SYNTHESIS OF CYCLIC SULFIDES

V.* SYNTHESIS OF ISOMERS OF 2,3-DIMETHYL-1-THIAHYDRINDANE AND 4-METHYL-1-THIADECALIN

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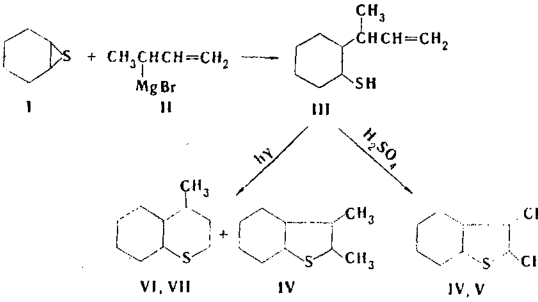
Two isomers of 2,3-dimethyl-1-thiahydrindane and two isomers of 4-methyl-1-thiadecalin were obtained by the reaction of cyclohexene episulfide with crotylmagnesium bromide and subsequent cyclization of the resulting 2-(α-methyl-β-propenyl)-1-cyclohexanethiol by the action of 75% sulfuric acid and UV irradiation.

In accordance with the scheme that we proposed in [1, 2], we obtained two isomers of 2,3-dimethyl-1-thiahydrindane (IV, V) and two isomers of 4-methyl-1-thiadecalin (VI, VII) by the reaction of cyclohexene episulfide (I) with crotylmagnesium bromide (II) and subsequent intramolecular cyclization of the resulting 2-(α-methyl-β-propenyl)-1-cyclohexanethiol (III).



Crotyl bromide, synthesized via the method in [4], was a mixture consisting of 85% 1-bromo-2-butene and 15% 3-bromo-1-butene [5, 6]. The crotylmagnesium bromide obtained from this mixture reacts with cyclohexene episulfide in one form – 3-bromomagnesio-1-butene [5] – which is confirmed by the structure of the thiabicyclans formed in the cyclization of III. Two methods were used to cyclize III: 1) the action of 75% sulfuric acid under nitrogen; 2) UV illumination. The cyclization of III via the first method proceeds selectively to give only thiabicyclans with a five-membered heterocycle, while cyclization via the second method is not selective, and a considerable amount of a thiabicyclan with a five membered heteroring is formed along with thiabicyclans with a six-membered ring. The cyclization of II by both the first and second methods does not proceed stereospecifically, in contrast to the cyclic mercaptans that we obtained by the reaction of cycloalkene episulfides with allylmagnesium bromide [1, 2]. The stereoisomerism of the thiabicyclans formed in the cyclization of III is apparently associated with the different orientation of the CH_3 group in the α-position relative to the cyclohexane ring. The presence of this group probably also promotes closure to a five-membered ring.

The thiabicyclans obtained by the cyclization of III were isolated in chromatographically pure form by rectification on a column or by preparative gas-liquid chromatography and were characterized by their

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*See [3] for communication IV.

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TABLE 1. Characteristics of the Thiabicyclans

Compound	Name	Bp, °C (mm)	n_D^{20}	d_4^{20}	MR_D		Empirical formula	Found, %			Calc., %		
					found	calc.		C	H	S	C	H	S
IV	2,3-Dimethyl-1-thiahydrindane	130,5—131,5 (48)	1,5066	0,9713	51,96	51,90	$C_{10}H_{18}S$	70,4	10,6	18,6	70,6	10,6	18,8
V	2,3-Dimethyl-1-thiahydrindane	140 (45)	1,5121	0,9811	52,0	51,90	$C_{10}H_{18}S$	70,4	10,4	18,5	70,6	10,6	18,8
VI	4-Methyl-1-thiadecalin	146 (49)	1,5173	0,9896	52,0	51,90	$C_{10}H_{18}S$	70,4	10,4	18,6	70,6	10,6	18,8
VII	4-Methyl-1-thiadecalin	150 (49)	1,5235	0,9975	52,12	51,90	$C_{10}H_{18}S$	70,8	10,6	18,9	70,6	10,6	18,8

physical chemical properties (Table 1). Complexes with mercuric chloride [7] methiodides [8], and sulfones [9] (Table 2) were obtained and characterized for them. The structures of the thiabicyclans were confirmed by the IR and mass spectra and also by identification of the hydrocarbons formed during their hydrodesulfuration. The IR spectra of IV–VII, respectively, contain the absorption maxima characteristic for the skeletal vibrations of cyclic sulfides (1280, 1260 and 1270, 1280, and 1275 cm^{-1}), absorption maxima corresponding to the CH stretching (2870 and 2965, 2866 and 2973, 2863 and 2980, and 2865 and 2965 cm^{-1}) and deformation (1380, 1380, 1380, and 1385 cm^{-1}) vibrations of the CH_3 group, the CH stretching (2933, 2935, 2930, and 2935 cm^{-1}) and deformation (1452, 1450, 1450, and 1450 cm^{-1}) vibrations of the CH_2 groups, and the CH deformation (1330, 1325, 1350, and 1330 cm^{-1}) vibrations of the CH group. The intensities of the peaks of the $C_5H_9S^+$ fragment ion in the mass spectra of IV–VII are 4.7, 6.8, 79.0, and 42.0% of the maximum peak, from which it can be concluded that IV and V have five-membered rings, while VI and VII have six-membered rings.

In the hydrodesulfuration of IV–VII, isobutylcyclohexane, the mass spectrum of which was identical to that described in [10], was obtained in all cases; one peak was noted in the gas-liquid chromatogram of a mixture of it with synthesized isobutylcyclohexane [11], while two peaks were observed on the chromatogram of a mixture with n-butylcyclohexane [11].*

EXPERIMENTAL

Crotyl Bromide. This compound was obtained by our modification of the method in [4]. Butadiene was saturated with hydrogen bromide, initially at −10 to 0° and then at 30° for 3 h. A 160-ml [103 g (1.9 mole)] sample of butadiene gave 179 g (70%) of crotyl bromide with bp 99.7-101.5° (746 mm) and n_D^{20} 1.4780. According to GLC,† the crotyl bromide was a mixture of 1-bromo-2-butene (85%) and 3-bromo-1-butene (15%).

2-(α-Methyl-β-propenyl)-1-cyclohexanethiol (III). This compound was obtained by the method described for the synthesis of 2-allyl-1-cyclohexanethiol [1]. Compound III was cyclized after removal of the solvent from the ether extract by distillation.

Cyclization of III. The cyclization was carried out by two methods until the mixtures gave a negative test for mercaptan [12]. A. Compound III was cyclized by the action of 75% sulfuric acid via the method described for 2-allyl-1-cyclopentanethiol [2] to give a reaction product with bp 99-108° (16 mm) and n_D^{20} 1.5078, which, according to GLC,‡ contained 36.4% IV and 63.6% V. The overall yield of IV and V was 45.5%.

B. Compound III was illuminated with a PRK-2 mercury-quartz lamp for 8 h. Vacuum distillation of the cyclization product gave a fraction with bp 104.5-108.5° (20 mm) and n_D^{20} 1.5160, which, according to GLC,‡ contained 16.2% IV, 34.8% VI, and 49% VII. The overall yield of IV, VI, and VII was 50%. Mixtures of IV, V and IV, VI, and VII were fractionated with a column filled with a glass packing to give chromatographically pure IV and V and VI and VII

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* The chromatography was performed with a Tswett chromatograph with a 25 m long capillary column with a squalane liquid phase at 54°, a nitrogen flow rate of 60 ml/min, and a flame ionization detector.

† Performed with a UKh-2 chromatograph with a 4 m long (4 mm in diameter) column packed with 10% dinonyl phthalate on INZ-600 at 70° with a hydrogen flow rate of 60 ml/min.

‡ Performed with a UKh-2 chromatograph with a 2.5 m long column (4 mm in diameter) packed with 10% diethylene glycol succinate on Cellite 545 at 136° with a hydrogen flow rate of 60 ml/min.

TABLE 2. Thiabicyclan Derivatives

Compound	Derivative	Mp, °C	Empirical formula	S (J), %	
				found	calc.
IV	Complex with $HgCl_2$	132,5—133,5	$C_{10}H_{18}S \cdot HgCl_2$	7,2	7,2
	Sulfone	—*	$C_{10}H_{18}SO_2$	15,9	15,8
	Methiodide	105—108	$C_{11}H_{21}IS$	(40,4)	(40,7)
V	Complex with $HgCl_2$	118—119	$C_{10}H_{18}S \cdot HgCl_2$	7,0	7,2
	Sulfone	76,5—77,5	$C_{10}H_{18}SO_2$	15,6	15,8
	Methiodide	117,5—118,5	$C_{11}H_{21}IS$	(40,2)	(40,7)
VI	Complex with $HgCl_2$	141—142	$C_{10}H_{18}S \cdot HgCl_2$	8,0	7,2
	Sulfone	—*	$C_{10}H_{18}SO_2$	15,6	15,8
	Methiodide	120,5—122	$C_{11}H_{21}IS$	(40,6)	(40,7)
VII	Complex with $HgCl_2$	161—162 (dec.)	$C_{10}H_{18}S \cdot HgCl_2$	7,4	7,2
	Sulfone	98—99	$C_{10}H_{18}SO_2$	15,5	15,8
	Methiodide	138—139 (subl.)	$C_{11}H_{21}IS$	(40,2)	(40,7)

*The sulfone of IV had bp 157-159° (2 mm), n_D^{20} 1.5053, and d_4^{20} 1.1377; MR_D found 52.66, calculated 52.85. Sulfone VI had n_D^{20} 1.5070. The composition of the sulfones of IV-VII was confirmed by additionally determining the percentage of C and H.

with purities of 90 and 93%, respectively. Chromatographically pure VI and VII were preparatively isolated with a UKh-2 chromatograph with a 4 m long (4 mm in diameter) column packed with 10% E=301 on Chromosorb W at 156° and a hydrogen flow rate of 40 ml/min.

The mass spectra were recorded with an MKh-1306 mass spectrometer at an electron ionizing energy of 50 eV, an emission current of 0.7 mA, and an ionization chamber temperature of 250°. The IR spectra were recorded with a UR-20 spectrophotometer (the liquid-layer thickness was 0.013 mm).

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