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**Preliminary communication**

# SILICON—CARBON BOND FORMATION BY THE REACTION OF DISILANES WITH HALOBENZENES IN THE PRESENCE OF TETRAKIS-(TRIPHENYLPHOSPHINE)PALLADIUM(0)

HIDEYUKI MATSUMOTO*, SHIGERU NAGASHIMA, KAZUO YOSHIHIRO and YOICHIRO NAGAI
*Department of Chemistry, Gunma University, Kiryu, Gunma 376 (Japan)*

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## Summary

Cleavage of disilanes with halobenzenes such as bromobenzene and chlorobenzene to afford arylsilanes was found to occur under the catalytic influence of tetrakis(triphenylphosphine)palladium(0).

Although cleavage of silicon—silicon bonds by the attack of nucleophiles such as alcohols and metal alkoxides has been the subject of much concern [1], little attention has been directed to the cleavage of polysilanes by organic halides* (eqn. 1).

$$\equiv\text{Si—Si}\equiv + \equiv\text{C—X} \rightarrow \equiv\text{Si—C}\equiv + \equiv\text{Si—X} \qquad (1)$$

(X = Cl, Br, I)

Thermochemical consideration of reaction 1 ** might lead to the prediction that this reaction would occur in the presence of an appropriate catalyst which activates silicon—silicon or carbon—halogen bonds. In this connection, it should be recalled that some low-valent Group VIII metal—phosphine complexes activate halobenzenes via oxidative addition processes [4]. Such complexes then are expected to act as effective homogeneous catalysts for the reaction of disilanes with halobenzenes. We have found that tetrakis(triphenylphosphine)palladium(0) effectively catalyzes the reaction of disilanes such as hexamethyldisilane, 1,1,2,2-tetramethyl-1,2-dichlorodisilane and 1,2-dimethyl-1,1,2,2-tetrachlorodisilane with some bromo- and chloro-benzenes (eqn. 2).

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*A patent claimed cleavage of disilanes by alkyl and aryl halides in the presence of Group VIII metal—phosphine complexes, but no examples for which tetrakis(triphenylphosphine)palladium(0) was utilized as a catalyst were mentioned [2].

**Enthalpies of the reactions estimated on basis of bond energy data [3] are −20 kcal/mol (X = Cl), −23 kcal/mol (X = Br) and −28 kcal/mol (X = I). Therefore, the reactions are concluded to be exothermic.

$$YC_6H_4X + Me_{6-n}Si_2Cl_n \xrightarrow{L_4Pd^0} YC_6H_4SiMe_{3-n}Cl_n + Me_{3-n}SiXCl_n \qquad (2)$$

(X = Cl, Br)

Thus, a mixture of 1.57 g (10.0 mmol) of bromobenzene, 1.02 g (7.0 mmol) of hexamethyldisilane, 40 mg (0.4 mmol) of tetrakis(triphenylphosphine)palladium(0) and 5 ml of toluene as a solvent was heated in a sealed glass tube to 140°C for 20 h. GLC analysis of the resulting solution indicated that hexamethyldisilane had been almost completely consumed and that phenyltrimethylsilane and trimethylbromosilane had been produced in yields of 100 and 99%, respectively. The reaction can be conducted without any added solvent, but the use of a solvent such as toluene and benzene gave somewhat better results.

Under almost the same conditions, the reaction of 1,1,2,2-tetramethyl-1,2-dichlorodisilane with bromobenzene afforded an equimolar mixture of phenyldimethylchlorosilane and dimethylbromochlorosilane in 98% yield. Similarly, heating a mixture of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane and bromobenzene gave phenylmethyldichlorosilane in 81% yield. *p*-Bromoanisole reacted with hexamethyldisilane to afford *p*-anisyltrimethylsilane in 39% yield. In this case, a considerable amount (45%) of anisole also was produced. The formation of this compound is likely due to protodesilylation [5] of *p*--anisyltrimethylsilane, since trimethylbromosilane reacts readily with moisture to give hydrogen bromide (eqns. 3-5).

$$p\text{-}MeOC_6H_4Br + Me_3SiSiMe_3 \rightarrow p\text{-}MeOC_6H_4SiMe_3 + Me_3SiBr \qquad (3)$$

$$2Me_3SiBr + H_2O \rightarrow (Me_3Si)_2O + 2HBr \qquad (4)$$

$$p\text{-}MeOC_6H_4SiMe_3 + HBr \rightarrow p\text{-}MeOC_6H_5 + Me_3SiBr \qquad (5)$$

The cleavage of hexamethyldisilane by chlorobenzene did not proceed at 140° C to any significant extent, and more drastic conditions were required to induce the reaction (see Table 1). However, introduction of an electron-withdrawing substituent, i.e., the nitro group, increased the reactivity of chlorobenzene. Thus, heating a mixture of hexamethyldisilane and *p*-nitrochlorobenzene in the presence of the complex to 140°C for 18 h led to formation of *p*-nitrophenyltrimethylsilane (100% yield) and trimethylchlorosilane (90% yield). The reaction is of some value since nitration of phenyltrimethylsilane can only be achieved with great difficulty [6].

All the arylsilanes obtained were readily identified by comparing their physical constants with reported values after isolation by GLC.

Cleavage of hexamethyldisilane by iodobenzene did not proceed under comparable conditions. The result may be attributed to the stability of the oxidative adduct of iodobenzene to the complex [7], and in fact, iodo(phenyl)bis(triphenylphosphine)palladium(II) did not react with hexamethyldisilane at temperatures of 100-120°C.

Dichlorobis(triphenylphosphine)palladium(II) also was found to initiate the reaction of hexamethyldisilane with bromobenzene, but the catalyst was not as active as the Pd° complex. This is implied by the fact that with the divalent complex the reaction went to only 40% completion at 140°C in 20 h.

TABLE 1

REACTIONS OF DISILANES WITH HALOBENZENES IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0)

| Disilane | Halobenzene | Conditions | Product (yield, %) [d] | | Conversion (%) [g] |
|---|---|---|---|---|---|
| $\mathrm{Me_3SiSiMe_3}$ [a] | $\mathrm{C_6H_5Br}$ | 140°C, 20 h | $\mathrm{C_6H_5SiMe_3}$ | (100) | 99 |
| | | | $\mathrm{Me_3SiBr}$ | ( 99) | |
| $\mathrm{Me_3SiSiMe_3}$ [c] | $\mathrm{C_6H_5Br}$ | 140°C, 33 h | $\mathrm{C_6H_5SiMe_3}$ | ( 99) | 92 |
| | | | $\mathrm{Me_3SiBr}$ | (100) | |
| $\mathrm{Me_3SiSiMe_3}$ [b] | $\mathrm{4\text{-}CH_3OC_6H_4Br}$ | 130°C, 20 h | $\mathrm{4\text{-}MeOC_6H_4SiMe_3}$ | ( 39) [e] | 100 |
| | | | $\mathrm{C_6H_5OMe}$ | ( 45) [e] | |
| | | | $\mathrm{Me_3SiBr}$ | ( 95) | |
| $\mathrm{ClMe_2SiSiMe_2Cl}$ [a] | $\mathrm{C_6H_5Br}$ | 140°C, 20 h | $\mathrm{C_6H_5SiMe_2Cl}$ | ( 98) | 100 |
| | | | $\mathrm{Me_2SiBrCl}$ | ( 98) | |
| $\mathrm{Cl_2MeSiSiMeCl_2}$ [a] | $\mathrm{C_6H_5Br}$ | 145°C, 25 h | $\mathrm{C_6H_5SiMeCl_2}$ | ( 81) | 76 |
| | | | $\mathrm{MeSiBrCl_2}$ | (— ) [f] | |
| $\mathrm{Me_3SiSiMe_3}$ [a] | $\mathrm{C_6H_5Cl}$ | 170°C, 30 h | $\mathrm{C_6H_5SiMe_3}$ | ( 98) | 10 |
| | | | $\mathrm{Me_3SiCl}$ | (100) | |
| $\mathrm{Me_3SiSiMe_3}$ [b] | $\mathrm{4\text{-}NO_2C_6H_4Cl}$ | 140°C, 18 h | $\mathrm{4\text{-}NO_2C_6H_4SiMe_3}$ | (100) [e] | 66 |
| | | | $\mathrm{Me_3SiCl}$ | ( 95) | |
| $\mathrm{Me_3SiSiMe_3}$ [a] | $\mathrm{C_6H_5I}$ | 120°C, 20 h | $\mathrm{C_6H_5SiMe_3}$ | (— ) | < 1 |

[a] Reactions were carried out in toluene with a 1/1.5 mixture of a disilane and a halobenzene, the catalyst concentration being 0.5 mol % based on the disilane charged. [b] A 1.5/1 mixture of a disilane and a halobenzene was used. [c] No solvent was used. [d] Yields are based on the disilane used (via GLC) unless otherwise indicated. [e] Yields are based on the halobenzene used. [f] Not determined. [g] Conversion was (moles of disilane consumed)/(moles of disilane charged).

The present system thus may furnish a convenient method for converting disilanes (which are obtained as undesirable by-products from direct synthesis for making methylchlorosilanes) to potentially useful arylsilanes.

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