Organomagnesium Synthesis of *sec*-Butyl- and *tert*-Alkylchlorogermanes and Their Reaction with Ethynylmagnesium Bromide

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Abstract—The limits of application of organomagnesium synthesis to the substitution of chlorine atoms in tetrachlorogermane with bulky alkyl groups are established. The reaction of tetrachlorogermane with 2-butylmagnesium chloride leads to the substitution of one, two, or three chlorine atoms, yielding the corresponding alkylchlorogermanes $(MeEtCH)_nGeCl_{4-n}$. The reaction of $GeCl_4$ with *tert*-alkylmagnesium halides leads to the substitution of only one chlorine atom, yielding *tert*-alkyltrichlorogermanes RMe_2CGeCl_3 (R = Me, Et, Bu). *tert*-Butyltrichlorogermane reacts with ethylmagnesium bromide to give ethyl(*tert*-butyl)dichlorogermane. Isopropyltrichlorogermane reacts with *tert*-butylmagnesium chloride to give isopropyl(*tert*-butyl)dichlorogermane. This shows that the organomagnesium synthesis does allow linking of two bulky substituents to the germanium atom. The reaction of *tert*-alkyltrichlorogermanes and 2-butyltrichlorogermane in THF with ethynylmagnesium bromide, in which the hydrocarbon group is the most sterically accessible, allows substitution of all the three chlorine atoms, yielding the corresponding alkyl(triethynyl)germanes. The latter compounds react with the Grignard reagent and trimethylchlorosilane to give the corresponding alkyl(trimethylsilylethynyl)germanes.