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ALKYLATION OF 1-TRIMETHYLSILYLVINYL ALUMINATES WITH "UNREACTIVE" ALKYL HALIDES MEDIATED BY CUPROUS IODIDE-TRIMETHYL PHOSPHITE COMPLEX

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Abstract: Cuprous iodide-triethyl phosphite complex was found to be effective as a catalytic or equimolar reagent for the alkylation of 1-trimethylsilylvinyl aluminates with "unreactive" alkyl halides.

In 1976, several papers appeared elaborating methods for the hydrometalation-alkylation of 1-trialkylsilylalkynes. The products of these reactions, 1,2-dialkylvinyl-trialkylsilanes, are important intermediates in the stereocontrolled synthesis of trisubstituted olefins.[1]

Utimoto[2] demonstrated that the successful regiocontrolled hydroalumination of 1-trialkylsilylalkynes was solvent dependent, requiring the coordinating solvent ether for cis addition of diisobutylaluminum hydride (DIBAL) while hexane afforded trans hydroalumination products. Although alkylation of the resultant aluminate (from addition of methyllithium) was readily achieved with allylic halides, poor yields were obtained with "unreactive" ethyl and butyl iodide. Similarly, Eisch[3] reported that added N-methylpyrrolidine preserves the stereochemical integrity of the kinetic, cis hydroalumination product of 1-trialkylsilylalkynes in hexane, however, the derived aluminate was only alkylated effectively (50-75% yield) with methyl and allyl iodide. The alkylation of the closely related E-alkenylaluminates were found by Negishi[4] to undergo effective alkylation in THF with methyl, allyl, propargyl, and benzyl halides, but only moderate yields were obtained in alkylations employing octyl iodide (49%) or mesylate (41%). Utimoto[5] was able to circumvent these difficulties associated with trimethylsilylvinyl aluminates by successively exposing the analogous boronate to stoichiometric cuprous iodide, triethylphosphite, HMPA, and alkyl halide. Under these conditions, "unreactive" n-alkyl halides underwent efficient alkylation.

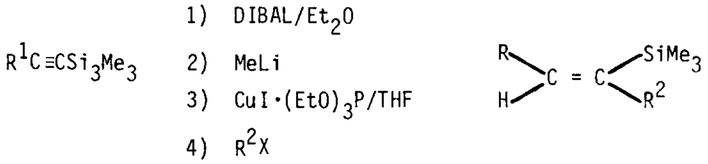
In this Letter we report an experimental procedure which permits efficient, stereocontrolled alkylation of trimethylsilylvinyl aluminates with primary alkyl halides in the presence of catalytic amounts of cuprous iodide triethylphosphite complex.[6] Representative examples are illustrated in the Table.

Commercial DIBAL in hexane solution was found to be inefficient for hydroaluminations in ether.[7] Neat DIBAL dissolved in ether was vastly superior. Tetrahydrofuran-ether was a better solvent than ether in the alkylation step. The alkylation using 25 mol % CuI $(EtO)_3P$ was as efficient as the stoichiometric reaction, while the absence of copper gave little or no alkylation.

The preparation of Z-3-trimethylsilyl-3-decene is representative. To a stirred solution of 20 mL of dry ether (Na benzophenone ketyl) and 1-trimethylsilyl-1-octyne (1.82 g, 10 mmol) maintained at -20°C under argon was added (syringe-septum) DIBAL (1.85 mL, 10 mmol). The reaction mixture was refluxed for 2h, cooled to 0°C, and treated with 11 mmol of methyllithium (10 mL, 1.1 M in ether). The mixture was allowed to warm to room temperature over 0.5 h and stirred for an additional 1 h. To the reaction mixture at -78°C was added $CuI{\cdot}(EtO)_3P$ (3.57 g, 10 mmol) dissolved in 50 ml of dry THF (Na benzophenone ketyl). To the resulting dark brown mixture was added ethyl iodide (0.13 mL, 16.5 mmol) at -78°C. The reaction mixture was allowed to warm to room temperature over 18 h. The mixture was acidified with dilute HCl/ice , extracted with ether, washed with sat. aq. NH_4Cl and brine, dried over $MgSO_4$, evaporated, and chromatographed on silica gel (hexane) to afford 1.87 g (78%) of the vinylsilane whose NMR spectrum was in agreement with reported data.[5b]

Table

Stereoselective Synthesis of Z-1,2-Dialkylvinylsilanes



1 2

Entry	$R^1C{\equiv}CSiMe_3$	R^2X	Yield,[a] %	Isomer Ratio,[b] %
1	R^1=n-C_6H_{13}, R^2=CH_3	C_2H_5I	78	98[d]
2		C_2H_5I	76[c]	94
3		C_2H_5Br	72	94
4		C_4H_9I	82	98[d]
5	R^1=$(CH_2)_2$OTHP, R^2=CH_3	CH_3I	84[c]	98[d]

a) Isolated yield after column chromatography, b) determined by integration (270 MHz NMR), c) 25 mol % of CuI·$(EtO)_3P$ was used, d) stereoisomer not detected by 270 MHz NMR, d) after removal of the protecting group, the alcohol was purified by column chromatography.

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7. Commercial solutions of DIBAL in hexane were standardized by reduction of excess benzaldehyde followed by isolation and NMR integration. Although the molarities agreed with those claimed, as many as two "equivalents" of DIBAL were required for complete reduction within measurable reaction time.

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