Some Hemithio-dithioacetal Derivatives of Tetrahydropyran. J. Kansikas, K. Sipilä, Laboratory of Inorganic Chemistry and 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-tetrahydropyranyllithio)propan-2-ol, C₉H₁₄O₂S (1), 2-naphthylthio-1-phenyl-2-(2-tetrahydropyranyllithio)ethanol, C₁₃H₁₈O₂S₂ (2) and 2-[1-butyl-1-(2-naphthylthio)-pentylthio]-tetrahydropyran, C₁₄H₂₄O₂S₄ (3) are determined.

Compound 1 was synthesized from 2-(phenylthio)tetrahydropyran and separated from the mixture of diastereoisomers with HPLC. The starting material for 2 and 3, 2-(2-naphthylthio)ethyltetrahydropyran was prepared from 2-(chloromethyl)naphthylsulfide and 2-(acetylthio)tetrahydropyran. The deprotonations were performed with LDA (1 and 2) or n-BuLi (3) and the anions quenched with acetonaphone, benzaldehyde 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 β=93.37(3)°], 2 [a=9.903(2), b=10.564(2), c=10.201(2) Å and β=107.29(3)°] and 3 [a=10.778(2), b=23.743(5), c=9.017(2) Å and β=90.22(3)°] at 193 K will be compared to another diastereoisomer of 2-phenyl-1-phenylthio-1-(2-tetrahydropyranyllithio)propan-2-ol (4) and the four diastereoisomers of 1-phenyl-2-phenylthio-2-(2-tetrahydropyranyllithio)ethanol (5-8).

The sulfur side chain in the tetrahydropyran ring is axial in compounds 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 P₂₁/c, compound 2 in P₂₁, compound 4 in P₂₁/n, compounds 5 and 6 in P2₁/2₁/2 and compound 8 in Pna2₁.

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.


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.

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(CH₃)]BF₄, (system I) and ethylurotropinium tetrafluoroborate, [(CH₂)₄N(C₂H₅)]BF₄ (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) Å³, reflections/parameters ratio 1018/124, R₁ = 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) Å³, reflections/parameters ratio 1190/124, R₁ = 0.059. In the both structures, alkylurotropinium cation and BF₄⁻ 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.