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Silylation of 1-Alkynes with Chlorosilanes Promoted by Zinc: Preparation of Alkynylsilanes in a Single Step

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Abstract: The direct silylation of 1-alkynes with chlorosilanes smoothly takes place in the presence of zinc powder in acetonitrile, giving good yields of alkynylsilanes. The reactions are tolerant of a wide range of functionalities such as carboxylic acid, ester, alcohol, and chlorine in the 1-alkynes.

Alkynylsilanes have been extensively used as versatile reagents[1] for Lewis acid promoted alkynylation of a variety of electrophiles,[2] protecting groups for terminal alkynes,[3] and substrates for the palladium catalyzed alkynylation of organic halides or triflates,[4] and have also found numerous applications in recent literatures.[5] These compounds have been usually synthesized through the reaction of a suitable chlorosilane with an alkynylmetal, prepared by the metalation of 1-alkyne with organometallic reagents such as butyllithium or Grignard reagents.[6] However, the use of a stoichiometric amount of organometallic reagents in these procedures has made it difficult to carry out a large scale preparation of alkynylsilanes in laboratories and in industry. We wish to report that the direct silylation of terminal alkynes with chlorosilanes takes place in the presence of zinc powder in acetonitrile to give the corresponding alkynylsilanes in good yields.[7]

$$R_nSiCl_{4-n} + H-C\equiv C-R' \xrightarrow[\text{MeCN, 120 °C}]{\text{Zn powder}} R_nSi\left(C\equiv C-R'\right)_{4-n} \qquad (1)$$

R, R' = alkyl, aryl

Various combinations of metals and solvents were examined for the reaction of phenylethyne (0.50 mmol) with chlorotrimethylsilane (1.0 mmol) in order to optimize the reaction conditions (Table 1). The choice of the metals strongly influenced the conversion to alkynylsilane. The best results were obtained by using zinc powder in acetonitrile; the reaction proceeded smoothly at 120 °C in a sealed tube to complete within 5 h, giving (trimethylsilyl)phenylethyne in 98% yield (entry 1). Although the reaction with Zn-Cu couple[8] took place at 80 °C in acetonitrile to afford the same product in 94% yield (entry 2), this procedure caused a significant reduction of the carbon-carbon triple bond of the 1-alkyne in several cases (e.g., Table 2, entry 6). The reaction using magnesium powder in acetonitrile at 120 °C failed to give rise to a detectable amount of the product (entry 3). When the reaction was carried out in ether with sodium at room temperature, the alkynylsilane was obtained in 68% yield (entry 4). However, the silylation of aliphatic 1-alkynes by this procedure gave rather unsatisfactory

Table 1. Reactions of Chlorotrimethylsilane with Phenylethyne[a]

Entry	Metal	Solvent	Conditions	Yield of (trimethylsilyl)phenylethyne (%)[b]
1	Zn	acetonitrile	120 °C, 5 h	98
2	Zn-Cu couple	acetonitrile	80 °C, 5 h	94
3	Mg	acetonitrile	120 °C, 5 h	0
4	Na	ether	r.t., 12 h	68
5	Zn	toluene	120 °C, 5 h	0
6	Zn	DMF	120 °C, 5 h	0
7	Zn	THF	120 °C, 5 h	0[c]

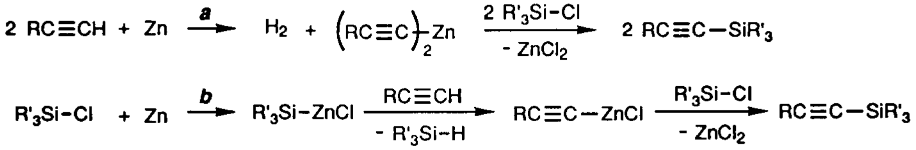
[a] Reactions were carried out in 2 ml of solvent with 1.0 mmol of chlorosilane, 0.50 mmol of phenylacetylene and 2.0 mmol of metal powder in a sealed tube . [b] Isolated yields.
[c] Fair amount of the ring-opening product of THF was obtained.

Table 2. Reactions of Chlorosilanes with 1-Alkynes[a]

Entry	Chlorosilane	1-Alkyne	Product	Yield (%)[b]
1	Me_3SiCl	$HC\equiv CPh$	$Me_3SiC\equiv CPh$	98
2	Me_3SiCl	$HC\equiv C(CH_2)_5CH_3$	$Me_3SiC\equiv C(CH_2)_5CH_3$	86
3	Me_3SiCl	$HC\equiv C(CH_2)_7CH_3$	$Me_3SiC\equiv C(CH_2)_7CH_3$	98 (22)[c]
4	Me_3SiCl	$HC\equiv C(CH_2)_3Cl$	$Me_3SiC\equiv C(CH_2)_3Cl$	80
5[d]	Me_3SiCl	$HC\equiv C(CH_2)_3OH$	$Me_3SiC\equiv C(CH_2)_3OH$	98
6[d]	Me_3SiCl	$HC\equiv C(CH_2)_2COOH$	$Me_3SiC\equiv C(CH_2)_2COOH$	44 (52)[e]
7	Me_3SiCl	1,4-$(HC\equiv C)_2(C_6H_4)$	1,4-$(Me_3SiC\equiv C)_2(C_6H_4)$	70
8	Et_3SiCl	$HC\equiv C(CH_3)_3$	$Et_3SiC\equiv C(CH_3)_3$	32
9	Et_3SiCl	$HC\equiv C(CH_2)_2COOMe$	$Et_3SiC\equiv C(CH_2)_2COOMe$	46
10[f]	Me_2SiCl_2	$HC\equiv CPh$	$Me_2Si(C\equiv CPh)_2$	98
11	$ClMe_2SiSiMe_2Cl$	$HC\equiv CPh$	$(PhC\equiv C)Me_2SiSiMe_2(C\equiv CPh)$	76
12	$PhMe_2SiCl$	$HC\equiv C(CH_2)_7CH_3$	$PhMe_2SiC\equiv C(CH_2)_7CH_3$	96

[a] Reactions were performed in acetonitrile at 120 °C for 5 h in a sealed tube, by using 1.0 equiv of 1-alkyne, 2.0 equiv of chlorosilane, and 4.0 equiv of Zn powder unless otherwise noted. [b] Isolated yields. [c] Yield in parentheses was obtained from the reaction using sodium in ether at room temperature. [d] The reaction was performed by using 4.0 equiv of chlorotrimethylsilane. [e] Yield in parentheses was obtained by using Zn-Cu couple under the same conditions. The reaction gave a fair amount of 4-pentenoic acid. [f] The reaction was performed by using 1.0 equiv of dichlorodimethylsilane and 2.0 equiv of phenylethyne.

Scheme 1. Proposed Mechanism for Silylation of Alkynes



$$2\ RC\equiv CH + Zn \xrightarrow{a} H_2 + \left(RC\equiv C\right)_2 Zn \xrightarrow[-\ ZnCl_2]{2\ R'_3Si\text{-}Cl} 2\ RC\equiv C\text{—}SiR'_3$$

$$R'_3Si\text{-}Cl + Zn \xrightarrow{b} R'_3Si\text{-}ZnCl \xrightarrow[-\ R'_3Si\text{-}H]{RC\equiv CH} RC\equiv C\text{—}ZnCl \xrightarrow[-\ ZnCl_2]{R'_3Si\text{-}Cl} RC\equiv C\text{—}SiR'_3$$

results (e.g., Table 2, entry 3). The conversion to alkynylsilanes is also very sensitive to the nature of solvent used; the silylation of phenylethyne did not occur in toluene or *N,N*-dimethylformamide (DMF) (entries 5 and 6). The reaction in tetrahydrofuran (THF) led to extensive ring-opening reaction of THF (entry 7).

The reaction conditions thus optimized (acetonitrile, Zn powder, 120 °C for 5 h) have been applied to a number of the reactions of 1-alkynes with chlorosilanes (Table 2). The following procedure for the preparation of 5-chloro-1-trimethylsilyl-1-pentyne is representative (Table 2, entry 4). To a suspension of 2.61 g (40 mmol) of zinc powder (obtained from Merck Chem. Co.) in 10 ml of acetonitrile (distilled from CaH_2) was added 1.03 g (10 mmol) of 5-chloro-1-pentyne and 2.17 g (20 mmol) of chlorotrimethylsilane (distilled from CaH_2). The resulting mixture was heated at 120 °C for 5 h in a sealed tube. The small scale reaction (<20 mmol) can be conveniently carried out in a pyrex glass tube (60-100 ml) with a plastic cap. For the larger scale preparation, the use of a glass autoclave is recommended . After removal of excess zinc by filtration, the filtrate was condensed under reduced pressure. Crude product was purified by bulb-to-bulb distillation (bp 120-150°C (50 mmHg)) to afford 1.40 g (80%) of 5-chloro-1-trimethylsilyl-1-pentyne as a colorless liquid.[9]

Trimethylsilylation (entries 1-7), triethylsilylation (entries 8 and 9) and dimethyl(phenyl)silylation (entry 12) of the 1-alkynes have been effectively performed by using a two-fold excess of the corresponding chlorosilanes in the presence of the four-fold excess of zinc powder, giving the high yields of the corresponding alkynylsilanes. Double silylation of 1,4-diethynylbenzene with chlorotrimethylsilane also effectively proceeded under the same conditions (entry 7). Smooth reaction of 1,2-dichloro-1,1,2,2-tetramethyldisilane with phenylethyne apparently indicates that the Si-Si bond remains intact under the reaction conditions (entry 11). The present results have proved the utility of this method as a general route to a wide variety of alkynylsilanes. An important feature of the zinc-promoted silylation of 1-alkynes is the high chemoselectivity; the reaction tolerates a variety of functionalities such as chlorine (entry 4), alcohol (entry 5), carboxylic acid (entry 6), and ester (entry 9), thus, providing a straightforward route to alkynylsilanes bearing various functional groups.

With the aim of revealing the reaction mechanism, a series of experiments were carried out. An attempt to prepare a silylzinc species from the reaction of chlorotrimethylsilane with zinc powder in acetonitrile at 120 °C was unsuccessful; chlorotrimethylsilane remained unchanged under the reaction conditions. In order to establish the stoichiometric relationship of the reaction, 1.0 mmol of chlorotriethylsilane was subjected to the reaction with 2.0 mmol of phenylethyne under the same conditions; the reaction gave 0.64 mmol of (triethylsilyl)phenylethyne (64%) and 0.09 mmol of hexaethylsiloxane (18%). These results strongly suggest that the reactive intermediate of the silylation is an alkynylzinc species, generated *in situ* from the direct metalation of 1-alkynes with zinc (Scheme 1, path ***a***). An alternative pathway which involves the participation of a silylzinc species (path ***b***) is unlikely, since according to this mechanism, the conversion of 1 mole of the 1-alkynes requires 2 moles of the chlorosilanes. The path ***a*** is also supported by the following experiment. The reaction of phenylethyne (1.0 mmol) with a large excess of benzaldehyde (10 mmol) in the presence of zinc powder (10 mmol) in acetonitrile at 120 °C for 5 h gave 1,3-diphenyl-1-propyne-3-ol in 13% (eq 2). This result can be explained in terms of the participation of phenylethynylzinc species which reacts with benzaldehyde, giving the corresponding adduct.[10]

$$\mathrm{PhCHO} \quad + \quad \mathrm{HC{\equiv}CPh} \quad \xrightarrow[\text{MeCN, 120 °C}]{\text{Zn powder}} \quad \mathrm{PhCH(OH)(C{\equiv}CPh)} \qquad (2)$$

In conclusion, the zinc-promoted silylation of 1-alkynes with chlorosilanes provides an efficient, general and practical route to a wide variety of alkynylsilanes. The present method has offered several distinct advantages over the conventional syntheses of alkynylsilanes which require the use of a stoichiometric amount of organometallic reagents and protection-deprotection procedure for functional groups in starting materials. Furthermore, we have proposed an alkynylzinc species as a reactive intermediate, generated from the direct metalation of the 1-alkynes with zinc.[11] Studies on its application to organic synthesis and mechanistic details are currently undertaken in our laboratory.

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9. ^{1}H NMR (200 MHz, CDCl3) δ 0.15 (s, 9H), 1.97 (m, 2H), 2.41 (t, J = 6.8 Hz, 2H), 3.65 (t , J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 0.05, 17.3, 31.3, 43.5, 85.6, 105.1; IR (neat) 2950, 2170, 2124, 840, 755 cm^{-1}. Anal. Calcd for $C_8H_{15}ClSi$: C, 54.99; H, 8.65. Found: C, 55.04; H, 8.88.
10. Step-wise reaction where benzaldehyde was added to the reaction mixture after heating of phenylethyne and zinc in acetonitrile at 120 °C failed to give the adduct. This result would be due to the decomposition of phenylethynylzinc species at the high reaction temperature.
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