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CONFORMATIONAL ANALYSIS OF THE STEREOISOMERS OF 3-METHYL-2-OXO-2-THIABICYCLO[4.4.0]DECANE

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The conditions for the separation of the stereoisomeric sulfones and sulfoxides of 3-methyl-2-thiabicyclo[4.4.0]decane were found by means of capillary gas—liquid chromatography, and the relative thermodynamic stabilities of the latter were determined. The configuration of the stereoisomeric sulfoxides was established on the basis of oxidation data, the characteristics of the physicochemical properties, and the Kerr effect.

In developing the stereochemistry of thiabicycloalkanes that model petroleum sulfides and their derivatives [1] we obtained sulfones from four of the stereoisomers of 3-methyl-2-thiabicyclo[4.4.0]decane [2] and sulfoxides from two of them and established the configuration of the latter.

For uniformity in the nomenclature of the thiabicycloalkanes we will subsequently use the IUPAC nomenclature for bicyclic hydrocarbons with a condensed system of rings. The three-dimensional orientation of the substituents is most conveniently examined with respect to the hydrogen atom attached to the angular carbon atom with which numbering is commenced. In this case it is most illustrative to compare the three-dimensional orientation of the angular hydrogen atom and the hydrogen atom attached to the tertiary carbon atom bonded to the alkyl substituent. The cis configuration of the alkyl group is assigned to this isomer when the latter have identical orientations.

TABLE 1. Stereoisomers of 3-Methyl-2,2-dioxo-thiabicyclo-[4.4.0]decane

Compound	Configuration	mp, °C (solvent)	Retention time, min
III	cis, trans	102,5—103,5[a]	31,23
IV	cis, trans	—[b]	31,35
V	trans, trans	69—71[a]	34,57
VI	trans, cis	92—94[c]	39,75

[a] From ethanol. [b] n_D^{20} 1.5098. [c] From methanol.

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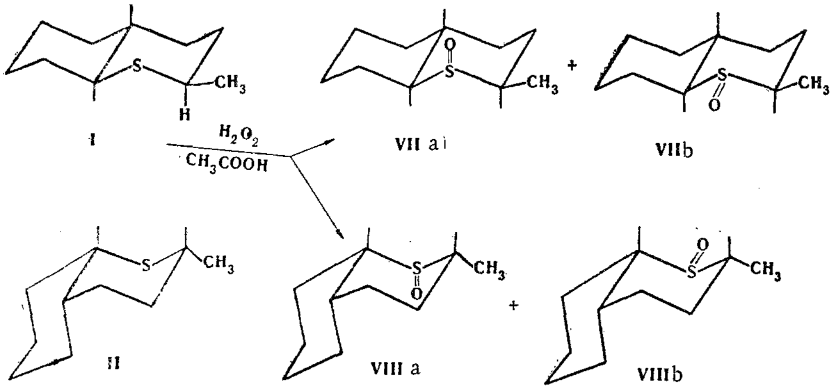
Sulfones III-VI (Table 1) were obtained by oxidation of the stereo-isomers of 3-methyl-2-thiabicyclo[4.4.0]decane (I, II) by the method in [3].

cis, trans-3-Methyl-2-thiabicyclo[4.4.0]decane (1) and the cis, cis isomer (II) were oxidized with hydrogen peroxide in glacial acetic acid [1] to the corresponding sulfoxides VII and VIII:



A portion of stereoisomer VIIb, which crystallized out at normal temperature, was separated, and the residue was separated by means of column chromatography. Stereoisomer VIIa was also obtained as a result of inversion of the configuration of sulfoxide VIIb by the method in [4] by alkylation of the sulfoxide group with triethyloxonium tetrafluoroborate and subsequent hydrolysis of the ethoxysulfonium salt.

In the case of sulfide I it is easier for the attacking molecule of hydrogen peroxide to approach the unshared electron pair of the sulfur atom from the side opposite to the methyl substituent, and it may therefore be assumed that stereoisomer VIIb has an equatorial sulfoxide group and that VIIa has an axial sulfoxide group. The approach of the hydrogen peroxide molecule to the sulfur atom in sulfide II can be realized only from the exo side of the bicyclic system and from the side opposite to the methyl position. Stereoisomer VIIIb, which constitutes 95% of the mixture, like VIIb, probably has a configuration with an equatorial sulfoxide group (Table 2).

Quantitative analysis of the mixtures of sulfoxides VII and VIII was accomplished by capillary gas — liquid chromatography (GLC), during which stereoisomers VIIb and VIIIb had longer retention times than, respectively, VIIa and VIIIa. Inasmuch as the equatorial isomer has higher polarity and, consequently, a longer retention time and a lower R_f value than the axial isomer, it may be assumed that stereoisomer VIIb has an equatorial sulfoxide group and that VIIa has an axial sulfoxide group. Judging from the melting point, stereoisomer VIIb should have cis-oriented methyl and sulfoxide groups; this orientation is possible if the SO group is equatorial. For the same reasons, stereoisomer VIIIb has a structure with an equatorial sulfoxide group.

Treatment of each sulfoxide (VIIa and VIIb) by the method in [5] with hydrochloric acid in dioxane leads to the formation of an equilibrium mixture of isomers, which was analyzed

TABLE 2. Relative Percentages of the Stereoisomeric 3-Methyl-2-oxo-thiabicyclo[4.4.0]decane in the Mixtures after Oxidation and Their Physicochemical Properties

Sulfoxide	Percentage	mp, °C	Dipole moment, D	Molar Kerr constant, $mK \cdot 10^{12}$	
				found	calc. (conformation)
VIIa	21	98—99[a]	4.02	−56	−77 (*a*)
VIIb	79	76—77[b]	4,55	277	269 (*e*)
VIIIa	5	—[c]	—	—	−187 (*a*)
VIIIb	95	—[d]	4,59	355	366 (*e*)

[a] From hexane. [b] From isooctane [c] Not isolated. [d] n_D^{20} 1.5661.

by GLC. In this case it was observed that stereoisomer VIIa with an axial sulfoxide group ($\Delta J^\circ = -0.34$ kcal/mole) is the preferred isomer. The composition of the mixture did not change when sulfoxides VII were heated at 253°.

In order to prove the above conclusions regarding the three-dimensional structures of the sulfoxides we investigated the double-beam refractions in an electrical field (the Kerr effect) [6] of sulfoxides VIIa, b and VIIIb in carbon tetrachloride.

The molar Kerr constant (mK) is calculated from the formula

$$mK = \frac{2\pi N_A}{9}(\theta_1 + \theta_2), \tag{1}$$

where θ_1 and θ_2 are the anisotropic and dipole currents, respectively, and

$$\theta_1 = \frac{1}{45kT} \cdot \frac{P_D}{P_e} \left[(b_{xx} - b_{yy})^2 + (b_{yy} - b_{zz})^2 + (b_{zz} - b_{xx})^2 + 6(b_{xy}^2 + b_{xz}^2 + b_{yz}^2)\right]; \tag{2}$$

$$\begin{aligned}\theta_2 = \frac{1}{45k^2T^2} + [m_x^2(2b_{xx} - b_{yy} - b_{zz}) + m_y^2(2b_{yy} - b_{xx} - b_{zz}) + m_z^2(2b_{zz} -\\ - b_{xx} - b_{yy})^2 + 6m_x m_y b_{xy} + 6m_x m_z b_{xz} + 6m_y m_z b_{yz}];\end{aligned} \tag{3}$$

here, b_{ii}, ..., b_{jk} are the components of the matrix of the molecular polarizability tensor found on the basis of tensor-additive summation of the bond polarizability ellipsoids, and m_i is the component of the molecular dipole moment.

The geometry of the sulfoxide-containing ring was taken from the data in [7], and the geometry of the cyclohexane fragment was taken from the data in [8]. The direction of the dipole moments was determined on the basis of the method in [9]. The C—H bonds were considered to be anisotropically polarizable — $b_e = b_t = 0.64$ Å^3; $b_e = 0.98$ Å^3 and $b_t = 0.27$ Å^3 for the C—C bond [6]. No data are available on the polarizability ellipsoid of the sulfoxide group.

Considering that the θ_1 value is negligibly small [9], it is easy to represent Eq. (1) for sulfoxides that do not contain additional polar substituents in the form

$$mK = 45^{-1}k^{-2}T^{-2}\{\Sigma[m_i^2(2b_{ii} - b_{jj} - b_{kk} + 6m_i m_j b_{ij}]\}_{\mathrm{C-C}} + mK_{(\mathrm{CH_6})_2\mathrm{SO}}.$$

The experimentally found mK constant for dimethyl sulfoxide in carbon tetrachloride [10] is $144 \cdot 10^{-12}$. The experimentally found Kerr constants and the values calculated for the possible three-dimensional structures are presented in Table 2. It is apparent that stereoisomer VIIa has an axial sulfoxide group, whereas VIIb and VIIIb have an equatorial sulfoxide group. Thus stereoisomer VIIa is cis, trans, trans-, VIIb is cis, cis, trans-, and VIIIb is cis, cis, cis-3-methyl-2-oxo-2-thiabicyclo[4.4.0]decane.

EXPERIMENTAL

The sulfoxides were subjected to GLC with a Tsvet-4 chromatograph with a flame-ionization detector in a 55-m long steel capillary column with a diameter of 0.25 mm; the stationary phase was polyethylene glycol 20 M, the carrier gas was helium, and the thermostat temperature was 200°. The sulfones were subjected to GLC with a Tsvet-4 chromatograph with a 30-m long column with a diameter of 0.25 mm; the stationary phase was γ-nitrilosilicone rubber, the carrier gas was helium, and the thermostat temperature was 225°.

The dipole moments and the Kerr constants were measured in carbon tetrachloride at 20° in analogy with the method in [11].

3-Methyl-2,2-dioxo-2-thiabicyclo[4.4.0]decanes (III-VI) (Table 1). These compounds were obtained by oxidation of the isomeric sulfides with hydrogen peroxide as described in [3] for sulfone III.

3-Methyl-2-oxo-2-thiabicyclo[4.4.0]decanes (VII, VIII). These compounds were obtained by oxidation of sulfides I and II, respectively. Stereoisomer VIIb crystallized out partially from the mixture (21% VIIa and 79% VIIb); it was separated, and the residue was separated by means of column chromatography with activity III neutral aluminum oxide and elution with acetone–carbon tetrachloride (1:4). Two fractions were obtained: the first fraction was stereoisomer VIIa with mp 98-99° (after repeated recrystallization from hexane), and the second fraction was VIIb with mp 76-77° (from isooctane) (according to the data in [1], the first fraction had n_D^{20} 1.4986, and the second fraction had mp 74.5-76°).

The reaction mixture, which contained 9% VIIIb, was purified by means of column chromatography as described above.

Inversion of Stereoisomer VIIb to VIIa. This was accomplished by the method in [4]. A mixture of 1.9 g (12 mmole) of sulfoxide VIIb and 2.3 g (12 mmole) of triethyloxonium in 50 ml of dichloromethane was stirred at 25° for 1.5 h, after which water was added, and the solution of ethoxysulfonium salt was titrated with 0.1 N sodium hydroxide solution with phenolphthalein as the indicator. The mixture was salted out with sodium chloride and extracted with dichloromethane; the extract was dried with anhydrous sodium sulfate, and the dichloromethane was removed by distillation to give sulfoxide VIIa. The yield after recrystallization from hexane was 0.96 g; repeated recrystallization from hexane gave a product with mp 98-99°.

Investigation of the Equilibrium VIIa $\rightleftarrows$ VIIb. A) A mixture of 0.6 ml of concentrated hydrochloric acid, 1.2 ml of dioxane, and 0.1 g of sulfoxide VIIb was stirred at room temperature for 24 h, after which 10 ml of water was added, and the mixture was thoroughly extracted three times with dichloromethane. The extract was dried with calcined potassium carbonate, the solvent was removed by distillation, and the residue was analyzed by GLC, which revealed that the mixture consisted of 64% VIIa and 36% VIIb.

B) A 50 mg sample of isomer VIIa was stirred in 0.3 ml of concentrated hydrochloric acid and 0.6 ml of dioxane at room temperature for 24 h. After the usual extraction, the mixture was analyzed by GLC, which revealed that it consisted of 65% VIIa and 35% VIIb.

C) A 1% solution of sulfoxides VII in $n\text{-}C_{14}H_{30}$ was heated at 250° for 2 h in a stream of nitrogen. The solution was analyzed by GLC as described above. No change in the isomer ratio was observed.

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