4,5-Dichloroanthrone (3). A suspension of quinone **1** (0.56 g, 2 mmol) in dioxane (10 mL) and then $Na_2S_2O_4 \cdot 2H_2O$ (1,26 g, 6 mmol) were added to a solution of NaOH (0.48 g, 12 mmol) in water (50 mL) heated to 100 °C. The mixture was stirred for 20 min with boiling and then cooled. The residue was separated and recrystallized from benzene. Anthrone **3** was obtained (0.29 g, 59%), m.p. 196—201 °C (*cf.* Ref. 2: m.p. 198 °C). ^{1}H NMR ($CDCl_3$), δ: 4.17 (s, 2 H, CH_2), 7.42 (br.t, 2 H, H(2), H(7), J = 8.0 Hz), 7.67 (br.d, 2 H, H(3), H(6), J = 8.0 Hz), 8.25 (br.d, 2 H, H(1), H(8), J = 8.0 Hz). IR (KBr), ν/cm^{-1}: 1660 (C=O). MS, *m/z*: 262 [M]$^+$.

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The first example of Ge—Ge and Sn—Sn bond cleavage by arylmagnesium halides

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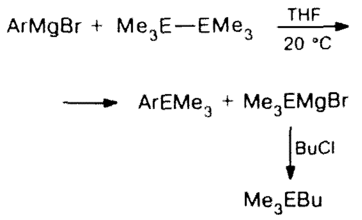
It is known[1,2] that E—E bonds (E = Ge, Sn) can be cleaved by the action of organolithium compounds, alkali metals, their alkoxides, hydroxides, and fluorides to form metal-centered anions R_3E^-. In this work, we report on the first example of E—E bond (E = Ge, Sn) cleavage by Grignard reagents under mild conditions. The reaction found suggests the intermediate formation of organogermanium (organotin) Grignard reagents of the R_3EMgX type (E = Ge, Sn) and can serve as a new method for generation of these poorly studied organometallic compounds.[1,2]

Hexamethyldistannane and hexamethyldigermane react readily with PhMgBr (THF, 20 °C) to form a mixture of equimolar amounts of the corresponding $PhEMe_3$ and Me_3EBu or Me_3EH (E = Ge, Sn) in high yields (according to the data of GC-MS and ^{1}H NMR spectroscopy) after treatment of the reaction mixture with n-BuCl (or H_2O).



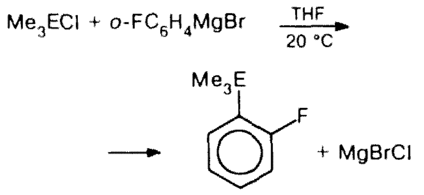
(1)

E = Ge, Sn; Ar = Ph; o-FC_6H_4

The formation of Me_3EBu (or Me_3EH) when n-BuCl (or H_2O) is added to the reaction mixture is significant evidence that organogermanium (organotin) Grignard reagents Me_3EMgBr are involved in the reactions of ArMgX with Me_6E_2 (E = Ge, Sn).

Under similar conditions (THF, 20 °C), the Si—Si bond in Me_6Si_2 does not cleave under the action of o-FC_6H_4MgBr.

Reaction (1) occurs fairly readily. Thus, even the very labile Grignard reagent from o-bromofluorobenzene (o-FC_6H_4MgBr) cleaves the E—E bonds in Me_6E_2 (E = Ge, Sn) in THF at 20 °C more rapidly than it decomposes to give MgBrF and dehydrobenzene.[3] According to the data of GC-MS, the reaction products (o-$FC_6H_4EMe_3$ and Me_3EBu) are formed in quantitative yields after treatment of the reaction mixture with n-BuCl. The intermediate participation of labile o-fluorophenylmagnesium bromide in the transformations described above was proved by trapping reactions. o-Bromofluorobenzene reacts readily with Me_3ECl (E = Si, Sn)



E = Si, Sn

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in the presence of magnesium (THF, 20 °C) to give products corresponding to the reaction of the latter with *o*-fluorophenylmagnesium bromide, *o*-$FC_6H_4EMe_3$ (E = Si, Ge). Both compounds were isolated preparatively (yields 80—90 %) and identified by mass spectrometry and ^1H NMR spectroscopy.

Unlike arylmagnesium halides, methylmagnesium iodide does not cleave the E—E bonds in Me_6E_2 (E = Ge, Sn).

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