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Synthesis of Small-Ring Sulfur Compounds Containing Germanium and Tin

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SYNTHESIS OF SMALL-RING SULFUR COMPOUNDS CONTAINING GERMANIUM AND TIN

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Abstract Synthesis of some novel types of four-membered organosulfur compounds containing germanium and tin by [2+2]cycloaddition of germanethione $(R_1R_2Ge=S)$ and stannanethione $(R_1R_2Sn=S)$ intermediates is reported.

1,2,4,3-Trithiametallolanes (2) were synthesized by the reaction of 1,2,3,4,5-tetrachalcogenametallolanes (1)¹ with diphenyldiazomethane followed by dechalcogenation with a trivalent phosphorus reagent. 3 and 4 were reacted with $P(NMe_2)_3$ to give 2.

36%

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16%

2 (Ar=Tip, M=Sn) reacted with dimethylacetylene dicarboxylate (DMAD) upon heating to give a new type of sulfur heterocycles 5 and 6 containing tin, suggesting the intermediacy of Tb(Tip)Sn=S and Tb(Tip)SnS₂. 2(M=Ge) underwent a similar reaction with DMAD.

Reaction of germylene (7, M=Ge) or stannylene (7, M=Sn), generated *in situ* in solutim, with styrene episulfide followed by addition of thiocumulenes (S=C=Y; Y=S, NPh) afforded novel heterocycles 9 via [2+2]cycloaddition of 6 with the thiocumulenes.

Dechalcogenation of 1 (Ar=Mes) with triphenylphosphine (3 eq.) gave *cis*-10 stereospecifically.

Some structures of newly obtained 5, 9, and 10 were determined by X-ray crystallography.

Some four-membered selenium compounds of similar structures were also synthesized.

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