J.C.S. Снем. Сомм., 1976

Optically Active Silylanions. Evidence for the Formation of Analogues of Silyl Grignard Reagents

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Summary The preparation and reactions of an analogue of R_3SiMgX are reported; its reactions proceed with 55% retention of configuration and those of the analogous R_3SiLi 70%.

SILVL anions offer a versatile synthetic route to organosilanes and have been widely studied¹ e.g., the 'S-system' of Calas and Dunoguès² offers a large variety of synthetic possibilities. We describe here a possible new route to silyl anions, and particularly to R_3SiMgX . The formation of this species has never been established but was reasonably invoked by West³ and Gilman⁴ and their co-workers.

Treatment of $[(CO)_4CoSiPh_3]^5$ with a tenfold excess of a Grignard or alkyl-lithium reagent led to the formation of the corresponding anionic reagent (reaction 1). The reactions

$$[(CO)_4 CoSiPh_3] \xrightarrow{\text{RM}} M-SiPh_3 \tag{1}$$

M = MgBr, R = Me, Et, or allyl; M = Li, R = Me

of these derivatives are shown in Scheme 1. Hydrolysis with D₂O yields only the deuteriated silane, showing that the silane is formed from an anionic species, since hydrolysis of the cobalt-silicon complex gives the silanol quantitatively. The reactions of the alkyl halides gave further proof that the coupling reactions did proceed through a silvl anion, since they are unreactive towards Co-Si bonds.



SCHEME 17

Treatment of the optically active compound $[(+)-(CO)_4-$ CoSiMePh(α -Np)], $[\alpha]_{D}^{25} + 2.7^{\circ 6}$ with a Grignard reagent yielded a silyl Grignard reagent of low optical activity (Scheme 2). Treatment with MeLi gave, after hydrolysis, a silane with 70% retention of configuration. These results should be compared with those obtained by Sommer and Mason⁷ for the preparation of an optically active silvllithium.

Surprisingly, treatment of [(CO)₄CoGePh₃],⁸ m.p. 158-160 °C, with MeMgBr led to substitution on Ge, while allylmagnesium bromide led to the germyl Grignard reagent (Scheme 3).



The behaviour of these complexes is surprising since we had expected nucleophilic attack on silicon or germanium to occur. In fact treatment of both types of compounds with LiAlH₄ led to formation of the corresponding Si-H or Ge-H bond. The reaction takes place9 with inversion of configuration in the case of the optically active cobalt-silicon compound.



SCHEME 3

The magnesium or lithium alkyl probably attacks the carbonyl ligands,¹⁰ the silicon unit being displaced as a silvl anion.

(Received, 18th December 1975; Com. 1397.)

† Reactions marked with an asterisk (*) in Schemes 1 and 3 take place in ca. 40% yield. We presume that this corresponds to the yield of the silyl or germyl anion formed. After hydrolysis ca. 40 % yields of the silanol or germanol byproduct are formed. Some tar is formed in all cases.

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