

SHORT
COMMUNICATIONS

Selective Synthesis of Mixed Haloalkyl- and Haloarylgermanes

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Organogermanium compounds of $R_2R'GeX$ type are prepared by successive dealkylation of mixed fully substituted organogermanium compounds with various agents [1]. However the publication concerning the synthesis of these compounds are scarce.

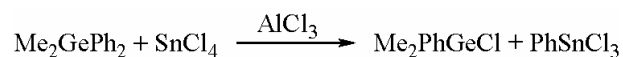
Here we report on the results of preparation of unsymmetrical germanium compounds of $R_2R'GeCl$, type where $R = Me$, $R' = Ph$, $t-Bu$, from Me_2GeCl_2 (**I**) and corresponding Grignard reagents or organolithium compounds. The initial compound **I** was obtained by direct method using the known procedure [1] from metallic germanium and methyl chloride in the presence of copper catalyst.

Reaction of compound **I** with phenyllithium at 1 : 1 ratio in dilute ethereal solution even at cooling to 0°C, slow addition of PhLi and vigorous stirring afforded Me_2GePh_2 (**II**) in 53% yield. Therewith the target product chlorodimethylphenylgermane $Me_2PhGeCl$ (**III**) formed only in 4% yield due to the nonselective character of the reaction. Besides some unreacted compound **I** was recovered.

The other synthetic procedure consisted in treating compound **I** in ether with PhMgBr at molar ratio 1 : 1. The reaction was performed by slow addition of phenylmagnesium bromide to compound **I** within 5–6 h at vigorous stirring. In this case we obtained chlorodimethylphenylgermane (**III**) in 30% yield, and compound **II** in 15% yield.

The results of the above experiments and the difficulties in separation of compounds **II**, **III** led us to conclusion that the best way to compound **III** consists in preliminary alkylation of dimethylgermanium dichloride with replacement of both chlorine atoms by phenyl groups with subsequent dealkylation of compound **II** by treating with $SnCl_4$ in the presence of

aluminum chloride without solvent. The reaction was selective and completed in 3 h.



The yield of the target product was 70%. The composition and structure of compound **III** were proved by elemental analysis and IR and 1H NMR spectra

Synthesis of $t-Bu_nGeCl_{4-n}$, by treating $GeCl_4$ with $t-BuLi$ was described before [2].

We established that the introduction of a sterically hindering substituent can be performed selectively with the use of a Grignard reagent that in this case is more available.

Thus *tert*-butylmethylchlorogermane, $t-BuMe_2GeCl$ (**IV**), was obtained by reaction of compound **I** with $t-BuMgCl$ in THF at reagents ratio 1 : 1 in 25% yield. The other components of the reaction mixture were $t-Bu_2Ge?$ and unreacted compound **I**. Compound **IV** obtained was identified by IR spectrum, GLC, and elemental analysis.

Chlorodimethylphenylgermane (III). Into a three-neck flask equipped with a stirrer, a reflux condenser, and a dropping funnel was charged in an argon flow 53.7 g (0.3 mol) of compound **I** in 100 ml of ether, and at cooling to 0°C was added dropwise while stirring 26 g (0.3 mol) of PhLi in 200 ml of ether. On completing the reaction (2 h) the mixture was boiled on a water bath for 2.5 h, the precipitate was separated, the ether was distilled off, and the residue was subjected to a vacuum distillation. We obtained 21.44 g of compound **II**. Yield 53%, bp 142°C (10 mm Hg). To 21.44 g (0.08 mol) of compound **II** was added 0.3 g of $AlCl_3$ and 21.8 g (0.08 mol) of $SnCl_4$, and the mixture was heated under reflux for 3 h. Within this time the temperature of the reaction mixture grew to 135°C. The

precipitate was separated, and the product was distilled in a vacuum. Yield of compound **III** 12.5 g (69%), bp 105–107°C (9 mm Hg) n_D^{20} 1.5458. IR spectrum, ν , cm^{-1} 3050, 1480, 1430, 1090, 740, 700, 460 (GePh); 2970, 2900, 1400, 1240, 830, 810, 615, 590 (GeMe); 380 (GeCl). ^1H NMR spectrum (CDCl_3), δ , ppm: 0.92 s (6H, Me), 7.41, 7.54 m (5H arom). Found, %: C 44.42; H 5.01; Ge 34.12. $\text{C}_8\text{H}_{11}\text{ClGe}$. Calculated, %: C 44.69; H 5.11; Ge 33.74.

tert-Butylmethylchlorogermane (IV). Under conditions described above to 30.2 g (0.17 mol) of compound **I** in 50 ml of THF was added 20.4 g (0.17 mol) of *t*-BuMgCl in 100 ml of THF in the course of 2 h. After 2 h of boiling on cooling of the reaction mixture it was diluted with 50 ml of hexane to attain full separation of precipitate. The precipitate was washed with 50 ml of benzene, the filtrates were combined, the

solvents were removed, and the residue was distilled. We obtained 8.8 g (25%) of compound **IV**, bp 145–150°C, n_D^{20} 1.4620. IR spectrum, ν , cm^{-1} : 1215, 1250, 1375 (*t*-Bu–Ge); 380 (Ge–Cl). Found, %: C 36.61; H 7.42; Ge 37.48. $\text{C}_6\text{H}_{15}\text{ClGe}$. Calculated, %: C 36.92; H 7.68; Ge 37.20.

IR spectra were registered on spectrometer Perkin Elmer 557, ^1H NMR spectra were measured on Bruker DPX-200 instrument (200 MHz), internal reference TMS.

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2. Wojnowska, M., Noltemeyer, M., F'Ilgrabe, H.I., and Meller, A., *J. Organomet. Chem.*, 1982, pp. 228, 229.