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To the memory of A.A.Petrov

Reaction of 4-(*N,N*-Dimethylaminophenyl)magnesium Bromide with Palladium Tetrakis(triphenylphosphine)*

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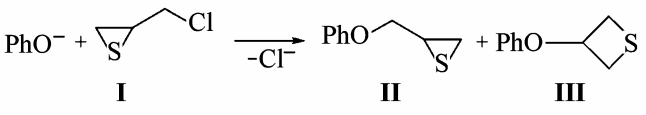
Abstract—(α-Chloroalkyl)thiiranes react with sodium phenolates at heating in water-alcohol mixtures furnishing phenoxymethylthiiranes, 3-phenoxythietanes (resulting from thiirane-thietane rearrangement), or their mixture. The increased polarity of solvent favors the thiirane-thietane rearrangement. 2,2-Dimethyl-3-(chloromethyl)thiirane forms an exclusion for it does not afford (phenoxymethyl)thiirane even in anhydrous ethanol. Diastereomeric erythro- and threo-(1-chloroethyl)thiiranes react stereospecifically giving 2-methyl-3-phenoxymethylthiiranes or 2-methyl-3-phenoxythietanes of *trans*- and *cis*-configuration respectively. Specific features of these reactions are discussed from the viewpoint of solvent polarity effect on the competition between formal chlorine substitution along "recyclization" mechanism or through thiirane-thietane rearrangement.

We established previously that epithiohalohydrins and their simplest homologs reacted with morpholine through a mechanism of cycle opening cycle closure («recyclization») of the thiirane ring affording at equimolar amount of reagents rearranged (morpholinomethyl)thiiranes similar to behavior of epihalohydrins [2].

At the same time (chloromethyl)thiirane (**I**) is known to react fairly unusual with harder nucleophiles of phenol type providing either arylthioglycidyl ethers (**II**), or 3-phenoxythietanes (**III**), or mixtures thereof depending on the reaction conditions [3].



I **II** **III**

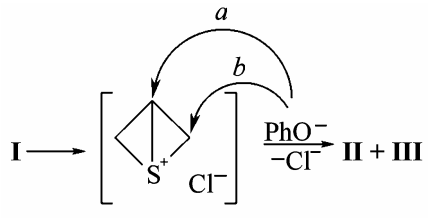
The latter direction, the so-called thiirane-thietane rearrangement, is quite unexpected in the epihalohydrin series. In the general case the course of the process is governed both by the character of nucleophile, polarity of solvent, and the nature of the leaving group.

The reaction may occur either giving rise to thiiranes, or to thietanes, or to their mixture. Thiiranes are formed in reactions of thiolates [4–9], secondary amines [9, 10], N,N-dialkyldithiocarbamates [11], and alcoholates [12, 13]. Thietanes formation was first revealed in reactions with alkali [14] and salts of carboxylic acids [15]. Further studies showed that with such nucleophiles as phenolates [3], *N,N*-dialkyldithiophosphates [16–18], and thioacetates [15] arose both thiiranes and thietanes depending on the conditions. It was presumed that the structure of the product originated from different directions of thiirane ring opening in different media: in water at the secondary, and in aprotic solvents at the primary carbon atom, and this behavior was ascribed to dissimilar character of thiirane (**I**) solvation. However this assumption on the different places of ring opening of the thiirane ring was disproved, for the later data [2, 19] indicated that the ring opened at the primary carbon atom. Detailed kinetic study of (chloromethyl)thiirane solvolysis in aqueous dioxane demonstrated that the reaction corresponded to S_N1 mechanism [8].

In this connection the target of this study is acquisition of new data on reaction mechanism of (α-chloroalkyl)thiiranes and phenolate anions and investigation of new synthetic opportunities of the thiirane-thietane rearrangement. One problem concerns the elucidation whether exists a possibility of (phenoxymethyl)thiiranes formation by an attack of the phenolate anion on the atom *2* of the intermediately arising

* For communication II see [1].

1-thioniabicyclobutane (path b), or its opening always occurs at the central C–S bond (path *a*) giving rise to



3-phenoxythietanes, and (phenoxymethyl)tiiranes are generated independently.

As the easiest way to clear this problem we regarded a reaction of 2-(chloromethyl)thiirane-3,3-d_2 (**Ia**) [2] with sodium phenolate under conditions where both thiirane and thietane formed simultaneously. Here the distribution of the label in the (phenoxymethyl)thiirane would suggest whether the thiirane formation be an independent process [in case of label transition to the exocyclic carbon atom of the (phenoxymethyl)thiirane, (path *c*)], or occurs a concurrent opening of thioniabicyclobutane in both directions (paths *a* and *b*).

The thiirane/thietane ratio we planned to measure by GLC. Therefore we synthesized individual unlabeled (phenoxymethyl)thiirane (**II**) and 3-phenoxythietane (**III**). Thiirane **II** was obtained from glycidyl phenyl ether (**V**) via isothiuronium salt (**s**). 3-Phenoxythietane (**III**) was obtained by treating thiirane **I** with aqueous sodium phenolate [3]. The ratio of these products strongly depeds on the solvent, and the mixture thiirane/thietane of desired ratio according to [3]

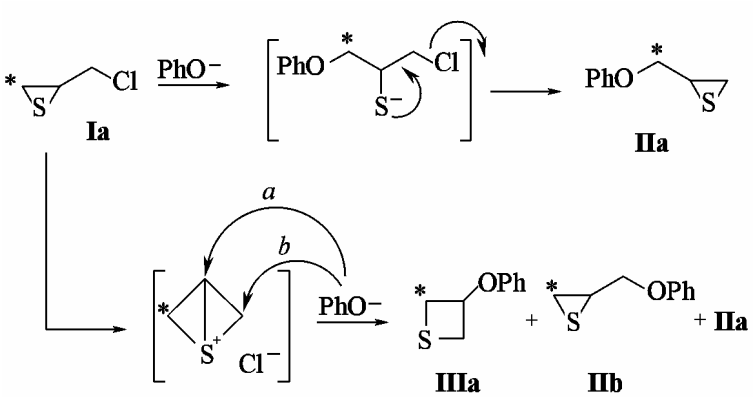
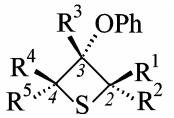


Table 1. [1]H NMR spectra of solutions of 3-phenoxythietanes **III, X, XII, XVIa, b** in $CDCl_3$, δ, ppm, *J*, Hz



Compd. no.	R^1	R^2	R^3	R^4	R^5	H arom	$^2J_{12}$	$^3J_{13}$	$^3J_{23}$	$^3J_{34}$	$^3J_{35}$	$^2J_{45}$	^4J
III[a]	3.56	3.36	5.28	3.36	3.56	7.1–7.7	9.8	7.9	7.6	7.6	7.9	9.8	1.7
X	3.09	3.90	1.73	3.09	3.90	7.1–7.7	9.7	–	–	–	–	9.7	–
XII	1.45	1.61	4.91	3.25		7.1–7.7	–	–	–	8.0	8.0	–	–
XVIa	4.23	1.63	4.98	3.49	3.53	7.1–7.7	6.0	–[b]	–[b]	–[b]	–[b]	–[b]	–
XVIa[c]	4.11	1.34	4.68	3.04	3.22	7.1–7.7	6.5	7.2	–	8.1	8.4	8.3	–
XVIb	1.53	3.87	5.32	3.34	3.65	7.1–7.7	6.9	–	7.8	7.8	7.8	9.5	1.7

[a] The spectrum was recorded at operating frequency 100 MHz.
[b] Coupling constants not determined.
[c] The spectrum was recorded in C_6D_6 solution.

Table 2. ^{13}C NMR spectra of 3-phenoxythietanes **III, X, XII, XVIa, b,** δ, ppm, *J*, Hz

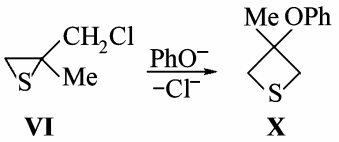
Compd. no.	R^1	R^2	R^3	C^2	C^3	C^4	C arom
III	–	–	–	35.7	74.1	35.7	115.2, 121.6, 129.7, 156.5
X	–	–	23.3	40.0	80.3	40.0	118.5, 121.7, 129.2, 154.5
XII	30.5	24.3	–	56.3	78.3	31.1	115.3, 121.3, 129.4, 156.9
XVIa	–	21.4	–	47.2	78.4	32.5	115.3, 121.4, 129.5, 156.6
XVIb	16.8	–	–	45.6	71.6	33.0	114.7, 121.2, 129.5, 156.6

should form in acetonitrile. However under these conditions we obtained and identified by GLC as the only product thiirane **II**. The reaction carried out in anhydrous ethanol also furnished only thiirane **II** although in [3] was indicated that here thietane **III** should be the prevailing product. In this situation we were obliged to chose the proper solvent by ourselves; it turned out to be 85% aqueous ethanol. The ratio of compounds **II/III** in the product was according to GLC 5 : 2, convenient for the analysis of the spectra. In this connection we are obliged to mention that the analytical procedure used in [3] to determine the composition of reaction mixture obviously gave incorrect results (it was based on «selective» iodometric titration of thiiranes [3]). Actually 3-aryloxythietanes form only in the presence of water; in all anhydrous solvents, even in alcohols, arise only thiiranes and products of their further transformations. This is due apparently to stringent requirements of 1-thioniabicyclobutane toward solvation. ^{13}C NMR spectrum of the obtained mixture of products **IIa**, and **IIIa** unambiguously showed that the label was transmitted into the α-position with respect to the thiirane ring, thus evidencing insignificant role of path *b*.

Thus (phenoxymethyl)thiiranes form independent of 3-phenoxythietanes, and as in the case of N-nucleophiles the reaction proceeds through «recyclization» mechanism.

It was reasonable to assume that introduction of additional substituents (in the simplest case methyl groups) both into the thiiraane ring proper and into α-position to it would affect both the selectivity and rate of reactions between (α-haloalkyl)thiiranes and nucleophiles. However we could not predict the extent of such influence: the homologs of (chloromethyl)thiirane we were the first to synthesize, and comparison with oxygen-containing analogs not always suggested correct prediction of behavior of sulfur analogs. In order to elucidate the character of this influence we studied the reaction of the simplest homologs of (chloromethyl)thiirane (**I**): 2-methyl-2-(chloromethyl)thiirane (**VI**), 2,2-dimethyl-3-(chloromethyl)thiirane (**VII**), and diastereomeric erythro- and threo-(α-chloroethyl)-thiiranes (**VIII**) and (**IX**) with phenolate anion in water-alcohol mixtures of various compositions.

Reaction of thiirane **VI** with sodium phenolate even in anhydrous ethanol gave rise only to 3-methyl-3-phenoxythietane (**X**) which structure nambiguously follows from its ^1H and ^{13}C NMR spectra (Tables 1, 2).



VI **X**

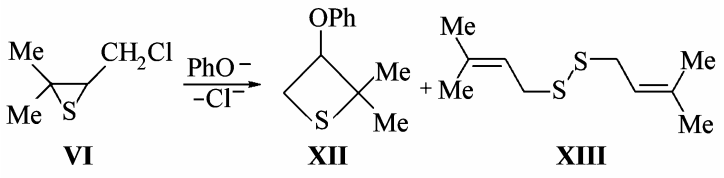
In the ^1H NMR spectrum of thietane X appears a singlet from three protons of a methyl group (δ 1.73 ppm) and AA' system with $^3J_{HH}$ 9.7 Hz from nonequivalent protons at C^2 and C^4 ($H_{a'}$ and $H_{a'}$) belonging to thietane ring (δ 3.09–3.90 ì.ä.). In the upfield region of the ^{13}C NMR spectrum are present only three signals of carbon atoms. The mass spectrum is also consistent with the structure of 3-methyl-3-phenoxythietane (**X**): the lack of a peak with *m/z* $[M-33]^+$ is unusual for thiiranes but common for thietanes[20].

Thiirane **VII** in reaction with sodium phenolate in water-alcohol mixtures of various compositions (50–100% of ethanol) furnished a mixture of two compounds in 1 : 1 ratio, insensitive to the ethanol–water ratio. It was first assumed that the products mixture contained 2,2-dimethyl-3-(phenoxymethyl)thiirane (**XI**) and thietane (**XII**).

However it seemed dubious because of nearly complete insensitivity of the products ratio to the solvent composition: with (chloromethyl)thiirane (**I**) in its reaction with phenolate the influence of the medium character on the ratio of products is very pronounced. Besides thiirane **XI** might arise here only from direct replacement of chlorine because the «recyclization» mechanism for 2,2-dimethyl-3-(chloromethyl)thiirane (**VII**) is inconsistent with Krasusky rule. The products

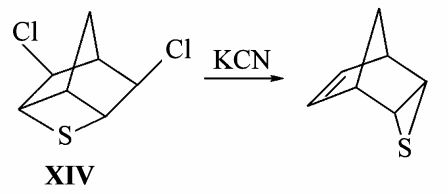
mixture was separated by means of preparative TLC on silica gel. Analysis of ^{1}H and ^{13}C NMR spectra of the products revealed that one of them actually was 2,2-dimethyl-3-phenoxythietane (**XII**). Its ^{1}H NMR spectrum contains a system AX_2, where a signal of δ 4.91 ppm (1H, $^3J_{HH}$ 8 Hz) obviously corresponds to the proton attached to C^3 of the thietane ring, but not to methylene protons of the phenoxymethylene group (their resonances are located in the region 3.5-4.5 ppm). The mass spectrum is consistent with structure **XII** for it lacks a peak of *m/z* $[M-33]^+$characteristic of thiirane spectra.

The ^{13}C and ^{1}H NMR spectra of the second product lack carbon and proton signals belonging to the phenoxy group. The ^{1}H NMR spectrum is consistent with a structure containing a 3-methyl-2-butenyl fragment where the signal of a single olefin proton is split with an extremely characteristic remote coupling constant $^4J_{HH}$ 1 Hz. In the ^{13}C NMR spectrum appears a set of five signals: two downfield and three upfield. It may be stated basing on these data and also on the mass spectrum of the compound (*m/z* 202, $[M]^+$) that it is bis(3-methyl-2-butenyl) disulfide (**XIII**).



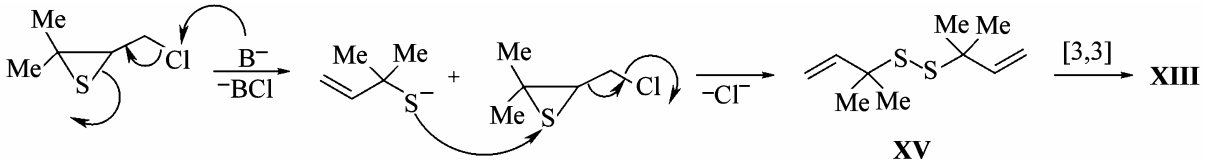
VI **XII** **XIII**

The way of its generation can be suggested only tentatively. An example is known of dechlorination of compound **XIV** at its treating with a base (apparently as a result of a halophilic attack) [21].



XIV

Probably in our case occurs the following process.



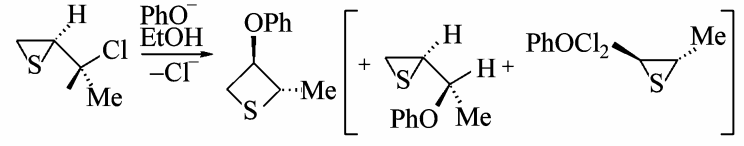
XV

According to data of [22] compound **XV** at room temperature spontaneously rearranges into disulfide **XIII**.

Very peculiar route takes reaction with sodium phenolate of diastereomeric thiiranes **VIII** and **IX**. erythro-Diastereomer **VIII** in anhydrous ethanol furnishes one product (see scheme).

It was identified as thietane (**XVIa**) proceeding from the data of ^{13}C and ^{1}H NMR . Firstly, in the ^{1}H NMR spectrum appears a signal at δ 4.98 ppm charac-

Scheme.



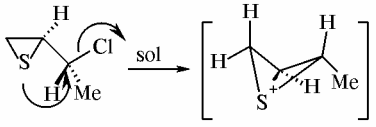
teristic of a proton attached to C^3 atom of a 3-phenoxy-substituted thietane, but not of methylene protons of (phenoxymethyl)thiirane (δ 3.4-4.5 ppm). This signal looks like a «correct quartet», $^3J_{HH}$ 7.6 Hz in C_6D_6 excluding both structure **XVIIIa** where the most deshielded proton of the PhO-C<u>H</u>-Me moiety should appear as a signal of five lines, and structure **XVIIa** in whose spectrum any of the methylene protons from the phenoxymethyl group at thiirane ring should be split either into a doublet of doublets or into a triplet. However sometimes a doublet of doublets looks like a quartet. Then we would be obliged to decide that the second proton of the methylene group has a signal at δ 3.04 or 3.22 ppm that is quite unreasonable for a phenoxymethyl group. The ^{13}C NMR spectrum also testifies to thietane structure **XVIa**. In a 2,3-disubstituted thiirane **XVIIa** the chemical shifts of the carbon atoms in the ring according to our data should fall into the range 35-40 ppm and have very close values. Unlike that in thietane **XVIa** the difference between the chemical shifts of carbons C^2 and C^4 should be significantly greater, as it is actually observed (δ 32.5 and 47.2 ppm respectively). Mass spectrum of the compound is in agreement with the structure of thietane **XVIa.** It does not contain a peak of *m/z* $[M-33]^+$ that is unusual for thiiranes, and the fragmentation of its molecular ion has the pattern that we already have observed for thietanes **X** and **XII** (see EXPERIMENTAL). The *trans*-configuration of the thietane **XVIa** obtained we may now only suggest proceeding from the known stereochemistry of oxirane-oxetane rearrangement observed on erythro-α-methylglycidyl 2,4-dinitrobenzoate [23]. Constant of the coupling between protons attached to C^2 and C^3 of the thietane ring ($^3J_{HH}$ 7.2 Hz, C_6D_6) in this case does not permit determination of compound **XVIa** configuration with the use of the known Karplus expression. The application of Overhauser effect also did not provide unambiguous result due to the spatially close position of all the protons in the ring.

Reaction of threo-diastereomer **IX** with sodium phenolate in anhydrous ethanol also furnished a single product. In the ^{13}C NMR spectrum recorded in the DEPT 135 mode in the upfield region appear in different phases signals of δ 15.7, 35.0 and 36.4 ppm on the one sude and of δ 67.9 on the other side. The latter signal can be definitely assigned only to the carbon atom of the methylene group of the phenoxymethylene fragment in **XVIIb** structure.Taking into account the mechanism of reaction between thiirane **IX** and morpholine [2] we can state that the obtained 2-methyl-3(phenoxymethyl)thiirane (**XVIIb**) has *cis*-configuration. There are no reasons why the stereochemistry of "recyclization" mechanism should change to the opposite in going from amine to phenolate anion. It is confirmed by coupling constant of the protons attached to C^2 and C^3 of the thiirane ring having the value of 6.6 Hz in $CDCl_3$ and 6.8 Hz in C_6D_6.

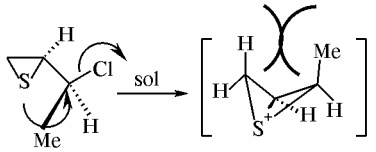
It should be noted that for compounds **IX** and **X** in strongly polar proton solvents sharply grows the probability of direct chlorine replacement as compared to the «recyclization» mechanism due to more efficient solvation of the charged intermediate state.

Thiirane **IX** afforded thietane **XVIb** (with 10% impurity of thiirane **XVIIb**) only in 50% aqueous methanol. The ^{13}C NMR spectrum of the minor component completely coincided with thaat of thiirane **XVIIb**. The **XVIIIb** structure should be rejected because the signal of the methine proton of the phenoxyethyl group would be a multiplet of no less than five lines. Taking into account the structure of the initial thiirane and the mechanism of rearrangement [23] we assume for obtained thietane **XVIb** the *cis*-configuration. Here like in the case of thietane **XVIa** the coupling constant between the protons at C^2 and C^3 atoms permits no unambiguous conclusion with respect to the configuration of compound obtained. The use of Overhauser effect also did not allow uniquely determined result.

However some reasons indicate the validity of the assumptions on the configurations of the corresponding thietanes. Firstly, it is the fact of formation of thiirane **XVIIb** and not thietane **XVIb** from threo-thiirane **IX** in the anhydrous ethanol medium. Let us consider the intermediate of the thiirane-thietane rearrangement, 1-thioniabicyclobutane, for each instance.



VIII VIIIa

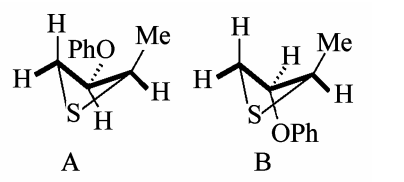


IX IXa

It is seen that in the case of threo-diastereome **IX** in the intermediate **IXa** exists a destabilizing repulsion

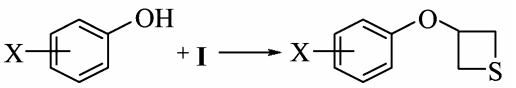
between the pseudoaxial proton at C^4 and pseudoaxial methyl group attached to C^2. This interaction should increase the energy of intermediate **IXa** as compared to that of diastereomeric intermediate **VIIIa** arising from erythro-diastereomer **VIII**. Since the initial thiranes **VIII** and **IX** are approximately equal in energy the difference in the energy of the intermediates should affect the value $\Delta\Delta G^{\neq}$ in keeping with Hammond postulate. The solvation in anhydrous ethanol is insufficiently efficient for the rearrangement to occur in the case of thiirane **IX**, but is amply enough for rearrangement in the reaction of erythro-diastereomer **VIII**. In a water-methanol solution the solvation is more strong , and thiirane-thietane rearrangement occurs also with threo-thiirane **IX**.

Secondly, the remote coupling constant observed in the ^{1}H NMR spectrum of 2-methyl-3-phenoxythietane (**XVIb**) obtained from threo-thiirane **IX** may originate from spin-spin coupling of the W-type in the envelope conformation, i.e. we are dealing with $^4J_{2e',4e'}$. This is possible if exist conformations A and B in thietanes **XVIa** and **XVIb** respectively.



However the B conformation of *trans*-isomer **XVIa** is a lot less favorable than the A conformation of *cis*-isomer **XVIb** due to pseudoaxial location of the phenoxy and methyl groups. In the *cis*-isomer the corresponding A conformation is more feasible because the phenoxy group takes the pseudoequatorial position, and occurrence of configuration with W-type coupling between the protons at C^2 and C^4 seems more probable.

To show the practical application of this rearrangement to organic synthesis we prepared several 3-(aryloxy)thietanes. It should be noted that a series of similar compounds was synthesized before [3], but there were used the simplest phenoles (mono- and polyhalo-substituted, cresols, and methoxyphenols). Besides no information was published on the yields and constants of the compounds obtained (save the data on 3-phenoxythietane), and identification of the substances was performed basing on the elemental analyses for the products of their oxidation, sulfones. In this study we prepared 3 and 4-(thietan-3-yloxy)benzaldehydes (**XIX**), (**XX**), and also 4-(thietan-3-yloxy)-benzoic acid (**XXI**) and its methyl ester **XXII**.



XIX–XXII

X = 3-CHO (**XIX**), 4-CHO (**XX**), 4-CO_2H (**XXI**), 4-CO_2Me (**XXII**).

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker AC 200 at operating frequencies 200 and 59.28 MHz respectively from solutions in $CDCl_3$ with HMDS as internal reference (if not indicated otherwise). In description of DEPT 135 spectra «+» means positive phase (methyl or methine carbon atom), "–" means negative phase (methylene carbon atom), "q" means a lack of DEPT signal (quaternary carbon atom). Mass spectra were measured on GC-MS instrument LKB 2091S, ionizing electrons energy 70eV, ionization current 25μA, accelerating voltage 35 kV, separator temperature 150°C, temperature of ion source 150°C. Glass column 1800 × 2 mm, stationary phase 2% SE-30 on Chromosorb W (80-100 mesh). Oven temperature 50–150°C, vaporizer temperature 200°C. Carrier gas helium, flow rate 30 ml/min. Elemental analyses were carried out on C,H,N-analyzer Hewlett-Packard HP-185B. Reaction progress was monitored and the purity of substances was checked by GLC on chromatograph LKhM-80 equipped with glass columns 2000×3 mm, stationary phase 5% SE-30 on Chromatrone Super 0.125–0.160 mm and 5% XE-60 on Chromatrone N-AW 0.16-0.20 mm; carrier gas helium, flow rate 39 ml/min, detector katharometer. The identification of compounds was performed on two columns. Preparative thin-layer chromatography (PTLC) was carried out on silica gel 40–160 mesh.

(Chloromethyl)thiirane (**I**), 2-(chloromethyl)-thiirane-3,3-d_2 (**Ia**), 2-methyl-2-(chloromethyl)thiirane (**VI**), 2,2-dimethyl-3-(chloromethylthiirane (**VII**), and diastereomeric racemic erythro- and threo-1-(chloroethyl)thiiranes (**VIII**) and (**IX**) were prepared along published procedures [2].

S-(2-hydroxy-3-phenyloxypropyl)isothiuronium sulfate (IV). In a mixture of 3 ml (0.06 mol) of concn. H_2SO_4 and 40 ml of water was dissolved at heating 8.4 g (0.11 mol) of thiourea, the mixture was cooled to 10°C, and to the dispersion obtained was added drop-

wise 15 g (0.1 mol) of phenyl glycidyl ether (**V**). The mixture was then stirred at cooling with ice water for 20 min. The precipitate was filtered off and washed on the filter first with ice water and then with cold acetone. Yield 26 g (98%). T. decomp. > 300°C.

(Phenoxymethyl)thiirane (II). To a suspension of 26 g (0.1 mol) of salt **IV** in 110 ml of water was added dropwise at stirring a solution of 11 g (0.08 mol) of K_2CO_3 in 50 ml of water within 10 min. Then the mixture was stirred for 10 min at 50°C, 50 ml of benzene-pentane mixture, 1:1, was added, and the stirring was continued for 40 min. The organic phase was separated, the water phase was extracted with benzene. The combined organic solutions were dried by sodium sulfate. The solvents were distilled off, the residue was distilled . Yield 11.5 g (70%), bp 100–101°C (2 mm Hg), n_D^{20}1.5778. Published data [24]: bp 106°C (1 mm Hg), n_D^{20} 1.5735. ^{1}H NMR spectrum (100 MHz, CCl_4), δ, ppm: 2.12 d.d (1H, *J* 1.0, *J* 4.5 Hz), 2.40 d.d (1H, *J* 1.0, *J* 6.1 Hz), 2.83 m (1H), 3.66 d.d (1H, *J* 7.0, *J* 10.0 Hz), 4.06 d.d (1H, *J* 5.4, *J* 10.0 Hz), 7.1–7.7 m (5H). ^{13}C NMR spectrum (25.142 MHz, $CDCl_3$), δ, ppm3.8, 31.4, 72.6, 114.8, 121.3, 129.6, 158.5.

3-Phenoxtthietane (III). To a solution of 14.1 g (0.15 mol) of phenol and 6.0 g (0.15 mol) of NaOH in 20 ml of H_2O at stirring within 30 min was added 16.3 g (0.15 mol) of thiirane **I**. The mixture was stirred for 2 h at 70°C, cooled, extracted with ether, the extracte was washed with 5% water solution of NaOH, with water, and dried with Na_2SO_4. The ether was distilled off, the residue was subjected to distillation. Yeidl 6 g (24%), bp100–101°C (2 mm Hg), mp 39–40°C. Published data [3]: bp 130–140°C (12 mm Hg), mp 39°C.

Reaction of 2-(chloromethyl)thiirane-3,3-d_2 (Ia) with sodium phenolate. To emulsion of 4,8 g (44 mmol) of thiirane **Ia** in 30 ml of 85% (by volume) aqueous ethanol was added dropwise while stirring at 44-45°C within 1 h a solution of 44 mmol of sodium phenolate [1.05 g (44 mmol) of sodium and 4.18 g (44 mmol) of phenol] in 30 ml of 85% ethanol. Ethanol was distilled off at reduced pressure, to the residue was added 20 ml of water, the mixture was extracted with ether, the extract was washed with 50 ml of 5% cold solution of KOH, with saturated solution of Na_2SO_4 till neutral washings, and dried with Na_2SO_4. The ether was removed, the residue was distilled. Yield 2.3 g (30%), bp 100–105°C (2 mmHg). We obtained a mixture of 2-(phenoxymethyl)thirane-d_2 (**IIa**) and 3-phenoxythietane-d_2 (**IIIa**) in molar ratio 5 : 2 (GLC).

^{13}C NMR spectrum (25.142 MHz, $CDCl_3$), δ, ppm of compound **IIa**: 23.8, 31.3, 71.9 ê (*J* 24 Hz), 114.8, 121.3, 129.4, 158.6.

3-Methyl-3-phenoxythietane (X). To a solution of 1.15 g (9 mmol) of thiirane **II** in 5 ml of 96% ethanol was added a solution of sodium phenolate [0.95 g (10 mmol)] of phenol and 0.22 g (9.5 mmol) of sodium] in 20 ml of 95% ethanol. The mixture was heated at reflux to complete disappearance of the original thiirane (GLC monitoring, about 40 min). Ethanol was evaporated, the reaction product was extracted into ether, the combined extract were washed with 5% solution of KOH, with saturated solution of NaCl, and dried with sodium sulfate. Ether was evaporated, the residue was distilled. Yield 1.0 g (61%), bp 95–100°C (1.5 mmHg.), n_D^{20} 1.5666. Mass spectrum, *m/z* (I_{rel}, %): 180 $[M]^+$ (3), 94 (28), 87 (100), 65 (9), 59 (10), 53 (13), 47 (9), 45 (25), 41 (13), 39 (24). Found, %: C 56.68; H 9.63. $C_{10}H_{12}OS$. Calculated, %: C 56.78; H 9.53.

Reaction of thiirane (VII) with sodium phenolate. To a solution of sodium phenolate [0.35 g (15 mmol) of sodium and 1.6 g (17 mmol) of phenol] in 30 ml of 96% ethanol at 60°C was added dropwise within 30 min a solution of 20 g (15 mmol) of thiirane **VII** in 5 ml of 96% ethanol. The mixture was heated at reflux on a water bath for 2 h. The ethanol was distilled off in a vacuum, and the residue was diluted with 5 ml of water. The reaction product was extracted into ether, the extract was washed with 5% water solution of KOH and dried with sodium sulfate. On evaporation of ether 1.2 g was obtained of a mixture containing 2,2-dimethyl-3-phenoxythietane (**XII**) and bis(3-methyl-2-butenyl) disulfide (**XIII**) at molar ratio 1 : 1 (GLC). The mixture was separated by PTLC method (eluent ether-pentane, 1 : 3). Mass spectrum of compound **XII**, *m/z* ($I_{rel.}$, %): 194 $[M]^+$ (3), 101 (100), 94 (57), 85 (13), 67 (33), 65 (13), 59 (44), 55 (14), 45 (13), 41 (26), 39 (24); *m** 34.5, 44.6. (XIII). Mass spectrum of compound XIII, *m/z* ($I_{rel.}$, %): 202 $[M]^+$ (3), 101 (20), 94 (14), 69 (100), 68 (24), 67 (35), 53 (27), 43 (12), 41 (87), 40 (14), 39 (33).

***trans*-2-Methyl-3-phenoxythietane (XVIa)**. To a solution of sodium phenolate [0..5 g (22 mmol) of sodium and 2.35 g (25 mmol) of phenol] in 50 ml of anhydrous ethanol while boiling at reflux was added within 5 min dropwise a solution of 2.45 g (20 mmol) of thiirane **VIII** in 10 ml of anhydrous ethanol. The boiling of the mixture was continued for 2 h more, ethanol was distilled off, and the residue was diluted with 10 ml of water and extracted with ether. The extracts were combined, washed with

5% solution of KOH, and dried with sodium sulfate. The ether was distilled off, and the residue was subjected to distillation. Yield 1.0 g (28%), bp 98–105°C (1.5 mm Hg). Mass spectrum, *m/z* (I_{rel}, %): 180 $[M]^+$ (20), 94 (21), 88 (9), 87 (100), 77 (9), 59 (12), 53 (13), 47 (9), 45 (37), 39 (13). Found, %: C 59.00; H 10.00. $C_{11}H_{14}OS$. Calculated, %: C 58.76; H 9.86.

***cis*-2-Methyl-3-phenoxythietane (XVIb)**. To a solution of sodium phenolate [0..4 g (10 mmol) of NaOH and 1.0 g (11 mmol) of phenol] in 50% aqueous methanol heated at reflux was added within 5 min dropwise a solution of 0.3 g (2..5 mmol) of thiirane **IX** in 5 ml of 50% aqueous methanol. The mixture was refluxed for another 1 h, the methanol was distilled off, the reaction product was extracted into ether, the extract was washed with 15% solution of NaOH, the ether was evaporated, and water was distilled off with benzene (20 ml). The residue was distilled. Yield 0.2 g (44%), bp 73–75°C (1.5 mm Hg). A mixture of compounds **XVIb** and **XVIIb** was obtained at molar ratio 9:1 (^{1}H NMR). Mass spectrum, *m/z* (I_{rel}, %): 180 $[M]^+$ (8), 134 (3), 120 (5), 94 (15), 87 (100), 77 (2), 59 (3), 53 (11), 47 (2), 45 (28), 41 (2), 39 (11). Found, %: C 58.06; H 9.66. $C_{10}H_{12}OS$. Calculated, %: C 58.76; H 9.86.

***cis*-2-Methyl-3-(phenoxymethyl)thiirane (XVIIb)**. To a solution of 1.2 g (10 mmol) of thiirane **IX** in 5 ml of anhydrous ethanol at reflux was added dropwise within 15 mim a solution of sodium phenolate [0.15 g (11 mmol) of sodium and 1.2 g (13 mmol) of phenol] in 7 ml of anhydrous ethanol. The boiling mixture was refluxed for 30 min more, ethanol was evaporated, the residue was diluted with 10 ml of 10% water solution of NaOH and extracted with ether. The combined extracts were washed with 10% water solution of NaOH and dried with $CaCl_2$. The ether was distilled off, and the residue was subjected to distillation. Yield 0.75 g (42%), bp 95–97°C (2 mm Hg), n_D^{20} 1.5630. ^{1}H NMR spectrum, δ, ppm: 1.54 d (3H, *J* 6.2 Hz), 3.13 quintet (1H, *J* 6.3 Hz), 3.30 d.d.d (1H, *J* 5.2, *J* 6.6, *J* 8.5 Hz), 3.93 d.d (1H, *J* 8.5, *J* 10.4 Hz), 4.38 d.d (1H, *J* 5.2, *J* 10.1 Hz), 7.1–7.7 m (5H). ^{13}C NMR spectrum, δ, ppm: 15.7 (+), 35.0 (–), 36.4 (+), 67.9 (–), 114.6 (+), 121.1 (+), 129.4 (+), 158.4 (q). Mass spectrum, *m/z* (I_{rel}, %): 180 $[M]^+$ (5), 149 (16), 94 (100), 87 (97), 77 (14), 71 (5), 69 (4), 55 (37), 51 (11), 45 (37). Found, %: C 59.05; H 9.99. $C_{10}H_{12}OS$. Calculated, %: C 58.76; H 9.86.

3-(Aryloxy)thietanes. General procedure. To a solution of an appropriate sodium phenolate (0.11 mol of substituted phenol and 0.1 mol of NaOH) in 100 ml of 90% (by volume) aqueous methanol was added dropwise while stirring at 45–55°C within 1.5 h a (chloromethyl)thiirane (0.09 mol). After the end of addition the stirring of the heterogeneous mixture was continued for 2 h at the same temperature. Then the reaction mixture slowly cooled, and therewith the reaction product precipitated as crystals. It was filtered off, washed on the filter with water till neutral washings, and recrystallized from an appropriate solvent.

3-(Thietan-3-yloxy)benzaldehyde (XIX). Yield 61%, mp 41–43°C (from aqueous EtOH), bp 141–143°C (1.5 mm Hg). ^{1}H NMR spectrum, δ, ppm: 3.41–3.46 m (2H), 3.56–3.62 m (2H), 5.37 quintet (1H, *J* 7.3 Hz), 6.92 d (2H, *J* 8.8 Hz), 7.84 m (1H, *J* 9.8 Hz), 9.89 s (1H). ^{13}C NMR spectrum, δ, ppm: 35.8 (–), 72.0 (+), 113.8 (+), 122.6 (+), 124.7 (+), 130.8 (+), 138.3 (q), 157.3 (q), 192.2 (+). Found, %: C 62.06; H 5.16. $C_{10}H_{10}O_2S$. Calculated, %: C 61.83; H 5.19.

4-(Thietan-3-yloxy)benzaldehyde (XX). Yield 69%, mp 54–56°C (from aqueous EtOH), bp 145–147°C (1.5 mm Hg). ^{1}H NMR spectrum, δ, ppm: 3.40–3.47 m (2H), 3.57–3.65 m (2H), 5.40 quintet (1H, *J* 10.9 Hz), 7.12 d.t (1H, *J* 2.0, *J* 7.3 Hz), 7.29 m (1H), 7.38–7.52 m (2H), 9.97 s (1H).^{13}C NMR spectrum, δ, ppm: 35.6 (–), 71.9 (+), 115.6 (+), 130.9 (q), 132.5 (+), 161.6 (q), 191.0 (+). Found, %: C 62.00; H 5.10. $C_{10}H_{10}O_2S$. Calculated, %: C 61.83; H 5.19.

Methyl 4-(thietane-3-yloxy)benzoate (XXI). Yield 68%, mp 66–68°C (from aqueous EtOH). ^{1}H NMR spectrum, δ, ppm: 3.39–3.47 m (2H), 3.57–3.64 m (2H), 3.90 s (1H), 5.38 quintet (1H, *J* 7.6 Hz), 6,84 d (2H, *J* 7.6 Hz), 8.00 d (2H, *J* 8.6 Hz). ^{13}C NMR spectrum, δ, ppm: 35.7 (–), 52.3 (+), 71.8 (+), 114.9 (+), 123.8 (q), 132.2 (+), 160.4 (q), 167.1 (q). Found, %: C 59.09; H 5.55. $C_{11}H_{12}O_3S$. Calculated, %: C 58.91; H 5.39.

4-(Thietane-3-yloxy)benzoic acid (XXII) was obtained by alkaline hydrolysis of ester **XXI** followed by treating the reaction mixture with hydrochloric acid. Yield 93%, mp 211-213°C (from BuOH). ^{1}H NMR spectrum, δ, ppm: 3.40–3.55 m (4H), 5.41 quintet (1H, *J* 7.3 Hz), 6.87 d (2H, *J* 8.9 Hz), 7.86 d (2H, *J* 8.9 Hz), 11.7–12.8 br.s (1H, COOH).^{13}C NMR spectrum, δ, ppm: 35.6 (–), 71.7 (+), 115.1 (+), 124.8 (q), 132.2 (+), 160.0 (q), 167.5 (q). Found, %: C 57.09; H 4.65. $C_{10}H_{10}O_3S$. Calculated, %: C 57.13; H 4.79.

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