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On the Mechanism of Uncatalyzed Reduction of Triphenylmethyl Chloride with Triethylgermane[1]

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Synopsis. Reduction of triphenylmethyl chloride with triethylgermane in benzene proceeds by a free-radical mechanism as evidenced by the observation of an ESR spectrum of the triphenylmethyl radical. However, the reduction involves apparently an ionic mechanism in a polar solvent such as dichloromethane and nitromethane.

Corey and West first reported that triphenylmethyl chloride can be reduced with hydrosilanes in high yield under moderate conditions without any added catalyst.[2]

$$Ph_3CCl + R_3SiH \longrightarrow Ph_3CH + R_3SiCl$$

Ionic mechanisms, especially a four-centered[2,3] and an ion-pair mechanism[4] have been proposed to this reaction.

The fact that triphenylmethyl chloride can also be reduced with hydrogermanes without catalyst is not surprising because of the known capability of hydrogermanes to reduce organic halides.[5] However, we report here that the reduction proceeds through a free radical mechanism in non-polar solvents such as benzene.

Reduction of triphenylmethyl chloride with triethylgermane was affected strongly by the nature of a solvent employed. Thus, in a polar solvent such as dichloromethane and nitromethane, the reduction takes place very rapidly even at room temperature.

$$Ph_3CCl + Et_3GeH \longrightarrow Ph_3CH + Et_3GeCl$$

However, in benzene it was required to raise the reaction temperature to 80 °C for completion of the reduction. Interestingly, a strong ESR signal of the triphenylmethyl radical was observed as shown in Fig. 1 after a benzene solution of triphenylmethyl chloride containing triethylgermane in an ESR tube was heated for a few seconds at 80 °C. This fact strongly indicates that the reduction with organogermane in benzene should proceed by a free-radical mechanism.

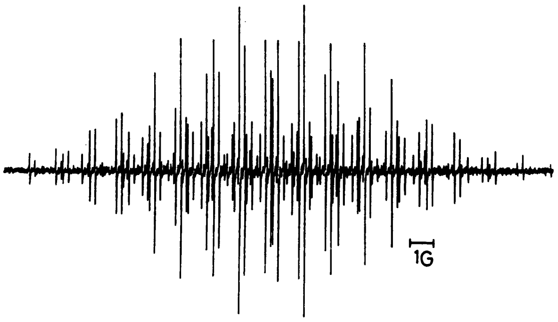

Fig. 1. ESR spectrum of the triphenylmethyl radical, $a_{o\text{-H}}=2.53G$, $a_{m\text{-H}}=1.11G$, $a_{p\text{-H}}=2.77G$.

$$Et_3GeH \longrightarrow Et_3Ge\cdot + (\cdot H)$$

$$Ph_3CCl + Et_3Ge\cdot \longrightarrow Ph_3C\cdot + Et_3GeCl$$

$$Ph_3C\cdot + Et_3GeH \longrightarrow Ph_3CH + Et_3Ge\cdot$$

However, when dichloromethane, nitromethane, or diethyl ether was employed as a solvent, instead of benzene, no ESR signal was observed under various conditions. When triphenylmethyl chloride was dissolved in dichloromethane or nitromethane, color of the solution immediately turned to deep yellow due to the formation of the triphenylmethyl cation. Addition of triethylgermane to the colored solution caused immediate fading with concurrent formation of both triphenylmethane and triethylchlorogermane. These facts suggest that the reduction of triphenylmethyl chloride with hydrogermane in a polar solvent proceeds by an ionic mechanism.

The nature of the initiation step is uncertain, but probably a trace amount of oxygen plays a role. Photochemical generation of the triphenylmethyl radical from triphenylmethyl chloride is known,[6] but no free radical was detected by ESR for a solution of triphenylmethyl chloride in benzene heated at 80 °C. Therefore, thermal generation of the triphenylmethyl radical is unimportant at least under the conditions.

Incidentally, the ESR spectrum of the triphenylmethyl radical obtained in this study is extremely well-resolved compared to those reported previously.[7] Generation of free radicals for the ESR studies by reduction with triorganosilanes is well documented,[8] but no modification using hydrogermane has been reported. We have found recently that reduction of organic halide with hydrogermane has several advantages even for generation of very unstable radicals.[9]

Experimental

Materials. Triethylgermane[10] and triphenylmethyl chloride[11] were prepared according to the literature.

Reduction of Triphenylmethyl Chloride with Triethylgermane in Dichloromethane. Triphenylmethyl chloride (0.17 g, 0.60 mmol) was added to a solution of triethylgermane (0.48 g, 3.01 mmol) in dichloromethane (2.0 ml). The mixture was kept at room temperature for 30 min. GLC analysis showed formation of triphenylmethane (0.13 g, 0.53 mmol) in 88.0% yield.

Another run with a mixture of triphenylmethyl chloride (0.030 g, 0.10 mmol) and triethylgermane (0.160 g, 1.0 mmol) in dichloromethane (0.5 ml), which was subjected to react for 5 min at room temperature, gave triphenylmethane in 46% yield.

Reaction of Triphenylmethyl Chloride with Triethylgermane in Benzene. A mixture of triphenylmethyl chloride (0.49 g, 1.74 mmol) and triethylgermane (1.40 g, 8.71 mmol) in benzene (2.0 ml) was placed in an ampoule which was bubbled with dry nitrogen, sealed and immersed in a constant-temperature bath kept at 80 °C for 2 h. Triphenylmethane (0.37 g, 1.52 mmol, 87.4% yield) was identified and analyzed by GLC.

Another mixture of triphenylmethyl chloride (0.030 g, 0.1 mmol) and triethylgermane (0.160 g, 1.0 mmol) in benzene (0.5 ml) was heated at 80 °C for a few second. GLC analysis showed formation of triphenylmethane in 41% yield.

ESR Measurement. Triethylgermane (0.100 g, 0.62 mmol) was added to a solution of triphenylmethyl chloride (0.011 g, 0.045 mmol) in benzene (0.01 ml) placed in an ESR tube. The tube was bubbled with dry nitrogen and immersed in a constant-temperature bath kept at 80 °C for a few second. Then the ESR spectrum of triphenylmethyl radical was recorded with a Varian E-12 spectrometer.

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