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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-dihydrothiochromene (I) [1]. Under acid-catalysis conditions ($CH_3COOH/HClO_4$, CF_3COOH) benzohydrothiochromene 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 sulfone 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, β = 90.29(1)°, V = 2055.7(5) $Å^3$, M = 388.7, d_{calc} = 1.26 g/cm^3, z = 4, and symmetry space group $P2_1/c$.

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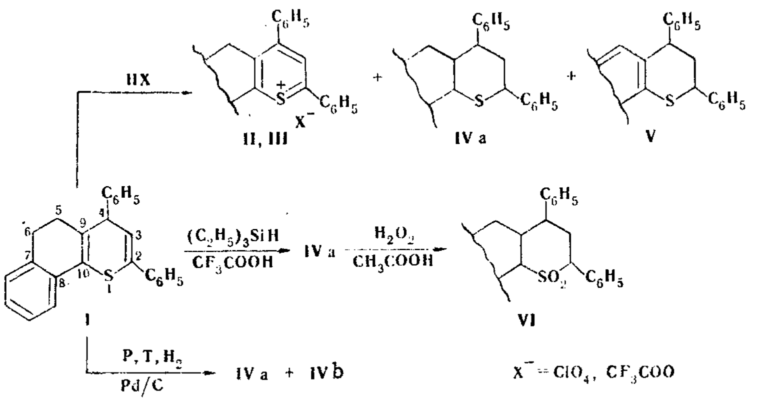

IVa,b — benzohexahydrothiochromene isomers

The coordinates of the atoms of sulfone VI are given in Table 1, the bond lengths and angles are presented in Fig. 1, and the stereochemistry of the molecule along with the torsion angles is shown in Fig. 2.

A comparison of the structure of VI and the structure of the known tetrahydrothiopyrone sulfone [2] shows that the lengths of the S—C bonds and the endocyclic CSC angle in these molecules coincide within the limits of 3σ. The lengths of the S—O bonds [1.411(4) and 1.440(4) Å] in VI (Fig. 1) coincide with those in thioxanthene sulfone [3]. The OSO angle in all of the previously investigated sulfones range from 115.4 to 119.1°, and the angle found for the sulfone VI molecule [116.5(2)°] is found within the same limits. The lengths of the C—C bonds of various types coincide with the corresponding standard values [4].

Tetrahydrothiopyran ring A has a chair conformation that is appreciably distorted because of fusion with the adjacent ring and the presence of an S atom with a smaller (than in the case of the carbon atom) bond atom. The orientation of the phenyl substituents is equatorial.

TABLE 1. Coordinates of the Atoms (•10^4)* of Sulfone VI

Atom	x	y	z	Atom	x	y	z
S	6806 (1)	380 (1)	8 122 (1)	$H_{(1)}$	7255	2493	8 794
$O_{(1)}$	7883 (3)	−137 (4)	8 015 (2)	$H_{(2)}$	7040	2273	7 300
$O_{(2)}$	5968 (3)	−702 (4)	8 227 (2)	$H_{(3)}$	4801	1630	7 540
$C_{(1)}$	6732 (4)	1667 (5)	8 865 (3)	$H_{(3')}$	5272	2997	7 067
$C_{(2)}$	6452 (4)	1524 (5)	7 357 (2)	$H_{(4)}$	6063	3967	8 195
$C_{(3)}$	5416 (4)	2348 (5)	7 496 (3)	$H_{(5)}$	5007	1598	8 839
$C_{(4)}$	5422 (4)	3291 (5)	8 185 (3)	$H_{(6)}$	4716	3683	9 589
$C_{(5)}$	5589 (4)	2357 (5)	8 867 (3)	$H_{(6')}$	6042	3890	9 661
$C_{(6)}$	5441 (5)	3165 (6)	9 596 (3)	$H_{(7)}$	4812	1426	10 168
$C_{(7)}$	5466 (5)	2078 (7)	10 215 (3)	$H_{(7')}$	5425	2621	10 688
$C_{(8)}$	6477 (5)	1171 (6)	10 214 (3)	$H_{(9)}$	6430	710	11 325
$C_{(9)}$	6868 (7)	555 (7)	10 869 (3)	$H_{(10)}$	8011	−661	11 385
$C_{(10)}$	7815 (7)	−190 (8)	10 912 (4)	$H_{(11)}$	9244	−829	10 324
$C_{(11)}$	8504 (6)	−350 (7)	10 292 (4)	$H_{(12)}$	8517	76	9 168
$C_{(12)}$	8088 (5)	228 (7)	9 626 (3)	$H_{(15)}$	7638	2030	6 169
$C_{(13)}$	7129 (4)	984 (6)	9 588 (3)	$H_{(16)}$	7586	876	5 003
$C_{(14)}$	6447 (4)	684 (6)	6 650 (3)	$H_{(17)}$	6317	−1097	4 790
$C_{(15)}$	7120 (5)	1189 (6)	6 076 (3)	$H_{(18)}$	5195	−1954	5 757
$C_{(16)}$	7095 (7)	535 (9)	5 405 (3)	$H_{(19)}$	5334	−854	6 943
$C_{(17)}$	6362 (6)	−633 (10)	5 286 (3)	$H_{(21)}$	5243	6042	7 787
$C_{(18)}$	5713 (6)	−1121 (8)	5 844 (4)	$H_{(22)}$	3716	7586	7 706
$C_{(19)}$	5782 (5)	−462 (7)	6 531 (3)	$H_{(23)}$	1935	6726	8 067
$C_{(20)}$	4428 (4)	4238 (6)	8 185 (3)	$H_{(24)}$	1744	4274	8 493
$C_{(21)}$	4505 (5)	5662 (6)	7 933 (3)	$H_{(25)}$	3356	2711	8 574
$C_{(22)}$	3628 (6)	6550 (7)	7 889 (4)				
$C_{(23)}$	2587 (6)	6067 (10)	8 096 (4)				
$C_{(24)}$	2481 (4)	4665 (11)	8 344 (4)				
$C_{(25)}$	3419 (5)	3735 (8)	8 391 (4)				

*The number of the H atoms coincides with the numbering of the corresponding carbon atoms; the second atoms of the CH_2 group are given with apostrophes.

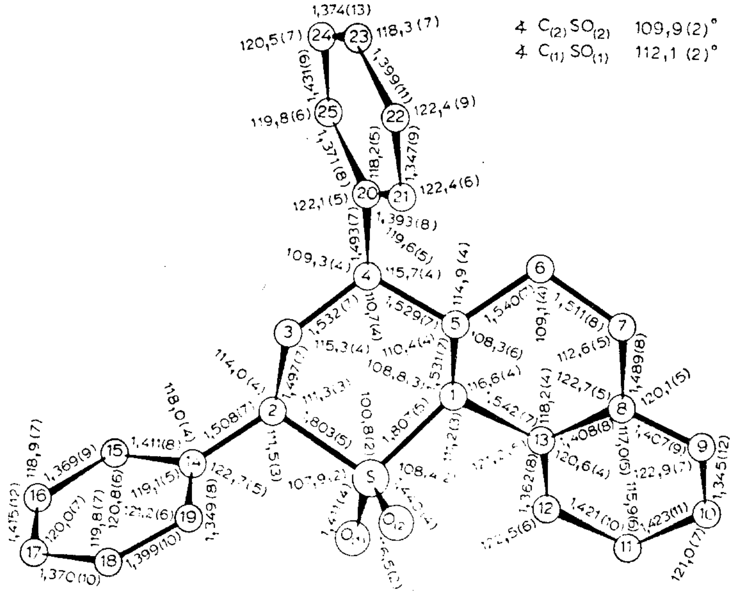

Fig. 1. Geometry of the VI molecule: bond lengths and angles.

According to the torsion angles (Fig. 2), cyclohexene ring B has a distorted half-chair conformation. The A and B rings have trans fusion. Benzene rings C, D, and E are planar.

It is known that products involving cis addition of hydrogen to the double bonds are more often observed in the case of catalytic hydrogenization, and one might therefore expect the formation of isomer IVb with cis fusion of the heteroring and alicyclic ring with a high probability in the reduction of benzodihydrothiochromene I. In fact, the following facts constitute evidence in favor of this. Absorption bands of C=C bonds at 1590-1640 cm^{-1} are absent in the IR spectrum of sulfide IVb, and signals of vinyl protons at 5.50-6.05 ppm are absent in the PMR spectrum, thereby attesting to the saturated nature of the heteroring. With respect to their position and form, the three one-proton signals in the middle of the PMR spectrum of benzohexahydrothiochromene IVb, viz., a doubled doublet at 4.03 ppm with SSCC 3.5 and 11 Hz, a singlet at 4.45 ppm, and a doubled triplet at 3.10 ppm with SSCC 3.5 and 11 Hz, were assigned to the 2-H, 10-H, and 4-H protons, respectively. An analysis of the SSCC of the protons indicated above (2-H and 4-H) demonstrated that they do not depend on the polarity of the solvent [CCl_4 and $(CD_3)_2CO$] and that they take on extremal values; this evidently indicates the absence of conformational transitions in the benzohexahydrothiochromene IVb molecule. Proceeding from general theoretical premises, it may be assumed that the heteroring in the indicated system has a puckered chair form [5]. The splitting of the 2 H proton in the spectrum of IVb is probably due to diaxial and axial-equatorial interaction with the methylene protons attached to C_3 and provides a basis for the assumption that the aryl substituent attached to C_2 is pseudoequatorially oriented. The phenyl group attached to C_4 is also similarly oriented, which follows from the SSCC of the 4-H and 3a-H protons ($^3J_{aa}$ = 11 Hz), which is characteristic for a diaxial interaction. However, the splitting of the signal into a triplet ($^3J_{ae}$ = 3.5 Hz) makes it possible to assert that the 9-H proton is pseudoequatorial, a consequence of which is cis fusion of the heteroring and alicyclic ring of IVb. The singlet form of the 10-H signal serves as an additional confirmation. The construction of Dreiding models shows that the dihedral angle between the 9-H and 10-H protons is close to 80°C and, in conformity with the correlation in [6] of the $^3J_{9,10}$ constant, should be less than 1 Hz.

Thus, the PMR spectroscopic data confirm our assumption [1] of cis addition of a hydrogen atom to the double bonds of the heteroring in 2,4-diphenyl-7,8-benzo-5,6-dihydrothiochromene (I) during its catalytic hydrogenation on Pd/C.

EXPERIMENTAL

The synthesis of I-VI was described in [1]. Isomers IVa, b, which were obtained as a mixture in the catalytic hydrogenation of I, were isolated in different forms — needles of IVa and polygons of IVb (mp 155-157 and 119-121°C, respectively) — in the case of recrystallization from alcohol. Analysis by gas-liquid chromatography was carried out with an LKhM-

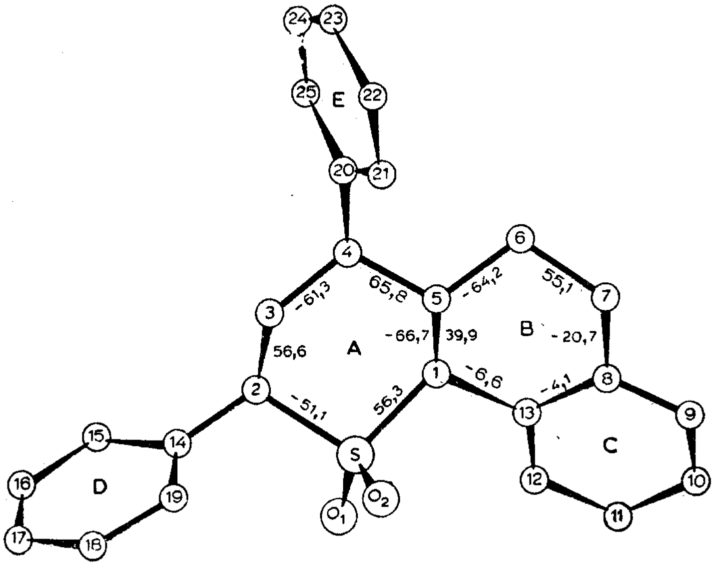

Fig. 2. Geometry of the VI molecule: torsion angles.

8MD chromatograph with a stainless steel column (100 by 0.3 cm) filled with 0.2% Apiezon L on quartz sand at 250°C; the hydrogen flow rate was 60 ml/min, and the carrier-gas (helium) flow rate was 110 ml/min. The retention times of sulfides IVa and IVb were 22.7 and 16.6 min, respectively. The PMR spectra of solutions of isomer IVb in CCl_4 and $(CD_3)_2CO$ were recorded with an RYa-2306 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The x-ray diffraction study was carried out with a Hilger—Watts four-circle automatic diffractometer guided by a PDP 8/1 minicomputer (with λ Cu K_α, a graphite monochromator, and $\theta/2\theta$ scanning with $1° \leq \theta < 57°$). A total of 2277 independent reflections with $I \geq 2\sigma$ were used in the calculation. The structure was decoded by the heavy-atom method and was refined by the method of least squares within the total-matrix anisotropic approximation. All of the hydrogen atoms were uncovered by differential synthesis and were included in the calculation of F_{calc} with the coordinates calculated from the obvious geometrical considerations; the position and heat parameters of the H atoms were disregarded (it was assumed that $B_{iso} = 5.0$ Å²). The final R value was 0.068 ($R_W = 0.072$).

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