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

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UDC 547.892'379.07

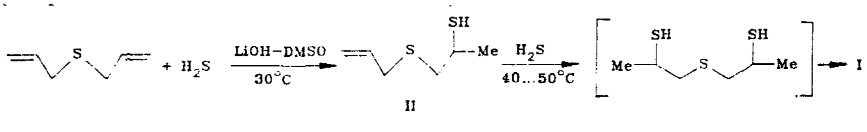
Preparative methods have been developed for the synthesis of 3,7-dimethyl-1,2,5-trithiacycloheptane and 4-thia-1-heptene-6-thiol from diallyl sulfide and hydrogen sulfide in a system containing an alkali metal hydroxide and DMSO.

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).

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TABLE 1. Effect of the Conditions of the Reaction of Diallyl Sulfide with Hydrogen Sulfide on the Yield of I and II*

Experiment No.	Starting reagents			Temperature, °C	Reaction products, g (yield, %)		Conversion of diallyl sulfide, %
	diallyl sulfide	MOH					
		M	g (mole)		I	II	
2	7,4 (0,06)	Li	2,0 (0,08)	50	4,6 (40,3)	0,6 (8,2)	97
3	8,1 (0,07)	K	4,5 (0,08)	50	2,8 (34,1)	0,4 (7,2)	66,6
4	7,4 (0,06)	Li	2,0 (0,08)	80	2,7 (24,1)	Traces	96
5	8,2 (0,07)	Na	3,2 (0,08)	50	4,7 (39,8)	1,4 (18,4)	91
6	6,6 (0,05)	—	—	50	—	—	—
7	6,8 (0,05)	Li	0,02 (0,0008)	50	Traces	Traces	—
8	6,6 (0,05)	Li	5,0 (0,2)	50	4,1 (41,4)	0,5 (7,9)	95
9†	8,7 (0,08)	Li	2,0 (0,08)	40	8,8 (64,2)	0,6 (6,8)	99

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*In 100 ml DMSO. The reaction time was 6 h and hydrogen sulfide was introduced until a saturated solution was obtained.

†Diallyl sulfide was added dropwise to the reaction mixture during the reaction.

In previous work [5], we showed that the yield of di(propen-1-yl) sulfide (III) upon the isomerization of diallyl sulfide in the MOH—DMSO system (M = K, Na, and Li) depends largely on the nature of the alkali metal (90, 65, and 0.5% for KOH, NaOH, and LiOH, respectively). A study of the effect of the basicity of the MOH—DMSO system (Table 1) on the reaction course showed that the nature of the alkali metal hydroxide is not a major factor controlling the yield of I (40, 39, and 34% for LiOH, NaOH, and KOH, respectively). This finding is related to the circumstance that hydrogen sulfide is a strong acid in DMSO (pK_a 14.7 [6]), which reduces the basicity of the MOH—DMSO system to such an extent that the prototropic isomerization of diallyl sulfide does not occur.

In the absence of alkali metal hydroxide, the reaction does not proceed. An increase in the reaction temperature to 80°C reduces the yield of I due to tar formation.

EXPERIMENTAL

The NMR spectra of I and II were taken in $CDCl_3$ on a Bruker WP-200SY spectrometer at 201 and 50.3 MHz for the ^1H and ^{13}C nuclei, respectively. The analytical chromatographic analysis was carried out on an LKhM-72 chromatograph on a 2 m × 4 mm column packed with Carbowax 20M on Chromaton N-AW-DMCS. The compounds for structural analysis were separated by preparative gas-liquid chromatography on a PAKhV-0.7 chromatograph using a 2 m × 6 mm column packed with Carbowax 20M on Chromaton N-AW-DMCS. The elemental analysis data corresponded to the calculated values.

Thiylation of Diallyl Sulfide. A mixture of 10.7 g (0.09 mole) diallyl sulfide, 1.9 g (0.08 mole) LiOH, and 100 ml DMSO was placed into a four-necked flask equipped with a reflux condenser and stirrer and hydrogen sulfide was slowly introduced for 5 h at 30°C. Then, the mixture was diluted with water and extracted with ether. The ethereal extracts were washed with water and dried over $CaCl_2$. Ether was distilled off and the residue was fractionated in vacuum to give 1.6 g (18.8%) I and 3.6 g (65.8%) II.

The results of the other experiments are given in Table 1.

3,7-Dimethyl-1,2,5-trithiacycloheptane, $C_6H_{12}S_3$, bp 82°C (1.3 hPa), n_D^{20} 1.5912. ^1H NMR spectrum: 1.30 (6H, d, 3,7-Me), 2.86 (2H, q, 4,6-H_a), 3.07 (2H, q, 4,6-H_e), 3.22 ppm (2H, m, 3,7-H), J_{gem} = 14.5, $J_{vic,trans}$ = 7.5, $J_{vic,cis}$ = 4.0. ^{13}C NMR spectrum: 20.0 (Me), 48.1 ($C_{(1)}$), 42.9 ppm ($C_{(2)}$). M^+ 180.

5-Thia-1-heptene-6-thiol. ^1H NMR spectrum: 1.42 (3H, d, Me), 1.98 (1H, d, SH), 2.68 and 3.19 (4H, d, CH_2), 3.01 (1H, m, CH), 5.16 (2H, m, 1-H), 5.19 ppm (1H, m, 2-H). ^{13}C NMR spectrum: 117.13 ($C_{(1)}$), 134.15 ($C_{(2)}$), 41.73 ($C_{(3)}$), 35.22 ($C_{(4)}$), 34.90 ($C_{(5)}$), 23.58 ppm (Me). M^+ 148.

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SYNTHESIS, STRUCTURE, AND PROPERTIES OF 2-THIO-4-IMINO-5-SPIROCYCLOHEXANEHYDANTOINS

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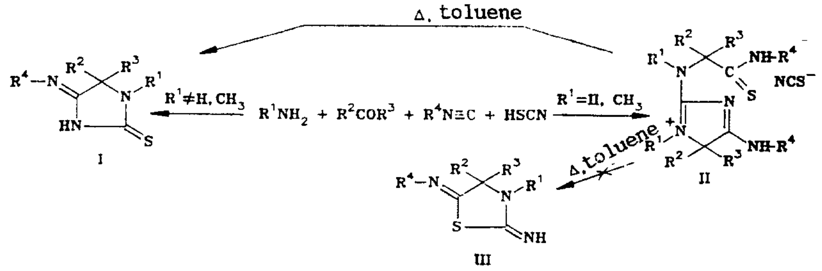
UDC 547.783'592'415'239.07:
548.737:543.51'422

The imidazolium salt, obtained by the multicomponent condensation of benzyl isonitrile, methylamine, cyclohexanone, and thiocyanic acid, undergoes thermal recyclization to 1-methyl-2-thio-4-imino-5-spirocyclohexanehydantoin. The stereochemical and structural features and properties of the 2-thiohydantoins are analyzed on the basis of the data of x-ray structural analysis and geometrical modeling.

It was shown [1] that the multicomponent condensation with the participation of ammonia or methylamine does not lead to the corresponding hydantoins (I), expected according to the Ugi reaction [2, 3], but is accompanied by the formation of the imidazolium salts (II). When they were boiled in toluene or benzene, the product, to which the thiazolidinimine structure (III) was assigned [1] on the basis of spectral data, was obtained. However, it was shown as a result of the x-ray structural investigation performed that the product of the thermal recyclization (IIa) has the thiohydantoin structure (Ia) (Tables 1-3).



Ia, b $R^1=CH_3$; Ic $R^1=CH_2Ph$; Ia–c $R^2+R^3=(CH_2)_5$; Ia, c $R^4=CH_2Ph$; Ib $R^4=4\text{-}CH_3C_6H_4$

The five-membered heterocycle of the molecule of (Ia) (Fig. 1) and the S, $N_{(3)}$, $C_{(4)}$, and $C_{(16)}$ atoms lie in one plane with the accuracy of ±0.02 Å. The strong p-π* conjugation appears as the following features: the significant [up to 1.331(3) Å (Table 1)] contraction of the $N_{(2)}$-$C_{(1)}$ bond, which is characteristic of the thioamide fragment [1, 4], the delocalization of the electron density of the amidine grouping – $N_{(1)}$-$C_{(2)}$ 1.318(3) Å and $N_{(3)}$-$C_{(2)}$ 1.324(3) Å, the fact that the $N_{(1)}$-$C_{(1)}$ bond length of 1.376(3) Å is intermediate between that of N_{sp^3}-C_{sp^2} 1.45 Å (without the p-π* conjugation) [5] and N_{sp^2}-C_{sp^2} 1.33 Å (with p-π* conjugation), and the increase of the C=S bond length 1.681(3) Å by 0.01-0.03 Å by comparison with thioamides [1, 4].

It should be noted that hydrogen was not found at the $N_{(1)}$ atom in spite of the reliable localization of the hydrogen atoms, even at the periphery of the molecule. It can be proposed as an explanation of this result, as well as the equality of the $N_{(1)}$-$C_{(2)}$ and $N_{(3)}$-$C_{(2)}$ bonds, that the indicated hydrogen atom participates in the tautomeric equilibrium, since this is characteristic of amidines [6, 7]. The anti-orientation of the unshared electron pair of $N_{(3)}$

All-Union Scientific Research Institute of Chemical Agents for Plant Protection, Moscow 109088. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 485-492, April, 1989. Original article submitted June 25, 1987; revision submitted July 27, 1988.

0009-3122/89/2504-0403 $12.50