SYNTHESIS OF CYCLIC SULFIDES

VII.* SYNTHESIS OF 3-PHENYLTHIACYCLOHEXANE AND 2-METHYL-4-PHENYLTHIACYCLOPENTANE

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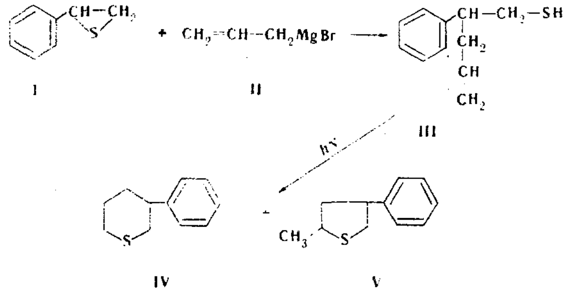
3-Phenylthiacyclohexane and 2-methyl-4-phenylthiacyclopentane were synthesized by reaction of styrene episulfide with allylmagnesium bromide and subsequent photochemical cyclization of the resulting 2-phenyl-4-pentene-1-thiol.

In the present research we have shown the usefulness of a scheme, proposed by two of us [2], for the synthesis of aryl-substituted cyclic sulfides. 3-Phenylthiacyclohexane (IV) and 2-methyl-4-phenylthiacyclopentane (V) were obtained by reaction of styrene episulfide (I) with allylmagnesium bromide (II) and subsequent intramolecular cyclization of the resulting 2-phenyl-4-pentene-1-thiol (III).



In the reaction of I with II the bond between the sulfur atom and the carbon atom in the α position relative to the phenyl ring is cleaved, as confirmed by the structures of the cyclization products. In fact, the physical constants of the 3-phenylthiacyclohexane that we obtained differ from the physical constants reported for 2-phenylthiacyclohexane [3], which would be formed in the case of a different direction of cleavage of the C—S bond. A mixture consisting of 56% IV and 44% V is obtained by photocyclization of thiol III. Chromatographically pure IV and V were isolated by rectification of this mixture.

The IR spectra of IV and V contain the absorption maxima characteristic for the skeletal vibrations of cyclic sulfides (1240 and 1220 cm^{-1}, respectively), absorption maxima of CH stretching (2870-2940 cm^{-1}) and deformation (1430-1460 cm^{-1} for IV and 1460 cm^{-1} for V) vibrations of CH_2 groups, CH stretching (2970 cm^{-1}) and deformation (1380 cm^{-1}) vibrations of CH_3 groups (for V), out-of-plane deformation vibrations of the C—H bond of monosubstituted benzene (710, 740, and 770-780 cm^{-1}), and stretching vibrations of C=C (1500, 1600 cm^{-1}) and =CH (3040, 3080 cm^{-1}) bonds of an aromatic ring. Two multiplets of protons of a thiacyclohexane ring (1.02-2.24 and 2.24-3.16 ppm) and of phenyl protons (7.08-7.16 ppm) are observed in the PMR spectrum of IV, and their intensity ratio is 9 : 5. The spectrum of isomer V contains two doublets of methyl protons [1.34 ppm ($J = 6.4$ Hz) and 1.37 ppm ($J = 6.2$ Hz)] with a ratio of the equatorial methyl group to the axial methyl group of 58 : 42 (gravimetric method), a multiplet of protons of a thiacyclopentane ring (1.57-3.54 ppm), and a multiplet of phenyl protons (7.08-7.16 ppm).

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*See [1] for communication VI.

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EXPERIMENTAL

The IR spectra of liquid films of the compounds were recorded with a UR-20 spectrometer with NaCl and LiF prisms. The PMR spectra of CCl_4 solutions (at 26°) were recorded with a BS-487B spectrometer at an operating frequency of 80 MHz. The chemical shifts of the protons relative to hexamethyldisiloxane are expressed on the δ scale (in parts per million).

Styrene Episulfide (I). This compound was obtained by the method in [4]. The reaction was monitored by means of gas-liquid chromatography (GLC). A UKh-2 chromatograph with a column (4-m long and 4 mm in diameter) filled with 10% E-301 on Chromosorb W and a thermal-conductivity detector was used; the helium flow rate was 50 ml/min, and the column temperature was 216°. The reaction was complete after the disappearance of the styrene oxide peak on the chromatogram (after 3 h). The ether extract of I, obtained from 39 g (0.35 mole) of styrene oxide and 34.5 g (0.36 mole) of potassium thiocyanate was dried over fused potassium carbonate and used for the subsequent synthesis without distillation.

2-Phenyl-4-pentene-1-thiol (III). This compound was obtained by the method in [2]. Reaction of episulfide I with allylmagnesium bromide II, prepared from 33.6 g (1.4 g-atom) of magnesium and 60.5 g (0.49 mole) of allyl bromide in 170 ml of absolute ether gave (after removal of the ether by distillation) 51.35 g of crude thiol III with n_D^{20} 1.5669.

Cyclization of 2-Phenyl-4-pentene-1-thiol (III). Compound III was illuminated with a PRK-2 mercury-quartz lamp until it gave a negative test for mercaptan. Vacuum distillation of the cyclization product gave a fraction with bp 122-136° (5 mm) and n_D^{20} 1.5735, which, according to GLC data, contained 56% IV and 44% V. The mixture of isomers IV and V was rectified with a column filled with a glass packing (the efficiency of the column was 16 theoretical plates) to give chromatographically pure components. Isomer IV had 200° (132 mm), n_D^{20} 1.5810, and d_4^{20} 1.0642. Found: C 74.2; H 8.0; S 17.5%; MR_D 55.73. $C_{11}H_{14}S$. Calculated: C 74.2; H 7.9; S 18.0%; MR_D 55.12. The complex of IV with mercuric chloride had mp 133-134°. Found: S 7.5%. $C_{11}H_{14}S \cdot HgCl_2$. Calculated: S 7.1%. The methiodide of IV had mp 127-129°. Found: I 40.1%. $C_{12}H_{17}IS$. Calculated: I 39.7%. The sulfone obtained from IV had mp 157-158°. Found: C 63.1; H 6.6; S 14.9%. $C_{11}H_{14}O_2S$. Calculated: C 62.9; H 6.7; S 15.2%. The sulfoxide obtained from IV had mp 100-102°. Found: C 68.3; H 7.2; S 15.9%. $C_{11}H_{14}OS$. Calculated: C 68.0; H 7.2; S 16.5%. Isomer V had bp 195° (132 mm), n_D^{20} 1.5688, and d_4^{20} 1.0550. Found: C 74.1; H 8.0; S 17.4%; MR_D 55.04. $C_{11}H_{14}S$. Calculated: C 74.2; H 7.9; S 18.0%; MR_D 55.12. The complex of V with mercuric chloride had mp 192° (dec.). Found: S 7.6%. $C_{11}H_{14}S \cdot HgCl_2$. Calculated: S 7.1%. The methiodide of V was a liquid. Found: I 40.5%. $C_{12}H_{17}IS$. Calculated: I 39.7%. The sulfone of V had mp 154-155°. Found: C 62.8; H 6.7; S 15.2%. $C_{11}H_{14}O_2S$. Calculated: C 62.8; H 6.7; S 15.2%. The sulfoxide of V was a liquid with n_D^{20} 1.5752 and d_4^{20} 1.1410. Found: C 68.0; H 7.4; S 16.1%; MR_D 56.20. $C_{11}H_{14}OS$. Calculated: C 68.0; H 7.2; S 16.5%; MR_D 55.80.

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