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Facile Cleavage of Ge-C Bonds of N-(Germylmethyl)benzylamine Derivatives. Generation of Germyl Anions

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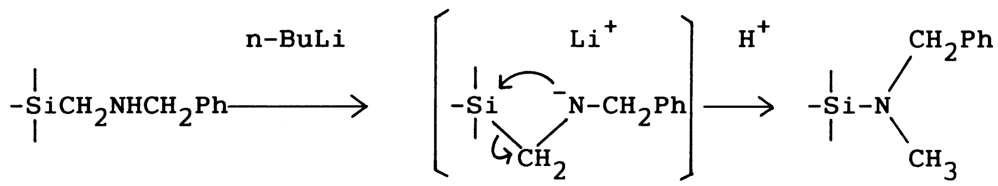
The reactions of N-(germylmethyl)benzylamine derivatives with butyllithium were carried out. Facile cleavages of Ge-C bonds of the N-benzylgermylmethylamine derivatives giving the corresponding germyl anions and N-pentylbenzylamine were observed. The reaction mechanism of the Ge-C bond cleavage was discussed.

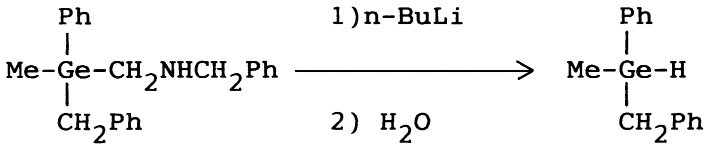
A.G.Brook et al. found that intramolecular rearrangements took place when N-(silylmethyl)benzylamine derivatives were treated with a catalytic amount of butyllithium (n-BuLi) (Scheme 1).$^{1)}$



Scheme 1.

Previously, we used the rearrangement reaction successfully to establish the configurations of new optically active organosilanes.$^{2)}$

In the course of our investigations on preparation and application of optically active organogermanium compounds, it was found that the reaction of N-(benzylmethylphenylgermylmethyl)benzylamine in the presence of n-BuLi in tetrahydrofuran (THF), followed by quenching with water, gave benzylmethylphenylgermane in a good yield (Scheme 2).3)

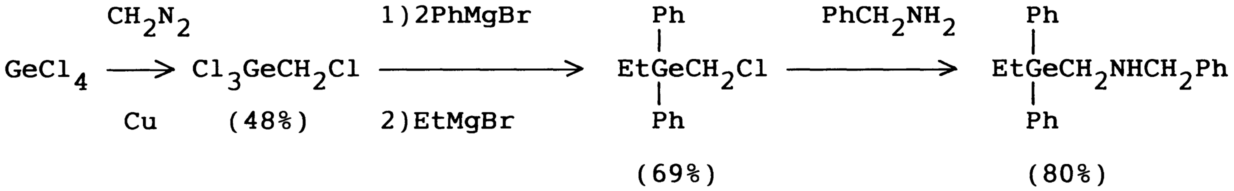


$$\mathrm{Me{-}\overset{\displaystyle Ph}{\underset{\displaystyle CH_2Ph}{Ge}}{-}CH_2NHCH_2Ph} \xrightarrow[\text{2) } H_2O]{\text{1) n-BuLi}} \mathrm{Me{-}\overset{\displaystyle Ph}{\underset{\displaystyle CH_2Ph}{Ge}}{-}H}$$

Scheme 2.

In this paper we wish to describe on the reactions of N-(germylmethyl)benzylamine derivatives, such as N-(ethyldiphenylgermylmethyl)benzylamine, N-(diethylphenylgermylmethyl)benzylamine, and N-(benzyldiethylgermylmethyl)benzylamine with n-BuLi.

N-(Ethyldiphenylgermylmethyl)benzylamine was prepared as follows;



$$\mathrm{GeCl_4} \xrightarrow[\text{Cu}]{CH_2N_2} \underset{(48\%)}{\mathrm{Cl_3GeCH_2Cl}} \xrightarrow[\text{2)EtMgBr}]{\text{1)2PhMgBr}} \underset{(69\%)}{\mathrm{Et\overset{\displaystyle Ph}{\underset{\displaystyle Ph}{Ge}}CH_2Cl}} \xrightarrow{PhCH_2NH_2} \underset{(80\%)}{\mathrm{Et\overset{\displaystyle Ph}{\underset{\displaystyle Ph}{Ge}}CH_2NHCH_2Ph}}$$

Scheme 3.

Other N-(germylmethyl)benzylamine derivatives employed here were synthesized by using the corresponding Grignard reagents in a similar manner described above.

Then the reactions of N-(germylmethyl)benzylamine derivatives with n-BuLi in THF were carried out. In contrast to the reactions of silcon derivatives with n-BuLi, 2 molar equivalents of n-BuLi were required for completion of the reactions in the case of the germanium derivatives.

In a typical experiment, a solution of n-BuLi (2.9 mmol, 1.55 M in hexane)(1 M = 1 mol $\mathrm{dm^{-3}}$) was added to a solution of N-(ethyldiphenylgermylmethyl) benzyl amine (1) (0.50 g, 1.3 mmol) in THF (4 ml) at 0℃ . The solution colored to reddish brown immediately. After stirring at 0℃ for 1 h, the reaction mixture was quenched with water. Organic layer was separated and dried over Na_2SO_4. Purification by column chromatography on silica gel gave ethyldiphenylgermane and N-pentylbenzylamine in 91 and 84% yields respectively.

The results of reactions for N-(germylmethyl)benzylamine derivatives with n-BuLi were summarized in Table 1.

Table 1. Reactions of N-(Germylmethyl)benzylamine Derivatives with Butyllithium

Run	$R_1R_2R_3GeCH_2NHCH_2Ph$	(mmol)	n-BuLi[a] (mmol)	Yield / % $R_1R_2R_3GeH$	$C_5H_{11}NHCH_2Ph$
1	$R_1=R_2=Ph$, $R_3=Et$	1.3	1.5	63	33
2	$R_1=R_2=Ph$, $R_3=Et$	1.3	2.9	91	84
3	$R_1=Ph$, $R_2=R_3=Et$	1.3	2.9	68	83
4	$R_1=CH_2Ph$, $R_2=R_3=Et$	1.5	3.2	83	67

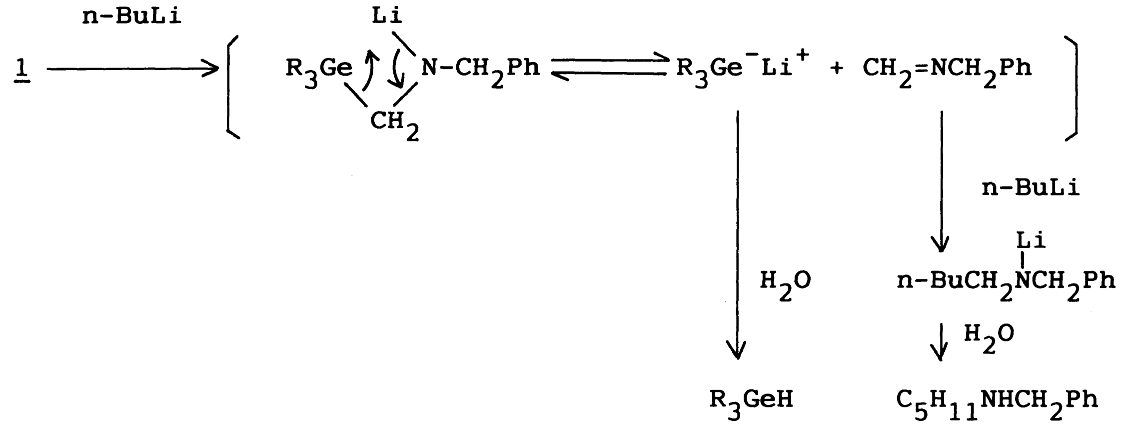
a) Hexane solution of n-BuLi (1.55 M) was employed.

When the reaction of 1 with an equimolar amount of n-BuLi was carried out under the similar reaction conditions (Run 1), ethyldiphenylgermane, N-pentylbenzylamine were isolated in 63 and 33% yields, respectively, in addition to unreacted 1 (27%). On the other hand, in the reaction of 1 with 2 molar equivalents of n-BuLi, both germanium hydrides and N-pentylbenzylamine were obtained in high yields (Runs 2-4), regardless of the kind of substituents on germanium.

From these observations, we considered the reaction mechanism as described in Scheme 4, because it is known that germyl anions give the corresponding hydrogermane derivatives on treatment with water,4) and because germyl anions may react with N-benzylmethyleneimine to reproduce lithium amide intermediates.

Although it is not clear that the reason why the Ge-C bonds cleave easily, it is interesting that germanium plays a part of nucleophile in the reaction to generate germyl anion species as an intermediate, while, in the reaction of N-(silylmethyl)benzylamine derivatives, silicon atom takes a role of electrophile (Scheme 1) under the similar reaction conditions.

These defferences of the reactivities between N-(germylmethyl)- and N-(silylmethyl)benzylamine derivatives may come from those in the electronegativities between Ge (2.0) and Si (1.8).[5)]



Scheme 4.

More detailed studies on the Ge-C cleavage reactions including stereochemistry are in progress.

References

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