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Diastereoselective conversion of alkynyl(trimethyl)silanes into substituted cyclopropanes affected by the *i*-Bu_3Al–CH_2I_2 reagent

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ABSTRACT

A highly convenient and diastereoselective method for the synthesis of cyclopropylaluminums has been described, which involves treatment of alkynyl(trimethyl)silanes with triisobutylaluminum and diiodomethane.

In previous notes, we have already reported on the high efficiency of the triethylaluminum-diiodomethane reagent for alkyne transformation to tri- and tetrasubstituted cyclopropanes.[1]

To extend the scope of this unusual reaction as well as to investigate the structural effect of the initial organoaluminum compounds (OAC) and alkynes, we studied the reaction of OAC and CH_2I_2 with readily accessible organosilicon derivatives of acetylenic compounds to prepare silyl-substituted cyclopropanes. Cyclopropanes are known to be versatile intermediates in organic synthesis and can be converted to a variety of useful products by cleavage of the three-membered ring.[2] Silylcyclopropanes particularly are very important reagents since many of their reactions occur with strictly defined stereochemistry.[3] Different approaches to their synthesis have been developed. It is noteworthy to mention the cycloalkylation reaction of (ω-halo-1-alkenyl)metal derivatives,[4a] the reaction of chloro- and bromo-alkyl substituted silanes $CCl_2XCH_2CHXSi(CH_3)_3$ with zinc,[4b] the preparation of cyclopropylsilanes from terminal alkenes with organochromium reagents,[4c] the catalytic addition of thialkylsilane to cyclopropenes,[4d] the cyclopropanation of olefins with trimethylsilyldiazomethane,[4e] and the cyclopropanation of vinylsilanes.

Here we wish to report a highly convenient and versatile method for the synthesis of substituted cyclopropanes from silylalkynes, which were found to exhibit unique diastereoselectivity. The method involves treatment of silylalkynes with triisobutylaluminum and diiodomethane (Fig. 1).

1-Hexynyl(trimethyl)silane reacted with diiodomethane and triisobutylaluminum in dichloromethane for 3 hours at room temperature followed by deuterolysis to give diastereomerically pure 2-butyl-3-deuterocyclopropyl(trimethyl)silane **2a** in 83% GC yield (Table 1, entry 1).[5]

Table 1
Alkynyl(trimethyl)silane cyclopropanation with *i*-Bu_3Al–CH_2I_2

Entry	Alkyne	R_3Al	Yield[a] (%)
1	$Me_3Si{-}C{\equiv}C{-}C_4H_9^{n}$	*i*-Bu_3Al	83 (74)
2	$Me_3Si{-}C{\equiv}C{-}C_5H_{11}^{n}$	*i*-Bu_3Al	80 (65)
3	$Me_3Si{-}C{\equiv}C{-}C_6H_{13}^{n}$	*i*-Bu_3Al	72 (62)
4	$Me_3Si{-}C{\equiv}C{-}C_8H_{17}^{n}$	*i*-Bu_3Al	65 (52)
5	$Me_3Si{-}C{\equiv}C{-}C_4H_9^{n}$	Et_3Al	59
6	$Me_3Si{-}C{\equiv}C{-}C_4H_9^{n}$	*i*-Bu_2AlCl	53[b]

The reaction conditions: [alkyne]–[CH_2I_2]–[R_3Al] = 1:3:3, CH_2Cl_2, 20–25 °C.
[a] GC (isolated) yield of OAC deuterolysis products.
[b] 48 h.

We have synthesized cis- and trans-isomers of 1-trimethylsilyl-2-butylcyclopropane by reduction[6] of hexynyl(trimethyl)silane with DIBAL-H followed by cyclopropanation procedure with CH_2N_2 to determine the stereoconfiguration of **3a**. Diazomethane was generated in situ according to a modified procedure.[7] This method is known to be stereospecific.[8] The isomers have identical mass spectra and different retention times on capillary GC column. The ^{13}C and ^{1}H NMR spectra of the synthesized cis-isomer were identical to those of **3a,** and these compounds had the same GC retention time. Thus, the cis-orientation of butyl and trimethylsilyl substitutents at the cyclopropane ring was established. Moreover, there was no evidence for the presence of a trans-isomer in the reaction mixture.

The complete structure elucidation[9] of product was carried out by a variety of correlation NMR methods (COSY, HSQC, and HMBC).[10] So, the cyclopropane ring was unambiguously assigned

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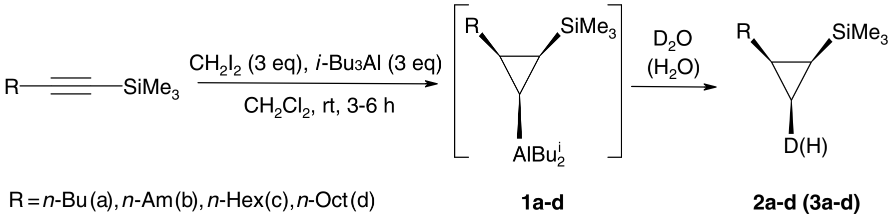

Figure 1. Alkynyl(trimethyl)silane cyclopropanation.

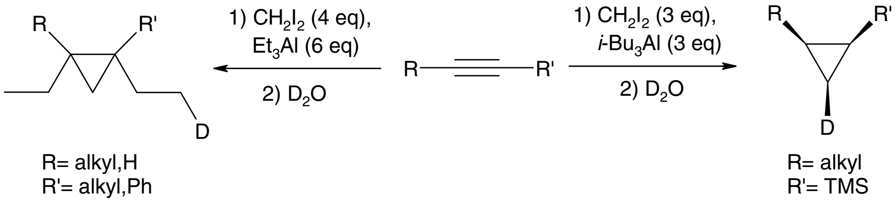

Figure 2. Different pathways for the reaction of alkynes with aluminum carbenoids.

based on cross peaks in COSY, HSQC, and HMBC spectra ($\delta_{HC(1)} = -0.45$ ppm, $\delta_{H'C(2)} = 0.70$ ppm, $\delta_{H''C(2)} = -0.01$ ppm, $\delta_{HC(3)} = 1.01$ ppm). The most shielded proton at C(1) shows a six line multiplet. The calculation of the coupling constants gave three J values: two of them are about 10 Hz, while the third one appears to be about 7 Hz that confirms the cis-orientation of alkyl and trimethylsilyl groups since cyclopropyl protons with a cis relationship give rise to larger couplings (7–10 Hz), when compared to those with a trans relationship (3–7 Hz).[11]

To determine the deuterium atom orientation in compound **2a**, The ^{1}H NMR spectrum was analyzed, where the most shielded signal at $\delta_{HC(1)} = -0.45$ ppm shows a triplet splitting with $J \sim 8$ Hz. This evidences that all three hydrogen atoms of the AMX spin system are in a cis relationship to each other.

In the same way, the products prepared via cyclopropanation of a variety of alkynylsilanes were identified (Table 1, entries 2–4). Diastereomerically pure 2-alkyl-3-deuterocyclopropyl(trimethyl)silanes **2** were obtained in good yield in all experiments. Trimethyl(2-phenylethynyl)silane failed to react under these reaction conditions. Thus, only alkyl-substituted alkynes were involved in the reaction to give cyclopropylaluminums.

We studied the influence of the OAC reactants on the yield and composition of the reaction products. It was established that the use of Et_3Al instead of i-Bu_3Al decreases yield of **2a** to 59% due to an incomplete conversion of the initial alkyne and the formation of side products. Attempted cyclopropanation of 1-hexynyl(trimethyl)silane with diisobutylaluminum chloride and diiodomethane in dichloromethane gave **2a** in lower yield (only 53% for 48 h; cf. entry 6 in the Table 1). The reaction of 1-hexynyl(trimethyl)silane with diiodomethane in the presence of DIBAL-H or Et_2AlCl did not afford cyclopropylaluminum compound **1a**.

We determined that the reaction selectivity depends on the solvent nature. The best results were obtained when the reaction was carried out in dichloromethane or hexane. The reaction in toluene affords mainly isobutylmethylbenzene identified by GC–mass spectrometry. The reaction does not take place in ether solvents (tetrahydrofuran, diethyl ether).

Although the i-Bu_3Al–CH_2I_2 system is analogous to the earlier proposed Et_3Al–CH_2I_2 reagent,[1a,b] we did not observe the formation of tri- and tetrasubstituted cyclopropanes in this reaction (Fig. 2). Thus, an earlier proposed mechanism[1c] for the reaction of mono- and dialkylsubstituted alkynes with Et_3Al–CH_2I_2 does not extend to alkynylsilanes. Our current research efforts are aimed at isolation and characterization of the reaction intermediates to clarify the mechanism of this interesting transformation.

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5. *The synthesis of 2-butyl-3-deuterocyclopropyl-(trimethyl)silane* (**2a**): To a solution of 1-hexynyl(trimethyl)silane (0.462 g, 3 mmol) and diiodomethane (0.72 mL, 9 mmol) in CH_2Cl_2 (15 mL), neat triisobutylaluminum (2.27 mL, 9 mmol) was added (caution: TIBAL is pyrophoric and can ignite on contact with air, water, or any oxidizer) at 0 °C under argon atmosphere. The mixture was stirred at room temperature for 4 h. The reaction was terminated by dilution with hexane (50 mL) followed by treatment with 15 wt. % solution of DCl in D_2O (10 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic layers were then washed with saturated $NaHCO_3$ solution and dried over anhydrous $CaCl_2$. The solvent was removed under reduced pressure and the residue distilled to yield 0.380 g of oily product (74% yield).
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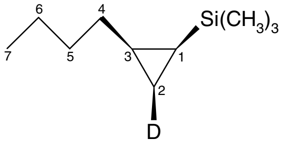
9. *2-Butyl-3-deuterocyclopropyl(trimethyl)silane* (**2a**): Bp 75–78 °C (15 Torr). ^{13}C NMR specter (δ, ppm): −0.10 (Me_3Si), 2.62 (C(1)), 8.78 (C(2)), 14.06 (C(7)), 16.92 (C(3)), 22.52 (C(6)), 31.94 (C(4)), 32.52 (C(5)). ^{1}H NMR (δ, ppm): −0.45 (t, $^3J_{CH} \sim 8$ Hz, 1 H, C(1)H), 0.03 (s, 9 H, Me_3Si), 0.65–0.75 (m, 1 H, C(2)H), 0.91 (t, $^3J_{CH} = 7.0$ Hz, 3 H, $C(7)H_3$), 0.95–1.1 (m, 2 H, C(3)H, $C(4)H_a$), 1.25–1.55 (m, 5 H,

C(4)H_b, C(5,6)H_2). Mass-spectra, *m*/*z*: 171 (1) $[M]^+$, 156 (3) $[M-CH_3]^+$, 128 (3) $[M-C_3H_7]^+$, 100 (9), 86 (7), 73 (100), 59 (35).



10. ^1H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions on spectrometer Bruker Avance 400 (400.13 MHz for ^1H and 100.62 MHz for ^{13}C).
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