NEW PATHWAY FOR THE DISPROPORTIONATION OF HYDROTHIOCHROMENES AND STRUCTURAL STUDIES OF THE RESULTING COMPOUNDS

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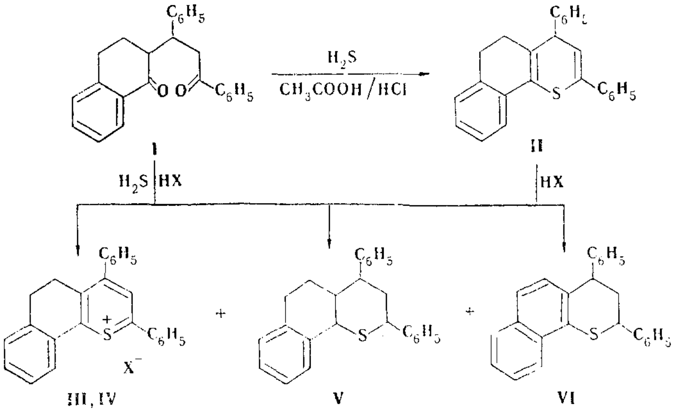
A new pathway for the disproportionation of hydrothiochromenes under the influence of protic acids, which consists in intermolecular hydride transfer of a hydrogen from the alicycle and leads to the development of a hydrothiochroman, was developed. Correlation results that confirm the structures and conformational peculiarities of the resulting compounds were obtained by PMR spectroscopy and x-ray diffraction analysis.

It is known [1, 2] that the reaction of "semicyclic" 1,5-diketones with hydrogen sulfide and acids concludes with the formation of products of partial or complete disproportionation of the intermediately formed 5,6-polymethylenethiopyrans.

We have established that in the case of the reactions of 2-(1,3-diphenyl-1-propanon-3-yl)-1-tetralone (I) with hydrogen sulfide and perchloric or trifluoroacetic acid, in addition to the well-known transformation that takes place with the formation of disproportionation products III, IV, and V [3], substance VI, which is a benzodihydrothiochromene derivative (II), is formed.



$HX = CH_3COOH/HClO_4$, CF_3COOH; $X^- - ClO_4$, CF_3COO

The structures of the benzohydrothiochromylium salts (III, IV) and the benzohexahydrothiochromene (V) were proved in [3, 4]. We obtained 2,4-diphenyl-7,8-benzo-2,3-dihydrothiochroman (VI) for the first time from a mixture of the latter with sulfide V by column chromatography and also as a result of repeated recrystallization.

The formation of VI constitutes evidence for the previously unobserved transformation of hydrothiochromenes under the influence of protic acids. Intermolecular hydride transfer of hydrogen from the C_5 or C_6 position, which leads to aromatization of the alicycle and can be represented by the scheme presented below, apparently occurs in this case.

The structure of benzohydrothiochroman VI was established by x-ray diffraction analysis and PMR spectroscopy.

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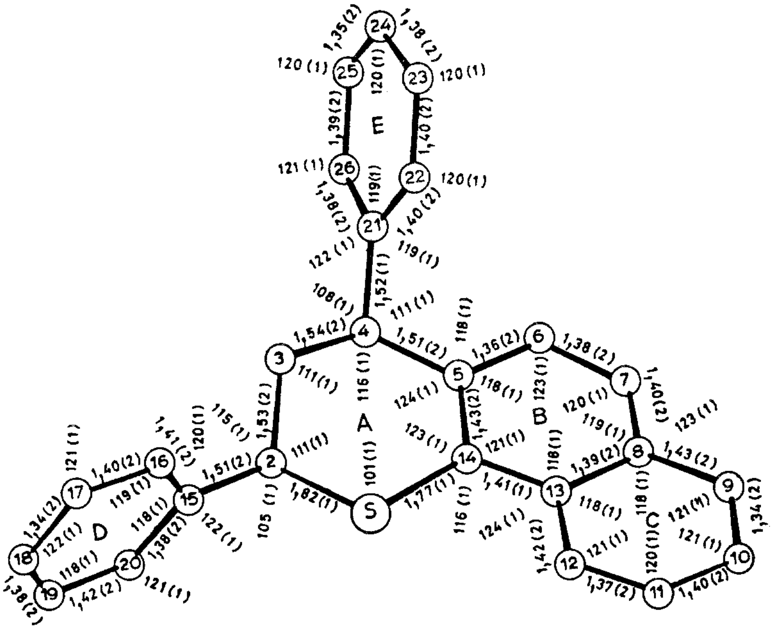
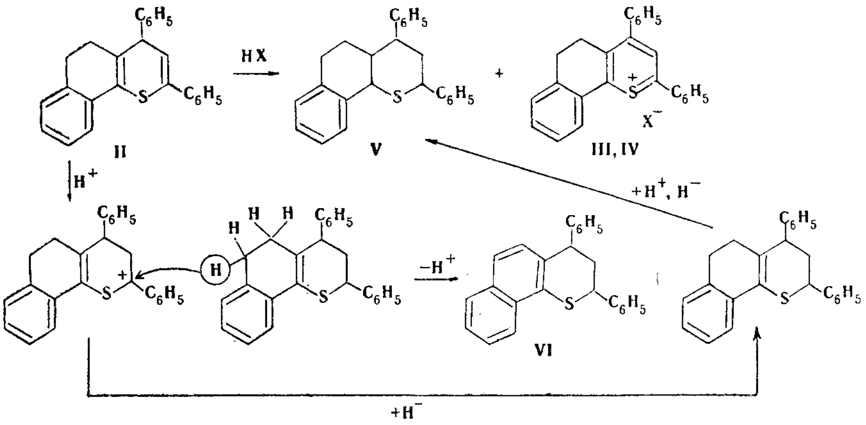


Fig. 1. Bond lengths and angles of the VI molecule.

The crystals of sulfide VI are monoclinic: a = 13.180(2), b = 19.389(3), c = 7.864(1) Å, γ = 111.72(1)°, V = 1867(1) $Å^3$, M = 354.5, d_{calc} = 1.15 g/cm^3, Z = 4, space group $P2_1/b$.



The coordinates of the atoms of VI are given in Table 1, and the bond lengths and angles are presented in Fig. 1.

According to the results of x-ray diffraction analysis, the lengths of the C–C bonds in the B and C rings (Fig. 1) clearly indicate their aromatic character; the bond angles, which correspond to trigonal sp^2 hybridization of the atoms of these rings, also constitute evidence in favor of this.

The observed delocalization of the π electrons over the two-ring B–C system [the average length of the C–C bonds is 1.39(2) Å] makes it possible to regard it as a naphthalene system (1.395 Å) [5] and consequently as a planar system (Fig. 1). As regards the lengths of the single bonds of the A ring [1.51(2)-1.54(2) Å], they coincide within the limits of 3σ with the value (1.521 Å) in cyclohexane [6]. The D and E phenyl rings have the usual geometry.

Because of the participation of the unshared pair of the sulfur atom in conjugation with the aromatic ring, the length of the $S-C_{14}$ bond [1.77(1) Å] is appreciably less than that of the $S-C_2$ bond [1.82(1) Å]. In thioxanthenes [7, 8] these lengths range from 1.746(5) to 1.773(4) Å, such that the length of the shortest $S-C_{14}$ bond in structure VI coincides with the upper limit. As expected, the length of the other $S-C_2$ bond with an sp^3-hybridized carbon atom is virtually equal to the value found in saturated sulfur-containing heterocycles [1.817(5) Å] [9].

TABLE 1. Experimental Coordinates of the Nonhydrogen Atoms and Calculated Coordinates of the Hydrogen Atoms* (all multiplied by 10^4)

Atom	*x*	*y*	*z*	B_{iso}	Atom	*x*	*y*	*z*
S	3117 (2)	2418 (2)	1307 (4)	†	H (2)	2050	3219	678
C (2)	2427 (8)	2888 (6)	14 (13)	4,1 (2)	H (3)	1050	2550	−1657
C (3)	1361 (8)	2334 (6)	−684 (14)	4,1 (2)	H (3′)	1519	1900	−1213
C (4)	519 (9)	2021 (6)	750 (13)	4,1 (2)	H (4)	367	2483	1195
C (5)	911 (9)	1713 (6)	2265 (15)	4,5 (2)	H (6)	−634	1187	3174
C (6)	155 (9)	1296 (6)	3412 (14)	4,7 (2)	H (7)	−145	778	5760
C (7)	427 (10)	1017 (6)	4884 (16)	5,3 (2)	H (9)	1195	398	7427
C (8)	1504 (9)	1069 (6)	5153 (15)	4,8 (2)	H (10)	3070	521	7762
C (9)	1809 (9)	710 (6)	6548 (15)	4,8 (2)	H (11)	4502	1206	5695
C (10)	2851 (11)	783 (7)	6774 (17)	6,2 (3)	H (12)	4077	1867	3424
C (11)	3672 (11)	1183 (8)	5624 (18)	6,3 (3)	H (16)	3423	4406	−311
C (12)	3430 (10)	1542 (6)	4266 (15)	4,9 (2)	H (17)	4846	5081	−2502
C (13)	2341 (9)	1497 (5)	3970 (13)	4,0 (2)	H (18)	5393	4436	−4546
C (14)	2034 (8)	1844 (5)	2599 (13)	3,8 (2)	H (19)	4685	3098	−4796
C (15)	3253 (8)	3312 (6)	−1303 (14)	4,4 (2)	H (20)	3299	2371	−2593
C (16)	3702 (10)	4092 (6)	−1245 (15)	5,3 (2)	H (22)	227	651	−330
C (17)	4480 (10)	4484 (7)	−2465 (17)	5,6 (3)	H (23)	−1312	−287	−1676
C (18)	4785 (11)	4123 (7)	−3695 (18)	6,0 (3)	H (24)	−2963	3	−2175
C (19)	4356 (10)	3360 (7)	−3821 (17)	5,6 (3)	H (25)	−3043	1149	−1257
C (20)	3593 (9)	2954 (6)	−2574 (15)	5,0 (2)	H (26)	−1466	2103	45
C (21)	−495 (8)	1441 (6)	−31 (14)	4,3 (2)				
C (22)	−475 (10)	747 (6)	−475 (15)	5,0 (2)				
C (23)	−1385 (10)	220 (6)	−1255 (16)	5,3 (2)				
C (24)	−2294 (11)	389 (7)	−1606 (16)	5,8 (3)				
C (25)	−2339 (11)	1041 (7)	−1107 (18)	6,0 (3)				
C (26)	−1442 (10)	1576 (6)	−325 (15)	5,1 (2)				

*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 CH_2 group).

†The anisotropic temperature factors (B_{aniso}) of the S atom: $T = \exp[-{}^1/_4(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^{**} + \ldots)]$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	4,5 (1)	5,9 (2)	3,5 (1)	0,5 (1)	0,5 (1)	1,8 (1)

Thiacyclohexene ring A has a half-chair conformation that is markedly distorted because of fusion with aromatic ring B and because of the presence of a sulfur atom with a bond angle that is smaller than in the case of carbon atoms.

To reduce the steric hindrance with heteroring A, phenyl substituents D and E form dihedral angles of 85.5 and 70°, respectively, with its planar fragment. For the same reason, D and E occupy pseudoequatorial positions relative to heteroring A.

Three groups of signals are observed in the PMR spectrum of VI (in CCl_4): a broad intense multiplet of aromatic protons at δ 6.80-8.0 ppm and multiplets at δ 4.45 and 2.60 ppm, the integral intensities of which are in a ratio of 8:1:1 and are characteristic for the structure of sulfide VI. It is apparent that the multiplet at δ 4.45 ppm corresponds to the protons attached to C_2 and C_4 of the heteroring.

To obtain a more accurate assignment of the signals in this region we obtained the PMR spectrum of a benzene solution of VI; this made it possible to determine the spin–spin coupling constants (SSCC) of the protons under consideration in the case of coupling with the methylene groups attached to C_3. It follows from the splitting diagram in Fig. 2 that the signal of the 2-H proton is a double doublet with SSCC of 4, 5, and 10 Hz (δ 2-H 4.17 ppm). The constants found make it possible to assume [10] that 2-H occupies a pseudoaxial position. One can arrive at a similar conclusion by examining the SSCC of the 4-H proton (δ 4.05 ppm) in the case of coupling with the methylene protons attached to C_3 ($^3J_{3e,4}$ = 7.5 Hz, $^3J_{3a,4}$ = 11.5 Hz), i.e., the phenyl substituents attached to C_2 and C_4 are both pseudoequatorially oriented.

We attempted on the basis of the data from the PMR spectrum to shed some light on the problem of the conformation of the dihydrothiopyran ring in the investigated system. In conformity with the correlation in [11] and taking into account the observed SSCC, one can estimate the dihedral angles between 4-H and 3-H: The angle between the 4-H and 3e-H protons is ≈30°, while the angle between the 4-H and 3a-H protons is ≈150°. In the Newman projec-

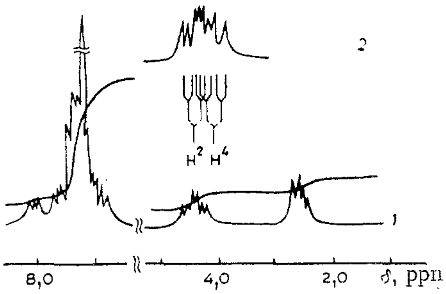


Fig. 2. PMR spectrum of VI: 1) in benzene; 2) in CCl_4.

tion for the C_4—C_3 fragment the carbon atom in the 2 position of the heteroring deviates ~30° from the plane of the C=C bond.

According to the data of Dashevskii [12], a distorted half-chair conformation in which the C_2 atom experiences the greatest shift relative to the plane of the C=C bonds, while the shift of C_3 is insignificant, corresponds to the indicated angle.

Thus, the indicated methods gave intercorrelating results and made it possible to assign the 2,4-diphenyl-7,8-benzo-2,3-dihydrothiochroman structure to VI.

EXPERIMENTAL

The synthesis of the substances was described in [3]. The mixture of sulfides V and VI was separated by column chromatography on activity III Al_2O_3 [elution with hexane—nitromethane (4:1)] or possibly by recrystallization from alcohol—acetone (2:1.5: (sulfide V had mp 156-157°C, while benzohydrothiochroman VI had mp 155-156°C). Analysis by gas—liquid chromatography (GLC) was carried out with an LKhM-8MD chromatograph with a stainless steel column (100 × 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 the peaks of sulfide V and VI were 22.74 and 31.74 min, respectively, and their percentages were 54.32 and 45.48%. The PMR spectrum of VI was recorded with an RYa-2306 spectrometer (80 MHz) at 25°C; 30% solutions of VI in CCl_4 and benzene were used with hexamethyldisiloxane as the internal standard.

The x-ray diffraction study was made with a Hilger—Watts four-circle automatic diffractometer guided by a PDP 8/1 minicomputer (with λCuK_α emission, a graphite monochromator, $\nu/2\nu$ scanning, and $1° \leqslant \nu \leqslant 57°$) no correction for absorption was introduced [$\mu(CuK\alpha) = 8.4\ cm^{-1}$]. A total of 1056 independent reflections with $I \geqslant 2\sigma$ were used in the calculation.

The structure was determined by the heavy-atom method and refined by the method of least squares initially within the fully matrix isotropic approximation to R = 0.120. Only the S atom was then subjected to fully matrix anisotropic refinement (the C atoms were not refined anisotropically because of the relatively small number of reflections). All of the hydrogen atoms were revealed by differential synthesis and were included in the calculation of F_{calc} with the coordinates calculated from geometrical considerations; the position and thermal parameters of the H atoms were not refined (it was assumed that B_{iso} = 5.0 Å [2]). The final R value was 0.085.

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TELLURAXANTHENE

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Telluraxanthene was obtained by intramolecular electrophilic cyclization of 2-trichlorotelluriodiphenylmethane with subsequent reduction of the intermediately formed 10,10-dichlorotelluraxanthene. The chemical reactions that occur at the tellurium atom and the methylene group of telluraxanthene were studied. The lower limit of the activation energy of pyramidal inversion at the onium tellurium atom in telluroniaxanthenyldimedone ylid was determined by PMR spectroscopy.

In contrast to xanthene and its thia and selena analogs, telluraxanthene and its derivatives were unknown until recently. An attempt by Renson [1] to obtain telluraxanthene by cyclization of 2-chlorocarbonyldiphenyl telluride led to rearrangement of the starting compound and the formation of 2-chloroelluriabenzophenone. For the synthesis of telluraxanthene we recently found [2] a new (for the chemistry of xanthenes) reaction, viz., intramolecular electrophilic cyclization of 2-trichlorotelluriodiphenylmethane (I) with subsequent reduction of the resulting 10,10-dichlorotelluraxanthene (which is formed in high yield) to the desired compound. This paper is devoted to a description of the synthesis of telluraxanthene and a study of its properties.

The starting Ia for the preparation of telluraxanthene was obtained from bis(2-benzylphenyl) ditelluride (II), which was synthesized in 60-80% yields by the reaction of 2-lithiodiphenylmethane [from 2-iodo(bromo)diphenylmethane and lithium in ether] with powdered tellurium in an argon atmosphere with subsequent spontaneous oxidation by air oxygen of the corresponding tellurophenol formed by hydrolysis with dilute hydrochloric acid. The higher yields of ditelluride II when 2-bromodiphenylmethane is used are due to the fact that when 2-iododiphenylmethane is used to obtain 2-lithiodiphenylmethane, part of the resulting organolithium derivative undergoes side reactions involving condensation with the halo derivative. The chlorination and bromination of ditelluride II to the corresponding trihalides Ia, b give the products in quantitative yields. An alternative method for the preparation of Ia, viz., reaction between 2-trimethylsilyldiphenylmethane and tellurium tetrachloride in toluene (by the method in [3]) leads to lower yields (~50%) of Ia based on the starting 2-halodiphenylmethane.

The cyclization of 2-trichlorotelluriodiphenylmethane (Ia) to 10,10-dichlorotelluraxanthene (IIIa) does not proceed as readily as the cyclization of 2-chlorotelluriodiphenyl sulfide [4] and 2-trichlorotelluriodiphenyl oxide [5]. The latter reactions, although they do take place under rather severe conditions (heating for many hours at 200-250°C), do not require the presence of catalysts because of the sufficiently strong activation of the ortho positions of the aryl rings to electrophilic attack by the electron-donor oxygen and sulfur atoms. However, Ia undergoes cyclization when it is heated in o-dichlorobenzene or 1,2,4-trichlorobenzene in the presence of one equivalent of anhydrous aluminum chloride. Attempts to bring about the cyclization of 2-trichlorotelluriodiphenylmethane at elevated temperatures in the absence of anhydrous aluminum chloride led to the production of IIIa in a very low and difficult-to-reproduce yield. The role of aluminum chloride evidently consists in a significant increase in the manifestation of the electrophilic properties of the trichlorotellurio group in Ia due to the formation of a complex, to which, in analogy with the product of the reaction

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