A new method for the synthesis of bicyclic sulfides consisting of the reaction of cycloolefin sulfides with vinylmagnesium or allylmagnesium bromides and the subsequent intramolecular cyclization of the resulting unsaturated mercaptans has been proposed. By using this method, from cyclohexene sulfide we have synthesized 1-thiadecalin and 2-methyl-1-thiahydrindan; and complexes of these substances with mercuric chloride, and their methiodides and sulfones have been obtained.

Syntheses of bicyclic sulfides are multistage processes which, in many cases, use difficulty accessible compounds and are not general. Two of us [1] proposed a general method for the synthesis of thiabicyclanes via the following stages: the reaction of cycloolefin oxides with vinylmagnesium or allylmagnesium bromides, the addition of hydrogen bromide to the resulting vinyl- or allylcycloalkanols in accordance with and contrary to Markovnikov's rule, the replacement of the hydroxyl by bromine, and the cyclization of the dibromides with sodium sulfide. In an experimental test of this method by the reaction of cyclohexene oxide with vinylmagnesium and allylmagnesium bromides we obtained vinyl- and allylcyclohexanols, respectively. However, it was found that even under UV irradiation hydrogen bromide adds to 2-allylcyclohexan-1-ol only in accordance with Markovnikov's rule. A similar anomaly has been reported in the literature and has been explained by the influence of the hydroxyl group [1]. The addition of hydrogen bromide to the vinyl- and allylcyclohexanols and the replacement of the hydroxyl by bromine gave, respectively, 1-bromo-2-(α-bromoethyl)- and 1-bromo-2-(β-bromopropyl)cyclohexanes. The structure of the latter was confirmed by IR spectroscopy. Analysis of the product of the cyclization of the dibromide with sodium sulfide by the GLC method** showed the absence of the 1-thiadecalin which could be formed from the isomeric i-bromo-2-(γ-propyl)cyclohexane.

The cyclization of the 1-bromo-2-(β-bromopropyl)cyclohexane was carried out with sodium sulfide and also by the action of caustic soda on the mercaptan formed by the reaction of the 1-bromo-2-(β-bromopropyl)cyclohexane with thiourea. In both cases, 2-methyl-1-thiahydrindan was obtained in the form of a mixture of the cis and trans isomers. The cyclization of 1-bromo-2-(α-bromoethyl)cyclohexane with sodium sulfide in dimethylformamide at 125° C gave polymerized products, as expected, since 2-methyl-1-thiabicyclo[4,2,0]nonane, which should have been formed, contains a four-membered ring with a sulfur atom, and such compounds tend to polymerize [3].

In this paper we put forward another method for the synthesis of thiabicyclanes, consisting of the reaction of cyclo-olefin sulfides with vinylmagnesium or allylmagnesium bromides and the subsequent intramolecular cyclization of the resulting mercaptans. This method has been tested for cyclohexene sulfide. The mercaptan formed by the reaction of cyclohexene sulfide with allylmagnesium bromide was subjected to cyclization in three ways: 1) on prolonged storage; 2) by the action of 75% sulfuric acid in an atmosphere of nitrogen; and 3) by UV irradiation. On cyclization by the first method a mixture of 1-thiadeacin (67%) and 2-methyl-1-thiahydrindan (33%) was obtained, the second method gave 2-methyl-1-thiahydrindan with a small amount of 1-thiadeacin as an impurity, and the third method gave 1-thiadeacin contaminated with 2-methyl-1-thiahydrindan. In all cases, cyclization took place stereo-specifically, and the 1-thiadeacin and the 2-methyl-1-thiahydrindan were each obtained in the form of a single stereoisomer. Their configurations have not yet been established.

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**UKh-1 instrument, 4 m column, filled with polyethylene glycol on Celite-22, temperature 120° C, rate of flow of hydrogen 60 ml/min.
1- Allylcyclohexan-1-ol. This was obtained by our modification of a published method [4]. In an atmosphere of nitrogen, 78.4 g (0.8 mole) of cyclohexene oxide [5] was added with stirring and cooling to the allylmagnesium bromide [6] [from 96 g (4 g-at.) of magnesium and 121 g (1 mole) of allyl bromide in 200 ml of absolute ether], the mixture was boiled for 2 hr 30 min and then left overnight; on the following day it was decomposed with a solution of 108 g of ammonium chloride in 400 ml of water. The ethereal layer was decanted off from the residue, and the latter was washed with ether (3 × 150–200 ml), the solvent was distilled off from the ethereal extracts, the residue was boiled with a solution of 18 g of caustic soda in 100 ml of water for 1 hr, the organic layer was separated off, the aqueous layer was extracted with ether, and the extract was combined with the main layer and dried over sodium sulfate. After the solvent had been driven off, the residue was distilled in vacuo to give 98.3 g (89%) of 2-allylcyclohexan-1-ol. Bp 91–93° C (15 mm); nD 1.4785; dD 0.9345; MRD 42.56. Literature data [4]: bp 94–96° C (15 mm); nD 1.4757.

2-Vinylcyclohexan-1-ol. Obtained in a yield of 52% by a method analogous to that described for 2-allylcyclohexan-1-ol, except that the vinylmagnesium bromide was prepared in tetrahydrofuran solution [7]. Bp 70–71.5° C (14 mm); nD 1.4735; dD 0.9422. Found, %: C 75.93; H 11.20. MRD 37.62. Calculated for C8H14O, %: MRD 38.00.

1-Bromo-2-(β-bromopropyl)cyclohexane. A mixture of 48 g (0.34 mole) of freshly distilled 2-allylcyclohexan-1-ol and 1 g of hydroquinone was saturated with hydrogen bromide at -20 to -30° C in an atmosphere of nitrogen (3 hr), then the temperature was slowly raised to 100° C, and saturation with hydrogen bromide was continued (4–5 hr). The mixture was poured into water, the reaction product was extracted with hexane, and the extract was washed with sodium bicarbonate solution and water, and was dried over calcium chloride. After the solvent had been driven off, vacuum distillation of the residue yielded 83.1 g (86%) of 1-bromo-2-(β-bromopropyl)cyclohexane, bp 99–100° C (2 mm); nD 1.5280; dD 1.5252. Found, %: C 38.03; H 5.63; Br 56.34. Calculated for C9H16Br2, %: C 38.19; H 5.70; Br 56.23. The IR spectrum of this compound has absorption bands characteristic for the C–H deformation vibrations in CH3 groups (1381 cm⁻¹), CH2 groups (in a ring) (1445 cm⁻¹), and CH groups (1334 cm⁻¹) and for a C–Br bond in the 500–600 cm⁻¹ region. A bromide with an identical IR spectrum was obtained by saturating 2-allylcyclohexan-1-ol with hydrogen bromide, first with ice cooling and UV irradiation and then without irradiation with a gradual rise in the temperature to 100° C. The yield was 89%, bp 103–104° C (2.5 mm); nD 1.5285.

1-Bromo-2-(α-bromoethyl)cyclohexane was obtained with a yield of 53% by a method analogous to that for the synthesis of 1-bromo-2-(β-bromopropyl)cyclohexane with UV irradiation. Bp 91.5–99° C (3 mm); nD 1.6235. Found, %: C 35.56; H 5.18; Br 59.25. Calculated for C8H14Br2, %: C 35.57; H 5.38; Br 59.07. MRD 52.07.

cis- and trans-2-Methyl-1-thiahydrindans. The water distilled off from a solution of 57.6 g (0.24 mole) of Na2S·9H2O in 200 ml of dimethylformamide, and at 125° C 22.4 g (0.08 mole) of 1-bromo-2-(β-bromopropyl)cyclohexane in 100 ml of dimethylformamide was added over 9 hr. Then the mixture was diluted with a fourfold volume of water and extracted with ether, and the extract was dried over sodium sulfate. After the solvent had been evaporated off and the residue had been vacuum distilled, 6.8 g (54%) of a mixture of cis- and trans-2-methyl-1-thiahydrindans was obtained. Bp 89–90° C (20 mm); nD 1.5609; dD 0.9783. Found, %: C 57.24; H 10.35. MRD 47.67. Calculated for C9H16S, %: C 57.22; H 10.25. MRD 47.33. Cyclization of the dibromide with sodium sulfide in dimethylformamide at 110 and 140° C gave a mixture of the cis- and trans-isomers of 2-methyl-1-thiahydrindan with yields of 28 and 34%, respectively. The same sulfides were obtained with yields of 30 and 51%, respectively, by the cyclization of the dibromide with anhydrous sodium sulfide in absolute ethanol [8], and by the action of a solution of caustic soda on the mercaptan formed by the reaction of the 1-bromo-2-(β-bromopropyl)cyclohexane with thiourea. In the last two cases, the sulfide was contaminated with low-boiling impurities.

2-Allylcyclohexan-1-thiol. Over 1 hr 30 min, 39.9 g (0.35 mole) of cyclohexane sulfide [9] was added to a mixture of allylmagnesium bromide [from 57.6 g (2.4 g-at.) of magnesium and 72.6 g (0.6 mole) of allyl bromide in 200 ml of absolute ether] cooled with a mixture of ice and salt. After the cooling bath was removed, the mixture was stirred at room temperature until condensate ceased to drip from the condenser, and then it was heated to the boil, boiled for 6–8 hr, and left overnight. On the following day, with cooling in a current of nitrogen, the mixture was decomposed with 10% HCl, the organic layer was separated off, the aqueous layer was extracted with ether, and the combined extract was dried over sodium sulfate. The 2-allylcyclohexan-1-thiol present in the ethereal extract was subjected to cyclization in three ways.

Cyclization of 2-allylcyclohexan-1-thiol. A) The solvent was distilled off from the ethereal solution of 2-