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A.HIGH YIELD SYNTHESIS OF METHYLTHIO AND METHYLSELENO DERIVATIVES OF SILICON, GERMANIUM, AND TIN

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The use of complex aluminates as synthetic reagents has been studied considerably in the last few years. Recently phosphino-,[1,2] alkylphosphino-,[3] silylphosphino-,[4] arsino-,[5,6] alkylarsino-,[7] silylarsino-,[7] alkylstibino-,[7] alkylamino-,[8] and alkoxy-[9] aluminates have been used in the preparation of group IV derivatives:

e.g. $4Me_3SiCl + LiAl(PH_2)_4 = 4Me_3SiPH_2 + LiCl + AlCl_3$.

The evolution of hydrogen on reaction of thiols with lithium tetrahydroaluminate is well known and methanethiol reacts to give lithium tetra(methylthio)aluminate. We find that the latter is an excellent reagent for the preparation of methylthio derivatives of silicon, germanium, and tin. (Recently the preparation of methyl(silyl)sulphide by this method was reported independently by Glidewell.[9])

We report the following reactions of mono- and di-halides with lithium tetra(methylthio)aluminate:

$$\mathrm{LiAl(SMe)_4 + 4RX = 4RSMe + LiX + AlX_3}$$

$$\mathrm{(R = Me_3Si,\ Me_3Ge,\ Me_3Sn,\ SiH_3,\ GeH_3,\ Si_2H_5;\ X = Cl,\ Br)}$$

$$\mathrm{LiAl(SMe)_4 + 2R'X_2 = 2R'(SMe)_2 + LiX + AlX_3}$$

$$\mathrm{(R' = Me_2Si,\ Me_2Ge,\ Me_2Sn,\ SiH_2)}$$

The yields are excellent and even for the reactions with the disilanyl and methyltin halides they are 70 - 80%.

The analagous reactions involving lithium tetra(methylseleno)aluminate with the monohalides also give excellent yields in the range 65 - 90%. However, the yields are very poor with the methyltelluro derivatives. Tellurium metal is deposited and the products apparently disproportionate to give dimethyltelluride and the appropriate group IV telluride.

EXPERIMENTAL

In a typical experiment, lithium tetrahydroaluminate (0.1 g, 2.5 mmoles) and methanethiol (12.0 mmoles) were left for 30 hr at room temperature in diethylether (ca. 10 ml) by which time the hydrogen (9.4 mmoles) had been evolved. The halide, e.g. bromo(trimethyl)germane (9.0 mmoles) was then added and the mixture stirred at $-45^{\circ}C$ for 30 - 45 min. The product, e.g.

methylthio(trimethyl)germane (8.1 mmoles) was separated on a fractionating column on the vacuum line.[10] With SiH_3Br, GeH_3Br, and Si_2H_5Br, the diethylether was replaced by diglyme before addition of the halide to facilitate separation. The procedures with methylselenol and methyltellurol were identical.

Yields.- Me_3SiSMe (92%); Me_3GeSMe (90%); Me_3SnSMe (81%); SiH_3SMe (95%); GeH_3SMe (89%); Si_2H_5SMe (73%); $Me_2Si(SMe)_2$ (84%); $Me_2Ge(SMe)_2$ (71%); $Me_2Sn(SMe)_2$ (72%); $H_2Si(SMe)_2$ (76%); $Me_3SiSeMe$ (66%); $Me_3GeSeMe$ (73%); $Me_3SnSeMe$ (69%); SiH_3SeMe (87%); GeH_3SeMe (74%); $Me_3SiTeMe$ (5%); $Me_3GeTeMe$ (15%); $Me_3SnTeMe$ (12%); SiH_3TeMe (17%); GeH_3TeMe (14%).

The products were identified by their molecular weights, by their cleavage reactions with hydrogen iodide, and by comparison of their ^1H n.m.r. and infrared spectra with literature values.[11]

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