARBOXYLIC ACIDS

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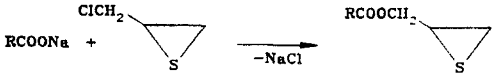
Thioglycidyl esters of monobasic carboxylic acids were synthesized by thioepoxidation of glycidyl esters of thiourea.

Despite the fact that data on the methods of synthesis and on the properties of thiirane compounds have been correlated and systematized in a monograph [1], the amount of data in the literature regarding thioglycidyl esters of monobasic carboxylic acids is small. Acetic acid thioglycidyl ester was obtained for the first time in [2] by the reaction of potassium acetate with thioepichlorohydrin. This method was then perfected [3]. Thioglycidyl esters of acetic, methacrylic, and benzoic acids were obtained by Arbuzov and coworkers [4, 5] by thioepoxidation of the corresponding oxiranes with thiourea.

In our search for new thiiranes and their amino derivatives [6], in the present research we carried out the synthesis of some thioglycidyl esters of monobasic carboxylic acids either by thioepoxidation of the corresponding glycidyl esters with thiourea or by reaction of thioepichlorohydrin with acid salts.

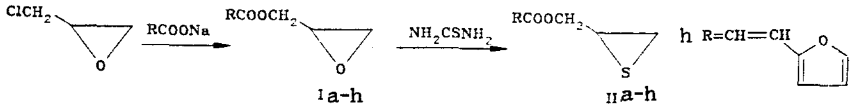
We observed that the yields of the corresponding thiiranes ranged from 10% to 20% in the reaction of thioepichlorohydrin with acid salts in aprotic solvents in the presence of catalysts (triethylbenzylammonium chloride, triethylamine):



IIb,f

IIb $R=C_3H_7$; f $R=CH_2C_6H_5$

In this connection it seemed expedient to synthesize thiiranes through the corresponding oxiranes. Using a known method [7, 8] we obtained the previously described oxiranes Ia-e and the unknown If-h:



Ia-h IIa-h

I, II a $R=CH_3$; b $R=C_3H_7$; c $R=C_4H_9$; d $R=C_7H_{15}$; e $R=C_6H_5$; f $R=CH_2C_6H_5$; g $R=C_6H_4Cl$-*o*

All of the synthesized oxiranes Ia-f were converted to the corresponding thiiranes by thioepoxidation with thiourea (see Tables 1 and 2).

The physicochemical constants of the synthesized thiiranes were identical to the constants of thiiranes obtained on the basis of the reaction of thioepichlorohydrin with acid salts in aprotic solvents. These results demonstrate that a thiirane–thietane rearrangement does not occur in the reaction of thioepichlorohydrin with acid salts in aprotic solvents.

Absorption bands at 830-860, 1020-1030, and 1235-1255 cm^{-1}, which are characteristic for the oxirane ring, and an intense absorption band of a carbonyl group at 1720-1745 cm^{-1} are observed in the IR spectra of oxiranes Ia-f. An intense absorption band that characterizes the stretching vibrations of the C–S bond in the thiirane ring of esters IIa-h is observed at 630-645 cm^{-1}.

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TABLE 1. Characteristics of the Synthesized If-h and IIa-h

Compound	Empirical formula	bp, °C (mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	R_f	Yield, %
If	$C_{11}H_{12}O_3$	160...161 (4)	1,5165	1,1396	51,20	50,98	0,70	70
Ig	$C_{10}H_9ClO_3$	145...146 (2,8)	1,5365	1,2850	51,60	51,45	0,66	55
Ih	$C_{10}H_{10}O_4$	143...144 (2,5)	1,5690	1,3231	48,04	48,23	0,64	50
IIa*	$C_5H_8O_2S$	52...53 (2,8)	1,4820	1,1436	33,14	33,45	0,85	78
IIb	$C_7H_{12}O_2S$	93...94 (3)	1,4760	1,0591	42,61	42,69	0,92	60
IIc	$C_8H_{14}O_2S$	58 (0,5)	1,4732	1,0378	47,05	47,31	0,82	57
IId	$C_{11}H_{20}O_2S$	134...136 (2,8)	1,4550	0,9629	60,86	61,16	0,92	55
IIe †	$C_{10}H_{10}O_2S$	125 (1)	1,5630	1,1898	53,03	52,94	0,87	56
IIf	$C_{11}H_{12}O_2S$	122 (0,8)	1,5502	1,1552	57,43	57,56	0,89	75
IIg	$C_{10}H_9ClO_2S$	146...148 (1,5)	1,5655	1,2942	57,55	57,81	0,88	54
IIh ‡	$C_{10}H_{10}O_3S$	142 (1)	1,6080	—	—	—	0,71	50

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*According to the data in [4], this compound had bp 71°C (12 mm) and n_D^{20} 1.4822 and was obtained in 61% yield.

†According to the data in [5], this compound had bp 117°C (0.2 mm) and n_D^{20} 1.5638 and was obtained in 35% yield.

‡This compound had mp 38-39°C.

TABLE 2. Spectral Characteristics of Thioglycidyl Esters IIa-h

Compound	IR spectrum, cm^{-1}		PMR spectrum, δ, ppm						
						R			
	C=O	C—C S	CH_2S	$O—CH_2$	CH	CH_2CO	CH_2, m	CH_3	Ar
IIa	1740	635	2,15; 2,40 d	3,90	2,85			2,0 s	
IIb	1745	630	2,30; 2,50 d	4,15	3,20	2,2d	1,30...1,80	0,9 m	
IIc	1745	640	2,15; 2,35 d	4,20	3,00	2,1 d	1,15...1,70	0,8 m	
IId	1740	635	2,10; 2,45 d	4,10	3,15	2,0 d	1,20...1,75	0,9 m	
IIe	1725	630	2,25; 2,45 d	4,10	3,00				7,10...7,70m
IIf	1745	645	2,15; 2,35 d	3,90	2,80	3,45 s			6,90 s
IIg	1725	630	2,15; 2,30 d	4,15	3,10				6,80...7,80m
IIh	1725	635	2,15; 2,40 d	3,90	3,10				

In the PMR spectra of thiiranes IIa-h signals of the protons of the CH_2 group attached to the thiirane ring show up in the form of two doublets at 2.10-2.30 ppm and 2.35-2.50 ppm and correspond to trans and cis protons. In addition to signals of protons of a thiirane fragment, the PMR spectrum of furyl-substituted thiirane IIh contains signals of protons of a vinyl radical — two doublets at 5.75 and 7.05 ppm ($J_{\alpha\beta}$ = 15 Hz). The signals of the β protons of the furan ring at 6.25 and 6.10 ppm show up in the form of a doublet and a doublet of doublets, respectively (J_{34} = 5 Hz and J_{45} = 2.2 Hz); the signal of the 5-H proton at 7.15 ppm appears as a poorly resolved doublet.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Varian T-60 spectrometer with tetramethylsilane (TMS) as the internal standard. The IR spectra of liquid films of the compounds were recorded with a Specord 75-IR spectrometer. The purity of the compounds was determined by GLC with a Tsvet-4 chromatograph: the stainless-steel column (200 by 0.3 cm) was packed with a 5% solution of polyphenyl ether on Chromaton N-AW with a grain size of 0.25-0.50 mm, the temperature was 160°C, the carrier gas was steam at a pressure of 0.10-0.15 kg/cm^2, and the sample introduced into the column had a volume V of 0.1 µl. The course of the reaction was monitored by TLC on Silufol UV-254 plates in ethanol—hexane (1:5). The results of elementary analysis of all of the newly synthesized compounds I and II were correct.

Thioepichlorohydrin was obtained by the method in [10] in 50% yield and had bp 135°C and n_D^{20} 1.5270 (n_D^{20} 1.5280 [10]). Oxiranes Ia-e were obtained by the methods in [7, 8].

The results of elementary analysis of I and II for C, H, and S were in agreement with the calculated values.

1,2-Epoxy-3-phenylacetoxypropane (If, $C_{11}H_{12}O_2$). A 4.6-g (0.2 mole) sample of sodium metal was added with vigorous stirring to a solution of 27.2 g (0.2 mole) of phenylacetic acid in 100 ml of benzene. After the sodium had undergone complete reaction, 1.1 g (0.005 mole) of triethylbenzylammonium chloride and 37 g (0.4 mole) of epichlorohydrin were added to the reaction mixture, and the mixture was heated with stirring for 2 h at 115-117°C. It was then cooled to room temperature, washed with water, and extracted with carbon tetrachloride. The organic layer was dried over sodium sulfate, the solvent was removed by distillation, and the reaction product was fractionated in vacuo.

The corresponding oxirane Ig was similarly synthesized from 31.3 g (0.2 mole) of o-chlorobenzoic acid and 37 g (0.4 mole) of epichlorohydrin. The reaction of 27.6 g of β-(α-furyl)-acrylic acid and 37 g of epichlorohydrin gave 18.5 g of oxirane Ih.

1,2-Epithio-3-phenylacetoxypropane (IIf). A 6.1-g (0.08 mole) sample of thiourea was added to a solution of 14.1 g (0.08 mole) of epoxide If in 50 ml of ethanol, and the mixture was stirred for 4 h at 35-40°C. The organic layer was washed with water and extracted with carbon tetrachloride, and the extract was dried over $MgSO_4$.

The other representatives of thioglycidyl esters IIa-h were similarly synthesized (see Tables 1 and 2).

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