REACTIONS OF SYM-OCTAHYDROTHIOXANTHYLIUM SALTS WITH BASES AND STRUCTURE OF 4-(SYM-OCTAHYDROTHIOXANTHEN-9-YL)-1,2,3,5,6,7,8-HEPTAHYDRO-2H-THIOXANTHENE

V. G. Kharchenko, A. A. Shcherbakov,
and Yu. T. Struchkov

UDC 547.818.6:548.737

The reaction of sym-octahydrothioxanthylium salts with pyridine or aqueous sodium bicarbonate leads to the formation of 4-(sym-octahydrothioxanthen-9-yl)-1,2,-3,5,6,7,8-heptahydro-2H-thioxanthene, whose structure was established by x-ray diffraction analysis.

Thiopyrylium salts and their condensed analogs in the presence of bases (pyridine or a mixture of pyridine and phosphorus polysulfide) are converted into compounds, containing a di(thiopyranylidene) fragment [1]. Thus, sym-octahydrothioxanthylium chloride (I) is converted by the action of pyridine or aqueous sodium bicarbonate into a dimer. IR and UV spectral analysis and chemical transformations indicated that this dimer is di(sym-octahydrothioxanthylene) [2, 3]. However, the PMR spectrum of this compound showed a vinyl proton singlet at

TABLE 1. Atomic Coordinates ($\times 10^4$)* For Dimer II

Atom	x	y	z	Atom	x	y	z
$S_{(1)}$	188 (1)	2036 (1)	1504 (1)	$H_{(2)}$	2914	5590	2109
$S_{(2)}$	−4460 (1)	2415 (1)	1959 (1)	$H_{(2')}$	3036	6905	1125
$C_{(1)}$	1221 (4)	5825 (3)	1891 (5)	$H_{(3)}$	3653	5481	−683
$C_{(2)}$	2490 (12)	6073 (18)	1193 (18)	$H_{(3')}$	2330	5630	−910
$C_{(3)}$	2733 (13)	5331 (14)	−152 (18)	$H_{(4)}$	2583	3233	472
$C_{(4)}$	2195 (3)	3917 (3)	265 (5)	$H_{(4')}$	2071	3913	−787
$C_{(5)}$	−2214 (3)	845 (3)	2631 (3)	$H_{(6)}$	−3632	182	4476
$C_{(6)}$	−3497 (3)	709 (3)	3504 (4)	$H_{(6')}$	−4078	282	2902
$C_{(7)}$	−3749 (3)	1951 (3)	3855 (4)	$H_{(7)}$	−4546	1799	4617
$C_{(8)}$	−2724 (3)	2748 (3)	4472 (4)	$H_{(7')}$	−3808	2413	2911
$C_{(9)}$	−681 (3)	4105 (3)	3136 (4)	$H_{(8)}$	−2674	2295	5431
$C_{(10)}$	503 (3)	4463 (3)	2097 (4)	$H_{(8')}$	−2886	3571	4693
$C_{(11)}$	965 (3)	3631 (3)	1320 (4)	$H_{(9)}$	−889	4763	3764
$C_{(12)}$	−1311 (3)	1913 (3)	2552 (4)	$H_{(14)}$	−2067	1325	−692
$C_{(13)}$	−1512 (3)	2984 (3)	3372 (4)	$H_{(14')}$	−983	605	−937
$C_{(14)}$	−1878 (3)	497 (3)	−858 (4)	$H_{(15)}$	−1729	671	−3203
$C_{(15)}$	−2233 (8)	124 (8)	−2331 (10)	$H_{(15')}$	−1980	−779	−2495
$C_{(16)}$	−3601 (9)	−217 (9)	−2086 (11)	$H_{(16)}$	−3972	581	−1380
$C_{(17)}$	−4207 (3)	−1365 (4)	−889 (4)	$H_{(16')}$	−4084	−193	−2846
$C_{(18)}$	−3753 (4)	−3540 (3)	4176 (5)	$H_{(17)}$	−4090	−2137	−1366
$C_{(19)}$	−2114 (8)	−3661 (8)	4212 (12)	$H_{(17')}$	−5120	−1473	−525
$C_{(20)}$	−1846 (7)	−2711 (9)	4998 (10)	$H_{(18)}$	−4558	−3574	4884
$C_{(21)}$	−1479 (3)	−1508 (3)	3915 (4)	$H_{(18')}$	−3851	−4298	3622
$C_{(22)}$	−2009 (2)	−285 (3)	1834 (3)	$H_{(19)}$	−1586	−3617	3445
$C_{(23)}$	−2588 (3)	−422 (3)	492 (3)	$H_{(19')}$	−2199	−4324	5145
$C_{(24)}$	−3630 (3)	−1265 (3)	466 (4)	$H_{(20)}$	−938	−2299	5470
$C_{(25)}$	−3390 (3)	−2383 (3)	3075 (4)	$H_{(20')}$	−2350	−2201	5936
$C_{(26)}$	−2366 (3)	−1458 (3)	2937 (3)	$H_{(21)}$	−1383	−764	4488
$H_{(1)}$	1171	6121	2922	$H_{(21')}$	−667	1495	3214
$H_{(1')}$	819	6311	1300	$H_{(22)}$	−1113	141	1412

*The numbering of the hydrogen atoms is in accord with the corresponding carbon atoms. The second hydrogen atoms of the CH_2 group are indicated by a prime sign.

N. G. Chernyshevskii Saratov State University, Saratov 410601. A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow 117813. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 479-482, April, 1989. Original article submitted June 10, 1987; revision submitted May 31, 1988.

 0009-3122/89/2504-0398$12.50

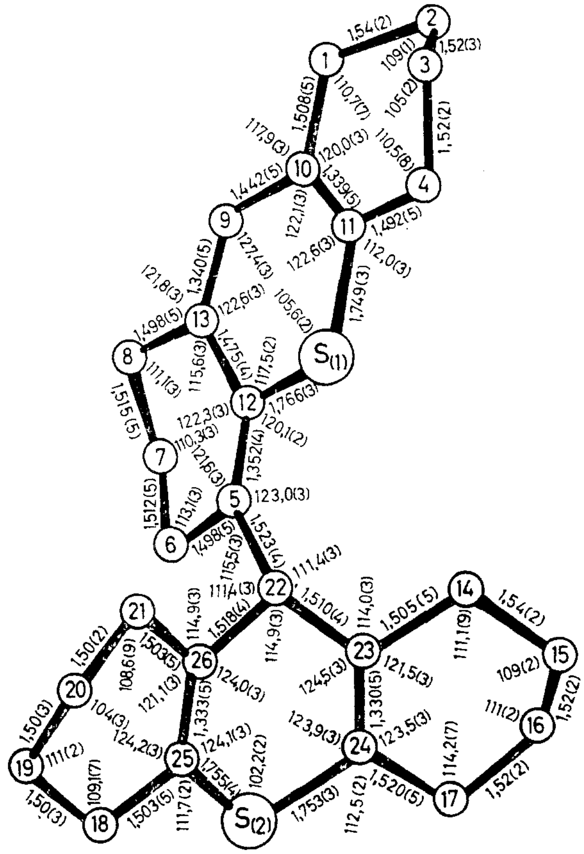
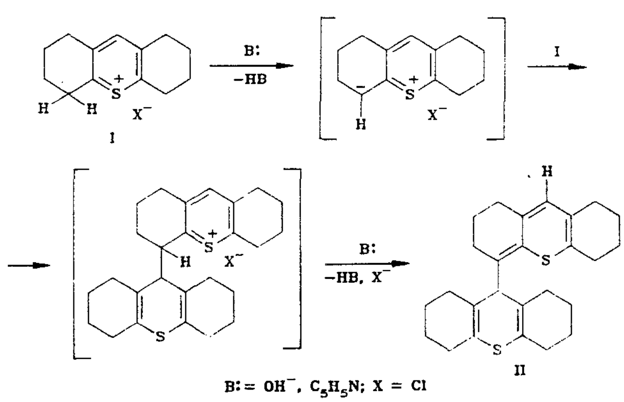


Fig. 1. Bond lengths and angles in II.



In order to determine this structure, we carried out an x-ray diffraction structural analysis of dimer I. This compound was found to be 4-(sym-octahydrothioxanthen-9-yl)-1,2,3,5,-6,7,8-heptahydro-2H-thioxanthene (II). The atomic coordinates of dimer II are given in Table 1, while the bond lengths and angles are given in Fig. 1. The molecular stereochemistry and torsion angles are given in Fig. 2.

The molecular geometry of II is generally unexceptional. The structural parameters are close to those found for mono-, bi-, and tricyclic thiopyrans [4-8]. We should note the contraction of the lengths of the $C_{(9)}-C_{(10)}$ and $C_{(12)}-C_{(13)}$ single bonds in ring B (Fig. 1) due to the cyclic conjugation chain including $S_{(1)}$ as well as the presence of the exocyclic $C_{(5)}=C_{(12)}$ double bond. For this reason, thiacyclohexadiene ring B is virtually planar. On the other hand, 4H-thiopyran ring E has distorted boat conformation, which is somewhat compressed at $S_{(2)}$ (Fig. 2).

The 2H-thioxanthenyl substituent at $C_{(22)}$ occupies an axial position and forms an angle of 72.9° with the planar fragment of heterocycle E in order to reduce the steric interactions between cyclohexene ring C and rings D and F.

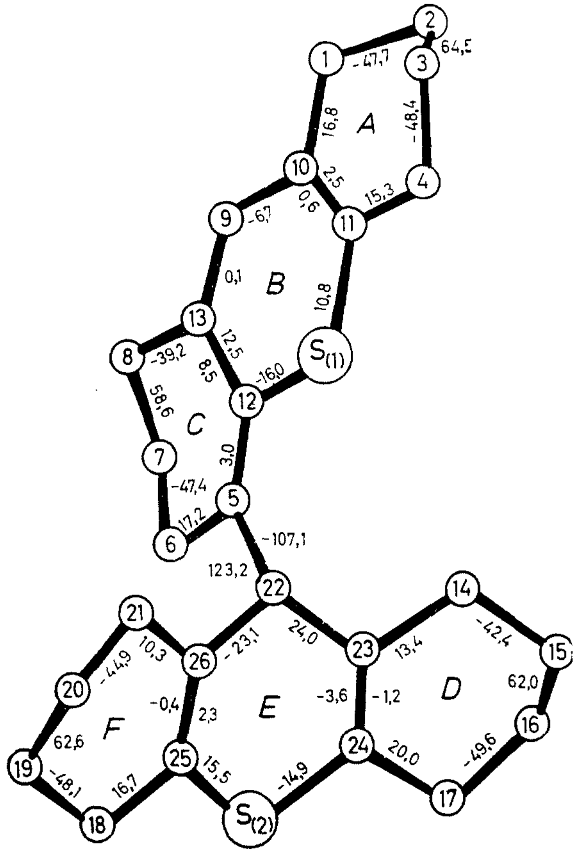


Fig. 2. Molecular stereochemistry of II with torsion angles.

Cyclohexene rings A, D, and F have half-chair conformation $^{2}H_{3}$, $^{15}H_{16}$, and $^{19}H_{20}$, respectively. On the other hand, ring C has a conformation intermediate between half-boat ^{8}HB and half-chair $^{7}H_{8}$ due to fusion with virtually planar ring B.

We may assume that the formation of II involves the initial loss of a proton from $C_{(5)}$ of the alicycle with subsequent electrophilic attack of the carbanion formed by the cation of (I). Dimer II arises upon the loss of a second proton from the same position.

EXPERIMENTAL

The synthesis of II was described in our previous work [2]. The unit cell parameters of triclinic crystals of II are as follows: $a = 11.570(1)$, $b = 11.078(1)$, $c = 9.130(1)$ Å, $\alpha = 87.28(1)$, $\beta = 77.95(1)$, $\gamma = 104.71(1)°$, $V = 1100.7(4)$ Å^3, $M = 409.5$, $d_{calc} = 1.23$ g/cm^3, $Z = 2$, space group $P\bar{1}$. The x-ray diffraction structural analysis was carried out on a Hilger–Watts four-circle automatic diffractometer controlled by a PDP 8/1 minicomputer using λCuK_{α} radiation, graphite monochromator, and $\theta/2\theta$ scanning: $\theta < 57°$. A total of 2401 independent reflections with $I \geq 2\sigma$ were used in the calculation. The structure was solved by the heavy atom method and refined by electron density maps and the method of least squares in the full-matrix anisotropic approximation. All the hydrogen atoms were revealed in the difference map and included in calculation of E_{calc} with coordinates calculated from obvious geometric considerations. The positional and thermal parameters of the hydrogen atoms were not refined; B_{iso} was taken to be 5.0 Å^2. The final $R = 0.049$ and $R_w = 0.062$. All the calculations were carried out using the INEXTL program set on an Eclipse S/200 computer [9].

LITERATURE CITED

1. G. A. Reynolds, C. H Chen,and J. A. V. Allon, J. Org. Chem., 44, 4456 (1979).
2. V. G. Kharchenko, T. I. Krupina, and A. F. Blinokhvatov, Thioxanthenes, Hydrothioxanthenes, and Their Derivatives [in Russian], Izd. Saratovsk. Gos. Univ., Saratov (1979).
3. V. G. Kharchenko and T. I. Krupina, Zh. Org. Khim., 3, 1710 (1967).
4. A. A. Shcherbakov, G. G. Aleksandrov, Yu. T. Struchkov, and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 11, 1470 (1979).

5. V. G. Kharchenko, A. P. Krivchenko, O. V. Fedotova, I. Ya. Evtushenko, A. A. Shcherbakov, G. G. Aleksandrov, and Yu. T. Struchkov, Khim. Geterotsikl. Soedin., No. 10, 1337 (1980).
6. T. V. Stolbova, S. K. Klimenko, A. A. Shcherbakov, G. G. Aleksandrov, Yu. T. Struchkov, and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 8, 1056 (1980).
7. T. V. Stolbova, S. K. Klimova, A. A. Shcherbakov, V. G. Andrianov, Yu. T. Struchkov, and V. G. Kharchenko, No. 10, 1342 (1981).
8. V. G. Kharchenko, N. I. Kozhevnikova, A. A. Shcherbakov, G. G. Aleksandrov, and Yu. T. Struchkov, Khim. Geterotsikl. Soedin., No. 3, 324 (1980).
9. R. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, 28, No. 5, 1029 (1983).

THIYLATION OF DIALLYL SULFIDE BY HYDROGEN SULFIDE IN THE ALKALI METAL HYDROXIDE–DMSO SYSTEM

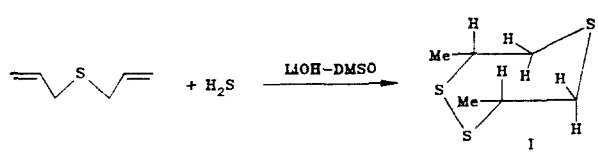
G. K. Musorin, S. V. Amosova, and G. A. Kalabin

UDC 547.892'379.07

Preparative methods have been developed for the synthesis of 3,7-dimethyl-1,2,5-trithiacycloheptane and 4-thia-1-heptene-6-thiol from diallyl sulfide and hydrogen sulfide in a system containing an alkali metal hydroxide and DMSO.

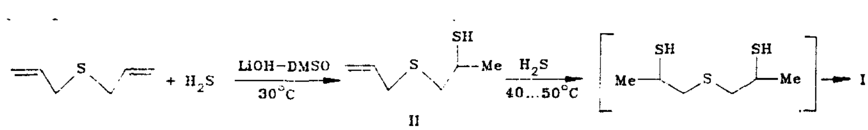
3,7-Dimethyl-1,2,5-trithiacycloheptane (I) is a promising inhibitor for the radiation aging of polymers [1] but the methods described for its synthesis are inefficient. Thus, the reaction of di(2-chloropropyl) sulfide with thiourea and treatment of the resultant mass with aqueous sodium hydroxide give dithiols, whose oxidation gives a mixture of structural isomers, which is difficult to separate [2]. These isomers may be obtained in low yield (~14%) by the reaction of di(2-chloropropyl) sulfide with sodium thiosulfate with subsequent treatment of the resultant salt with 25% hydrochloric acid in a nitrogen atmosphere [2].

We have discovered that diallyl sulfide reacts with hydrogen sulfide in the LiOH–DMSO system with the formation of I in yields up to 64% [3].



In the present work, experimental details of the synthesis of I are given.

The reaction of diallyl sulfide with hydrogen sulfide proceeds through intermediate 4-thia-1-heptene-6-thiol (II), which is obtained at 30°C in 65% yield. At 40-50°C, II adds a second hydrogen sulfide molecule apparently to form di(2-mercaptopropyl) sulfide, which is oxidized by DMSO to give I.



Using the Karplus equation [4] and taking account of the similarity of the electronegativities of sulfur and carbon, we may consider, in light of the coupling constants (J = 7.5 and 4.0 Hz), that the methyl groups in ring occupy equatorial positions (the ^{1}H NMR spectral data are given in the Experimental).

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 483-484, April, 1989. Original article submitted September 14, 1987; revision submitted June 6, 1988.

0009-3122/89/2504-0401$12.50