for 2 h. Water (20 ml) was added, and the mixture was extracted with chloroform. The chloroform was removed from the extract, 2 ml of alcohol was added to the residue, and the mixture was allowed to stand at 0° for 24 h. The resulting solid was removed by filtration to give 0.3 g (64%) of white needles with mp 64-65° (from alcohol). Found: C 56.9; H 5.8; N 10.7%. $C_{14}H_{17}NO_4S$. Calculated: C 56.9; H 5.8; N 10.9%.

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REACTION OF 1,5-DIKETONES

XIX.* 2,2'-DICYCLOHEXANONYL SULFIDE: SYNTHESIS, ISOMERIZATION TO A CYCLOKETOL, AND CONVERSION TO PERHYDROPHENOTHIAZINE

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2,2'-Dicyclohexanonyl sulfide and the isomeric 2-thiatricyclo[7.2.1.$0^{3,8}$]tridecan-8-ol-13-one were synthesized by reaction of α-chlorocyclohexanone with $Na_2S \cdot 9H_2O$. Both compounds form the same perhydrophenothiazine isomers under the conditions of the Leuckart reaction.

The previously undescribed 2,2'-dicyclohexanonyl sulfide (I) is a peculiar 1,5-diketone and the thia analog of the known [2] 2,2'-dicyclohexanonylmethane. In the present communication we present data that confirm that the structural analogy between these diketones also extends to some of their reactions.

Depending on the reaction conditions, diketone I or isomeric ketol II is obtained in the reaction of α-chlorocyclohexanone with sodium sulfide. When the temperature is lowered, one can obtain diketone I in yields up to 40%. Diketone I is unstable and can be stored only at low temperature in the dark. In light it decomposes after a few days. Ketol II, which is formed in 80% yield when a solution of sodium sulfide and α-chlorocyclohexanone is allowed to stand at room temperature for 2 days, is completely stable on storage.

The IR spectrum of diketone I contains an intense absorption band at 1710 cm^{-1} (C=O), and the IR spectrum of ketol II, in addition to this band, also contains absorption bands at 3600 and 3450 cm^{-1} (OH). The presence of two carbonyl groups in diketone I is confirmed by the formation of a bis derivative (III) on reaction of diketone I with malononitrile under the conditions of the Knoevenagel reaction. We were unable to obtain a dioxime from diketone I.

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*See [1] for communication XVIII.

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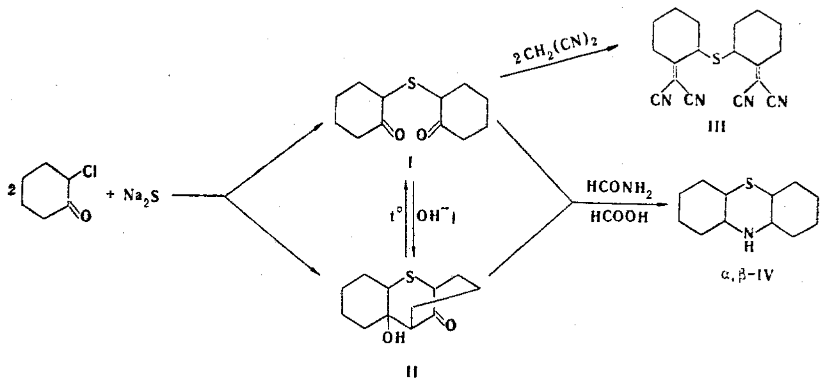

As in the case of 2,2'-dicyclohexanonylmethane [2, 3], diketone I is converted to ketol II on treatment with methanolic sodium methoxide as a result of an intramolecular aldol condensation; the reverse reaction occurs when II is vacuum distilled.

The same products – the α and β isomers of perhydrophenothiazine (IV) – are formed when diketone I or isomeric ketol II is treated with formamide under the conditions of the Leuckart reaction. Under these conditions ketol II apparently undergoes prior isomerization to diketone I, and the latter reacts with formamide to give perhydrophenothiazines α,β-IV. Other dicyclonylmethanes and their cycloketols also behave similarly in the Leuckart reaction [4-6].

Isomeric bases IV, which are formed in an overall yield of 50%, differ from one another with respect to the form of their crystals, melting points, and chromatographic behavior. The IR spectra of the α and β isomers differ only slightly in the "fingerprint" region, and the characteristic band belonging to the NH group appears only in the spectra of mineral oil suspensions of the compounds (at 3300 cm^{-1} for α-IV and 3320 cm^{-1} for β-IV).

The NMR spectrum of the α isomer contains four groups of signals at 0.65 (s), 1.5 (s), 2.33 (d), and 3.12 (s) ppm with an intensity ratio of 1 : 16 : 3 : 1, respectively. The NMR spectrum of the β isomer contains three groups of signals at 0.91 (s), 1.5 (s), and 2.31 (d) ppm with an intensity ratio of 1 : 16 : 4. In both cases the signals at weak field (0.65 and 0.91 ppm) belong to the protons of the NH group, inasmuch as they vanish when D_2O is added. The signals with chemical shifts ≥ 2.3 ppm apparently belong to the protons of the CH groups adjacent to the nitrogen and sulfur atoms.

EXPERIMENTAL METHOD

The IR spectra of CCl_4 solutions of the compounds were recorded with a UR-20 spectrometer. The NMR spectra of $CDCl_3$ solutions were recorded with a ZKR-60 spectrometer with tetramethylsilane as the internal standard. The R_f values were determined in a thin layer of Silufol (elution with ethyl acetate).

2,2'-Dicyclohexanonyl Sulfide (I). A solution of 20 g of $Na_2S \cdot 9H_2O$ in 60 ml of 50% methanol was added dropwise to a solution of 20 g of α-chlorocyclohexanone in 50 ml of methanol at such a rate that the temperature of the mixture did not exceed 15°. The mixture was then stirred for 15 min, diluted with water to 0.5 liter, and extracted with ether. The extract was dried with $MgSO_4$, and the ether was removed by distillation to give an oil that crystallized slowly. The crystals were removed from the oil by filtration, washed with a cold mixture of petroleum ether and diethyl ether, and recrystallized from hexane to give 7.0 g (41%) of a product with mp 71-73°. Found: C 63.6; H 7.9; S 14.0%. $C_{12}H_{18}SO_2$. Calculated: C 63.5; H 8.0; S 14.1%.

2-Thiatricyclo$[7.3.1.0^{3,8}]$tridecan-8-ol-13-one (II). A) A solution of 44 g of $Na_2S \cdot 9H_2O$ in 200 ml of 50% methanol was added in the course of 15 min with stirring and ice cooling to a solution of 40 g of α-chlorocyclohexanone in 100 ml of methanol, and the mixture was allowed to stand at room temperature for 2 days. It was then diluted with water to 1 liter, and the resulting solution was saturated with NaCl. The precipitated ketol crystals were removed by filtration and recrystallized from petroleum ether–CCl_4 to give 27 g (80%) of colorless crystals with mp 102-103°. Found: C 63.5; H 7.9; S 14.1%. $C_{12}H_{18}SO_2$. Calculated: C 63.5; H 8.0; S 14.1%.

B) A 6-g sample of diketone I was dissolved in 25 ml of a 0.5 M solution of $NaOCH_3$ in methanol, and the solution was allowed to stand at room temperature for 5 h. Saturated NaCl solution (200 ml) was added, and the precipitated crystals were removed by filtration and recrystallized from petroleum ether–CCl_4 to give the product in quantitative yield. The product was identical to ketol II obtained in the preceding experiment.

Di(2-dicyanomethylenecyclohexyl) Sulfide (III). A 2-g sample of diketone I, 1.3 g of malononitrile, and a few drops of piperidine were dissolved in 50 ml of alcohol, and the mixture was allowed to stand at room temperature for 2 days. The precipitated crystals were removed by filtration, washed with alcohol, and dried to give 1.5 g (52%) of III with mp 172-173° (acetonitrile). Found: C 66.7; H 5.8; N 17.3; S 10.0%. $C_{18}H_{18}N_4S$. Calculated: C 67.1; H 5.6; N 17.4; S 10.0%. IR spectrum: 2227 ($C \equiv N$) and 1605 ($C=C$) cm^{-1}.

Leuckart Reaction for I and II. A mixture of 26 g of diketone I or ketol II, 70 ml of formamide, and 70 ml of 85% formic acid was refluxed for 2 h, after which 400 ml of HCl (1 : 1) was added, and the mixture was refluxed for another hour. It was then cooled slowly to room temperature, and the precipitated crystals of α-IV hydrochloride were removed by filtration to give 9.3 g (37%) of a product with mp 253-255°. The mother liquor was cooled with ice to precipitate 3.2 g (13%) of β-IV hydrochloride with mp 301-302°. The hydrochlorides were dissolved in water, the solutions were made alkaline with NaOH, and the precipitated bases were recrystallized from 50% alcohol. The products were obtained in quantitative yield. The α isomer was obtained as colorless prisms with mp 71.5-72.5° and R_f 0.25. Found: C 67.7; H 10.2; N 6.4; S 15.4%. $C_{12}H_{21}NS$. Calculated: C 68.2; H 10.0; N 6.6; S 15.2%. The picrate had mp 188-189° (dec.). Found: N 13.0%. $C_{18}H_{24}N_4O_7S$. Calculated: N 12.7%. The β isomer was obtained as colorless plates with mp 99-99.5° and R_f 0.1. Found: C 67.6; H 10.1; N 6.3; S 15.0%. $C_{12}H_{21}NS$. Calculated: C 68.2; H 10.0; N 6.6; S 15.2%. The picrate had mp 198° (dec.). Found: N 13.0%. $C_{18}H_{24}N_4O_7S$. Calculated: N 12.7%.

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STUDY OF THE REACTION OF SULFUR HALIDES WITH UNSATURATED COMPOUNDS

XIII.* OXIDATION OF THIABICYCLOTRIDECENES

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The oxidation of thiabicyclotridecenes with various oxidizing agents proceeds selectively and, depending on the amount and strength of the oxidizing agent, gives sulfoxides, epoxy sulfoxides, or epoxy sulfones. The sulfur atom is initially oxidized, after which the double bond either undergoes epoxidation or hydroxylation.

The oxidation of sulfides is currently attracting considerable attention [1]. Research directed toward the study of the effect of the character of the oxidizing agent and steric factors on the degree of oxidation of the sulfur atom may be of particular interest. In this respect, convenient experimental subjects are 13-thia-

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*See [9] for communication XII.

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