Selective Synthesis of Chlorohydrogermanes from Mono-, Di-, and Trihydrogermanes

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Treatment of hydrogermanes, $R_{4-n}GeH_n$ (R = Hex, Et, Ph, n = 1–3), with 2 equiv of $CuCl_2$ in ether at room temperature or in toluene under reflux led to selective replacement of an H–Ge bond with a Cl–Ge bond, giving the corresponding chlorohydrogermanes, $R_{4-n}GeH_{n-1}Cl$, selectively.

Halogermanes are useful reagents in the synthesis of a variety of organogermanium compounds.[1] Of these, halohydrogermanes are of high importance, as exemplified by dehydrohalogenative coupling of chlorohydrogermanes forming a Ge–Ge bond.[2] A few methods for the synthesis of halohydrogermanes, including redistribution reactions of organohydrogermanes with tetrachlorogermane[3] and selective monohalogenation of dihydrogermanes with $HgCl_2$, $ClCH_2OCH_3$ in the presence of $AlCl_3$ as the catalyst, or *N*-bromosuccinimide (NBS), have been published to date.[4] However, these monohalogenation involves the use of toxic or costly reagents. Although partial hydrogenation of dihalogermanes has been also reported, it may be applied to only some special cases.[5] Recently, we have demonstrated that treatment of mono-, di-, and trihydrosilanes with 2 equiv of $CuCl_2$ in the presence of a catalytic amount of CuI ($2CuCl_2(CuI)$ reagent) leads to the selective transformation of an H–Si bond to a Cl–Si bond, providing a readily accessible route to bifunctional chlorohydrosilanes [eq (1)].[6] In this paper, we report the selective synthesis of chlorogermanes from hydrogermanes by $CuCl_2$ in the absence or presence of the CuI catalyst, in which one hydrogen atom on the germanium atom was selectively replaced with a chlorine atom with the use of 2 equiv of $CuCl_2$.

$$R_{4-n}SiH_n \xrightarrow{2\,CuCl_2(CuI)} R_{4-n}SiH_{n-x}Cl_x \quad (1)$$

$n = 1-3,\ x = 1-3$

When Hex_2GeH_2 was treated with $2CuCl_2(CuI)$ in toluene under reflux for 5 h, Hex_2GeHCl was obtained in 91% isolated yield [eq (2) and Table 1].[7] In this reaction, no other volatile products were detected by GLC analysis of the reaction mixture. The chlorination proceeded also in ether at lower temperature to give Hex_2GeHCl in good to high yields. In this reaction, however, a trace of $Hex_2Ge(OEt)Cl$ was found to be formed by GC–MS of the reaction mixtures. The ethoxy group would come from the solvent, ether. Similar treatment of Hex_2GeH_2 with 4 equiv of $CuCl_2(CuI)$ in toluene afforded Hex_2GeCl_2 in 87% isolated yield [eq (3)]. From the reaction of Et_2GeH_2 in ether and Ph_2GeH_2 in toluene, mono- and dichlorinated products were obtained again selectively, depending on the amount of $CuCl_2$ used. The reactions of Ph_2GeH_2 proceeded at a slower rate as compared with those of Hex_2GeH_2, i.e.; both the mono- and dichlorination of Hex_2GeH_2 completed in a shorter period than those of Ph_2GeH_2 under essentially the same conditions, respectively.

$$R_{4-n}GeH_n \xrightarrow[\text{ether or toluene}]{2\,CuCl_2} R_{4-n}GeH_{n-1}Cl \quad (2)$$

R = Hex, Et, Ph, n = 1–3

$$R_{4-n}GeH_n \xrightarrow[\text{ether or toluene}]{4\,CuCl_2\,(CuI)} R_{4-n}GeH_{n-2}Cl_2 \quad (3)$$

R = Hex, Et, Ph, n = 2–3

Monochlorination reactions occured also in the absence of CuI, although a longer reaction time was required to complete the chlorination, in particular for that in ether at room temperature. The required reaction time in ether may be reduced by heating the reaction mixture, although the yield dropped slightly, due to the formation of unidentified by-products. This is in marked contrast to the chlorination of hydrosilanes with the $CuCl_2(CuI)$ reagent which occurs only in the presence of the CuI catalyst. The starting hydrosilanes are recovered unchanged from the reactions in the absence of CuI under the same conditions. For the dichlorination of hydrogermanes, however, it was necessary to use the CuI catalyst [eq (3)]. Without the CuI catalyst, only monochlorinated products were obtained even when a large excess of $CuCl_2$ was used. Monohydrogermanes, Hex_3GeH and Et_3GeH were also readily chlorinated by similar treatment in ether.

Chlorination with the use of the $CuCl_2(CuI)$ reagent can be also applied to the selective chlorination of trihydrogermane $PhGeH_3$ as can be seen in Table 1 [eq (3), R = Ph, n = 3]. Thus, by changing the amount of the reagent, we could obtain desired chlorohydrogermanes with complete selectivity. Perchlorination of $PhGeH_3$ afforded $PhGeCl_3$ as the sole volatile product in 80% yield [eq (4)].

$$PhGeH_3 \xrightarrow{6\,CuCl_2\,(CuI)} PhGeCl_3 \quad (4)$$

The present chlorination of hydrogermanes may be explained by a mechanism shown in Scheme 1, as proposed for previously reported chlorination of hydrosilanes.[6] In the presence of the CuI catalyst, CuICl seems to be formed as the actual active species. The Ge–H bond would be initially converted to a Ge–I bond, which is then replaced with a Ge–Cl bond by the interaction with $CuCl_2$. Whereas, in the absence of CuI, the Ge–H bond may react directly with 2 equiv of $CuCl_2$ giving Ge–Cl and 2CuCl·HCl.

One might consider that a radical process is included in the chlorination. Although we have not yet obtained any direct evidences to support the reaction mechanism shown in Scheme 1, the high selectivities in the present system may exclude the possibility of a radical mechanism.

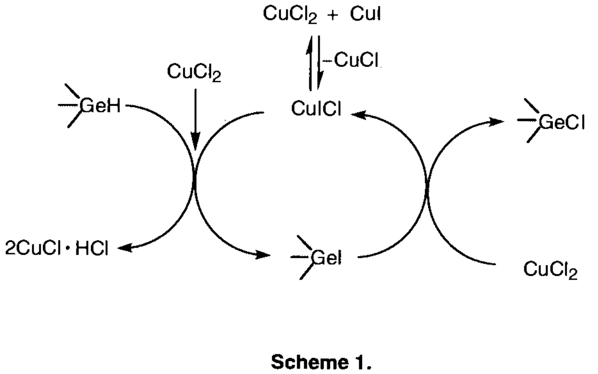
The present reaction is oxidative in nature and $CuCl_2$ acts as the oxidant. Presumably, replacement of the hydrogen atom

Table 1. Chlorination of hydrogermanes

Hydrogermane	$CuCl_2$/equiv	CuI/equiv	Solvent	Temp	Time/h	Product	Yield/%[a]
Hex_2GeH_2	2	0.03	toluene	reflux	5	Hex_2GeHCl	91
	2	none	toluene	reflux	19		90
	2	0.03	Et_2O	rt	3		65[b]
	2	none	Et_2O	rt	14 days		91[b]
	2	none	Et_2O	reflux	8 days		77[c]
	4	0.11	toluene	reflux	4 days	Hex_2GeCl_2	87
Hex_3GeH	2	0.03	Et_2O	rt	5	Hex_3GeCl	88
Et_2GeH_2	2	0.02	Et_2O	rt	1	Et_2GeHCl	73
	4	0.02	Et_2O	rt	8	Et_2GeCl_2	85
Et_3GeH	2	0.03	Et_2O	rt	3	Et_3GeCl	76
$PhGeH_3$	2	none	toluene	reflux	19	$PhGeH_2Cl$	84
	4	0.17	toluene	reflux	9 days	$PhGeHCl_2$	88
	6	0.18	toluene	reflux	17 days	$PhGeCl_3$	80
Ph_2GeH_2	2	none	toluene	reflux	31	Ph_2GeHCl	87
	4	0.14	toluene	reflux	6 days	Ph_2GeCl_2	86
Ph_3GeH	2	0.10	toluene	reflux	11 days	Ph_3GeCl	91

[a]Isolated yield. [b]A trace of $Hex_2Ge(OEt)Cl$ was formed. [c]Unidentified by-products, probably including $Hex_2Ge(OEt)Cl$, were formed.

of hydrohermanes with an electronegative chlorine atom suppresses the further chlorination to provide the high selectivities in the present reactions. The lower reaction rate of the chlorination of phenylgermanes than that of the respective hexylgermanes also seems to reflect the electronegative nature of the phenyl group compared to the hexyl group. Higher steric hindrance of phenyl group than hexyl group may also play a role in the slower reaction rate. This is in accordance with the slightly faster reaction progress of ethylgermanes as compared with hexylgermanes.



Scheme 1.

In conclusion, we have demonstrated that hydrogermanes can be converted selectively to chlorogermanes by treating them with $CuCl_2$ in the absence or presence of a catalytic amount of CuI. Chlorohydrogermanes seem to be of useful reagents for the synthesis of a variety of organogermanium compounds, because of their bifunctionality, i.e.; the Cl–Ge bond would allow rapid nucleophilic substitution, while the H–Ge bond is expected to undergo hydrogermylation with unsaturated organic compounds as well as rather slower substitution with nucleophiles. Studies to explore the synthetic utilities of chlorohydrogermanes are in progress.

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References and Notes

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7 Illustrative procedure for the chlorination of hydrogermanes is as follows. In a 100-mL flask fitted with a reflux condenser was placed a mixture of 0.98 g (4.00 mmol) of Hex_2GeH_2, 1.11 g (8.26 mmol) of $CuCl_2$, and 0.02 g (0.11 mmol) of CuI in 40 mL of toluene, and the mixture was stirred by magnetic stirrer under reflux for 5 h. After filtration of the resulting copper salts, the solvent was evaporated and the residue was distilled under reduced pressure to give 1.02 g (91% yield) of Hex_2GeHCl: bp 165–175 °C (1 mmHg); MS *m/z* 280 (M^+), 245 (M^+–Cl), 195 (M^+–Hex); ^{1}H NMR (δ in $CDCl_3$) 0.88 (t, J = 6.8 Hz, 6H, CH_3) 1.22–1.55 (m, 20H, CH_3) 5.53 (p, J = 2.3 Hz, 1H, GeH); ^{13}C NMR (δ in $CDCl_3$) 14.02, 18.92, 22.48, 24.35, 31.36, 31.93. Anal. Calcd for $C_{12}H_{27}ClGe$: C, 51.58; H, 9.74%. Found: C, 51.55; H, 9.71%.