SYNTHESIS OF CYCLIC SULFIDES

IV.* SYNTHESIS OF 5-METHYL-2-n-AMYLTHIACYCLOPENTANE AND 2-n-AMYLTHIACYCLOHEXANE

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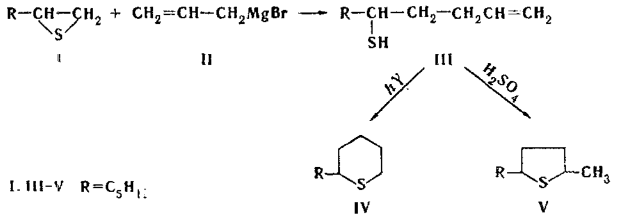
2-n-Amyl-5-methylthiacyclopentane and 2-n-amylthiacyclohexane, respectively, were synthesized by the reaction of 1-heptene episulfide with allylmagnesium bromide with subsequent cyclization of the resulting 1-decene-5-thiol by the action of 75% sulfuric acid and UV irradiation.

According to the scheme that we proposed in [1,2], the reaction of 1-heptene episulfide (I) with allylmagnesium bromide (II) with subsequent intramolecular cyclization of the resulting 1-decene-5-thiol (III) gave 2-n-amylthiacyclohexane (IV) and 2-n-amyl-5-methylthiacyclopentane (V).



Cleavage of the C – S bond in the reaction of 1-heptene episulfide with allylmagnesium bromide occurs between the sulfur and terminal carbon atom, as confirmed by the structure of the cyclization products obtained. 1-Decene-5-thiol (III) was subjected to intramolecular cyclization by two methods: 1) by the action of 75% sulfuric acid under nitrogen; 2) by UV illumination. As in the alkenethiols that we studied in [3], the cyclization of III proceeds nonselectively. The first method gives IV and V in a ratio of 1 : 4.6, while the second method gives them in a ratio of 3 : 1.

According to the results of gas-liquid chromatography (GLC), the cyclization of III to form 2-amyl-5-methylthiacyclopentane proceeds stereospecifically to form one of the two geometrical isomers. Thiacyclanes formed during the cyclization of III were isolated in pure form by preparative GLC.

The structures of IV and V were confirmed by IR spectroscopy. The spectra of IV and V contain absorption maxima that are characteristic for the skeletal vibrations of cyclic sulfides (1265 and 1260 cm^{-1}, respectively) and pendulum vibrations of the CH_2 groups in the C_5H_{11} radical (730 cm^{-1}).

EXPERIMENTAL

1-Heptene Episulfide (I). This compound was obtained in 43% yield by the method in [6] or in 37% yield by our modified method [7] for the synthesis of 1-hexene episulfide [3]; bp 100-102° (70 mm), n_D^{20} 1.4698, and d_4^{20} 0.8946. Compound I undergoes partial decomposition during distillation, and sulfur is formed.

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*See [3] for communication III.

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1-Decene-5-thiol (III). This compound was obtained by a method similar to that which we described for 2-allylcyclohexane-1-thiol [1]. The III thus obtained was subjected to intramolecular cyclization either after removal of the ether by distillation (method A) or in solution (method B).

Thiacycloalkanes (IV and V). A) A total of 280 g of 75% sulfuric acid was added under nitrogen at −10 to −13° to 1-decene-5-thiol (III), obtained from 60 g (0.46 mole) of 1-heptene episulfide. The subsequent methods used to carry out the reaction and isolate the product were similar to the methods that we described for the cyclization of 1-pentene-4-thiol [3]. A mixture [38 g (47%)] of 2-amylthiacyclohexane (IV) (18%) and 2-n-amyl-5-methylthiacyclopentane (V) (82%) was obtained.*

B) An ether solution of III was illuminated with a PRK-2 lamp until it gave a negative test for mercaptan [8]. Distillation gave a mixture (68.7%) of IV (75%) and V (25%).*

The mixture of IV and V was separated preparatively with a UKh-2 chromatograph (l 4 mm, d 4 mm, 20% dinonyl phthalate on INZ-600, 156°, hydrogen flow rate 60 ml/min). Chromatographically pure components were isolated. Compound IV had bp 109-110° (11 mm), n_D^{20} 1.4850, and d_4^{20} 0.9044. Found: C 69.7; H 11.8; S 18.5%; MR_D 54.50. $C_{10}H_{20}S$. Calculated: C 69.8; H 11.6; S 18.6%; MR_D 54.10. A complex of IV with mercuric chloride [4] and methyl iodide [4] was obtained as an oil. The sulfone [5] was also obtained as an oil with n_D^{20} 1.4810. Found: C 58.9; H 9.7; S 15.8%. $C_{10}H_{20}O_2S$. Calculated: C 58.8; H 9.8; S 15.7%. Compound V had bp 105-106° (11 mm), n_D^{20} 1.4740, and d_4^{20} 0.8900. Found: C 69.9; H 11.6; S 18.8%; MR_D 54.30. $C_{10}H_{20}S$. Calculated: C 69.8; H 11.6; S 18.6%; MR_D 54.1. The complex of V with mercuric chloride had mp 96.5-97.5°. Found: S 7.5%. $C_{10}H_{20}S \cdot HgCl_2$. Calculated: S 7.2%. The sulfone was obtained as an oil with bp 140-142° (7 mm), n_D^{20} 1.4720, and d_4^{20} 1.0311. Found: C 58.6; H 9.8; S 15.75%; MR_D 55.40. $C_{10}H_{20}O_2S$. Calculated: C 58.8; H 9.8; S 15.7%; MR_D 55.10.

IR spectra of IV: 2870, 2920 (stretching CH_2); 1444, 1460 (deformation CH_2); 2940 (stretching CH_3); 1383 (deformation CH_3); 1346 cm^{-1} (deformation CH). IR spectra of V: 2870, 2935 (stretching CH_2); 1460 (deformation CH_2); 2960 (stretching CH_3); 1380 (deformation CH_3); 1320 cm^{-1} (deformation CH).

LITERATURE CITED

1. V. I. Dronov, V. P. Krivonogov, and V. S. Nikitina, Khim. Geterotsikl. Soedin., 335 (1970).
2. V. I. Dronov and V. P. Krivonogov, Khim. Geterotsikl. Soedin., 1185 (1970).
3. V. I. Dronov and V. P. Krivonogov, Khim. Geterotsikl. Soedin., 1614 (1970).
4. R. D. Obolentsev, V. G. Bukharov, and N. K. Faizullina, in: Chemistry of Organosulfur and Organonitrogen Compounds in Petroleums and Petroleum Products [in Russian], Vol. 3 (1960), pp. 51 and 67.
5. R. D. Obolentsev, V. G. Bukharov, and M. M. Gerasimov, in: Chemistry of Organosulfur and Organonitrogen Compounds in Petroleums and Petroleum Products [in Russian], Vol. 3 (1960), p. 35.
6. E. E. Van Tamelen, J. Am. Chem. Soc., 73, 3444 (1951).
7. F. L. Bordwell and H. M. Andersen, J. Am. Chem. Soc., 19, 4959 (1953).
8. Houben-Weyl, Methoden Organischer Chemie [Russian translation], Moscow (1963), p. 585.

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*According to GLC (UKh-2 chromatograph, l 4 m, d 4 mm, 10% E-301 on Chromosorb W, 156°, hydrogen flow rate 60 ml/min).