SYNTHESIS OF HETEROCYCLIC SULFIDES.
II†. SYNTHESIS OF 1-THIABICYCLO[4,3,0]NONANE AND 2-METHYL-1-THIABICYCLO[3, 3, 0]OCTANE

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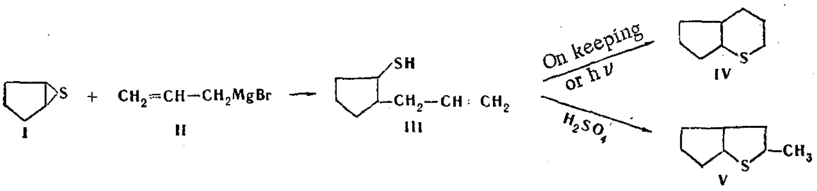
2-Allylcyclopentane-1-thiol is cyclized by treatment with 75% sulfuric acid and with UV light to 2-methyl-1-thiabicyclo[3, 3, 0]octane and 1-thiabicyclo[4, 3, 0]nonane, respectively. The cyclization is stereospecific.

Reaction of cyclopentene episulfide (I) with allylmagnesium bromide (II), followed by intramolecular cyclization of the resulting 2-allylcyclopentane-1-thiol (III), has given 1-thiabicyclo[4, 3, 0]nonane (IV) and 2-methyl-1-thiabicyclo[3, 3, 0]octane (V), according to the scheme which we have put forward [1].

The sulfide IV has been obtained from the thiol both by UV irradiation and by prolonged keeping under nitrogen. Cyclization of III by 75% sulfuric acid proceeds with great difficulty to give the sulfide V in 13% yield.



According to the GLC results, the cyclization of both III and 2-allyloxycyclohexanethiol [1] is stereospecific. According to [2-4], reaction of cycloolefin episulfides with II should give the trans-2-allyl-1-cycloalkanethiols, which on cyclization afford the trans-thiabicycloalkanes. This is confirmed by the low yield of V, since systems composed of two trans-fused five-membered rings are highly strained [2-4]. The position of the methyl group in V has not been established.

The structure of the sulfides IV and V is confirmed by their IR spectra. In IV, the absorption maxima correspond to vibrations of the C–H bond in the CH_2 and CH groups (2854-2954, 1433-1449, and 1334 cm^{-1}). In the spectrum of V, the maxima correspond to the stretching (2964 and 2876 cm^{-1}) and deformational (1376 cm^{-1}) vibrations of the C–H bond in CH_3, to the stretching (2926 cm^{-1}) and deformational (1458 cm^{-1}) vibrations of the C–H bond in CH_2, and to the deformational (1325 cm^{-1}) vibrations of the CH group. In the IR spectra of IV and V, maxima occur which are characteristic of the skeletal vibrations of cyclic sulfides [5], at 1261 and 1258 cm^{-1}, respectively. The absence of a band at 720-790 cm^{-1} shows the absence of a CH_2 group in a straight chain, which is further evidence for the cyclic structure of IV and V.

The structure of IV and V is also proved by their mass spectra (see Fig. 1). The breakdown of V under electron impact takes place according to the scheme given in [6]. Breakdown of IV occurs in a similar way.

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† For Part I, see [1].

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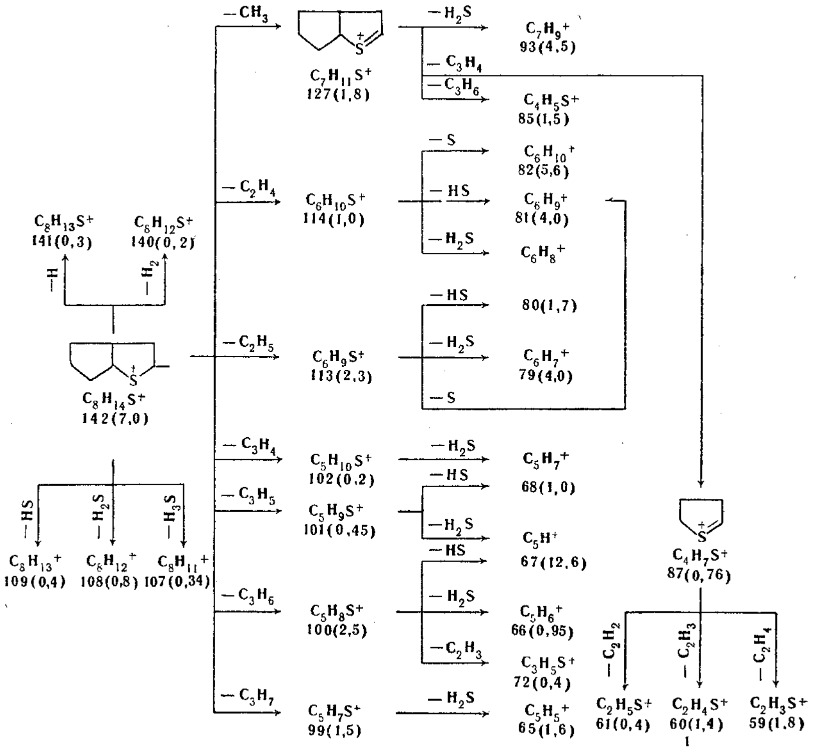

Breakdown of 2-Methyl-1-thiabicyclo[3, 3, 0]octane (the figures in parentheses, with the ionic mass values, indicate the peak intensities as a percentage of the total ion current).

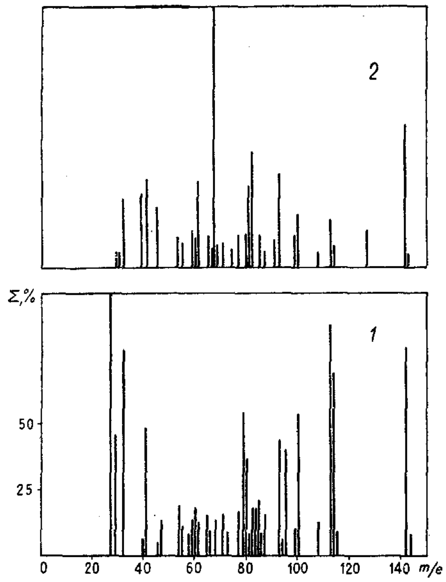

Fig. 1. Mass spectra. 1) 1-Thiabicyclo[4, 3, 0]nonane; 2) 2-methyl-1-thiabicyclo[3, 3, 0]octane.

EXPERIMENTAL

Cyclopentene Episulfide (I) was obtained according to [7], bp 68-69° (66 mm), n_D^{20} 1.5250, d_4^{20} 1.0502. Found: MR_D 29.18. Calculated, MR_D 29.52.

2-Allylcyclopentanethiol (III) was obtained by the method described for 2-allylcyclohexanethiol [1]. Reaction of 10 g (0.1 mole) of I with allylmagnesium bromide (prepared from 19.2 g [0.8 g-atom] of magnesium and 36 g (0.3 mole) of allyl bromide in 200 ml of dry ether) afforded, after drying the reaction mixture and removal of the ether, 8 g of a fraction bp 89-94° (33 mm). The thiol was not further characterized in view of its rapid cyclization.

Cyclization of 2-Allylcyclopentanethiol (III). a) Cyclization of III was complete after standing in a nitrogen atmosphere at room temperature for two weeks. Vacuum distillation of the cyclization product gave a fraction with bp 97.5-98.5° (25 mm), n_D^{20} 1.5195 and d_4^{20} 1.0078, containing 98% of IV and 2% of V by GLC (carried out on a column of length 4 m, diameter 4 mm, packed with 10% Apiezon L on Celite-545). The carrier gas was hydrogen. The overall yield of IV and V was 46%, calculated on I.

b) Cyclization of III with 75% sulfuric acid was carried out by the method described by us for 2-allylcyclohexanethiol [1], except that after stirring III for 3 h with sulfuric acid at room temperature, the mixture was diluted with cooling with twice its volume of water, then heated for 3 h at 40-50°, and kept overnight. The mixture was then steam-distilled, the distillate saturated with sodium chloride and extracted with ether, and the extract dried over sodium sulfate. Removal of the ether, followed by vacuum distillation of the residue, gave a fraction, bp 90-91.5° (23 mm), n_D^{20} 1.5100, d_4^{20} 0.9918, which contained 93% of V and 7% of IV by GLC. The overall yield of V and IV was 13%.

c) An ether solution of III was irradiated with a PRK-2 mercury-quartz lamp until a negative test for mercaptan was obtained (7-8 h). Vacuum distillation of the cyclization product gave a fraction, bp 92.5-93.5° (19 mm), n_D^{20} 1.5196, containing 97% of IV and 3% of V by GLC. The overall yield of IV and V was 42%.

IV was purified via its mercury complex, and was obtained chromatographically pure; bp 101-102° (25 mm); n_D^{20} 1.5212; d_4^{20} 1.0099; mp 7.6°. Found: C 67.8; H 9.9%; MR_D 42.8 $C_8H_{14}S$. Calculated: C 67.61; H 9.86%; MR_D 42.66. Mercuric chloride complex, mp 160.5-161°. Found: Hg 48.5%. $C_8H_{14}S \cdot HgCl_2$. Calculated: Hg 48.51%. Methiodide, mp 142.8-143.3° (sublimed). Found: I 44.8%. $C_9H_{17}IS$. Calculated: I 44.70%. Sulphone, mp 70-70.5°. Found: C 54.9; H 8.3%. $C_8H_{14}O_2S$. Calculated: C55.17; H 8.05%.

After purification via the mercury complex, V possessed the following contants: bp 89-90° (23 mm); n_D^{20} 1.5091; d_4^{20} 0.9904. Found: C 67.6; H 9.8%; MR_D 42.8. The mercuric chloride complex had mp 106.5-107°. Found: (for the molecular formula, see above (IV and its derivatives Hg 48.4%. Methiodide, mp 105-107°. Found: I 44.8%. Sulphone, bp 312° (753 mm) (determined by the Sivolobov method. The compound boiled with decomposition); n_D^{20} 1.5030. Found: C 54.94; H 8.04.

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