SYNTHESIS OF CYCLIC SULFIDES

III * SYNTHESIS OF ALKYL-SUBSTITUTED THIACYCLOPENTANES AND THIACYCLOHEXANES

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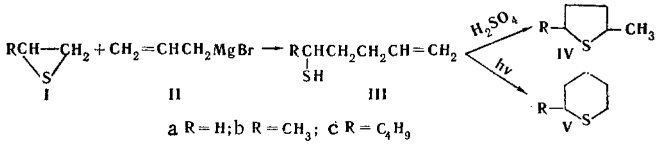
2-Methyl-, 2,5-dimethyl-, 2-n-butyl-5-methylthiacyclopentanes, thiacyclohexane, and 2-methyl- and 2-n-butylthiacyclohexanes were obtained by the reaction of ethylene, propene, and 1-hexane episulfides with allylmagneisum bromide with subsequent cyclization of the alkenethiols thus formed.

According to the scheme we proposed in [1,2], thiacyclopentanes (IV) and thiacyclohexanes (V) were obtained by the reaction of alkene episulfides (I) with allymagnesium bromide (II) and subsequent intramolecular cyclization of the alkenethiols (III) thus formed.



In the reaction of alkene episulfides with II the C−S bond is broken between the sulfur and the terminal carbon atom, as confirmed by the structure of the cyclization products obtained. Alkenethiols III were subjected to intramolecular cyclization via two methods: 1) by the action of 75% sulfuric under nitrogen; 2) by UV illumination.

In contrast to cycloalkenethiols, the cyclization of which proceeds selectively [1,2] (thiabicyclanes with the sulfur atom in a five-membered ring are formed via the first method, while thiabicyclanes with the sulfur atom in a six-membered ring are formed along with traces of the corresponding isomers via the second method), the cyclization of III is not selective. Compounds IV and V are obtained in almost equal amounts (1 : 1 or 3 : 2) via the first method; except for the cyclization of 4-pentene-1-thiol, IV are obtained in amounts commensurable with V (1: 2 or 1: 3) via the second method. However, V have higher boiling points than the isomeric IV, and their mixture can be separated by fractional distillation. The overall yields of the thiacyclanes formed by the cyclization of alkenethiols via the first method increase with an increase in the size of the hydrocarbon chain of the alkenethiole but decreases with increasing chain size via the second method.

The cyclization of alkenethiols to form 2,5-dialkylthiacyclopentanes proceeds stereospecifically and forms one of two geometrical isomers. In the cyclization of 4-hexene-1-thiol it was proved that cis-2,5-dimethylthiacyclopentane is obtained. All of the thiacyclanes formed by cyclization of the alkenethiols were isolated and characterized in the pure form and in the form of complexes with mercuric chloride (Table 1), obtained by the method in [5]. In spite of the assertion that 2-butylthiacyclohexane does not form a crystalline complex with methyl iodide [4], we were able to obtain this complex as well as a crystalline sulfone.

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*See [2] for Communication II.

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TABLE 1. Thiacycloalkanes (IV and V)

Compound	Name	Bp, °C (press., mm)	n_D^{20}	d_4^{20}	MR_D		Mercury complex	
					Found	Calc.	Empirical formula*	Mp, °C
IVa	2-Methylthiacyclopentane [3]	132 (755,6)	1,4915	—	—	—	$C_5H_{10}S \cdot 2HgCl_2$	157,5—159
IVb	cis-2,5-Dimethylthiacyclopentane [3]	142 (750)	1,4792	0,9207	35,77	35,63	$C_6H_{12}S \cdot 2HgCl_2$	178—178,5
IVc	2-n-Butyl-5-methylthiacyclopentane†	130 (76)	1,4772	0,9006	49,56	49,48	$C_9H_{18}S \cdot HgCl_2$	113,1—114
Va	Thiacyclohexane [3]	139—140 (755,6)	1,5068	0,9862	30,71	31,00	$C_5H_{10}S \cdot HgCl_2$	138—139
Vb	2-Methylthiacyclohexane [3]	149,5—150 (750)	1,4905	0,9427	35,60	35,63	$C_6H_{12}S \cdot HgCl_2$	101—102
Vc	2-n-Butylthiacyclohexane [4]†	139 (76)	1,4870	0,9185	49,47	49,48	$C_9H_{18}S \cdot HgCl_2$	oil

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*The empirical formulas of all of the complexes were confirmed by gravimetric determination of the mercury content.

† The empirical formulas of IVc and Vc were confirmed by elementary analysis (C, H, and S).

The structure of 2-butylthiacyclohexane (Vc) and the previoulsy unknown 2-butyl-5-methylthiacyclopentane (IVc) were confirmed by IR spectroscopy. The spectra of Vc and IVc contain absorption maxima characteristic for the skeletal vibrations of cyclic sulfides (1270 and 1260 cm^{-1}, respectively). The absorption maxima in the IR spectrum of Vc corresponds to the CH valence (2856-2920 cm^{-1}) and deformational (1446 and 1460 cm^{-1}) vibrations of the CH_2 groups, the CH valence (2948 cm^{-1}) and deformational (1386 cm^{-1}) vibrations of the CH_3 groups, and the CH deformational (1346 cm^{-1}) vibrations of the CH groups. The absorption maxima in the IR spectrum of IVc correspond to the CH valence (2860-2928 cm^{-1}) and deformational (1452 cm^{-1}) vibrations of the CH_2 groups, the CH valence (2928 cm^{-1}) and deformational (1384 cm^{-1}) vibrations of the CH_3 groups, and the CH deformational (1320 cm^{-1}) vibrations of the CH groups. The intensity of the band at 1386 cm^{-1} (CH_3 groups) is lower by a factor of two for Vc as compared with IVc. The spectra of these compounds also contain a band at ~730 cm^{-1}, which is the result of pendulum vibrations of the CH_2 group in C_4H_9. The intensity of this band is the same in the spectra of both compounds.

EXPERIMENTAL

Ethylene Episulfide and Propylene Episulfide. These were obtained via the methods in [6] and [7], respectively.

1-Hexane Episulfide. 1-Hexene oxide [25 g (0.25 mole)] was added in the course of 2 h with stirring and cooling to 0-5 deg to a solution of 20 g (0.2 mole) of thiourea, 7.5 ml of 94% sulfuric acid, and 88 ml of water, and the resulting mixture was heated to 20 deg after 2 h and stirred for another 2 h. A solution of 26.6 g (0.25 mole) of sodium carbonate in 125 ml of water was then added in the course of 25 min, and the mixture was heated for 5-10 min until the crystals dissolved. The resulting oil was separated, and the aqueous layer was treated via the method in [7]. The oil and extracts were combined, dried with anhydrous sodium sulfate, and distilled to give 21.5 g (74%) of 1-hexene episulfide with bp 106 deg (150 mm) and n_D^{20} 1.4700.

1-R-4-Pentenethiols (IIIa-c). A solution of 0.15 mole of the alkene episulfide in 50 ml of absolute ether was added during 1 h to a solution of allylmagnesium bromide [prepared from 24.0 g (1 g-atom) of magnesium and 42.35 g (0.35 mole) of allyl bromide in 190 ml of absolute ether] at -10 deg. The resulting mixture was stirred at room temperature for 1 h, refluxed for 5-6, allowed to stand overnight, and decomposed with 10% hydrochloric acid while cooling under nitrogen. The organic layer was separated rapidly, the aqueous layer was extracted with ether (two to three times with 100-ml portions), and the extracts were intramolecularly cyclized either after removal of the ether (method A) or without isolation (method B).

Thiacycloalkanes (IV and V). A. Sulfuric acid [99 g (75%)] was added to 4-pentenethiol (IIIa) obtained from 0.15 mole of ethylene epsulfide, under nitrogen at -10 to -13 deg, and the mixture was allowed to warm to room temperature in 2 h and stirred for another 3 h. A double volume of water was then added to the cooled mixture, the resulting mixture was heated at 40–50 deg for 3 h, allowed to stand overnight, and steam distilled. The distillate was saturated with sodium chloride and extracted with ether. The extract was dried with sodium sulfate, the ether was removed and the residue was distilled to give 8.2 g (53%) of a mixture of 2-methylthiacyclopentane (IVa) (58.6%)* and thiacyclohexane (Va) (41.4%)* with bp 131-137 deg (744 mm) and n_D^{20} 1.4959.

A mixture of 2,5-dimethylthiacyclopentane (IVb) (58.2%)† and 2-methylthiacyclohexane (Vb) (41.8%) was similarly obtained in 60% yield from 1-methyl-4-pentenethiol (IIIb); a mixture of 2-butyl-5-methylthiacyclopentane (IVc) (52%)‡ and 2-butylthiacyclohexane (Vc) (48%) was similarly obtained in 64% yield from 2-butyl-4-pentenethiol (IIIc).

B. An ether solution of IIIa was illuminated with a PRK-2 lamp until a test for mercaptan [8] was negative. Distillation yielded 12.9 g (84.3%) of a mixture of Va (90.8%) and IVa (9.2%)* with bp 137-141 deg (744 mm) and n_D^{20} 1.4969. A mixture of Vb (75.6%) and IVb (24.4%) was similarly obtained in 69.5% yield from IIIb, while IIIc gave 63.8% of a mixture of Vc (63%) and IVc (37%).

The mixtures of IVa with Va and IVb with Vb were distilled with a film reactification column (25 theoretical plates), while the mixture of IVc and Vc was distilled with a glass-packed wedge column (16 theoretical plates). Chromatographically pure components were isolated in this manner. A Vc–methyl iodide complex was obtained via the method in [9] and had mp 94-95 deg (sublimation). Found %: I 42.2. $C_9H_{18}S \cdot CH_3I$. Calc. %: I 42.3.

2-Butylthiacyclohexane Sulfone. This was obtained by the method in [10] and had mp 27-28.5 deg. Found %: C 56.9; H 9.3; S 16.6. $C_9H_{18}SO_2$. Calc. %: C 56.8; H 9.5; S 16.8.

IVc–Methyl Iodide Complex. This had mp 94.5-96 deg (sublimation). Found %: I 42.2. $C_9H_{18}S \cdot CH_3I$. Calc. %: I 42.3.

2-Butyl-5-methylthiacyclopentane Sulfone. This was obtained as an oil. It was purified by three precipitations from hexane solution on cooling with dry ice and evacuation of the solvent after each precipitation. The sulfone obtained was chromatographically pure and had bp 304 deg (742.5 mm, with decomposition),** d_4^{20} 1.0666, and n_D^{20} 1.4755. Found %: C 56.8; H 9.3; S 16.8; MR_D 50.20. $C_9H_{18}SO_2$. Calc. %: C 56.8; H 9.5; S 16.8; MR_D 50.43.

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*Gas-liquid chromatographic data: UKh-2 chromatograph, column (L 4 m, d 4 mm) filled with 20% dinodyl phthalate on INZ-600, 111 deg, helium flow rate 75 ml/min.

†Column temperature 117 deg.

‡With a column (L 4 m, d 4 mm) filled with 10% SE-30 on Chromosorb W at 174 deg.

**By the Sivolobov method [11].