SYNTHESIS AND PROPERTIES OF DICARBOXYLIC ACID BIS(THIETANYL) ESTERS

M. A. Allakhverdiev, N. A. Akperov, V. M. Farzaliev,
B. R. Gasanov, and V. V. Goryachev

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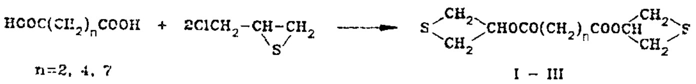
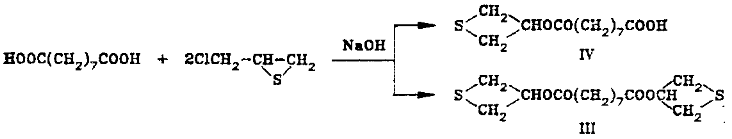
The reactions of some dibasic carboxylic acids with thioepichlorohydrins in the presence of interphase catalysts were studied. The first representatives of bis(thietanyl) esters of dicarboxylic acids were synthesized and characterized.

Thietanes are four-membered organosulfur heterocyclic compounds; methods for their synthesis have been correlated in a review [1]. No information regarding bis(thietanyl) esters of dicarboxylic acids is available in the literature.

In the present research we set out to synthesize some bis(thietanyl) esters of dicarboxylic acids and study their properties. For this, we investigated the reactions of some dibasic carboxylic acids with thioepichlorohydrin in the presence of benzyltriethylammonium chloride in a two-phase system with an equivalent amount of sodium hydroxide:



It is known [2] that a thirane–thietane rearrangement, which ultimately leads to the formation of the corresponding 3-thietanyl ester, occurs in the presence of alkali. In particular, in the reaction of azelaic acid with thioepichlorohydrin monosubstituted thietane IV is also formed in addition to symmetrical 3-thietanyl ester III:



The structures of the compounds obtained were proved by IR and PMR spectroscopy, and their characteristics are presented in Table 1.

The synthesized dicarboxylic acid bis(thietanyl) esters are white crystalline substances that are quite soluble in diethyl ether, acetone, and ethanol and insoluble in cold hexane.

A characteristic absorption band in the form of a doublet at 1710 and 1740 cm^{-1}, which corresponds to the carbonyl group in the molecules of the compounds, is observed in the IR spectra of 3-thietanyl esters I-III. The absorption band at 1470 and 1035 cm^{-1} characterizes the C–S bond in the thietane ring [3].

In the PMR spectra of I-III the signals of the protons of the $(CH_2)_n$ fragment when n = 2 appear at strongest field at 2.33 ppm in the form of a singlet, whereas when n = 4 and n = 7 the signals of the same protons are observed in the form of a multiplet at 1.4 ppm. The signals of the protons of the two methylene groups bonded to the C=O group are observed in the form of a triplet at 2.35 ppm. The signals of the protons of the two methylene groups in the thietane ring show up in the form of two doublets at 3.35 ppm. The methylidyne proton in the thietane ring usually appears in the form of a quintet at 5.65 ppm.

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TABLE 1. Mass Spectra of I-VII

Compound	Empirical formula	mp, °C	R_f	Yield, %
I	$C_{10}H_{14}O_4S_2$	90	0,76	45
II	$C_{12}H_{18}O_4S_2$	76...77	0,72	47
III	$C_{15}H_{24}O_4S_2$	42...43	0,75	65
IV	$C_{12}H_{20}O_4S$	57...58	0,82	6,0

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*The peaks of ions with $I_{rel} \geq$ 10% are presented.

In the case of monosubstituted thietane IV, in contrast to the examined compounds, the signals of the protons of the methylene groups show up at weakest field at 10.25 ppm; the signal of the proton corresponding to the carboxy group is observed in the form of a broad signal.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a Specord 75 IR spectrometer. The PMR spectra of solutions in CCl_4 were recorded with a Varian T-60 spectrometer with tetramethylsilane (TMS) as the internal standard. The purity of the synthesized compounds was determined by GLC with a Tsvet-4 chromatograph. The conditions used for the analysis were as follows: the column was 200 by 0.3 cm and was packed with 5% polyphenyl ether on Chromaton N-AW with particle size 0.5-0.25 mm, the column temperature was 160°C, and the carrier gas was water vapor (P_{H_2O} = 0.1-0.5 kg/cm^2). The results of elementary analysis for C, H, and S correspond to the calculated values.

Thin-layer chromatography was carried out on Silufol UV-254 plates with hexane and ethanol in a ratio of 1:5 as the eluent. One spot was formed in the case of development with iodine vapors.

The thioepichlorohydrin was obtained by the method in [4]. The product was obtained in 50% yield and had bp 135°C and n_D^{20} 1.5270 (n_D^{20} 1.5280) [4].

1,2-Bis(thietanyloxycarbonyl)ethane (I). A 12-g (0.1 mole) sample of succinic acid and 8 g (0.2 mole) of sodium hydroxide dissolved in 30 ml of distilled water were placed in a three-necked flask, the reaction mixture was heated with vigorous stirring to 70°C for 1 h, 1 g (0.005 mole) of benzyltriethylammonium chloride (as the interphase catalyst) was added, and 22 g (0.2 mole) of thioepichlorohydrin was then added dropwise. The mixture was maintained at the indicated temperature for another 8 h. The course of the reaction was monitored by TLC. The reaction product was then extracted with ether and dried over anhydrous sodium sulfate. The solvent was removed by distillation, and the residue was recrystallized from hexane to give 12 g (45%) of succinic acid bis(thietanyl) ester I with mp 90°C.

The other representatives of 3-thietanyl esters (I-III) were similarly synthesized.

LITERATURE CITED

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