LETTERS TO THE EDITOR

SYNTHESIS OF CYCLIC SULFIDES

VI.* SYNTHESIS OF 9-METHYL-1-THIADECALIN AND 2,8-DIMETHYL-1-THIAHYDRINDAN

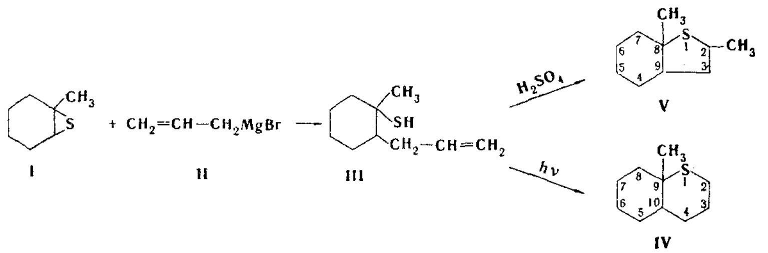
V. I. Dronov and V. P. Krivonogov

UDC 547.735'818.1.07:541.634

2,8-Dimethyl-1-thiahydrindan and 9-methyl-1-thiadecalin, respectively, were obtained by the reaction of 1-methyl-1-cyclohexene episulfide with allylmagnesium bromide and subsequent intramolecular cyclization of the resulting 1-methyl-2-allylcyclohexane-1-thiol by the action of sulfuric acid or UV irradiation. The cyclization proceeds stereospecifically.

9-Methyl-1-thiadecalin (IV) and 2,8-dimethyl-1-thiahydrindan (V) were obtained via the scheme that we proposed in [2,3] by the reaction of 1-methyl-1-cyclohexene episulfide (I) with allylmagnesium bromide (II) and subsequent intramolecular cyclization of the resulting 1-methyl-2-allylcyclohexane-1-thiol (III).

In the reaction of I with allylmagnesium bromide, the C–S bond is cleaved between the sulfur and the most hydrogenated carbon atom, which is confirmed by the formation of a mixture of cis and trans isomers of 1-methyl-2-propylcyclohexane during the hydrodesulfuration of IV or V.



The intramolecular cyclization of III proceeds with great difficulty during both UV illumination and under the influence of sulfuric acid, and the yields of IV and V are 26 and 14%, respectively. This is apparently associated with the steric hindrance to molecular cyclization exerted by the methyl group. As in the case of other allylcycloalkanethiols [2,3], the cyclization of III proceeds stereospecifically.

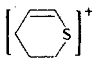
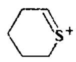
It is known that episulfides have the cis configuration [4] and that compounds with the trans configuration are formed in the reactions of cyclohexene cis-epoxide, which are accompanied by opening of the three-membered ring [5]. In this connection, in the reaction of I with II one should obtain III, in which the hydrogen atom and the CH_3 group attached to the cyclohexane ring are found in the trans orientation. It is also known that configuration changes do not occur in heterocyclization reactions during the interaction of the unshared electron pairs of sulfur with an unsaturated carbon atom [6]. Configuration changes apparently do not occur in the cyclization of III during both UV irradiation and under the influence of sulfuric acid, and IV and V, respectively, in which the hydrogen atom and the CH_3 group are found in the trans orientation on fusion of the rings, are formed. The orientation of the CH_3 group attached to C_2 in V still remains undetermined.

---

*See [1] for communication V.

Institute of Chemistry, Bashkirskii Branch, Academy of Sciences of the USSR, Ufa. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1186-1188, September, 1972. Original article submitted August 5, 1971.

The structures of IV and V were confirmed by the IR and mass spectra. The IR spectra of IV and V contain the absorption maxima characteristic for the skeletal vibrations of cyclic sulfides (1257 and 1250 cm^{-1}, respectively) and for the stretching and deformation vibrations of the C–H bonds in the CH_2 and CH_3 groups.

The fragmentation of IV and V under the influence of electron impact proceeds in accordance with the observations in [3, 7]. We found that the mass spectra of thiabicyclans with five- and six-membered heterorings [2,3] differ in that the latter, in contrast to the former, have intense peaks of fragment ions with masses of 100 or 101. We assign the  and  structures, respectively, to the fragment ions with masses 100 and 101. The intensities of the peaks of the fragment ions with masses 101 and 100 in the mass spectra of IV and V are, respectively, 27.4 and 42.2 and 1.07 and 1.0% of the maximum, on the basis of which it can be concluded that IV has a six-membered heteroring, while V has a five-membered heteroring.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrophotometer with NaCl and LiF prisms in dismountable liquid cuvettes with a layer thickness of 0.013 mm. The mass spectra were recorded with an MKh-1306 mass spectrometer at an ionizing electron energy of 50 eV, an emission current of 0.7 mA, and an ionizing chamber temperature of 250°.

1-Methyl-1-cyclohexene Episulfide (I). This compound was obtained via the method in [8]. The reaction was monitored by means of gas-liquid chromatography (GLC).* The reaction was terminated after the disappearance of the peak of 1-methyl-1-cyclohexene oxide on the chromatogram (50 h). A 156-g (1.37 mole) sample of 1-methyl-1-cyclohexene oxide and 193 g (2 mole) of potassium thiocyanate gave 77.1 g (43%) of I with bp 84-85° (37 mm), n_D^{20} 1.5130, and d_4^{20} 1.0125. Found: C 65.4; H 9.2; S 24.8%; MR_D 37.95. $C_7H_{12}S$. Calculated: C 65.6; H 9.4; S 25.0%; MR_D 38.1. Compound I decomposed to give sulfur and 1-methyl-1-cyclohexene [9] with bp 51.5° (110 mm), n_D^{20} 1.4505, and d_4^{20} 0.8110 during vacuum distillation with a rectification column.

1-Methyl-2-allylcyclohexane-1-thiol (III). This compound was obtained via the method in [2]. The reaction of 12.8 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 absolute ether, gave, after drying of the reaction mixture and removal of the ether, 4.5 g of a fraction with bp 70-102° (47 mm). The thiol was not characterized because of the rapid change it undergoes as a result of cyclization.

Cyclization of 1-Methyl-2-allylcyclohexane-1-thiol (III). A. The cyclization of III by the action of 75% sulfuric acid was carried out by the method in [3]. Vacuum distillation of the cyclization product yielded a fraction with bp 91-96.5° (16 mm), n_D^{20} 1.5100, and d_4^{20} 0.9826, which, according to GLC,† contains 97% 2,8-dimethyl-1-thiohydrindan (V) and 3% 9-methyl-1-thiadecalin (IV). The overall yield of IV and V was 14%.‡

B. Compound III was illuminated with a PRK-2 quartz mercury lamp until it gave a negative test for mercaptans (8 h). Vacuum distillation of the cyclization product yielded a fraction with bp 100-104° (18 mm), n_D^{20} 1.5170, and d_4^{20} 0.9965, which, according to GLC,† contained 92% IV and 8% V. The overall yield of IV and V was 26%.‡

Compound IV was purified through its mercury complex and was obtained chromatographically pure with bp 103.5-104.5° (18 mm), n_D^{20} 1.5220, and d_4^{20} 1.0059. Found: C 70.6; H 10.5; S 18.4%; MR_D 51.53. $C_{10}H_{18}S$. Calculated: C 70.6; H 10.6; S 18.8%; MR_D 51.90. The complex with mercuric chloride had mp 117.5-118.5°. Found: S 7.4%. $C_{10}H_{18}S \cdot HgCl_2$. Calculated: S 7.2%. The sulfone was obtained as an oil with n_D^{20} 1.5150. Found: C 59.4; H 8.8; S 15.6%. $C_{10}H_{18}O_2S$. Calculated: C 59.4; H 8.9; S 15.8%.

---

*With a UKh-2 chromatograph with a column (4 m long and 4 mm in diameter) filled with 10% E-301 on Chromosorb W at 111°. The helium flow rate was 70 ml/min.

†With a UKh-2 chromatograph with a column (2.5 m long and 4 mm in diameter) filled with 10% diethylene glycol succinate on Cellite-545 at 135°. The helium flow rate was 100 ml/min.

‡The yields were calculated on the basis of 1-methyl-1-cyclohexene episulfide.

Compound V had the following physical constants after purification through the mercury complex: bp 95-96.5° (16 mm), n_D^{20} 1.5118, and d_4^{20} 0.9836. Found: C 70.4; H 10.7; S 18.5%; MR_D 51.78. $C_{10}H_{18}S$. Calculated: C 70.6; H 10.6; S 18.8%; MR_D 51.90. The complex with mercuric chloride had mp 139.5-140° (dec.). Found: S 7.3%. $C_{10}H_{18}S \cdot HgCl_2$. Calculated: S 7.2%. The sulfone was obtained as an oil with n_D^{20} 1.5020 and d_4^{20} 1.1362. Found: C 59.6; H 8.9; S 16.0%; MR_D 52.50. $C_{10}H_{18}O_2S$. Calculated: C 59.4; H 8.9; S 15.8%; MR_D 52.85.

Hydrodesulfuration of IV and V. Freshly prepared Urusibar nickel [10] from 20 g of nickel–aluminum alloy (50% nickel) was placed in a flask, 20 ml of alcohol was poured over it, and a solution of 1 g of IV or V in 5 ml of alcohol was added. The mixture was heated on a water bath for 2 h below the boiling point and was then refluxed with monitoring of the reaction by means of GLC.* The reaction was terminated after the disappearance of the peak of IV or V on the chromatogram (1 h, 20 min). The catalyst was removed from the cooled mixture by filtration and washed with alcohol. The filtrate was diluted with an equal volume of water and extracted with n-hexane. The extract was dried with anhydrous magnesium sulfate, and the solvent was removed from the extract by distillation to give 0.7 g of a mixture, which, according to GLC,† contained 30% trans- and 70% cis-1-methyl-2-propylcyclohexane.

LITERATURE CITED

1. V. I. Dronov and V. P. Krivonogov, Khim. Geterotsikl. Soedin., 622 (1972).
2. V. I. Dronov, V. P. Krivonogov, and V. S. Nikitina, Khim. Geterotsikl. Soedin., 335 (1970).
3. V. I. Dronov and V. P. Krivonogov, Khim. Geterotsikl. Soedin., 1185 (1970).
4. L. Goodman and B. R. Baker, J. Am. Chem. Soc., 81, 4924 (1969).
5. Heterocyclic Compounds [Russian translation], Vol. 1, Inostr. Lit., Moscow (1953), p. 24.
6. Stereochemistry of Cyclohexane Derivatives [Russian translation], Inostr. Lit., Moscow (1958), p. 291.
7. E. S. Brodskii, R. A. Khmel'nitskii, A. A. Polyakova, and G. D. Gal'pern, Neftekhimiya, 9, 146 (1969).
8. E. E. van Tamelen, J. Am. Chem. Soc., 73, 3444 (1951).
9. A. F. Platé, A. L. Liberman, and N. A. Momma, Izv. Akad. Nauk SSSR, Ser. Khim., 689 (1953).
10. General Laboratory Manual of Organic Chemistry [in Russian], Mir, Moscow (1965), p. 615.

---

*With a UKh-2 chromatograph with a column (4 m long and 4 mm in diameter) filled with 30% Apiezon L on Chromosorb W at 188°. The helium flow rate was 60 ml/min.

†With a UKh-2 chromatograph with a column (3.5 m long and 4 mm in diameter) filled with 10% squalane on Cellite-545 at 144°. The hydrogen flow rate was 55 ml/min.