A Convenient Synthesis of Alkynylsilanes by Silylation of Copper(I) Alkynides

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Alkynylation of chlorosilanes with copper(I) alkynides takes place smoothly in the presence of triphenylphosphine, N, N, N', N'-tetramethylethylenediamine, or zinc powder to give a variety of alkynylsilanes in good yields.

Copper(I) alkynides are versatile reagents widely used for the general synthesis of conjugated acetylenic compounds,[1] because the copper reagents are stable to moisture and can be prepared by the reaction of 1-alkyne with an ammonia solution of copper(I) chloride. Thanks to their easy preparation, the Castro reaction and the Glaser reaction are extremely versatile. However, use of copper(I) alkynide for the synthesis of organosilicon compounds have been scarce to date.[2] For this purpose, alkynylmetals of Li, Na, and Mg[3] have been employed generally. As these alkynylmetals are highly nucleophilic and attack a variety of functional groups, these are not without limitations. We report a novel alkynylation reaction of chlorosilanes using copper(I) alkynides.

$$\mathrm{n\ Cu{-}C{\equiv}C{-}R} + \mathrm{R'_{4-n}SiCl_n} \longrightarrow \mathrm{R'_{4-n}Si{(}{-}C{\equiv}C{-}R{)}_n}$$

R = alkyl, aryl; R' = H, alkyl, aryl; n = 1, 2

The reaction of phenylethynylcopper with chlorotrimethylsilane was first studied in various solvents. Results are summarized in Table 1. The one in acetonitrile, benzene, or triethylamine failed to give rise to a detectable amount of the alkynylsilane (entries 1-3). When the reaction was carried out in pyridine that was successfully used for the Castro reaction, the alkynylsilane was obtained in 71% yield (entry 5). Although N,N-dimethylformamide (DMF) also can be utilized for the Castro reaction, the alkynylation of chlorotrimethylsilane did not occur in DMF (entry 4). We were pleased to find that a certain additive strongly accelerated the silylation reaction. The excellent results were obtained with triphenylphosphine (2 mol equiv), N, N, N', N'-tetramethylethylenediamine (TMEDA, 2 mol equiv), or zinc powder (8 mol equiv) in acetonitrile. The reaction proceeded smoothly at 100 °C to give 1-phenyl-2-(trimethylsilyl)ethyne in nearly quantitative yields (entries 6-8). A catalytic amount of triphenylphosphine or zinc powder was not effective enough. Although the combination of diethyl ether, tetrahydrofuran (THF), benzene, or DMF with triphenylphosphine gave the alkynylsilane, the conversion was rather unsatisfactory.

Following procedure for the preparation of 1-phenyl-2-(triethylsilyl)ethyne is representative. To a suspension of copper(I) phenylethynilide (0.5 mmol) in acetonitrile (2 ml) were added chlorotriethylsilane (0.6 mmol) and TMEDA (1.0 mmol). The mixture was heated under an argon atmosphere at 100 °C for 12 h in a sealed tube. The resulting mixture was concentrated and purified by column chromatography on silica gel to give 1-phenyl-2-(triethylsilyl)ethyne in 65% yield. The reaction conditions thus optimized were then applied to various copper(I) alkynides and chlorosilanes. Results are summarized in Table 2.

Table 1. Synthesis of 1-(Trimethylsilyl)-2-phenylethyne[a]

Entry	Solvent	Additive (equiv)	Yield (%)[b]
1	MeCN	—	0
2	C_6H_6	—	0
3	NEt_3	—	0
4	DMF	—	0
5	pyridine	—	71
6	MeCN	PPh_3 (2)	98
7	MeCN	Zn (8)	98
8	MeCN	TMEDA (2)	86

[a]Reactions were performed in a solvent (2 ml) with copper(I) phenylacetylide (1.0 equiv), chlorotrimethylsilane (4.0 equiv) at 100 °C in a sealed tube unless otherwise noted. [b]Isolated yields are given.

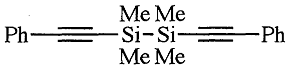
Phenylethynylation of chlorodimethylphenysilane, benzylchlorodimethylsilane, and chlorodimethylvinylsilane has been performed in the presence of two-fold excess of TMEDA and gave the corresponding alkynylsilanes in good yields (entries 3, 5, and 6). When the reaction of chloro(methyl)phenylsilane with copper(I) phenylacetylide was carried out in the presence of two-fold excess of triphenylphosphine, 1-(methylphenylsilyl)-2-phenylethyne was obtained in 36% yield (entry 4). Double phenylethynylations of dichlorodimethylsilane also effectively proceeded by applying three-fold molar excess of copper(I) acetylide and gave a high yield of the corresponding dialkynylsilane (entry 7). Both 1,2-dichloro-1,1,2,2-tetramethyldisilane and 1,3-dichloro-1,1,3,3-tetramethyldisiloxane reacted with the copper(I) acetylide to form the corresponding dialkynyldisilane and dialkynyldisiloxane respectively (entries 8 and 9). 1-(Trimethylsilyl)-1-octyne is accessible in high yield by the reaction of the corresponding copper(I) alkynide with chlorotrimethylsilane in the presence of triphenylphosphine (entry 10). Special attention should be paid to the of copper(I) alkynides bearing a functional group such as hydroxyl or chlorine. These tolerated the reaction and gave the corresponding alkynylsilanes in good yield (entries 11 and 12).

In conclusion, the alkynylation of chlorosilanes with copper(I) alkynides provides a novel route to a wide variety of alkynylsilanes. Studies on its synthetic application and mechanistic details are now in progress.[4]

References and Notes

1 a) K. Sonogashira, in "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), vol. 3, p. 521 and 551; b) W. Carruthers, in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, E. W. Abel, Pergamon Press, Oxford (1982), vol. 7, p. 691; c) R. D. Stephens and C. E.

Table 2. Reactions of Copper (I) alkynides with Chlorosilanes[a]

Entry	Copper (I) alkynide	Chlorosilane	Additive[b]	Product	Yield (%)[c]
1	$Cu{-}{\equiv}{-}Ph$	Me_3SiCl[d]	Zn	$Me_3Si{-}{\equiv}{-}Ph$	98
2	$Cu{-}{\equiv}{-}Ph$	Et_3SiCl	TMEDA	$Et_3Si{-}{\equiv}{-}Ph$	65
3	$Cu{-}{\equiv}{-}Ph$	$PhMe_2SiCl$	TMEDA	$PhMe_2Si{-}{\equiv}{-}Ph$	92
4	$Cu{-}{\equiv}{-}Ph$	$PhMeHSiCl$	PPh_3	$PhMeHSi{-}{\equiv}{-}Ph$	36
5	$Cu{-}{\equiv}{-}Ph$	$PhCH_2SiMe_2Cl$	TMEDA	$(PhCH_2)Me_2Si{-}{\equiv}{-}Ph$	84
6	$Cu{-}{\equiv}{-}Ph$	$(H_2C{=}CH)SiMe_2Cl$	TMEDA	$(H_2C{=}CH)Me_2Si{-}{\equiv}{-}Ph$	81
7[e]	$Cu{-}{\equiv}{-}Ph$	Me_2SiCl_2	TMEDA	$Me_2Si{-}({\equiv}{-}Ph)_2$	98
8[e]	$Cu{-}{\equiv}{-}Ph$	$ClMe_2SiSiMe_2Cl$	TMEDA	 $Ph{-}{\equiv}{-}\underset{Me\,Me}{\overset{Me\,Me}{Si{-}Si}}{-}{\equiv}{-}Ph$	57
9[e]	$Cu{-}{\equiv}{-}Ph$	$ClMe_2SiOSiMe_2Cl$	TMEDA	 $Ph{-}{\equiv}{-}\underset{Me\;Me}{\overset{Me\;Me}{SiOSi}}{-}{\equiv}{-}Ph$	34
10	$Cu{-}{\equiv}{-}(CH_2)_5CH_3$	Me_3SiCl[d]	PPh_3	$Me_3Si{-}{\equiv}{-}(CH_2)_5CH_3$	73
11	$Cu{-}{\equiv}{-}(CH_2)_3Cl$	Me_3SiCl[d]	Zn	$Me_3Si{-}{\equiv}{-}(CH_2)_3Cl$	57
12	$Cu{-}{\equiv}{-}(CH_2)_3OH$	Me_3SiCl[d]	Zn	$Me_3Si{-}{\equiv}{-}(CH_2)_3OH$	74

[a] Reactions were carried out in acetonitrile with copper(I) alkynide (1.0 equiv), and chlorosilane (1.2 - 2.0 equiv) at 100 °C in a sealed tube unless otherwise noted. [b] Zn: 8.0 equiv; TMEDA: 2.0 equiv; PPh_3: 2.0 equiv. [c] Isolated yields. [d] The reaction was performed by using four-fold molar excess of chlorotrimethylsilane. [e] The reactions were performed by using copper (I) phenylacetylide (3.0 equiv) and chlorosilanes (1.0 equiv).

Castro, *J. Org. Chem.*, **28,** 3313 (1963); d) C. E. Castro, E. J. Gauhan, and D. C. Owsley, *J. Org. Chem.*, **31,** 4071 (1966); e) H. Hopf and N. Krause, *Tetrahedron Lett.*, **26,** 3323 (1985); f) K. -H. Duchene and F. Vogtle, *Synthesis*, **1986,** 659.

2 a) Calas and his coworkers reported that chlorosilanes reacted with 1-alkynes leading to the corresponding alkynylsilanes in the presence of catalytic amounts of copper(I) chloride. However, the reaction must be carried out under severe conditions for prolonged period: G, Deleris, J. Dunogues, and R. Calas, *J. Organomet. Chem.*, **80,** C45 (1974); b) Yamaguchi and his coworkers reported the trimethylsilylation of 1-alkynes by using a combination of chlorotrimethylsilane and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of copper(I) chloride: Y. Taniguchi, J. Inanaga, and M. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **54,** 3229 (1981); c) Liu and Harrod have reported the copper(I) chloride catalyzed cross-dehydrocoupling reactions between silanes and ethynyl compounds: H. Q. Liu and J. F. Harrod, *Can. J. Chem.*, **68,** 1100 (1990).

3 a) G. Zweifel and W. Lewis, *J. Org. Chem.*, **43,** 2739 (1978); b) R. B. Miller and T. Reichenbach, *Tetrahedron Lett.*, **1974,** 543; c) L. Birkofer and O. Stuhl, in "The Chemistry of Organosilicon Compounds," ed by S. Patai and Z. Rappoport, John Wiley and Sons, New York (1989), p. 655.

4 Although no direct evidence concerning the mechanism is available, breakdown of the polymeric structures of copper(I) alkynides triggered the reactivity by the addition of external ligands such as triphenylphosphine or TMEDA.
The silylation of copper alkynides in the presence of zinc powder may be rationalized by the reaction of chlorosilanes with zinc alkynides, generated from the transmetalation of metallic zinc onto copper(I) alkynides. In our previous work, we have reported a convenient method for the preparation of alkynylsilanes by the direct silylation of 1-alkynes with chlorosilanes promoted by metallic zinc. We have proposed an alkynylzinc species as a reactive intermediate in the reaction: H. Sugita, Y. Hatanaka, and T. Hiyama, *Tetrahedron Lett.*, **36,** 2769 (1995).