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# SYNTHESIS AND STEREOCHEMISTRY OF SOME NEW 1,3-OXATHIANES OBTAINED FROM 1,4-DIMERCAPTOTHREITOL

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**ABSTRACT.** The synthesis and the stereochemistry of some new 1.3-oxathianes with *cis* decaline skeleton are disscused. The NMR investigations revealed the anancomeric structure of compounds.

## INTRODUCTION

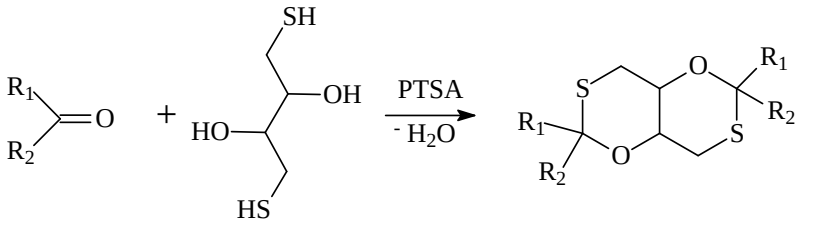
In the last years [1-7] the 1,3,5,7-tetraoxadecaline (TOD) system was intensively studied, beeing used as "building-block" in a series of macromolecular host compounds. The TOD system exists in *trans* (rigid, obtained from erythritol) and *cis* (flipping, yielded from threitol) configurations.

The similar tetraaza [8] and dioxadiaza [9] systems were also investigated, similar results being reported.

It was considered of interest to study the stereochemistry of the 1,5-dioxa-3,7-dithiadecaline, containing two 1,3-oxathiane units because of two main resons: our interest in the stereochemistry of 1,3-oxathiane derivatives (including the ring-chain tautomerism) [10-12] and the "construction" of macrocycles using these derivatives as substrates.

## RESULTS AND DISCUSSION

The compounds were obtained using the condensation reaction between 1,4-dimercaptothreitol (1) and *p*-nitrobenzaldehyde and *p*-nitroacetophenone, respectively (Scheme 1).



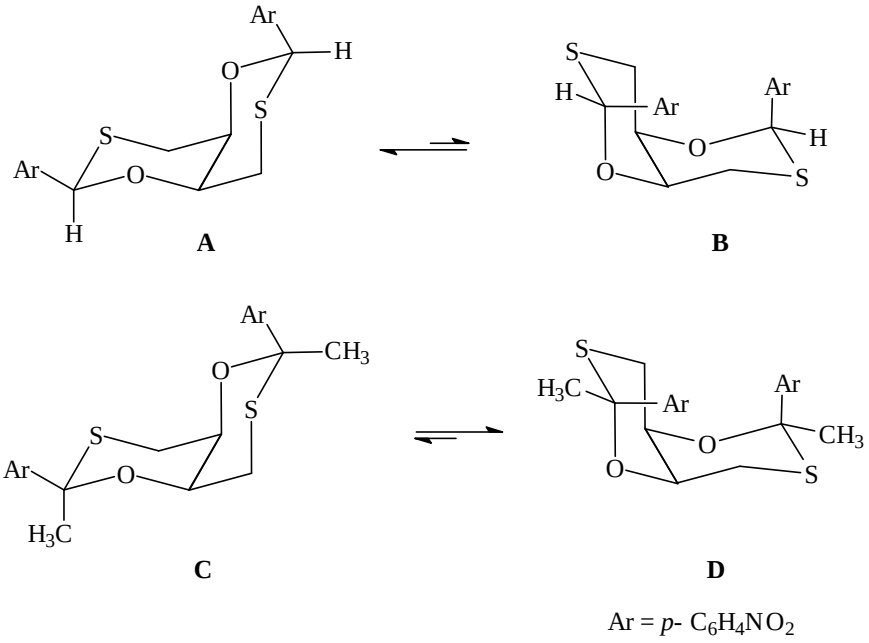

$R_1 = H \quad R_2 = p\text{—}C_6H_4\text{—}NO_2$ **2**

$R_1 = CH_3 \quad R_2 = p\text{—}C_6H_4\text{—}NO_2$ **3**

**Scheme 1**

The conformational analysis for compounds **2** and **3** shows anancomeric structures. For compound **2,** the conformational equilibrium is shifted towards the conformation A, with the phenyl groups in equatorial position, whereas compound **3** prefers the conformer D with the phenyl groups in axial orientation.

The anancomeric structure of the compounds determines the recording in the NMR spectra of different signals for the axial and equatorial protons of 1,3-oxathiane rings.




**Scheme 2**

As an example, the $^{1}$H-NMR spectrum of compound **3** (Figure **1**) shows an AB system for the aromatic protons ( $\delta$ =8.21, $\delta$ =7.68 ppm) and a multiplet ( $\delta$ =4.34 ppm) belonging to the protons 9 and 10. The spectrum also exhibits two doublets of doublets ( $\delta_{ax}$=3.18, $\delta_{eq}$=3.07 ppm) associated with the methylene protons of the two $CH_2S$ groups and a singlet ( $\delta$ =1.94 ppm) for the methyl groups.

## CONCLUSIONS

The NMR investigations of compounds **2,3** revealed anancomeric structures due to the presence of different substituents in positions 2 and 6. The aryl groups prefer the equatorial orientation when they are the unique substituents at positions 2 and 6 and the axial position when the second substituent at these positons are methyl groups (compound **3**).

## EXPERIMENTAL

$^{1}$H and $^{13}$C spectra were recorded at room temperature, using $CDCl_3$ as solvent, in 5 mm tubes, on a Bruker NMR spectrometer, equipped with a multinuclear head, operating at 300 MHz for protons and at 75 MHz for carbon atoms.

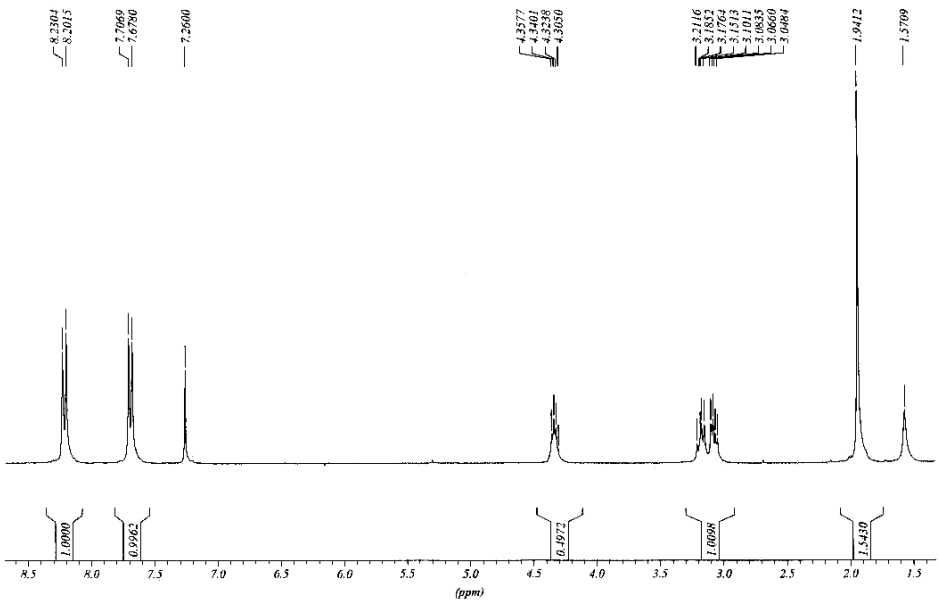



**Fig. 1**. *$^1$H NMR spectrum of compound **3***

Melting points were measured with Kleinfeld Apotec melting point apparatus and are uncorrected.

New compounds **2,3** general procedure

Stoechiometric amounts of 1,4-dithiathreitol and carbonyl compound (0.05 mol) with catalytic amounts of *p*-toluenesulphonic acid (0.05 g) were solved in 20 ml toluene and refluxed until 80% of the theoretical amount of water was separated by the Dean Stark trap. After cooling at room temperature, the catalyst was neutralized (under stirring 0.5 h) with KOH 0.1 M (20 ml). The organic layer was washed twice with 20 ml water. The toluene was removed and the 1.3-oxathiane compounds were purified by flash chromatography.

*2.6-Di(p-nitrophenyl)-1.5-dioxa-3.7-dithia-biciclo[4.4.0]decane (cis, RR, SS) **2***

White crystals, m.p. 235.1-235.2$^0$C. Yield 27%. $C_{18}H_{16}O_6S_2N_2$ found C 51.20, H 3.53, N 6.81, S 15.08 , required C 51.42, H 3.84, N 6.66, S 15.25

$^1$H NMR ($CDCl_3$, δppm): 3.2-3.4 (4H, dd, overlapped signals, 4, 8-$CH_2$), 4.50 (2H, m, 9, 10-H), 6.24 (2H, s, 2,6-H), 7.63 (4H, d, J = 8.7 Hz, aromatic protons), 8.21 (4H, d, J = 8.7 Hz, aromatic protons); $^{13}$C NMR ($CDCl_3$, ppm): 35.46 ($C^{4,8}$), 84.37 ($C^{9,10}$), 85.73 ($C^{2,6}$), 124.20, 127.79 (tertiary aromatic carbon atoms), 148.59, 159.31 (quaternary aromatic carbon atoms)

*2.6-Dimethyl, 2.6-di(p-nitrophenyl)-1.5-dioxa-3.7-dithia-biciclo[4.4.0]decane (cis, RR, SS) **3***

White crystals, m.p. 119-120$^0$C. Yield 33%. $C_{20}H_{20}O_6S_2N_2$ found C 53.73, H 4.25, N 6.18, S 14.52, required C 53.46, H 4.49, N 6.25, S 14.30

$^{1}$H NMR ($CDCl_3$, δppm): 1.94(6H, s, 2,6-$CH_3$), 3.07 (2H, dd, J = 10.5, J'= 5.2 Hz, 4,8-$H_{eq}$), 3.18 (2H, dd, J = 10.5, J'= 5.2 Hz, 4,8-$H_{ax}$), 4.34 (2H, m, 9, 10-H), 7.68 (4H, d, J = 8.7 Hz, aromatic protons), 8.21 (4H, d, J = 8.7 Hz, aromatic protons); $^{13}$C NMR ($CDCl_3$, ppm): 32.48 (2,6-$CH_3$) 35.35 ($C^{4,8}$), 83.04 ($C^{9,10}$), 95.48 ($C^{2,6}$), 123.86, 126.15 (tertiary aromatic carbon atoms), 147.33, 154.02 (quaternary aromatic carbon atoms)

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