Notes

Syntheses of 1,3-Disilaindanes, 1,4-Disilatetralines, and 1,3-Disila-1,3-dihydroisobenzofuranes Using Cobalt-Catalyzed [2+2+2] Cycloadditions

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Summary: A simple catalytic system for [2+2+2] alkyne cycloadditions consisting of cobalt(II) iodide and zinc powder in acetonitrile was applied to the direct synthesis of hydroxyalkyl-substituted 1,3-disilaindanes, 1,4-disilatetralines, and 1,3-disila-1,3-dihydroisobenzofuranes starting from silicon-containing diynes and unprotected propargyl alcohols. Silicon-containing diynes were efficiently coupled with propargyl alcohols with a terminal or internal monoyne moiety. The method reported allows efficient, one-step syntheses of the title compounds.

Introduction

The catalytic [2+2+2] cyclotrimerization of alkynes is an attractive method for synthesizing polysubstituted benzene derivatives[1,2] and is demonstrated here to be an efficient method for the synthesis of hydroxyalkyl-substituted 1,3-disilaindanes, 1,4-disilatetralines, and 1,3-disila-1,3-dihydroisobenzofuranes. As we have recently demonstrated, compounds with a 1,1,3,3-tetramethyl-1,3-disilaindane or 1,1,4,4-tetramethyl-1,4-disila-1,2,3,4-tetrahydronaphthalene skeleton are of great interest because of their potential application as pharmaceuticals[3] or fragrances,[4] and 1,3-disila-1,3-dihydroisobenzofuranes have been reported to be valuable reagents in the generation of benzynes.[5]

Recently, we have shown that cobalt(II) iodide in the presence of zinc powder in acetonitrile can efficiently catalyze arene syntheses by [2+2+2] cycloaddition of monoynes with diynes,[6] and neither additional zinc iodide nor additional ligands are necessary for this reaction (in this context, see also ref 2d). In these syntheses, an alkynylborolane or THP-protected propargyl alcohols were used as the monoynes. In the present study we demonstrate that non-protected propargyl alcohols can also be used in these [2 + 2 + 2] cycloadditions (in this context, see also ref 7), and the protection/deprotection steps[6a] can be omitted.

Results and Discussion

As shown in Scheme 1 and Table 1, a series of cobalt-catalyzed [2+2+2] cycloaddition reactions of the diynes **1a**−**c** with the alcohols **2a**−**d** were performed to give compounds **3a**−**l**. A detailed procedure for the synthesis of **3a** and analytical data (^{1}H, ^{13}C, and ^{29}Si NMR; C,H analyses) for **3a**, **3e**, and **3i** are reported in the Experimental Section.

The reactions proceeded very fast and were complete within ca. 5 min. The products were isolated in satisfying yields (44−66%, not yet optimized), although they are lower compared to those obtained with the respective THP-protected substrates.[6a] Because of their relatively high polarity, the products **3a**−**l** could be easily separated from the byproducts by column chromatography.[8] Both terminal (**2a**, **2d**) and internal monoynes (**2b**, **2c**) could be used in these syntheses. The yields of compounds **3a**−**d** (1,3-disilaindane skeleton; Table 1, entries 1−4) and **3i**−**l**

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(8) Diyne "dimers" and "trimers" were typical byproducts of the [2+2+2] cycloadditions described in this paper.

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Scheme 1

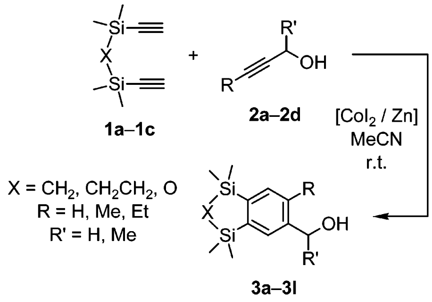

Table 1. Yields of the Arenes 3 Obtained in the Reaction of the Diynes 1 with the Propargyl Acohols 2 in Acetonitrile Using a CoI_2/Zn System for Catalysis[a,b]

entry	diyne	X	monoyne	R	R′	product (%)[c]
1	**1a**	CH_2	**2a**	H	H	**3a** (65)
2	**1a**	CH_2	**2b**	Me	H	**3b** (60)
3	**1a**	CH_2	**2c**	Et	H	**3c** (58)
4	**1a**	CH_2	**2d**	H	Me	**3d** (63)
5	**1b**	CH_2CH_2	**2a**	H	H	**3e** (44)
6	**1b**	CH_2CH_2	**2b**	Me	H	**3f** (51)
7	**1b**	CH_2CH_2	**2c**	Et	H	**3g** (50)
8	**1b**	CH_2CH_2	**2d**	H	Me	**3h** (47)
9	**1c**	O	**2a**	H	H	**3i** (64)
10	**1c**	O	**2b**	Me	H	**3j** (52)
11	**1c**	O	**2c**	Et	H	**3k** (62)
12	**1c**	O	**2d**	H	Me	**3l** (59)

[a] Ratio of reagents: **1** (mmol)/**2** (mmol)/CoI_2 (mmol)/Zn (mmol)/MeCN (mL): 1/1.4/0.025/0.1/2. [b] Reaction required cooling in a water or an ice bath (depending on the scale) to keep the temperature below 40 °C. [c] Isolated yield.

(1,3-disila-1,3-dihydroisobenzofurane skeleton; Table 1, entries 9−12) are higher than those of compounds **3e−h** (1,4-disilatetralin skeleton; Table 1, entries 5−8) as in the case of the THP-protected substrates.[6a]

In summary, we have discovered that a simple catalytic system consisting of commercially available cobalt(II) iodide and zinc powder can efficiently catalyze [2+2+2] cycloadditions of unprotected propargyl alcohols, containing terminal or internal monoyne moieties, with diynes. The reactions can be performed under mild conditions, and a relatively low (2.5%) catalyst load gives almost complete consumption of the starting materials in a very short time. Moreover, the reaction does not need to be performed at high dilution, and the workup and isolation are straightforward.

Experimental Section

General Procedures. All syntheses were carried out under dry nitrogen. Acetonitrile was dried and purified according to standard procedures and stored under dry nitrogen. The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded at 22 °C on a Bruker Avance 400 NMR spectrometer (^1H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz), and $CDCl_3$ was used as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^1H, δ 7.24), internal $CDCl_3$ (^{13}C, δ 77.0), or external TMS (^{29}Si, δ 0). Assignment of the ^1H NMR data was supported by $^1H,^1H$ gradient-selected COSY, $^{13}C,^1H$ gradient-selected HMQC and gradient-selected HMBC, and $^{29}Si,^1H$ gradient-selected HMQC experiments (optimized for $^2J_{SiH}$ = 7 Hz). Assignment of the ^{13}C NMR data was supported by DEPT 135 and the aforementioned $^{13}C,^1H$ correlation experiments.

Example: Synthesis of 5-(Hydroxymethyl)-1,1,3,3-tetramethyl-1,3-disilaindane (3a). Bis(ethynyldimethylsilyl)methane (**1a**) (902 mg, 5.00 mmol), prop-2-yn-1-ol (**2a**) (392 mg, 6.99 mmol), and cobalt(II) iodide (39 mg, 125 μmol) in acetonitrile (630 μL) were added one after another to a stirred suspension of zinc (33 mg, 505 μmol) in acetonitrile (10 mL). When the reaction mixture started to warm up (after ca. 1 min), it was cooled in an ice bath. After 5 min, the cooling bath was removed, and triethylamine (100 μL) was added. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (63−200 μm; eluent, *n*-pentane/diethyl ether (1/1 (v/v))) to afford **3a** (769 mg, 65%) as a white solid. ^1H NMR: δ −0.04 (s, 2 H, $SiCH_2Si$), 0.275 (s, 6 H, $SiCH_3$), 0.282 (s, 6 H, $SiCH_3$), 1.64 (t, $^3J_{HH}$ = 6.0 Hz, 1 H, O*H*), 4.70 (d, $^3J_{HH}$ = 6.0 Hz, 2 H, CH_2OH), 7.35−7.38 (m, 1 H, *H*C-6), 7.54−7.58 (m, 2 H, *H*C-4, *H*C-7). ^{13}C NMR: δ −2.4 ($SiCH_2Si$), 0.53 (2 C, $SiCH_3$), 0.54 (2 C, $SiCH_3$), 65.7 (CH_2OH), 127.5 (H*C*-6), 130.2 (H*C*-4), 132.0 (H*C*-7), 140.9 (*C*-5), 150.0 and 151.1 (*C*-3a, *C*-7a). ^{29}Si NMR: δ 8.7, 8.9. Anal. Calcd for $C_{12}H_{20}O_2Si_2$: C, 60.95; H, 8.53. Found: C 60.5; H 8.4.

Analytical Data for 6-(Hydroxymethyl)-1,1,4,4-tetramethyl-1,4-disila-1,2,3,4-tetrahydronaphthalene (3e). ^1H NMR: δ 0.21 (s, 6 H, $SiCH_3$), 0.22 (s, 6 H, $SiCH_3$), 0.99 (s, 4 H, $SiCH_2C$), 1.60 (t, $^3J_{HH}$ = 6.0 Hz, 1 H, O*H*), 4.67 (d, $^3J_{HH}$ = 6.0 Hz, 2 H, CH_2-OH), 7.32−7.35 (m, 1 H, *H*C-7), 7.46−7.48 (m, 1 H, *H*C-5), 7.48−7.51 (m, 1 H, *H*C-8). ^{13}C NMR: δ −1.52 (2 C, $SiCH_3$), −1.49 (2 C, $SiCH_3$), 7.49 ($SiCH_2C$), 7.53 ($SiCH_2C$), 65.6 (CH_2OH), 126.8 (H*C*-7), 131.9 (H*C*-5), 133.8 (H*C*-8), 140.3 (*C*-6), 145.3 and 146.3 (*C*-4a, *C*-8a). ^{29}Si NMR: δ −7.0, −6.9. Anal. Calcd for $C_{13}H_{22}OSi_2$: C, 62.34; H, 8.85. Found: C, 62.0; H, 8.7.

Analytical Data for 5-(Hydroxymethyl)-1,1,3,3-tetramethyl-1,3-disila-2-oxaindane (3i). ^1H NMR: δ 0.34 (s, 6 H, $SiCH_3$), 0.35 (s, 6 H, $SiCH_3$), 1.74 (t, $^3J_{HH}$ = 5.7 Hz, 1 H, O*H*), 4.72 (d, $^3J_{HH}$ = 5.7 Hz, 2 H, CH_2OH), 7.38−7.43 (m, 1 H, *H*C-6), 7.54−7.59 (m, 2 H, *H*C-4, *H*C-7). ^{13}C NMR: δ 0.99 (4 C, $SiCH_3$), 65.5 (CH_2-OH), 127.9 (H*C*-6), 129.4 (H*C*-4), 131.2 (H*C*-7), 141.4 (*C*-5), 147.5 and 148.7 (*C*-3a, *C*-7a). ^{29}Si NMR: δ 15.4, 15.5. Anal. Calcd for $C_{11}H_{18}O_2Si_2$: C, 55.41; H, 7.61. Found: C, 55.1; H, 7.3.

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