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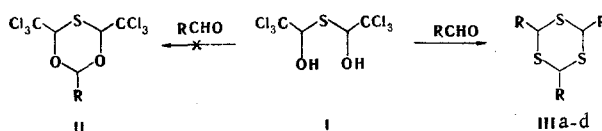
## SYNTHESIS OF THE $\beta$ ISOMERS OF 2,4,6-TRISUBSTITUTED 1,3,5-TRITHIANES

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The condensation of bis( $\alpha$ -hydroxy- $\beta$ , $\beta$ , $\beta$ -trichloroethyl) sulfide with aldehydes under acid catalysis conditions gives 2,4,6-trisubstituted 1,3,5-trithianes. The latter are realized only in the thermodynamically more favorable  $\beta$  forms.

It is known [1] that the addition of  $H_2S$  to carbonyl compounds frequently gives 1:2 adducts. When we carried out the condensation of the  $CCl_3CHO-H_2S$  adduct (I) with aldehydes we obtained derivatives of the 1,3,5-trithiane series (IIIa-d) instead of the expected 1,3,5-dioxathiane systems (II).



III a R =  $CH_3$ ; b R =  $C_6H_5$ ; c R =  $p\text{-ClC}_6H_4$ ; d R =  $p\text{-NO}_2C_6H_4$

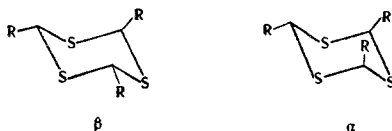
A sufficiently large number of methods for the synthesis of 1,3,5-trithianes are presented in the literature, and the most widely used method is the reaction of  $H_2S$  with aldehydes [2]. The formation of polymeric impurities should be considered to be the only disadvantage of the "hydrogen sulfide" method. In accordance with our synthetic method, the yields of 1,3,5-trithianes in the case of aromatic aldehydes are close to quantitative, and practically pure substances are obtained. There is a reference in [3] that the introduction of a strong acceptor group in the aromatic ring does not promote the formation of thioaldehyde in the reaction of aldehydes with  $B_2S_3$  and  $SiS_2$ . We were able to obtain trithiane III d from sulfide I and p-nitrobenzaldehyde, but, because of its ex-

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ceptionally low solubility, it was found to be impossible to determine its molecular weight. Nevertheless, there are no data to argue against its trimeric structure.

Since 2,4,6-triaryl(alkyl)-1,3,5-trithianes can exist in the form of two isomeric chairlike  $\alpha$  and  $\beta$  forms (for example, see [4, 5]), it seemed of interest to ascertain the stereochemical trend of this reaction. According to [5], primarily the less stable  $\alpha$  isomers are formed in the "hydrogen sulfide" method. Although the mechanism of their formation is not at all clear [6], it is nevertheless assumed that the preferred formation of the less favorable forms is associated with the effect of kinetic and statistical factors. The trithioaldehydes obtained under our conditions have the stable  $\beta$  structure, as confirmed by the agreement between the melting points observed by us and the data presented in the literature for the  $\beta$  forms.



The PMR spectrum of trithiane IIIa in  $\text{CHCl}_3$ , in conformity with the literature data [7], contains a doublet ( $\delta$  1.60 ppm,  $J=7.5$  Hz) and a quartet ( $\delta$  4.11 ppm,  $J=7.1$  Hz); this characterizes the equivalent orientation of the methyl groups in the ring.

The available information on the synthesis of isomeric trithioacetaldehydes constituted evidence for the substantial effect of the preparative method on the yield of the isomeric forms [8-10]. From the fact of the formation of only the  $\beta$  isomers, it should be concluded that the reaction is thermodynamically controlled. In the final analysis, the production of the  $\beta$  forms does not exclude the formation, in the first step, of the  $\alpha$  isomers, which, due to a shift in the epimerization equilibrium, are converted to the thermodynamically more favorable structures. The irreversibility of this shift is stimulated by the considerably lower solubility of the  $\beta$  forms, as confirmed by the data in [2], in which the facile conversion of the  $\alpha$  to the  $\beta$  isomers under the influence of  $\text{I}_2$ ,  $\text{SO}_3$ , and  $\text{HCl}$  is demonstrated.

#### EXPERIMENTAL

**2,4,6-Trimethyl-1,3,5-trithiane (IIIa).** A mixture of 10 g (0.03 mole) of sulfide I [11], 1.32 g (0.03 mole) of acetaldehyde, and 70 ml of dry benzene was heated with a catalytic amount of *p*-toluenesulfonic acid in a tube at 80-90° for 2 h, after which the liquid was removed from the resulting solution by distillation, and the residue was recrystallized from ethanol to give 0.75 g (41%) of a product with mp 125° (mp 126° [8]).

**2,4,6-Triphenyl-1,3,5-trithiane (IIIb).** A mixture of 10 g of sulfide I, 3.25 g (0.03 mole) of benzaldehyde, 70 ml of benzene, and a catalytic amount of *p*-toluenesulfonic acid was refluxed with stirring with removal of the water in a Dean-Stark trap. The starting sulfide dissolved completely, and a precipitate began to form after 40-50 min. At the end of the reaction, the mixture was cooled and filtered, and the solid material was recrystallized from xylene to give IIIb, with mp 232-233° (mp 230-231° [12]), in 100% yield. Found: C 69.3; H 4.9; S 26.5%.  $\text{C}_{24}\text{H}_{18}\text{S}_3$ . Calculated: C 68.8; H 4.9; S 26.2%.

**2,4,6-Tri(*p*-chlorophenyl)-1,3,5-trithiane (IIIc).** This compound, with mp 188-189° (from xylene) (mp 195° [5], 190° [13]), was obtained in quantitative yield by the method used to prepare IIIb.

**2,4,6-Tri(*p*-nitrophenyl)-1,3,5-trithiane (III d).** This compound, which was obtained as a pale-rose powder with mp 195-197°, was obtained in quantitative yield by the method used to prepare IIIb. Found: N 8.4; S 19.1%.  $\text{C}_{24}\text{H}_{15}\text{N}_3\text{O}_6\text{S}_3$ . Calculated: N 8.4; S 19.2%.

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ROLE OF THE 3d ORBITALS OF SULFUR  
IN THE THIAPYRYLIUM CATION

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The electronic structure of the thiapyrylium cation with allowance for and neglect of the 3d orbitals of sulfur was investigated by the self-consistent field MO LCAO method within the CNDO/2 (complete neglect of differential overlap) approximation. Inclusion of the 3d AO of sulfur in the basis leads to slight redistribution of the electron density to favor equalization of the charges on the carbon atoms. A qualitative correlation of the calculated populations of the atoms with the chemical shifts of the PMR spectrum of the thiapyrylium cation was obtained.

It was recently observed [1] that the PMR spectrum of the thiapyrylium cation (I) differs substantially from the spectrum of its analogs, pyrylium (II) and ethylpyridinium (III) cations (Table 1). The superimposition of the signals of the  $\gamma$  and  $\beta$  protons of I is explained by equality of the charges on the  $\gamma$ - and  $\beta$ -carbon atoms. In the opinion of Yoneda and co-workers, the reason for this peculiar electronic structure of the thiapyrylium cation is strong interaction of the 2p orbitals of the carbon atoms with the vacant 3d orbitals of sulfur. A conclusion regarding the substantial role of the 3d AO of sulfur in the thiapyrylium cation was drawn on the basis of a calculation of its electronic structure by the extended Huckel method (EHM).

It is known that the EHM, without self-consistency with respect to the charges and configurations, usually poorly conveys the charge distribution in heteroatomic ionic molecules [2]. A comparison of the charge distribution in I and II, obtained by the EHM, confirms this fact. In the thiapyrylium cation the calculated negative charge on the heteroatom and the contribution of carbonium valence structures to resonance are of a high order of magnitude (Table 2), despite the fact that the sulfur atom has a lower electronegativity than oxygen.

The EHM displays disadvantages especially markedly in the study of the problem of the 3d AO of elements of the third period. The absence of reliable methods for evaluation of the parameters for the outer vacant 3d orbitals usually leads to a considerable overestimation of their role in the formation of chemical bonds [4]. Ac-

TABLE 1. Chemical Shifts ( $\delta$ ) of the PMR Spectra of Thiapyrylium (I), Pyrylium (II), and N-Ethylpyridinium (III) Cations in Trifluoroacetic at 60 MHz

	I	II	III
$\alpha$ -H	10,20	9,70	8,81
$\beta$ -H	9,11	8,53	8,22
$\gamma$ -H	9,11	9,36	8,60

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