STEREOISOMERS OF 2-METHYL-1-THIADECALIN

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A mixture of the geometrical isomers of 2-methyl-1-thiadecalin has been separated by a combination of adsorption column chromatography and preparative gas–liquid chromatography. The configuration of each isomer has been established by mass spectrometry and PMR spectrometry with the application of the Auwers–Skita rule.

In order to study the properties of thiabicyclanes modeling the sulfides of the middle fractions of petroleum, 2-methyl-1-thiadecalin has been obtained previously [1] by the reduction of a mixture of the geometric isomers of 2-methyl-1-thiadecalin-4-one, the product of this reaction consisting of a mixture of all possible geometric isomers (Fig. 1).

The following system of nomenclature for the geometric isomers has been adopted in the present paper: the relative positions of the hydrogen atoms (cis or trans) are considered – first the configuration of the hydrogen in position 2 relative to the hydrogen bound to the nearest α-angular carbon atom is considered, and then the relative arrangement of the atoms of hydrogen attached to the α- and β-angular carbon atoms, which characterizes the configuration of the ring linkage.

The amounts of each of the geometric isomers in the mixture have been determined previously [2]. From a mixture of 2-methyl-1-thiadecalin-4-ones (precursors of the 2-methyl-1-thiadecalins) on cooling the most stable 2-methyl-1-thiadecalin-4-one (mp 77.5°C) separated out. Its reduction gave an individual geometric isomer of 2-methyl-1-thiadecalin. By analogy with 2-methyldecalin [3] it may be assumed that this isomer has the cis,trans configuration. We started from the assumption that the introduction of a sulfur atom into the ring does not change the general laws characteristic for decalin derivatives. A procedure was also developed [4] permitting the isolation of another isomer, presumably cis,cis-2-methyl-1-thiadecalin, by preparative thin-layer chromatography. According to preliminary results [5], the other geometric isomers present in the mixture must possess the trans,trans and trans,cis configurations.

In development of preceding investigations [1, 2, 4, 5] in the present work we have obtained results of the separation of the geometric isomers of 2-methyl-1-thiadecalin and the determination of their configurations.

By the use of adsorption column chromatography and preparative gas–liquid chromatography, from a mixture we have isolated all four geometric isomers of 2-methyl-1-thiadecalin; their characteristics are given in Tables 1 and 2. Assuming the possibility of extending the Auwers rule applying to hydroaromatic compounds (the trans isomer has the higher melting point but the lower boiling point and the lower refractive index) to the 2-methyl-1-thiadecalin-4-ones, it may be assumed that both crystalline thiadecalinones (mp 77.5 and 64°C; they were first obtained by Nazarov et al. [6]) have the trans linkage of the ring and the two liquid isomers the cis linkage. Of the two crystalline isomers of 2-methyl-1-thiadecalin-4-one, the isomer with the trans-oriented methyl group with respect to the closest angular hydrogen must have the higher melting point; the mutual position of the hydrogen atoms on the corresponding carbon atoms must then be cis. Consequently, the isomer of 2-methyl-1-thiadecalin-4-one with mp 77.5°C can be ascribed the cis, trans and the isomer with mp 64°C the trans, trans structure.

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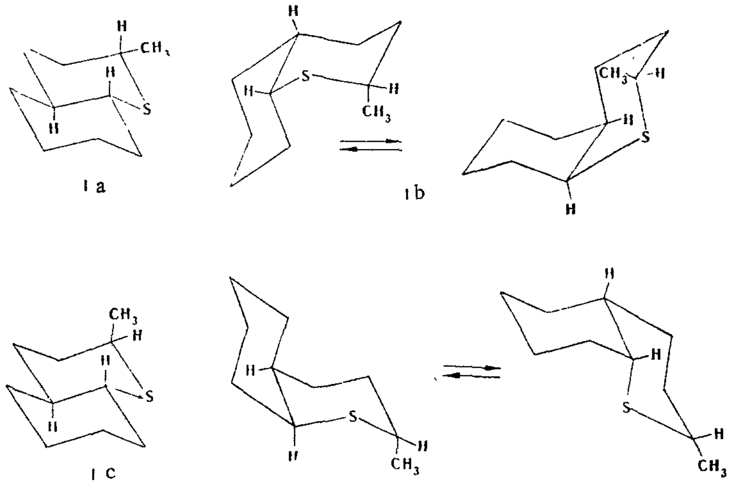

Fig. 1. Stereoisomers of 2-methyl-1-thiadecalin: cis,trans isomer (Ia); cis,cis isomer (Ib); trans,trans isomer (Ic); trans,cis isomer (Id).

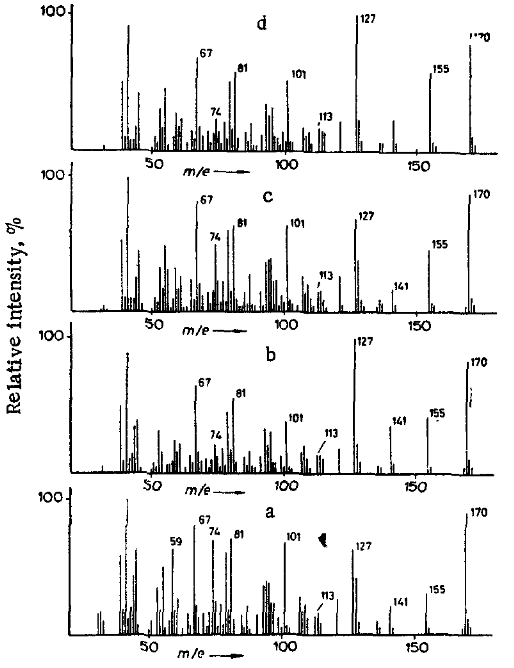

Fig. 2. Mass spectra of 2-methyl-1-thiadecalins: a) cis,trans isomer; b) cis,cis isomer; c) trans,trans isomer; d) trans,cis isomer.

The products of the reduction of the oxo group in the 2-methyl-1-thiadecalinones – 2-methyl-1-thiadecalins – retain the configuration of the oxo sulfides. Thus, on the basis of the Auwers rule, the isomer (Ia) with the smallest retention time will have the cis, trans and the isomer Ic the trans, trans configuration. In the pair of isomers with the cis linkage of the rings, the isomer (Ib) with the lower values of the retention time and of the boiling point apparently has the cis orientation of the α-hydrogen atom and the cis, cis configuration, while the isomer (Id) has the trans orientation of the α-hydrogen atom and the trans, cis configuration.

In the dissociative ionization of 2-methyl-1-thiadecalin under the action of electron impact, the ring not containing the sulfur atom decomposes first [7]. The mass spectra of the geometric isomers show considerable differences in the intensities of the peaks of the ions formed. It is known that the probability of the processes of cleavage of bi- and polycyclic systems with the cis linkage of the rings under the action of electron impact is higher than for those with a trans linkage of the rings [8, 9]. In the spectra of the isomers (Ia) and (Ic) the intensities of the peaks of the ions $(M-C_2H_5)^+$ with mass 141, $(M-C_3H_7)^+$ with mass 127, and $(M-C_4H_9)^+$ with mass 113 are considerably smaller than in the mass spectra of the isomers (Ib) and (Id) (Fig. 2). Consequently, the trans linkage of the rings is probable for the isomers (Ia) and (Ic) and the cis linkage for (Ib) and (Id).

The orientation of the methyl group can be deduced from a consideration of the dependence of the probability of the cleavage of the cyclic system on the thermodynamic stability of the geometric isomers. Characteristic for systems with a more highly strained configuration is a relatively high intensity of the peaks formed by the cleavage of the bicyclic system [9] (as compared with similar but less strained configurations). Starting from the hypothesis that the sulfur atom does not apparently change the thermodynamic stability of the given bicyclic system, on the basis of the total relative intensity (in percentages of the total ion current) of the peaks of the ions with mass 141, 127, and 113 of the geometric isomers of 2-methyl-1-thiadecalin (Table 2), they can be ascribed the cis,trans; the cis,cis; the trans,trans; and the trans,cis configurations, respectively.

TABLE 1. Physicochemical Characteristics of the Geometric Isomers of 2-Methyl-1-thiadecalin

Configuration	Relative retention volumes*	n_D^{20}	Found, %†		
			C	H	S
cis,trans (Ia)	1,29	1,5089	70,5	11,2	18,3
trans,trans (Ic)	1,57	1,5181	70,7	10,5	18,5
cis,cis (Ib)	1,36	1,5180	70,8	10,9	18,4
trans,cis (Id)	1,69	1,5198	70,7	10,5	18,6

* Standard $C_{16}H_{14}$.

† $C_{10}H_{16}S$. Calculated, %: C 70.6; H 10.6; S 18.8.

TABLE 2. Spectral Characteristics of the Geometric Isomers of 2-Methyl-1-thiadecalin

Configuration	Positions of the methyl groups	Sum of the intensities of the ions of masses 113, 127, 141	PMR spectra	
			half-width of the signal of the ring protons, ppm	chemical shift of the protons of the methyl group, ppm*
cis,trans (Ia)	*e*	5,07	0,93±0,03	1,08
trans,trans (Ic)	*a*	5,79	0,72±0,03	1,38
cis,cis (Ib)	$a \rightleftarrows e$	9,45	0,25±0,03	1,12
trans,cis (Id)	$a \rightleftarrows e$	9,39	0,49±0,03	1,09

* Doublet (J = 7 ± 1 Hz).

In the PMR spectra of the methyl-substituted thiacyclanes, such as the 2-alkyl-4-methyl- and 2-alkyl-4,6-dimethyl-1,3-dithianes [12], and also in the spectrum of cis-4,6-dimethyl-1,3-thioxane [13], the signals of the protons of an axial methyl group are found in a weaker field than the signal of the protons of an equatorial methyl group. A similar difference in the chemical shifts of the protons of the methyl groups is observed for the 2-methyl-1-thiadecalins with the same type of ring linkage but with different orientations of the methyl groups. By comparing the chemical shifts of the methyl protons in the isomers (Ia) and (Ic) (Table 2) it may be concluded that in the isomer (Ia) the methyl group is equatorial and in (Ic) it is axial (Fig. 1), which is the case if (Ia) has the cis, trans configuration and (Ic) the trans, trans configuration.

Each geometric isomer with the cis linkage of the rings may exist in two conformations between which rapid inversion takes place. However, since the energetically more favorable conformation must be that with the equatorial position of the substituent, the shifts of the signals of the methyl groups of the cis isomers, both b and d, are close to the shift of the signal of the equatorial methyl group of the isomer a, and therefore a choice between the configurations of the isomers b and d cannot be made from the PMR spectra.

The investigation performed shows that in their properties the four geometric isomers of 2-methyl-1-thiadecalin are divided into two groups, inclusion in which is determined by the configuration of the ring linkage. Within each group is reflected the thermodynamic stability of the configuration, which is connected with the relative position of the methyl group. The assignments of the configurations made with the aid of different physicochemical methods agree completely.

EXPERIMENTAL

The mass spectra were obtained on an MKh-1303 mass spectrometer at energies of the ionizing electrons of 70 eV, an emission current of 1.5 mA, an accelerating voltage of 2 kV, and a temperature of the ionization chamber of 250°C and of the inlet system of 150°C. The PMR spectra were obtained on an experimental specimen of an NMR spectrometer with a working frequency of 60 MHz produced by VNIIA-CherMet [All-Union Scientific-Research Institute for the Automation of Ferrous Metallurgy].

2-Methyl-1-thiadecalin-4-one (modification of a previous method [1]). An autoclave was charged with 40 g (0.29 mole) of propenyl cyclohexenyl ketone, 6.5 g (0.097 mole) of anhydrous sodium acetate, 0.5 ml (0.005 mole) of piperidine, and 0.1 liter of ethanol, and then it was cooled with a mixture of acetone and carbon dioxide, and 40 ml (1.19 mole) of liquid hydrogen sulfide was added. The mixture was kept at 0°C for 12 h and was then worked up as before [1]. The yield of the oxo sulfide fraction was 85%.

The reduction of cis,trans-2-methyl-1-thiadecalin-4-one (mp 77.5°C) was performed as described previously [1], with the difference that diethylene glycol was used instead of triethylene glycol. The yield of cis,trans-2-methyl-1-thiadecalin was 83%, bp 94°C (8 mm).

Isolation of cis,cis-2-Methyl-1-thiadecalin (Ib) from the Mixture of Geometric Isomers. The separation of the mixture of geometric isomers was performed with the aid of adsorption column chromatography. The adsorbent was neutral alumina (70-200 mesh) of Brockmann activity grade II. On 230 g of the adsorbent was deposited 1.005 g of the mixture of isomers (solution in hexane). Hexane was used as the eluent. The total yield after chromatography was 95%. The fractions obtained were 0.317 g (33%) of cis,cis-2-methyl-1-thiadecalin, 0.527 g (56%) of a mixture of three of the isomers (without the cis,cis isomer), and 0.105 g (11%) of a mixture of the four isomers.

The separation of the mixture of cis,trans-, trans,trans-, and trans,cis-2-methyl-1-thiadecalins by preparative GLC was performed on a PAKhV-04 chromatograph made by SKB INKhS AN SSSR [Special Design Bureau of the Institute of Petrochemical Synthesis of the Academy of Sciences of the USSR] under the following conditions: column length 9 m, diameter 8 mm; INZ-600, 15% of poly(ethylene adipate); rate of flow of helium 135 ml/min; temperature 174.5°C. The experiment was performed on 12.36 g of the mixture of geometric isomers impoverished in the cis,cis isomer as described in the preceding experiment. The separation of 10.86 (89%) of the mixture gave the following individual isomers: 8.92 g (82%) of (Ia), 0.92 g (8.5%) of (Ib), 0.71 g (6.5%) of (Ic), and 0.31 g (2.9%) of (Id).

LITERATURE CITED

1. E. N. Karaulova, V. Sh. Shaikhrazieva, and G. D. Gal'pern, Khim. Geterotsikl. Soedin., 51 (1967).
2. E. N. Karaulova, G. D. Gal'pern, V. Sh. Shaikhrazieva, T. S. Bobruiskaya, and I. V. Cherepanova, in: Physical and Physicochemical Methods of Analyzing Organic Compounds [in Russian], Nauka, Moscow (1970), p. 76.
3. L. N. Stukanova, T. N. Shan'gina, and Al. A. Petrov, Neftekhimiya, 9, 196 (1969).
4. E. N. Karaulova, G. D. Gal'pern, and V. Sh. Shaikhrazieva, Neftekhimiya, 7, 812 (1967).
5. E. N. Karaulova, G. D. Gal'pern, V. D. Nikitina, I. V. Cherepanova, and L. R. Barykina, Neftekhimiya, 12, 104 (1972).
6. I. N. Nazarov, A. I. Kuznetsova, and I. A. Gurvich, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 118 (1948).
7. E. S. Brodskii, R. A. Khmel'nitskii, A. A. Polyakova, and G. D. Gal'pern, Izv. Akad. Nauk SSSR, Ser. Khim., 2188 (1969).
8. H. Budzikiewicz, C. Djerassi, and D. Williams, Interpretation of Mass Spectra of Organic Compounds, Holden-Day, San Francisco (1964).
9. I. M. Lukashenko, E. S. Brodskii, I. A. Musaev, É. Kh. Kurashova, V. G. Lebedevskaya, and P. I. Sanin, Neftekhimiya, 13, 163 (1973).
10. J. Emsley, J. Feeney, and L. Sutcliffe, High Resolution NMR Spectroscopy, Pergamon, Oxford (1965, 1966).
11. E. M. Banas, A. W. Weitkamp, and N. S. Bhacca, Anal. Chem., 38, 1783 (1966).
12. E. L. Eliel and R. O. Hutchins, J. Amer. Chem. Soc., 91, 2703 (1969).
13. J. Gelan and M. Antennis, Bull. Soc. Chim. Belges, 79, 313 (1970).