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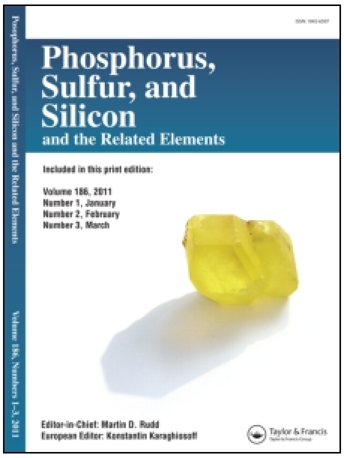

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REACTIONS OF 3-THIA(SELENA)PENTANE-1,5-DIONES WITH LEWIS ACIDS

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3-Thia(selena)pentane-1,5-diones react with Lewis acids by heteroatom. In these reactions soft Lewis acids such as tin tetrachloride and antimony pentachloride form adducts but hard Lewis acid such as phosphorus pentachloride oxidizes chalcogen atom of 3-thia(selena)-pentane-1,5-dione. Carbon analogues of these diketones form pyrylium salts in the reactions with these Lewis acids.

Keywords: 3-thiapentane-1,5-diones, 3-selenapentane-1,5-diones, pentane-1,5-diones, Lewis acids.

INTRODUCTION

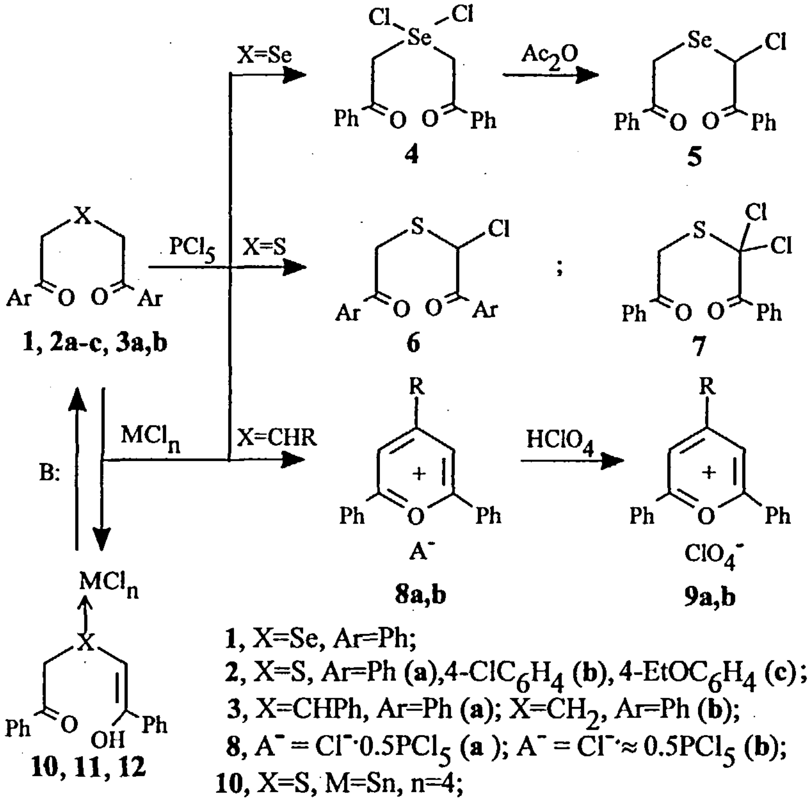
3-Thia(selena)pentane-1,5-diones have two possible reaction centers for attack by Lewis acids. We showed previously [1,2], that 3-selenapentane-1,5-dione formed 3,3-dichloride 4 under the action of PCl_5 in dichloromethane, but sulfur analogue of diketone 1 underwent Stiwens rearrangement leading to corresponding α-chloroderivatives 6, 7. Pentane-1,5-diones 3 reacted with PCl_5 by carbonyl groups and formed corresponding pyrylium salts 8 [1,2].

RESULTS AND DISCUSSION

We suggest that 3-thia(selena)pentane-1,5-diones form heteroatom adducts as intermediates at the first stage of the reaction with PCl_5.

Such intermediates are supposed to be very unstable because organic sulfides and selenides are soft Lewis bases but PCl_5 is hard Lewis acid. So the oxidation process is observed.

It is possible that adducts of 3-thia(selena)pentane-1,5-diones with soft Lewis acids are more stable. This fact can confirm above-mentioned supposition. In fact, tetrachlorostannates <u>10</u>, <u>11</u> and pentachloroantimonate <u>12</u> are isolated from the reaction of selenide <u>1</u> with $SnCl_4$ and $SbCl_5$ and from the reaction of sulfide <u>2</u> with $SnCl_4$ in absolute dichloromethane.



1, X=Se, Ar=Ph;
2, X=S, Ar=Ph (**a**),4-ClC_6H_4 (**b**), 4-$EtOC_6H_4$ (**c**);
3, X=CHPh, Ar=Ph (**a**); X=CH_2, Ar=Ph (**b**);
8, $A^- = Cl^-\cdot 0.5PCl_5$ (**a**); $A^- = Cl^-\cdot\approx 0.5PCl_5$ (**b**);
10, X=S, M=Sn, n=4;
11, X=Se, M=Sn, n=4;
12, X=Se, M=Sb, n=5.

SCHEME 1

It is to be noted that pentane-1,5-diones <u>3</u> react with these Lewis acids as well as with PCl_5 producing pyrylium salts which are identified in the form of corresponding perchlorates.

Spectral data show that one carbonyl group of these complexes is enolized. Valence oscillation bands of carbonyl group at 1680-1660 cm^{-1} are observed in IR spectra of all synthesized complexes. This band appears in the approximately same field as the band of initial diketones but its intensity in spectra of complexes is considerably less. Besides, valence oscillation bands of hydroxyl at 3500-3600 cm^{-1} and double C=C-bond at 1604-1624 cm^{-1} also appear in IR spectra of complexes.This fact allows to draw a conclusion about existence of these complexes in enol form.

Enol form of complexes confirms the donor-acceptor bond between chalcogen and tin or antimony atoms: π-p conjugation is possible in such structures and it compensates the decrease of electron density at chalcogen atom. Besides the affinity of chalcogens to studied acceptors (class B) is increased in the order $O<<S\approx Se\approx Te$, because Sn (IV) and Sb (V) are soft Lewis acids, oxygen containing ligands are hard Lewis bases, whereas sulfur, selenium and tellurium are soft Lewis bases. So the coordination between these elements and oxygen is doubtful. Although PCl_5 is hard Lewis acid (class A) it is probable that enolization stabilizes intermediate, which is complex of 3-chalcogenapentane-1,5-diones with PCl_5.

^1H NMR spectra of tetrachlorostannates <u>10</u> and <u>11</u> indicate their low stability in solutions and their ability to easy hydrolysis. Spectra of these compounds have signals of initial diketones, whereas signals of trace amounts of water in CD_3CN are disappeared, however new wide intensive signal is appeared in the field 6,6-6,9 ppm, which is identified as protons of $SnCl_4$ hydrolisys products. Antimonate <u>12</u> is more stable to hydrolisys and in its ^1H NMR spectrum there are signals of phenyl group (10H, m) and signals of enol form protons at 5.68 ppm (4H, m).

Although adducts <u>10-12</u> are isolated and characterized they are unstable and we observed its destruction in some days. Besides the treating of compounds <u>10-12</u> with ethanolic solution of triethylamine easy leads to initial chalcogenides <u>1,2</u> with high yields.

Thus, Lewis acids attack heteroatom of 3-thia(selena)pentane-1,5-diones, whereas carbon analogues of these diketones form pyrylium salts under the same conditions.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded at 80 MHz on Varian FT-80A spectrometer using tetramethylsilane as internal reference. The IR spectra were recorded using Specord-M80 instrument.

Typical procedure for the reaction of 3-thia(selena)pentane-1,5-diones with tin tetrachloride or antimony pentachloride.

Tin tetrachloride (20 mmol) is added under stirring to the solution of 10 mmol of diketone **1** or **2** (or antimony pentachloride is added under stirring and cooling to the solution of 10 mmol of diketone **1**) in 30 ml of absolute dichloromethane. Immediately precipitated white powder is filtered, washed with dichloromethane and dried. Adducts **10**,**11**,**12** are unstable and are stored above P_2O_5.
10: yield 75%, m.p. 98-101°C; Found,% (Calc.,%): C 36.20 (36.76); H 2.66 (2.87); S 6.03 (5.91); Cl 26.70 (26.76); Sn 28.38 (27.62).
11: yield 98%, m.p. 143-145°C Found,% (Calc.,%): C 33.26 (32.86); H 2.44 (2.73); Cl 23.50 (22.78); Sn 26.07 (26.51).
12: yield 62%, m.p. 74-76°C. Found,% (Calc.,%): C 31.18 (31.19); H 2.29 (2.71); Cl 28.80(29.02); Sb 18.80 (17.36).

Typical procedure for the reaction of pentane-1,5-diones with tin tetrachloride or antimony pentachloride.

Tin tetrachloride or antimony pentachloride (50 mmol) is added under stirring to the solution of diketone **3a** or **3b** (10 mmol) in 30ml of absolute dichloromethane. Yellow crystals, which are precipitated after 1.5 h are filtered, washed with ether and dried. Synthesized salts **8** are dissolved in hot 70 % $HClO_4$. After the cooling of solution perchlorate **9** is precipitated, filtered and washed with ether. All physical constants of salt **9** are the same as described [3].

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