## INTERACTION OF CERTAIN $\alpha$ -DICARBONYL COMPOUNDS WITH ETHANEDITHIOL AND STERIC STRUCTURE OF THE PRODUCTS FORMED

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 $\alpha$ -Dicarbonyl compounds in the reaction with 1, 2-ethanedithiol give mono and dimercaptals [1-4]. Compounds with a tetrathiadecalin structure, isomeric to 2, 2'-bis-1, 3-dithiolane, are not formed. In an attempt to produce 1, 4, 5, 8-tetrathiadecalin by directed synthesis, it was found that the only product in reactions of glyoxal sulfate [5] and 2, 3-dichloro-1, 4-dioxane [6] with ethylene glycol is naphthodioxane. The reactions of glyoxal sulfate and 2, 3-dichloro-1, 4-dioxane with 1, 2-ethanedithiol that we conducted under conditions of formation of naphthodioxane led only to bis-1, 3-dithiolane, described earlier [2, 7]. A mercaptal is not formed from diacetyl and 1, 2-ethanedithiol as a result of oxidation of the diketone by the mercaptan [4]. In the reaction of diacetyl with thiophenol, only diphenyl disulfide was isolated [8]. We succeeded in producing 2-methyl-2-acetyl-1, 3-dithiolane by conducting the reaction in water acidified with H<sub>2</sub>SO<sub>4</sub>. An analogous monomercaptal is also formed from benzil [3]. We were interested in using a mixed diketone in this reaction. The reaction with 1-phenylpropane-1, 2-diol, however, led to a compound with a bis-1, 3-dithiolane structure and 2-ethyl-2-phenyl-1, 3-dithiolane. The latter should be considered as a result of reduction of the dicarbonyl compound by the mercaptan. Thus, tetrathiadecalin structures, in contrast to oxygen-containing compounds, are not realized under these conditions.

We used the method of dipole moments (DM) to study the steric structure of certain 1, 3-dithiolanes (I)-(V).

(I) - (III)  $R^1 = R^2 = H (I)$   $R^1 = H, R^2 = C_6 H_5 (II)$  $R^1 = CH_3, R^2 = C_6 H_5 (III)$ 

(IV), (V) R=CH<sub>3</sub>(IV), C<sub>6</sub>H<sub>5</sub>(V)

On the basis of the PMR data [9], rotational spectra [10], as well as x-ray diffraction stydy [11], a halfchair structure (a) is assigned to the 1,3-dithiolane ring. However, after investigating 2-phenyl- and 2p-chlorophenyl-1,3-dithiolanes by the method of DM and Kerr constants, the authors of [12] arrived at the conclusion that the dithiolane ring is an envelope (b) with a small angle of the fold



The DM method does not permit an unambigous selection to be made between conformers (a) and (b). But if we use the effective vector of the DM of the dithiolane ring in the calculation of the theoretical values of the DM, then regardless of whether it is a half-chair or a highly flattened envelope, the effective DM practically coincides both in direction (dissectrix of the angle S-C-S) and in magnitude for the two structures.

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TABLE 1

Compound	DM <sub>calc,</sub> D, gauche	DM <sub>exp</sub> , D	Compound	DM <sub>calc</sub> , D		
				R	S	DMexp, D
(I) (II) (111)	1,40 1,33 1,33	1,35 1,50 1,37	(IV) (V)	3,75 3,72	2,77 3,03	2,71 3,36

Such an approach is justified in the case when the question either of the mutual orientation of the dithiolane rings or of the arrangement of the exocyclic polar substituents at the second carbon atom is resolved.

To calculate the effective vector of the ring we used the experimental DM of 2-phenyl-1, 3-dithiolane (1.34 D) and 2-p-chlorophenyl-, 3-dithiolane (2.4D) [13]. The value found was 1.05 D, assuming a tetra-hedral arrangement of the bonds at the  $C_2$  atom. For bis-1, 3-dithiolanes (I)-(III), the gauche- and transforms were taken into consideration. Shielded forms were not considered as less real.



A comparison of the experimentally obtained values with those calculated theoretically (Table 1) permits us to consider that compounds (I) - (III) exist in the gauche-form. Table 1 does not cite the DM of the transforms, since for compounds (I) - (III) they are close to zero. It should be noted that a gauche-structure was also assigned to bis-1, 3-dioxalane by the PMR method [14]. The PMR spectrum of bis-1, 3-dithiolane takes the form analogous to the spectrum of bis-1, 3-dioxalane [15], characteristic of systems of the type of AA'BB'. The conclusions on the gauche-form of bis-1, 3-dithiolane compounds do not contradict the generally accepted stereochemical concepts. The recently advanced concept of the "gauche-effect," [16-18], according to which compounds containing neighboring polar bonds and (or) unshared electron pairs have a minimum energy in the presence of a maximum gauche-interaction is probably also extended to bis-1, 3-dithio-lane systems.

Compounds containing a carbonyl group exist primarily in a shielded conformation [19]. We also considered such conformers for compounds (IV) and (V)



The conformers conditionally denoted as R and S are characterized by shielding of the carbonyl group by a methyl(phenyl) group in the molecule and by C-S bonds of the ring, respectively. From Table 1 it is evident that for 2-phenyl-2-benzoyl-1, 3-dithiolane (V), the conformational equilibrium is practically entirely shifted in the direction of the S-conformer. Compound (IV) is a conformational mixture of isomers containing  $\sim 50\%$  of the R and 50% of the S-conformer.

The question of the conformational equilibria induced by rotation around the  $C_{sp^3}-C_{sp^2}$  bond, even for acyclic molecules, is not entirely clear, since the question of the stability of various shielded conformers has not been resolved unambiguously. In our case the fraction of the S-conformer is substantial, although for acyclic molecules the shielding of the sulfide sulfur by the carbonyl group is not characteristic [19]. One of the evidences in support of the S-conformer may be the presence of conjugation in the system -S-C-C-R [20]. Such hyperconjugation can shift the equilibrium in the direction of the S-conformer.

I II R O

## EXPERIMENTAL METHOD

Compound (II) was synthesized according to [1], mp 109-111°. 2-Phenyl-2-benzoyl-1, 3-dithiolane (V) was produced according to the method of [3], mp 94-95°.

TABLE 2

Compound	α	β	P <sub>op</sub> ,	μ, D
(I)	1,0451	0,0921	37,5606	1,35
(II)	1,0830	0,2170	46,1882	1,50
(III)	0,8178	0,1312	38,5875	1,37
(IV)	7,7333	0,1387	231,3835	3,36
(V)	3,1172	0,3229	150,2214	2,71

<u>2,2'-Bis-1,3-dithiolane (I)</u>. a) A 1 g portion of glyoxal sulfate in 5 ml of water was boiled for 4 h with 3.2 ml of 1,2-ethanedithiol. After cooling, the reaction mass was diluted with 10 ml of water. The product was extracted with  $CHCl_3$ , and dried over  $CaCl_2$ . After distilling off the solvent, the residue was purified by recrystallization (ethanol) or sublimation under vacuum. White plates were obtained, yield 0.35 (40%), mp 135-136°, cf. [7].

b) The reaction of 2, 3-dichloro-1, 4-dioxane with 1, 2-ethanedithiol was conducted under the conditions of [6]. White crystals were obtained, mp 135-136°. A mixed sample with the substance produced according to method a) gave no depression of the melting point.

<u>2-Methyl-2-acetyl-1,3-dithiolane (IV).</u> The reaction was conducted according to the method a), on the basis of 1 ml diacetyl, 1.95 ml 1,2-ethanedithiol, and 5 ml water, slightly acidified with  $H_2SO_4$ . We obtained 0.8 g (42%) of a colorless liquid, bp 74-76° (2 mm);  $n_D^{20}$  1.5522;  $d_4^{20}$  1.1984. Found: C 44.79; H 5.98; S 39.62%.  $C_6H_{10}OS_2$ . Calculated: C 44.44; H 6.17; S 39.50%. PMR spectrum ( $\delta$ , ppm): 1.80 (3H, singlet, CH<sub>3</sub>), 2.26 (3H, singlet, CH<sub>3</sub>CO), 2.96 (4H, singlet, ring protons).

<u>2-Methyl-2'-phenyl-2, 2'-bis-1, 3-dithiolane (III).</u> A total of 4 ml of  $BF_3 \cdot (C_2H_5)_2O$  was added slowly in parts with cooling with cold water to 3.7 ml of 1-phenylpropane-1, 2-diole and 4.12 ml 1, 2-ethanedithiol in 10 ml glacial CH<sub>3</sub>COOH. After 12 h of standing, two layers were formed in the reaction mass. The lower colorless layer was removed and placed in a refrigerator. After several days, white plates crystallized out, yield 3g, mp 94-95° (from ethanol). Found: C 52.00; H 5.34; S 42.67%. C<sub>13</sub>H<sub>16</sub>S<sub>4</sub>. Calculated: C 52.24; H 5.33; S 42.50%. After redistillation, 2g of 2-ethyl-2-phenyl-1, 3-dithiolane was obtained from the filtrate [21], bp 118-119° (1 mm); n<sub>D</sub><sup>25</sup> 1.6046. PMR spectrum ( $\delta$ , ppm): 0.92 (3H, triplet, CH<sub>3</sub>), 2.37 (2H, quartet, -CH<sub>2</sub>-), 2.8 (4H, singlet, ring protons).

The dipole moments were measured in benzene at 25°. The experimental DM were calculated according to the Guggenheim-Smith method. The coefficients of the calculation equations are cited in Table 2.

## CONCLUSIONS

1. 1-Phenylpropane-1, 2-dione gives a bis-1, 3-dithiolane derivative in the reaction with 1, 2-ethanedithiol, analogously to glyoxal and phenylglyoxal. Diacetyl and benzil give the corresponding monomercaptals.

2. 1-Phenylpropane-1, 2-dione is reduced in the reaction with 1, 2-ethanedithiol, forming 2-ethyl-2-phenyl-1, 3-dithiolane.

3. Bis-1, 3-dithiolane derivatives of 1-phenylpropane-1, 2-dione, glyoxal, and phenylglyoxal exist in the gauche-form; 2-keto-1, 3-dithiolanes from diacetyl and benzil have shielded structures with predominance of the S-conformer.

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