

**o.m12.p9** **Some Hemithio-dithioacetal Derivatives of Tetrahydropyran.** J. Kansikas<sup>a</sup>, K. Sipilä<sup>b</sup>, <sup>a</sup>Laboratory of Inorganic Chemistry and <sup>b</sup>Laboratory of Organic Chemistry, Department of Chemistry, University of Helsinki, POBox 55, 00014, University of Helsinki, Finland.

Keywords: hemithioacetal, dithioacetal, diastereoisomer.

The structures of 2-phenyl-1-phenylthio-1-(2-tetrahydropyran-2-ylthio)propan-2-ol, C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub> (**1**), 2-naphthylthio-1-phenyl-2-(2-tetrahydropyran-2-ylthio)ethanol, C<sub>23</sub>H<sub>24</sub>O<sub>2</sub>S<sub>2</sub> (**2**) and 2-[1-butyl-1-(2-naphthylthio)-pentylthio]-tetrahydropyran, C<sub>24</sub>H<sub>33</sub>OS<sub>2</sub> (**3**) are determined.

Compound **1** was synthesized from 2-(phenylthiomethylthio)tetrahydropyran<sup>1</sup> and separated from the mixture of diastereoisomers with HPLC. The starting material for **2** and **3**, 2-(2-naphthylthiomethylthio)tetrahydropyran, was prepared from 2-(chloromethyl)naphthylsulfide<sup>2</sup> and 2-(acetylthio)tetrahydropyran<sup>1</sup>. The deprotonations were performed with LDA (**1** and **2**) or *n*-BuLi (**3**) and the anions quenched with acetophenone (**1**), benzaldehyde (**2**) or 1-bromobutane (**3**) in tetrahydrofuran at 195 K under argon atmosphere. The crystals for the structure determinations were obtained after several slow recrystallizations from ethanol.

Tetrahydropyran derivatives **1** and **2** have three chiral carbon atoms each in the -O-C\*-S-C\*(C\*)-S- moieties. The configuration for **1** is *rel-SRR* and for **2** *SRR* in the respective order of atoms. In compound **3** there is one chiral carbon atom in the tetrahydropyran ring and the crystals are racemic. Structures **1** [*a*=9.244(4), *b*=19.239(5), *c*=10.682(4) Å and  $\beta$ =93.37(3)°], **2** [*a*=9.903(2), *b*=10.564(2), *c*=10.201(2) Å and  $\beta$ =107.79(3)°] and **3** [*a*=10.778(2), *b*=23.743(5), *c*=9.017(2) Å and  $\beta$ =90.22(3)°] at 193 K will be compared to another diastereoisomer of 2-phenyl-1-phenylthio-1-(2-tetrahydropyran-2-ylthio)propan-2-ol (**4**)<sup>1</sup> and the four diastereoisomers of 1-phenyl-2-phenylthio-2-(2-tetrahydropyran-2-ylthio)ethanol (**5-8**)<sup>3,4</sup>.

The sulfur side chain in the tetrahydropyran ring is axial in compounds in **1**, **2**, **7** and **8**. An intramolecular hydrogen bond is present in compounds **4**, **5** and **6**.

Compounds **1**, **3** and **7** crystallize in the space group *P2<sub>1</sub>/c*, compound **2** in *P2<sub>1</sub>*, compound **4** in *P2<sub>1</sub>/n*, compounds **5** and **6** in *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* and compound **8** in *Pna2<sub>1</sub>*.

Compounds **2**, **5**, **6** and **8** crystallize as conglomerates of enantiomeric crystals. The selection of the given enantiomer is based on the near zero value of the Flack parameter.

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**o.m12.p10** **X-ray Study of the Products of Urotropin N-alkylation in Water Catalysed by Tetrafluoroborate Anion.** E. Kosterina, V. Rybakov, S. Troyanov, L.A. Aslanov, Department of Chemistry, Moscow State University, Moscow, Russia, e-mail address: kat@struct.chem.msu.ru.

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The interactions of urotropin with sodium tetrafluoroborate (system I) and tetrafluoroboric acid (system II) in water solution were studied. According to the data of X-ray crystal structure determination, the formation of methylurotropinium tetrafluoroborate, [(CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>(CH<sub>3</sub>)]BF<sub>4</sub>, (system I) and ethylurotropinium tetrafluoroborate, [(CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>(C<sub>2</sub>H<sub>5</sub>)]BF<sub>4</sub> (system II) was established.

The compounds have the following crystallographic characteristics: for system I — orthorhombic, space group *Pnma*, *a* = 11.970(3) Å, *b* = 8.746(1) Å, *c* = 9.921(3) Å, *V* = 1038.6(4) Å<sup>3</sup>, reflections/parameters ratio 1018/124, *R<sub>i</sub>* = 0.045; for system II — orthorhombic, space group *Pnma*, *a* = 7.987(1) Å, *b* = 6.527(1) Å, *c* = 20.659(4) Å, *V* = 1077.0(3) Å<sup>3</sup>, reflections/parameters ratio 1190/134, *R<sub>i</sub>* = 0.059. In the both structures, alkylurotropinium cation and BF<sub>4</sub><sup>-</sup> anion are situated on a crystallographic mirror plane. The crystal structures, the features of syntheses in comparison with the known data for analogous compounds are discussed in the report in detail.