INTERCONVERSIONS, REACTIVITIES, AND STRUCTURES OF ISOMERIC HYDROTHIOCHROMENES

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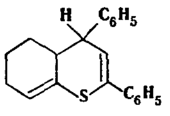
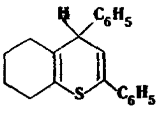
2,4-Diphenyl-5,6,7,9-tetrahydrothiochromene was isomerized to 2,4-diphenyl-5,6-tetramethylene-4H-thiopyran in the presence of HCl and DCl. The relative thermodynamic stabilities of 2,4-diphenyl-5,6-tetramethylene-6H-thiopyran and the compound thus obtained were studied. The reactivities of the isomers of all three compounds in oxidation, disproportionation, and alkylation reactions are discussed. The structures of 2,4-diphenyl-5,6,7,9-tetrahydrothiochromene and 2,4-diphenyl-5,6-tetramethylene-4H-thiopyran were established by x-ray diffraction analysis.

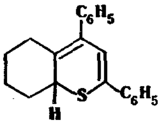
Isomeric sulfides I-III were obtained as described in [1-3]; 2,4-diphenyl-5,6-tetramethylene-4H- and -2H-thiopyran structures, respectively, were erroneously assigned to isomers I and II [1, 2].



I



II

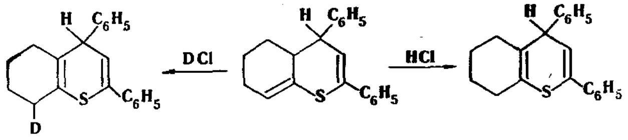


III

In the present paper we present some chemical transformations, spectral characteristics, and data from x-ray diffraction analysis for isomers I and II, on the basis of which we were able to establish their structures.

We have demonstrated [4] that in the reaction of 2,4-diphenyl-5,6,7,9-tetrahydrothiochromene (I) with perchloric acid it undergoes disproportionation to 2,4-diphenyl-5,6-tetramethylenethiopyrylium perchlorate and 3,5-diphenyl-2-thia-bicyclo[4.4.0]dec-$\Delta^{1,6}$-ene, whereas in the reaction with trifluoroacetic acid it undergoes disproportionation to 2,4-diphenyl-5,6-tetramethylenethiopyrylium trifluoroacetate and 3,5-diphenyl-2-thiabicyclo[4.4.0]decane. These results cannot be interpreted without taking into account migration of the "carbocyclic" double bond in the heteroring, i.e., isomerization of sulfide I to 4H-thiopyran II.

In order to confirm the possibility of the isomerization of sulfide I under the conditions mentioned above we studied its behavior with respect to HCL and DCl. We found that isomer I is converted easily and irreversibly to 4H-thiopyran II or 8D-2,4-diphenyl-5,6,7,8-tetrahydro-4H-thiochromene (IIa).



IIa I II

Sulfide IIa was characterized by the results of elementary analysis and data from the IR and PMR spectra. Absorption bands at 2110 and 2200 cm^{-1}, which correspond to the stretching vibrations of the C—D bond, are observed in the IR spectrum of sulfide IIa. The presence of deuterium in the alicycle is also confirmed by a comparison of the PMR spectra of sulfides II and IIa, the difference between which consists only in the signals of the alicyclic

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TABLE 1. Coordinates of the Atoms ($\times 10^4$) in Structure I

Atom	X	Y	Z	Atom	X	Y	Z
S	4862 (3)	1935 (3)	9 214 (2)	C12	1924 (10)	2576 (11)	8677 (6)
C2	4297 (10)	3605 (12)	8 770 (6)	C13	622 (11)	2435 (12)	8328 (7)
C3	5005 (10)	4893 (13)	8 769 (6)	C14	309 (10)	3155 (15)	7678 (6)
C4	6421 (10)	5153 (13)	9 165 (7)	C15	1297 (12)	4020 (14)	7382 (6)
C5	8503 (10)	4087 (13)	9 826 (6)	C16	2596 (12)	4201 (13)	7713 (6)
C6	9072 (12)	2675 (14)	10 247 (7)	C17	7201 (10)	6347 (12)	8785 (6)
C7	8130 (11)	2028 (14)	10 716 (6)	C18	7108 (10)	7848 (15)	9030 (5)
C8	6742 (11)	1822 (14)	10 329 (6)	C19	7810 (12)	9025 (13)	8679 (6)
C9	7165 (11)	3747 (13)	9 381 (6)	C20	8584 (11)	8646 (15)	8128 (7)
C10	6397 (9)	2540 (11)	9 712 (5)	C21	8686 (11)	7193 (16)	7892 (6)
C11	2880 (9)	3457 (11)	8 392 (6)	C22	7985 (11)	6088 (13)	8223 (6)

TABLE 2. Coordinates of the Atoms ($\times 10^4$)for the S Atom and $\times 10^4$ for the C Atoms) in Structure II

Atom	X	Y	Z	Atom	X	Y	Z
S	−1115 (9)	1464 (7)	16 049 (10)	C12	2098 (3)	401 (2)	4775 (4)
C2	488 (2)	29 (2)	3 170 (3)	C13	2897 (3)	839 (2)	5246 (4)
C3	2170 (3)	−340 (2)	3 814 (3)	C14	2938 (3)	1402 (2)	4632 (4)
C4	−5870 (2)	−856 (2)	3 377 (3)	C15	2194 (4)	1558 (2)	3571 (4)
C5	−2028 (3)	−1339 (2)	1 633 (4)	C16	1393 (3)	1145 (2)	3097 (4)
C6	−2766 (5)	−1213 (4)	328 (6)	C17	−191 (2)	−1558 (2)	3785 (3)
C7	−2284 (5)	−1652 (3)	−502 (6)	C18	−444 (3)	−1936 (2)	4571 (4)
C8	−1670 (3)	−451 (2)	78 (4)	C19	−70 (4)	22 576 (3)	4917 (2)
C9	−1197 (2)	−242 (2)	2 034 (3)	C20	5471 (4)	−2857 (2)	4446 (5)
C10	−1042 (3)	−456 (2)	1 256 (3)	C21	786 (4)	−2487 (2)	3690 (5)
C11	1335 (3)	598 (2)	3 694 (3)	C22	437 (3)	−1851 (2)	3359 (4)

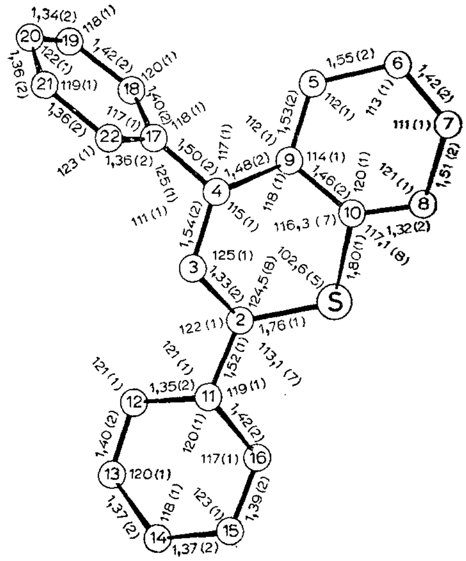


Fig. 1. Bond lengths and angles in structure I.

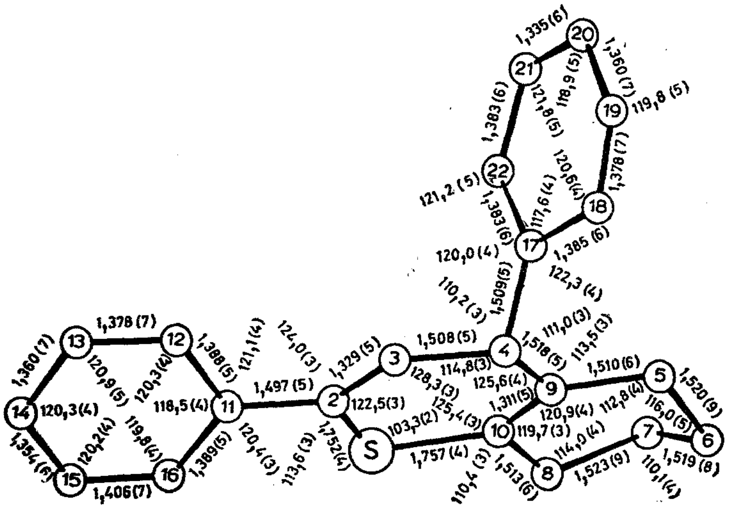
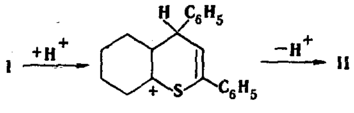


Fig. 2. Bond lengths and angles in structure II.

protons. The signals of the methylene protons in IIa are complicated significantly and are observed as a broad multiplet at δ 1.17-1.86 ppm.

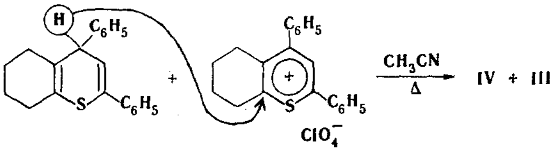
Protonation of the "carbocyclic" double bond with the formation of carbonium ion A and stabilization of the latter due to the ejection of a proton evidently occur in the isomerization of sulfide I.



A

Since sulfide I is obtained from 1,3-diphenyl-3-(2-oxocyclohexyl)-1-propane in the reaction with phosphorus pentasulfide in pyridine [1], it seemed of interest to ascertain the role of pyridine in its formation, which possibly proceeds through isomer II. However, sulfide II remains unchanged when it is refluxed in absolute pyridine in a stream of nitrogen.

We studied the relative thermodynamic stabilities of isomers I and II and 2,4-diphenyl-5,6-tetramethylene-6H-thiopyran (III); we used a known method [5, 6] to establish the relative stabilities of 4H- and 2H-(thio)pyrans. We carried out the reactions of isomers I-III with an equimolar amount of 2,4-diphenyl-5,7-tetramethylenethiopyrylium perchlorate (IV) by refluxing in acetonitrile. We found that under the conditions described 4H-thiopyran II undergoes conversion to give isomeric 6H-thiopyran III. The latter was isolated in quantitative yield. The isomerization of sulfide I is not observed.



II IV

The results obtained constitute evidence that 6H-thiopyran, being a conjugated system, is thermodynamically more stable than 4H-thiopyran II. In addition, the different degrees of interaction of the free electrons of the heteroatom with the multiple bonds should be reflected in the reactivities of isomers I-III. Thus it might be expected that the hydride ion in isomer III has greater lability. We have established that the disproportionation of 6H-thiopyran III with trifluoroacetic acid is complete in 1.5 h, as compared with 7.5 h in the case of isomers I and II. In the alkylation of isomers I-III with methyl iodide the corresponding sulfonium salts V-VII are obtained in 15, 10, and 0.5% yields, respectively, and this also makes it possible to form a judgment regarding the degree of participation of the free electrons of the heteroatom in conjugation.

Isomers I and II are readily oxidized to sulfones [1, 2]. 6H-Thiopyran III reacts with hydrogen peroxide to give, instead of the expected sulfone, an orange-red crystalline substance with mp 217-219°C, which is apparently a condensation product with an unknown structure.

The structures of sulfides I and II were established by x-ray diffraction analysis.

The crystals of 2,4-diphenyl-5,6,7,9-4H-thiochromene (I) are monoclinic with the following parameters: $a = 9.809(3)$, $b = 8.815(2)$, $c = 18.345(5)$ Å, $\beta = 93.55(2)°$, $V = 1583(4)$ Å^3, $M = 304.5$, $d_{calc} = 1.28$ g/cm^3, $z = 4$, and space group $P2_1/n$. The coordinates of the atoms of I are given in Table 1, and the bond lengths and angles are shown in Fig. 1

The crystals of 2,4-diphenyl-5,6-tetramethylene-4H-thiopyran (II) are monoclinic with the following parameters: $a = 15.165(1)$, $b = 19.692(1)$, $c = 12.199(1)$ Å, $\beta = 114.06(1)°$, $V = 3327(1)$ Å^3, $M = 304.5$, $d_{calc} = 1.22$ g/cm^3, $z = 8$, and space group $P2_1/c$; there are two independent molecules in the cell, but data for one of them are presented in the paper. The coordinates of the atoms of II are given in Table 2, while the bond lengths and angles are shown in Fig. 2.*

The geometrical parameters of the I and II molecules obtained in the present research are in agreement with the information regarding the geometry found in the 2,6-dimethyl-4-(3-cyanocyclopentadienylidene)-4H-thiopyran [7] and p-bromobenzyl 2H-thiopyrancarboxylate [8] structures. The lengths of the C—C bonds of various types are in agreement with the corresponding standard values [9].

The thiacyclohexane ring in structure I has a distorted half-chair conformation, while the 4H-thiopyran ring in the II molecule is virtually planar. The cyclohexane ring in I has

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*The numbering of the atoms used here differs from the generally accepted chemical numbering.

a boat structure, whereas it has a half-chair conformation in structure II.

The phenyl rings attached to the C_2 and C_4 atoms in the I molecule form dihedral angles of 35.0 and 82.1°, respectively, with the middle of the plane of the heteroring. The phenyl substituent attached to the C_4 atom in the II structure is oriented pseudocoaxially and forms a dihedral angle of 87.4° with the middle of the plane of the heteroring, while the phenyl ring attached to the C1 atom forms an angle of 22.4° with the middle of the plane of the heteroring, and this makes it possible to assume a certain amount of conjugation between the phenyl ring and the double bond.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The PMR spectrum of a solution of sulfide IIa in CCl_4 was obtained with a Tesla spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

The x-ray diffraction investigation of I and II was carried out with a Hilger-Watts four-circle automatic diffractometer guided by an PDP 8/1 minicomputer (λCu K_α, graphite monochromator, $\theta/2\theta$ scanning, $1° \leqslant \theta \leqslant 57°$). In the calculation for structure I we used 904 independent reflections with $1 > 2\sigma$, whereas we used 3427 independent reflections with $1 > 2\sigma$ for the II molecule. Structures I and II were elucidated by a direct method by means of the MULTAN program and were refined by the method of least square within a block-diagonal anisotropic approximation up to R = 0.095 for I and R = 0.057 for II.

Isomerization of 2,4-Diphenyl-5,6,7,9-tetrahydrothiochromene (I) to 2,4-Diphenyl-5,6-tetramethylene-4H-thiopyran (II). A solution of 0.2 g of sulfide I, obtained as described in [1], in 20 ml of ether was saturated with hydrogen chloride for 30 min. Ethanol (2 ml) was then added to the solution, and 0.13 g (65%) of sulfide II, with mp 89-91.5°C (from ethanol—ether), was isolated. No melting-point depression was observed for a mixture of this product with a genuine sample of II.

8D-2,4-Diphenyl-5,6,7,8-tetrahydro-4H-thiochromene (IIa). This compound was similarly obtained. The reaction of 0.2 g of sulfide I with DCl gave 0.156 g (78%) of IIa with mp 78-79°C (ethanol). Found: C 82.1; H 6.2; S 10.3%. $C_{21}H_{19}DS$. Calculated: C 82.6; H 6.3; S 10.5%.

S-Methyl-2,4-diphenyl-5,6,7,9-tetrahydro-4H-thiochromenium Nitrate (V). A 1-g sample of sulfide I was added to 20 ml of freshly distilled methyl iodide, after which 0.67 g of silver nitrate was added with vigorous stirring, and the mixture was allowed to stand for 24 h. The precipitate was removed by filtration and washed with hot methylene chloride. The filtrate and methylene chloride solutions were combined and evaporated in vacuo. Diethyl ether was added to the residue to give 0.18 g (15%) of S-methyl-2,4-diphenyl-5,6,7,9-tetrahydro-4H-thiochromenium nitrate with mp 160-161.5°C (CH_2Cl_2-ether). Found: C 69.2; H 6.0; N 3.6%. $C_{22}H_{23}O_3NS$. Calculated: C 69.3; H 6.1; N 3.7%.

S-methylsulfonium salts were similarly obtained from isomers II and III.

S-Methyl-2,4-diphenyl-5,6-tetramethylene-4H-thiopyranium Nitrate (VI). This compound, with mp 142-143°C (petroleum ether—diethyl ether), was obtained in a yield of 0.12 g (10%). Found: C 69.1; H 6.0; N 3.4%. $C_{22}H_{23}O_3NS$. Calculated: C 69.3; H 6.1; N 3.7%.

S-Methyl-2,4-diphenyl-5,6-tetramethylene-6H-thiopyranium Nitrate (VII). This compound, with mp 172-173°C (petroleum ether), was obtained in a yield of 0.06 g (0.5%). Found: C 69.3 ; H 5.9; N 3.6%. $C_{22}H_{23}O_3NS$. Calculated: C 69.3; H 6.1; N 3.7%.

Isomerization of 2,4-Diphenyl-5,6-tetramethylene-4H-thiopyran (II) to 2,4-Diphenyl-5,6-tetramethylene-6H-thiopyran (III). A mixture of 9 mmole of 4H-thiopyran II and 9 mmole of 2,4-diphenyl-5,6-tetramethylenethiopyrylium perchlorate (IV) was refluxed in 25 ml of acetonitrile for 8 h, after which it was diluted with ether to give starting perchlorate IV, which was identified by means of a mixed-melting-point determination with a genuine sample. The ether solution was evaporated, 5 ml of ethanol was added to the residue, and III, with mp 79-81°C [3], was isolated in 90% yield.

When an equimolar mixture of 2,4-diphenyl-5,6,7,9-tetrahydrothiochromene (I) and perchlorate IV was refluxed in acetonitrile, sulfide I was recovered unchanged.

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

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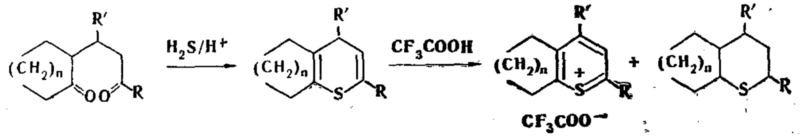
The PMR spectra of 3,5-diphenyl-2-thiabicyclo[4.4.0]decane and its 4,6-dideutero derivative and S-oxide in the presence of $Eu(dpm)_3$ were studied. It was established that 3,5-diphenyl-2-thiabicyclo[4.4.0]decane has a cis,cis,cis configuration. The extremal spin-spin coupling constants (SSCC) constitute 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-polymethylenethiopyrans 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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