Synthesis of Bromohydrosilanes: Reactions of Hydrosilanes with $CuBr_2$ in the Presence of CuI

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Reactions of hydrosilanes, $R_{4-n}SiH_n$ (R = alkyl or phenyl, n = 1–3), with 2 equiv of $CuBr_2$ in the presence of a catalytic amount of CuI led to selective replacement of an H–Si bond with a Br–Si bond giving R_3SiBr, R_2SiHBr, or $RSiH_2Br$, while treatment of R_2SiH_2 and $RSiH_3$ with 4 equiv of the reagent produced R_2SiBr_2 and $RSiHBr_2$, respectively. Similar reaction of $HEt_2SiSiEt_2H$ afforded $HEt_2SiSiEt_2Br$.

Organohalosilanes are important starting materials for building up organosilicon compounds as well as useful reagents in synthetic organic chemistry. Of these, organohalohydrosilanes have both Si–H and Si–halogen bonds and thus enables us to carry out independent reactions, such as hydrosilylation and nucleophilic substitution. Previously, we reported a convenient method for the synthesis of chlorohydrosilanes from hydrosilanes with the use of $CuCl_2$ in the presence of a catalytic amount of CuI,[1] and extended this method to the selective syntheses of fluorohydrosilanes[2] and chlorohydrogermanes.[3] We also reported Pd-catalyzed H/I exchange reactions of hydrosilanes with alkyl iodides to afford iodosilanes.[4]

As to bromosilanes, there have been reported several synthetic methods, such as reactions of polybromosilanes with Grignard reagents,[5] cleavage of Si–O bonds with PBr_3,[6] cleavage of Si–Ph bonds[7] or Si–Si bonds[8] with Br_2, Cl/Br exchange of chlorosilanes with $AlBr_3$[6a] or $MgBr_2$,[9] bromination of polyhydrosilanes with Br_2,[6a,10] HBr,[11] $HgBr_2$,[12] or NBS,[13] and partial reduction of 1,2-dibromodisilanes with trialkyltin hydrides,[14] but it is difficult to obtain selectively a desired type of bromohydrosilane by these methods.

In our continuing study on halogenation of hydrosilanes, we found that hydrosilyl groups can be transformed into bromosilyl groups with the use of $CuBr_2$, instead of $CuCl_2$, in the presence of a catalytic amount of CuI (thus $CuBr_2$(CuI) reagent), in a way analogous to chlorination.[1] When Et_3SiH was treated with 2 equiv of the $CuBr_2$(CuI) reagent in diethyl ether at room temperature for 1.5 h, Et_3SiBr was obtained in 82% yield after distillation of the reaction mixture (run 1 in Table 1).

$$Et_3SiH \xrightarrow[\text{ether}]{2\ CuBr_2(CuI)} Et_3SiBr$$

This reagent could be applied for the monobromination of dihydrosilanes.[15] Thus, when n-Hex_2SiH_2 was treated in diethyl ether with 2 equiv of the $CuBr_2$(CuI) reagent at room temperature, the starting silane disappeared within 1 h, and distillation of the resulting mixture afforded n-Hex_2SiHBr in 73% yield as the sole volatile product (run 2). Similar treatment of $MePhSiH_2$ for 9 h afforded MePhSiHBr in 68% yield, while the reaction of Ph_2SiH_2 in toluene for 7.5 h produced Ph_2SiHBr in 64% yield (runs 4 and 5).

$$R_2SiH_2 \xrightarrow[\text{ether or toluene}]{2\ CuBr_2(CuI)} R_2SiHBr$$
$$R_2 = n\text{-}Hex_2,\ MePh,\ \text{or}\ Ph_2$$

To obtain more information, we carried out dibromination of dihexylsilane and monitored the progress by GLC. When n-Hex_2SiH_2 was treated with 4 equiv of the $CuBr_2$(CuI) reagent in ether at room temperature, dihexylsilane disappeared soon after to generate n-Hex_2SiHBr as the primary product. The monobromide then diminished slowly and disappeared after 44 h, during which n-$Hex_2Si(OEt)H$ and n-$Hex_2Si(OEt)Br$ began to increase and became the final products, indicating that the

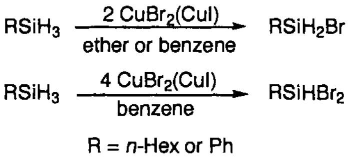
Table 1. Reaction of hydrosilanes with $CuBr_2$(CuI) reagent

Run	Hydrosilane	$CuBr_2$/equiv[a]	Solvent	Temp	Time/h	Product (yield/%)
1	Et_3SiH	2.0	Et_2O	r.t.	1.5	Et_3SiBr (82)
2	n-Hex_2SiH_2	2.0	Et_2O	r.t.	1	n-Hex_2SiHBr (73)
3	n-Hex_2SiH_2	4.0	benzene	reflux	34	n-Hex_2SiBr_2 (70)
4	$MePhSiH_2$	2.0	Et_2O	r.t.	9	MePhSiHBr (68)
5	Ph_2SiH_2	2.1	toluene	r.t.	7.5	Ph_2SiHBr (64)
6	n-$HexSiH_3$	2.1	Et_2O	r.t.	12	n-$HexSiH_2Br$ (64)
7	n-$HexSiH_3$	4.1	benzene	r.t.	1 week	n-$HexSiHBr_2$ (55)
8	$PhSiH_3$	2.0	benzene	r.t.	6	$PhSiH_2Br$ (72)
9	$PhSiH_3$	4.2	benzene	r.t.	40	$PhSiHBr_2$ (67)
10	$HEt_2SiSiEt_2H$	2.1	benzene	r.t.	4	$HEt_2SiSiEt_2Br$ (58)[b]

[a] CuI (1–2 mol%) was added as the catalyst. [b] Et_2SiHBr (10%) was formed as the byproduct.

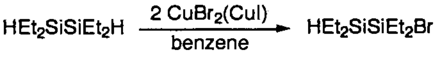
monobromination proceeds quite fast, while dibromination requires much longer time, and the bromide once formed reacts gradually with ether to give ethoxy derivatives.[16] To suppress undesired reactions, we changed the solvent from ether to benzene. When n-Hex_2SiH_2 was treated with 4 equiv of the $CuBr_2(CuI)$ reagent in benzene under reflux for 34 h, n-Hex_2SiBr_2 was obtained in 70% isolated yield (run 3).

Mono- and dibrominations of trihydrosilanes are also possible (runs 6–9). When n-$HexSiH_3$ was treated with 2 equiv of the $CuBr_2(CuI)$ reagent in ether at room temperature for 12 h, n-$HexSiH_2Br$ was obtained in 64% yield as the sole product after distillation. When n-$HexSiH_3$ was treated with 4 equiv of the $CuBr_2(CuI)$ reagent in benzene at room temperature for 1 week, n-$HexSiHBr_2$ was obtained in 55% isolated yield. Moreover, the reaction of $PhSiH_3$ with 2 equiv of the reagent in benzene at room temperature for 6 h afforded $PhSiH_2Br$ in 72% yield, while treatment with 4 equiv of the reagent in benzene at room temperature for 40 h produced $PhSiHBr_2$ in 67% yield.



On the other hand, attempted tribromination with this reagent did not take place. When $PhSiH_3$ was heated under reflux in benzene with 6 equiv of the $CuBr_2(CuI)$ reagent, dibromination completed within 3 h,[17] much faster than the case using 4 equiv of the reagent at room temperature. However, the reaction stopped at this stage, and no tribromide would be formed even after 1 week. Presumably, accumulation of electronegative bromine atoms on the same silicon center decreases the reactivity of the silicon center, as has been observed previously for the chlorination of fluorohydrosilanes.[2]

We also performed selective bromination of 1,2-dihydrodisilanes. Thus, when $HEt_2SiSiEt_2H$ was treated with 2 equiv of the reagent in benzene at room temperature for 4 h, $HEt_2SiSiEt_2Br$ was obtained in 58% isolated yield, together with a 10% yield of Et_2SiHBr (run 10).



The selectivity of the bromodisilane diminished in this case, but two products could be readily separated by distillation. The monosilane may be produced by the cleavage of an Si–Si bond of disilane with HBr generated during the reaction.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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15 A typical procedure is as follows. In a 300-mL flask, was placed a mixture of $MePhSiH_2$ (6.94 g, 56.7 mmol), $CuBr_2$ (25.66 g, 114.9 mmol), and CuI (0.48 g, 2.5 mmol) in 70 mL of diethyl ether under Ar, and the mixture was stirred at room temperature for 9 h. The mixture was filtered to remove Cu salts and concentrated. The residue was distilled under reduced pressure to give 7.75 g (38.6 mmol, 68%) of MePhSiHBr: b.p. 83–86 °C (16 mmHg); MS m/z 200 (M^+), 185 (M^+–Me), 123 (M^+–Ph), 121 (M^+–Br); ^1H NMR (δ in $CDCl_3$) 0.47 (3 H, d, J = 3.5 Hz, Me), 5.31 (1 H, q, J = 3.5 Hz, SiH), 7.42–7.71 (5 H, m, phenyl H); ^{13}C NMR (δ in $CDCl_3$) 0.36, 127.87, 128.25, 130.94, 133.84; ^{29}Si NMR (δ in $CDCl_3$) –2.98. Anal. Calcd for C_7H_9BrSi: C, 48.40; H, 4.51%. Found: C, 48.52; H, 4.60%.

16 Nevertheless, diethyl ether can be used as the solvent for bromination, unless the reaction requires longer reaction time. The reaction in ether is faster than in benzene, and subsequent work up is easy due to the low boiling point.

17 Dibromination of hexylsilane (run 7) may complete also faster under reflux conditions.