FORMATION OF 3,5-DIPHENYL-2-THIABICYCLO[4.4.0]DEC- $\Delta^{1,6}$ -ENE UNDER THE CONDITIONS OF THE PUMMERER REACTION AND ITS STRUCTURE

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The Pummerer rearrangement was investigated in the case of 3,5-diphenyl-2-thiabicyclo[4.4.0]decane S-oxide. It is shown that, of the two possible isomers, this compound forms only 3,5-diphenyl-2-thiabicyclo[4.4.0]dec- $\Delta^{1,6}$ -ene under the conditions of the Pummerer reaction; a secondary transformation, viz., disproportionation of the latter to 3,5-diphenyl-2-thiabicyclo[4.4.0]decane and 2,4-diphenyl-5,6-tetramethylenethiopyrylium acetate, is observed. 3,5-Diphenyl-2-thiabicyclo[4.-4.0]dec- $\Delta^{1,6}$ -ene was subjected to an x-ray diffraction study; it was proved unambiguously that the $C_1=C_6$ double bond has a length of 1.335 Å and that the dihydrothiopyran and cyclohexene rings have a distorted half-chair conformation: the dihedral angles between the phenyl rings and the planar fragment of the heteroring are 76.8 and 93.2°C.

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We have investigated the Pummerer rearrangement in the case of 3,5-diphenyl-2-thiabicyclo[4.4.0]decane S-oxide (I). In accordance with the generally accepted mechanisms of this reaction, one should expect the formation of isomeric 2-thiabicyclo[4.4.0]decenes II and III:



A mixture of two sulfides in a ratio of 10:1 is formed when S-oxide I is refluxed in acetic anhydride. The principal product displays an absorption band of an isolated double bond in its IR spectrum at 1620 cm⁻¹. However, the signal of a vinyl proton is absent in its PMR spectrum. The compound obtained was found to be 3,5-diphenyl-2-thiabicyclo[4.4.0]dec- $\Delta^{1,6}$ -ene (II). The second sulfide is 3,5-diphenyl-2-thiabicyclo[4.4.0]decane (IV), which is confirmed by data from IR and PMR spectroscopy and a mixed-melting point determination with a genuine sample [1].

The formation of saturated sulfide IV might have been explained by disproportionation of S-oxide I to sulfide IV and the corresponding sulfone. Thus, it is known [2] that alicyclic S-oxides can undergo this type of disproportionation. However, 3,5-diphenyl-2-thiabicyclo[4.4.0]decane S,S-dioxide was not detected in the reaction mixture. Another possible reason for the development of saturated sulfide IV under the reaction conditions may be disproportionation of sulfide II itself in an acidic medium. In fact, the formation of 3,5-diphenyl-2-thiabicyclo[4.4.0]decane (IV) and 2,4-diphenyl-5,6-tetramethylenethiopyrylium ace-

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Fig. 1. Bond lengths and angles in the II molecule,

tate (V), which was identified through perchlorate VI [1], is observed when 2-thiabicyclodecene II is refluxed in acetic anhydride—acetic acid (20:1).



Thus, of the two possible isomers II and III, S-oxide I forms only 3,5-diphenyl-2-thiabicyclo[4,4.0]dec- $\Delta^{1,6}$ -ene (II) under the conditions of the Pummerer reaction; a secondary transformation, viz., disproportionation of the latter to sulfide IV and salt V, is observed.

In view of the fact that the S-oxides of cis,trans- and trans,trans-3-methyl-2-thiabicyclo[4.4.0]decane form only 3-methyl-2-thiabicyclo[4.4.0]dec-3-ene, the solution of the problem of the position of the double bond in II seemed of particular interest. With this end in mind, we made an x-ray diffraction study of 3,5-diphenyl-2-thiabicyclo[4.4.0]dec- $\Delta^{1,6}$ -ene (II).

The crystals of II are monoclinic with $\alpha = 11.073(2)$, b = 8.476(1), c = 9.4498(2) Å, $\gamma = 108.22^{\circ}$, V = 842.4 Å³, M = 306.5, d_{calc} = 1.21 g/cm³, Z = 2, and space group P2₁. The coordinates of the atoms are given in Table 1, while the stereochemistry of the molecule with the bond lengths and bond angles is shown in Fig. 1.

The geometry of dihydrothiopyran ring A is close to that found in p-bromobenzyl 2H-thiopyrancarboxylate [4] and thioxanthenes [5, 6]. It was proved unambiguously that the $C_1=C_6$ double bond has a length of 1.335(9) Å, which coincides with the standard value. As regards the lengths of the ring single bonds of 1.502(8)-1.551(8) Å, within the limits of 3 σ they coincide with the value of 1.521 Å in cyclohexane [7]. The geometries of cyclohexene ring B and phenyl rings C and D are unusual. The A and B rings have a markedly distorted half-chair conformation. The exocyclic bonds have the following orientation: axial with H₄ and H₅, equatorial with C₁₁ and H₄, and pseudoequatorial with C₇. The dihedral angles between the C and D phenyl rings and the planar fragment of the heteroring are 76.8 and 93.2°, respectively.

The results make it possible not only to establish the structure of sulfide II but also to precisely determine the position of the double bond in 3,5-diary1-2-thiabicycloalkenes that are formed in the reactions of 1,3-diary1-3-(2-oxocycloalky1)-1-propanones with hydrogen sulfide and protic acids and previously described [1] as 3,5-diary1-2-thiabicyclo[4.4.0]dec-5-enes. No melting-point depression was observed for a mixture of the latter with sulfide II.

Atom	x	y	z	Atom	x	y	z
$\begin{array}{c} S\\ C_{(1)}\\ C_{(3)}\\ C_{(5)}\\ C_{(6)}\\ C_{(7)}\\ C_{(8)}\\ C_{(9)}\\ C_{(10)}\\ C_{(11)}\\ C_{(12)}\\ C_{(13)}\\ C_{(14)}\\ C_{(15)}\\ C_{(17)}\\ C_{(18)}\\ C_{(17)}\\ C_{(18)}\\ C_{(19)}\\ C_{(22)}\\ C_{(22)}\\ \end{array}$	$\begin{array}{c} 1931 \ (1) \\ 454 \ (5) \\ 1604 \ (5) \\ 319 \ (5) \\ -809 \ (5) \\ -634 \ (5) \\ -1804 \ (6) \\ -1573 \ (7) \\ -707 \ (7) \\ 578 \ (6) \\ 2699 \ (5) \\ 3672 \ (7) \\ 4677 \ (8) \\ 3726 \ (7) \\ 2745 \ (6) \\ -2015 \ (6) \\ -2994 \ (6) \\ -4075 \ (7) \\ -4214 \ (7) \\ -3252 \ (8) \\ -2172 \ (6) \end{array}$	$\begin{array}{c} 349 \ (2) \\ -1242 \ (6) \\ 1981 \ (7) \\ 2135 \ (6) \\ 581 \ (7) \\ -1038 \ (6) \\ -2532 \ (7) \\ -4207 \ (8) \\ -4185 \ (7) \\ -2894 \ (7) \\ 3582 \ (7) \\ 4035 \ (9) \\ 5487 \ (10) \\ 6516 \ (9) \\ 6084 \ (9) \\ 4602 \ (8) \\ 814 \ (7) \\ 904 \ (8) \\ 1177 \ (10) \\ 1349 \ (10) \\ 1256 \ (9) \\ 991 \ (8) \end{array}$	$\begin{array}{c} 2500 \ (0)\\ 2382 \ (8)\\ 1469 \ (7)\\ 1908 \ (7)\\ 1512 \ (7)\\ 1948 \ (6)\\ 1749 \ (8)\\ 1852 \ (9)\\ 3082 \ (8)\\ 2816 \ (8)\\ 2816 \ (8)\\ 1692 \ (7)\\ 706 \ (9)\\ 881 \ (11)\\ 2003 \ (12)\\ 2967 \ (10)\\ 2806 \ (8)\\ 2109 \ (6)\\ 1220 \ (8)\\ 1748 \ (10)\\ 3180 \ (11)\\ 4079 \ (8)\\ 3562 \ (7)\\ \end{array}$	$\begin{array}{c} H_{(3)} \\ H_{(4)} \\ H_{(4')} \\ H_{(5)} \\ H_{(7')} \\ H_{(7')} \\ H_{(8')} \\ H_{(9)} \\ H_{(9)} \\ H_{(10)} \\ H_{(10)} \\ H_{(10)} \\ H_{(10)} \\ H_{(13)} \\ H_{(13)} \\ H_{(13)} \\ H_{(15)} \\ H_{(16)} \\ H_{(16)} \\ H_{(18)} \\ H_{(19)} \\ H_{(22)} \\ \end{array}$	$\begin{array}{c} 1533\\ 306\\ -847\\ -2152\\ -2439\\ -1167\\ -2397\\ -556\\ -1071\\ 1045\\ 1110\\ 3666\\ 5386\\ 5341\\ 3726\\ 2044\\ -2924\\ -4754\\ -4988\\ -3344\\ -1492\end{array}$	$\begin{array}{c} 1680\\ 2324\\ 3118\\ 476\\ -2424\\ -2461\\ -4442\\ -5104\\ -3930\\ -3276\\ -2705\\ 3253\\ 5838\\ 7574\\ 6813\\ 4273\\ 764\\ 1298\\ 1536\\ 1373\\ 918 \end{array}$	$\begin{array}{r} 458\\ 2934\\ 1380\\ 444\\ 779\\ 2476\\ 965\\ 2010\\ 3190\\ 3980\\ 2054\\ 3710\\ -150\\ 123\\ 2098\\ 3836\\ 3565\\ 165\\ 1065\\ 3601\\ 5153\\ 4262\end{array}$

TABLE 1. Coordinates of the Atoms and Calculated Coordinates of the Hydrogen Atoms* $(\times 10^4)$.

*The numbers of the H atoms coincide with the numbers of the corresponding nonhydrogen atoms (with an apostrophe for the second hydrogen atom of the CH₂ group),

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Chromatography on Silufol UV-254 plates in hexane-ether (25:1) (for II and IV) and chloroform-hexane-acetone (5:1:1) (for I and the sulfone of IV) was used to evaluate the trend of the reaction and the individuality of the substances. The cell parameters and the intensities of 956 independent reflections with I > 20 were measured with a Hilger-Watts automatic four-circle diffractometer guided by a PDP 8/1 minicomputer (with λ Cu K_{α}, a graphite monochromator, and $\theta/2\theta$ scanning with $1^{\circ} \leq \theta \leq 57^{\circ}$). The structure was decoded by the heavy-atom method and was refined by the method of least squares within the total-matrix anisotropic approximation; corrections for anomalous scattering were taken into account for the S atom. All of the hydrogen atoms were uncovered by differential synthesis and were disregarded in the calculation of F_{calc} , the position and heat parameters of the H atoms were disregarded (it was assumed that $B_{iso} = 5$ Å²), and the final R value was 0.0526 ($R_W = 0.0630$). For the inverted structure with the same temperature factors, $R_{inv} = 0.0528$. Thus, in accordance with

the Hamilton test [8], the coordinates in the table correspond to the absolute structure and the absolute configuration of the molecule (in the specifically investigated individual crystal) with a probability of 98%. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of 5-10% solutions of the compounds in CCl₄ were obtained with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane as the standard.

3,5-Diphenyl-2-thiabicyclo[4,4.0]dec- $\Delta^{1,6}$ -ene (II). A 1-g sample of 3,5-diphenyl-2-thiabicyclo[4.4.0]decane 2-oxide [9] was refluxed in 10 ml of freshly distilled acetic anhydride for 30 min, after which the mixture was neutralized with sodium bicarbonate, and the precipitate was removed by filtration and recrystallized from acetone. The crystalline product, which consisted of needles and prisms, was separated mechanically, and each fraction was again recrystallized from alcohol-acetone (2:1) to give 0.35 g (37.2%) of sulfide II and 0.03 g (32%) of sulfide IV. Compounds II and IV were identified by means of their IR and PMR spectra and by mixed-melting-point determinations with genuine samples [1].

Disproportionation of 3,5-Diphenyl-2-thiabicyclo[4.4.0]dec- $\Delta^{1,6}$ -ene (II). A 0.1-g sample of sulfide II was refluxed in 3 ml of acetic anhydride-acetic acid (20:1) for 3 h after which sulfide IV was extracted with ether. The ether extracts were washed with water, dried with MgSO₄, and evaporated to give 0.05 g (50%) of 2-thiabicyclodecane IV, which was identified by means of the PMR spectrum and a mixed-melting-point determination with a genuine sample. A 0.2-ml sample of 70% HClO₄ was added to the acetic acid solution, 5 ml of water was added, and the precipitate was removed by filtration to give 0.03 g (25%) of perchlorate VI [1].

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STRUCTURAL INVESTIGATIONS OF ISOMERIC 2,4-DIPHENYL-7,8-BENZOHEXAHYDROTHIOCHROMENES

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Structural investigations were carried out by means of PMR spectroscopy and x-ray diffraction analysis, and the type of fusion of the heterorings and alicyclic rings in isomeric 2,4-diphenyl-7,8-benzohexahydrothiochromenes previously obtained by the disproportionation and ionic and catalytic hydrogenation of 2,4-diphenyl-7,8-benzo-5,6-dihydrothiochromene was established. The predominant realization of a diastereomer with trans-fused heterorings and alicyclic rings in all of the reactions mentioned above was demonstrated; the possibility of the formation of the cis isomer in the catalytic reduction of benzodihydrothiochromene was confirmed.

This communication is devoted to a study of the stereochemical peculiarities of isomeric 2,4-diphenyl-7,8-benzohexahydrothiochromenes. We observed different diastereomeric forms of the latter during a study of the chemical behavior of 2,4-diphenyl-7,8-benzo-5,6-dihydrothio-chromene (I) [1]. Under acid-catalysis conditions ($CH_3COOH/HClO_4$, CF_3COOH) benzohydrothio-chromene I. underwent disproportionation to give benzohexahydrothiochromene isomer IVa in addition to salts II and III and benzohydrothiochroman V. Sulfide IVa was synthesized in quantitative yield by ionic hydrogenation of benzohydrothiochromene I via a reaction modeling disproportionation. In the catalytic reduction of I, in addition to IVa, we isolated a second benzohexahydrothiochromene isomer, viz., IVb. The mixture consisted of 71.3 and 28.6% sulfides IVa and IVb, respectively. (See scheme, top, following page.)

Taking into account the fact that ionic hydrogenation is a reaction of the type that involves electrophilic trans addition to double bonds, we expressed the view that trans fusion of the heteroring and alicyclic ring of benzohexahydrothiochromene (IVa), which is observed primarily in all of the reactions mentioned above, is the most likely and favorable configuration for it [1]. The complex form of the signals of the 2-H and 10-H protons in the PMR spectrum of sulfide IVa at 4.14 ppm did not make it possible to obtain accurate values of the chemical shifts and the spin-spin coupling constants (SSCC). This assumption found confirmation in the results of x-ray diffraction analysis of the corresponding sulfore VI, which was obtained by oxidation of sulfide IVa with 30% hydrogen peroxide in acetic acid. The crystals of VI are monoclinic with a = 12.192(1), b = 9.2092(3), c = 18.310(2) Å, $\beta = 90.29(1)^{\circ}$, V =2055.7(5) Å³, M = 388.7, $d_{calc} = 1.26$ g/cm³, z = 4, and symmetry space group P2₁/c.

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