**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.

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The structures of 2-phenyl-1-phenylthio-1-(2-tetra-hydropyranylthio)propan-2-ol,  $C_{20}H_{24}O_2S_2$  (1), 2-naphthyl-thio-1-phenyl-2-(2-tetrahydropyranylthio)ethanol,

 $C_{23}H_{24}O_2S_2$  (2) and 2-[1-butyl-1-(2-naphthylthio)-pentylthio]-tetrahydropyran,  $C_{24}H_{33}OS_2$  (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-napthylthiomethylthio)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 1bromobutane (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-tetrahydropyranylthio)propan-2-ol (**4**)<sup>1</sup> and the four diastereoisomers of 1-phenyl-2-phenylthio-2-(2-tetrahydropyranylthio)ethannol (**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  $P2_1/c$ , compound 2 in  $P2_1$ , compound 4 in  $P2_1/n$ , compounds 5 and 6 in  $P2_12_12_1$  and compound 8 in  $Pna2_1$ .

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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[2] Tuleen, D.L. and Buchanan, D.N. AReactions of Methyl β-Napthyl Sulfides with N-Halosuccinimides@ J. Org. Chem., (1967), 32: 495-502.

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[4] Kansikas, J. and Sipilä, K. AStereochemical Studies on four Diastereomers of 1-Phenyl-2-phenylthio-2-(tetrahydropyran-2-ylthio)ethanol.@, 18th International Symposium on the Organic Chemistry of Sulfur, Abstracts, (1998), 63. o.m12.p10 X-ray Study of the Products of Urotropin Nalkylation 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. Keywords: catalytic N-alkylation, urotropin, X-ray single crystal structure.

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,  $[(CH2)_6N_4(CH_3)]BF_4$ , (system I) and ethylurotropinium tetrafluoroborate,  $[(CH2)_6N_4(C_2H_5)]BF_4$  (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.