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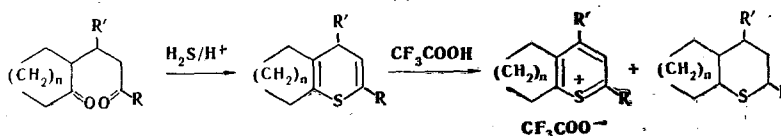
CONFIGURATION AND CONFORMATION OF 3,5-DIPHENYL-2-THIABICYCLO[4.4.0]DECANE

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The PMR spectra of 3,5-diphenyl-2-thiabicyclo[4.4.0]decane and its 4,6-dideutero derivative and S-oxide in the presence of Eu(dpm)_3 were studied. It was established that 3,5-diphenyl-2-thiabicyclo[4.4.0]decane has a cis,cis,cis configuration. The extremal spin-spin coupling constants (SSCC) constitute evidence for conformational rigidity of the investigated condensed system, which exists in the form of a puckered chair. The formation of the same cis,cis,cis isomer of 3,5-diphenyl-2-thiabicyclo[4.4.0]decane in the case of catalytic hydrogenation, disproportionation with trifluoroacetic acid, and ionic hydrogenation constitutes evidence for stereospecificity of the processes involving the reduction of the double bonds in 2,4-diphenyl-5,6-tetramethylene-6H-thiopyran.

Up until now, condensed thiacyclohexanes have been difficult to obtain. The catalytic hydrogenation of condensed thiopyrans [1], the reactions of 3-(2-oxocycloalkyl)-1-propanones with hydrogen sulfide and trifluoroacetic acid [2], and the disproportionation of 5,6-poly-methylenethiopyrans with trifluoroacetic acid [3] are relatively convenient methods for the synthesis of aryl- and diaryl-2-thiabicycloalkanes.



During a study of the reactions cited above, during which the double bonds in condensed thiopyrans are reduced, we directed our attention to the fact that, for example, the same 3,5-diphenyl-2-thiabicyclo[4.4.0]decane isomer (II), with mp 125-126.5°C, is formed in all cases from 2,4-diphenyl-5,6-tetramethylene-6H-thiopyran (I). The same isomer is also formed in the ionic reduction of 6H-thiopyran I with the trifluoroacetic acid-triethylsilane ion pair, which to a certain extent models reduction during disproportionation. The identical character of the saturated sulfides obtained from 6H-thiopyran I by three different methods, viz., by catalytic hydrogenation, by disproportionation of sulfide I with trifluoroacetic acid, and by ionic reduction (with triethylsilane-trifluoroacetic acid), was confirmed by their melting points and data from chromatography and the IR and PMR spectra. The formation of other isomers was not observed, and this constitutes evidence for the stereospecificity of the reduction of the double bonds in sulfide I in reactions that differ with respect to their nature.

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TABLE 1. Chemical Shifts and Spin-Spin Coupling Constants in the PMR Spectra of II-IV in CCl₄

Compound	δ , ppm					J , Hz		
	1-H	3-H	5-H	Ar	(CH ₂) _n	34	45	56
II	3,50 m	3,97 dd	2,90 dt	7,22	1,84 m	3,0, 12,0	12,0, 3,0	3,0
III	3,63 m	4,04 dt	2,91 m	7,22	1,83 m	3,0, 4,2		
IV	3,18	3,79 dd	3,31 dt	7,18, 7,35	1,68 m	3,0, 12,0	12,0, 3,0	3,0

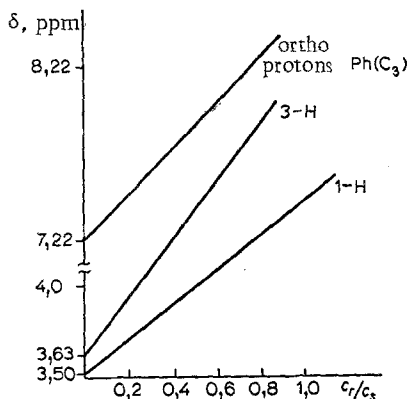
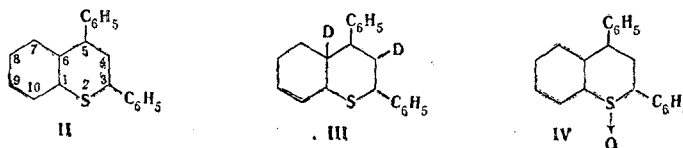


Fig. 1. Dependence of the chemical shifts of the protons of 3,5-diphenyl-2-thiabicyclo-[4.4.0]decane S-oxide (IV) in the presence of Eu(dpm) on the concentration ratio (c_T/c_S) at 80 MHz and room temperature with CCl₄ as the solvent.

All of the information stated above compelled us to investigate the structure of thiabicyclodecane II in order to ascertain which isomer is formed.

Little study has been devoted to the structure and conformational behavior of condensed thiacyclohexanes: isomeric 2-methyl-1-thiadecalins and their sulfoxides have been separated chromatographically and characterized [4, 5], the configuration and conformational equilibria of some substituted cis- and trans-1-thiadecalins have been investigated by ¹H and ¹³C NMR spectroscopy [6], the sulfonium salts of cis- and trans-2-thiadecalins have been subjected to conformational analysis [7], and the configuration of condensed thiacyclohexane S,S-dioxides has been established [8].

In the present research we investigated the PMR spectra of thiabicyclodecane II and its 4,6-dideutero derivative III and S-oxide IV, including the spectra in the presence of a paramagnetic shift reagent, which made it possible to establish the configuration and preferred conformation of sulfide II.



Data from the PMR spectra are presented in Table 1. The resonance signals were identified by total double resonance and integration of the spectra.

In the PMR spectrum of thiabicyclodecane II the double doublet at δ 3.97 ppm with SSCC 3.0 and 12.0 Hz should be assigned to the signal of the 3-H proton. The observed spin-spin coupling constants are characteristic for axial-equatorial and diaxial interactions of the vicinal protons in six-membered saturated cyclic compounds that exist primarily in the chair conformation. It is evident that the 3-H proton is axially oriented. The signal of the 1-H proton is observed at stronger field (3.57 ppm) and has the form of a broad singlet, which makes it impossible to draw any conclusion regarding its orientation.

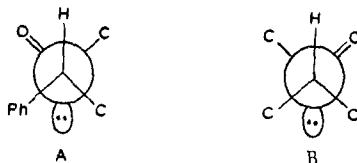
The double triplet at δ 2.90 ppm corresponds to the proton attached to C₅. The form of the signal (triplet $^3J_{ae} = 3.0$ Hz and doublet $^3J_{aa} \beta 12.0$ Hz) indicates that the 5-H proton is axially oriented, while the 6-H proton is equatorially oriented. An equatorial orientation of the angular 6-H proton is possible only in the case of cis fusion of the rings.

A comparison of the spectra of sulfides II and III provides evidence for a change in the forms of the signals of the 3-H and 5-H protons at δ 3.97 and 2.90 ppm, respectively.

The signal of the 3-H proton degenerates to a double triplet with ${}^3J_{HD} = 3.0$ Hz and ${}^3J_{3,4} = 4.2$ Hz, while the signal of the 5-H proton degenerates to a multiplet. Since splitting of the signals with SSCC 12.0 Hz is absent in the PMR spectrum of sulfide III, it should be assumed that the deuterium atom is axially oriented.

The relative orientation of the 1-H and 3-H protons cannot be established from the PMR spectra of II and III.

Shielding of the signals of the 1-H and 3-H protons (0.32 and 0.20 ppm, respectively) as compared with sulfide II is observed in the spectrum of sulfoxide IV (Table 1). This behavior of the signals of the 1-H and 3-H protons indicates their syn-axial orientation and is possible only in the case of an equatorial orientation of the S-O group, which is apparent from Newman projections along the C₃-S (A) and C₁-S (B) bonds:



The lower amount of shielding of the 3-H proton is apparently explained by the electronic effect of the phenyl group attached to C₃.

Thus it follows from an examination of the PMR spectra of II-IV that thiabicyclodecane II has a *cis,cis,cis* configuration.*

A study of the PMR spectrum of sulfoxide IV in the presence of the paramagnetic shift reagent Eu(dpm)₃ provides convincing evidence for the correctness of the configurational assignment made. Thus significant deshielding of the ortho protons of the phenyl group attached to C₃ is observed when Eu(dpm)₃, which coordinates with the oxygen atom of the sulfinyl group, is added, and this constitutes evidence for an equatorial orientation of the C₆H₅ and S-O groups. As a consequence of the latter, the signal of the 3-H proton is shifted to weak field by a greater factor (1.4) than the signal of the 1-H proton (Fig. 1). It is evident that the major magnetic axis of the resulting complex is shifted to favor an equatorial 3-phenyl group. In addition to the shift of the ortho protons of the phenyl substituent and the 1-H and 3-H protons, we noted a shift of the protons of the alicycle, and this hinders the assignment of the signals of the 4-H and 6-H protons.

The heteroring in sulfide II exists in the form of a puckered chair, as indicated by the R factor of 2.5 that we calculated. It is known [9] that R = 1.9-2.76 for six-membered heterocycles in the puckered chair form.

It is apparent from the PMR spectra that the J_{3,4}, J_{4,5}, and J_{5,6} spin-spin coupling constants of the protons of II and IV have extremal values, which indicates the absence of conformational transitions. The absence of conformational mobility for the *cis,cis,cis* isomer of sulfide II is evidently caused by destabilization of the other conformer due to 1,3-syn-axial interaction of the phenyl groups.

The formation of the *cis,cis,cis* isomer of sulfide II under the conditions of hydrogenation of 6H-thiopyran I on Pd/C can be explained by the known stereospecificity of this reaction. Thus, the hydrogenation of 2H-thiochromenes [10-13] and isothiochromenes [14] proceeds stereoselectively to give up to 85% amounts of products of *cis* addition of hydrogen to one double bond of the heteroring. The disproportionation and ionic hydrogenation of 6H-thiopyran I take place with the participation of carbonium ions formed as a result of protonation of the double bonds of the heteroring [15, 16] but still lead to *cis,cis,cis* isomer II. The production of the latter in reactions with such different natures as catalytic hydrogenation and disproportionation of 6H-thiopyran I evidently constitutes evidence that it is the most energetically favorable isomer because of the absence of an appreciable inter-

*The orientation of the hydrogen atom in the 3 position relative to the closest hydrogen atom bonded to the angular carbon atom is designated initially, after which the relative orientation of the α- and β-angular hydrogen atoms that characterized the type of ring fusion is designated, and, finally, the relative orientation of the β-angular hydrogen atom and the hydrogen atom attached to the C₅ atom is designated.

action between the substituents and the heteroatom. The construction of Dreiding models for all of the possible isomers confirms this assumption.

EXPERIMENTAL

The PMR spectra of solutions of sulfides II-IV in CCl_4 were recorded with a Tesla BS-487 spectrometer (80 MHz) at room temperature with hexamethyldisiloxane as the internal standard. In recording the PMR spectra of sulfoxide IV in CCl_4 we used $\text{Eu}(\text{dpm})_3$ in concentrations ranging from 0.01 to 0.05 mole/liter.

3,5-Diphenyl-2-thiabicyclo[4.4.0]decane (II). A) A 1-g sample of sulfide I was refluxed with 3 ml of trifluoroacetic acid for 5-10 h until the intermediate dihydrothiopyrans vanished, after which 10 ml of ether was added, the mixture was cooled, and 2 ml of 70% perchloric acid was added. Workup gave 2,4-diphenyl-5,6,7,8-tetrahydrothiochromylum perchlorate, with mp 183-184°C [15], in 59-62% yield. The ether extract was washed with water, dried with calcium chloride, and evaporated, and the residue was crystallized from alcohol to give 0.25 g (25%) of thiabicyclodecane II with mp 125-126.5°C (from ethanol). Found: C 81.0; H 8.0; S 10.2%. $\text{C}_{21}\text{H}_{24}\text{S}$. Calculated: C 81.8; H 7.8; S 10.4%.

B) A mixture of 1 g (0.003 mole) of sulfide I, 0.01 mole of triethylsilane, and 0.016 mole of anhydrous trifluoroacetic acid was refluxed for 5-8 h, after which it was extracted with ether. The extracts were washed with water, dried with calcium chloride, and evaporated to give 0.6 g (60%) of thiabicyclodecane II with mp 125-126.5°C (from ethanol).

C) Sulfide I was hydrogenated on Pd/C as described in [1]. Partial evaporation of the mother liquor gave sulfide II, with mp 125-126.5°C (from ethanol), in 70% yield.

4,6-Dideutero-3,5-diphenyl-2-thiabicyclo[4.4.0]decane (III). This compound, with mp 131-132°C (from ethanol), was obtained in 25% yield from sulfide I and deuterotrifluoroacetic acid (method A). IR spectrum: 2110, 2200 cm^{-1} (C-D). Found: C 81.2; H 8.5; S 10.2%. $\text{C}_{21}\text{H}_{21}\text{H}_{22}\text{D}_2\text{S}$. Calculated: C 81.3; H 8.4; S 10.3%.

3,5-Diphenyl-2-thiabicyclo[4.4.0]decane S-Oxide (IV). This compound was obtained as described in [2].

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