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CARBOMETALLATION OF 1,4-BIS(TRIMETHYLSILYL)-1,3-BUTADIYNE WITH TRIMETHYLALUMINIUM

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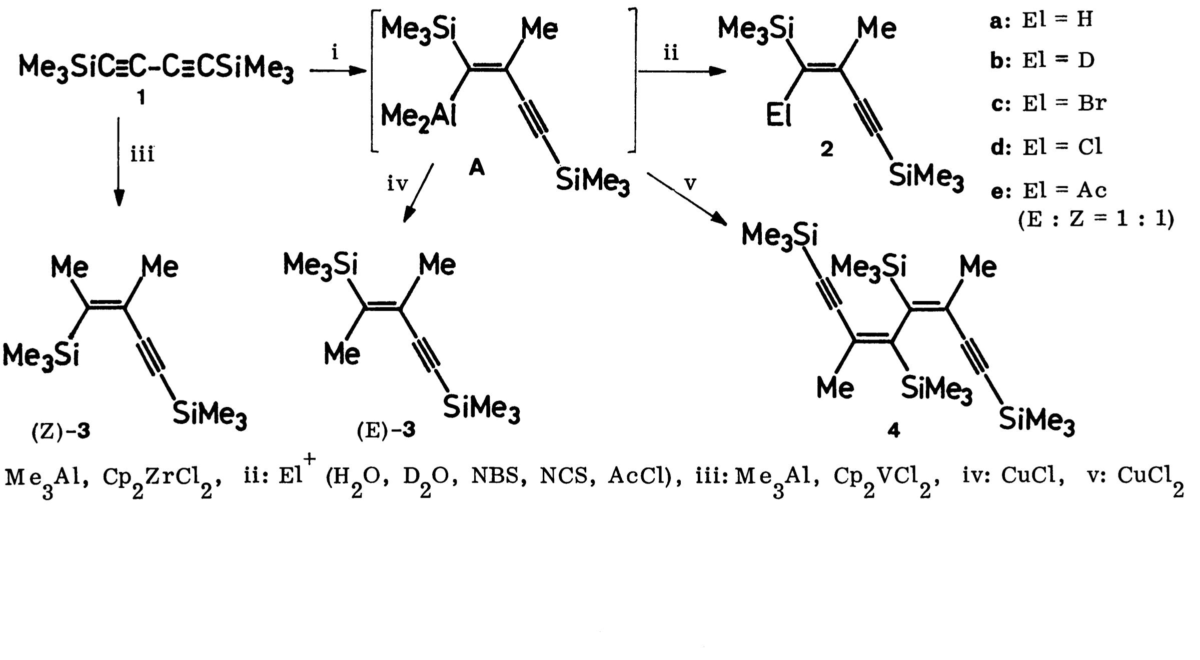
Carbometallation of 1,4-bis(trimethylsilyl)-1,3-butadiyne with Me_3Al in the presence of Cp_2ZrCl_2 catalyst produced selectively an alkenylaluminium intermediate which, upon treatment with water and various electrophiles, afforded 2-methyl-1,4-bis(trimethylsilyl)-1-buten-3-yne and its 1-substituted derivatives.

We report that zirconium-catalyzed carbometallation$^{1)}$ of 1,4-bis(trimethylsilyl)-1,3-butadiyne (**1**) with trimethylaluminium allows us to add one methyl group at C(2) and various electrophiles as well as methyl group at C(1) stereoselectively.

The reaction conditions originally found by Negishi$^{2)}$ were slightly modified and employed for the reaction: A hexane solution of Me_3Al (2.0 mol/dm^3, 1.6 ml, 3.2 mmol) was added to a solution of Cp_2ZrCl_2 (0.013 mmol) in 1,2-dichloroethane (DCE, 3 ml) at room temperature, and the mixture was stirred for 30 min. Then, a DCE (1 ml) solution of **1** (194 mg, 1.0 mmol) was added, and the resulting mixture was heated to reflux for 10 h. Quenching with 1 mol/dm^3 NaOH followed by workup and purification by preparative TLC gave (E)-2-methyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (**2a**) (145 mg, 69% yield)$^{3)}$ as the isolable product. The stereochemistry of the product was assigned by ^{13}C NMR ($^3J_{C-H}$ = 12.2 Hz$^{4,5)}$ and ^{1}H NMR (J ($\underline{H}C{=}CC\underline{H}_3$) = 1.1 Hz).$^{6)}$ Contamination of the (Z)-product was not detected. The regiochemistry of the carbometallation was clearly established by treatment of **2a** with 57% HI$^{7)}$ in C_6D_6 and observation of the olefinic signals at δ 5.00 and 5.35 typical to



i: Me_3Al, Cp_2ZrCl_2, ii: El^+ (H_2O, D_2O, NBS, NCS, AcCl), iii: Me_3Al, Cp_2VCl_2, iv: CuCl, v: $CuCl_2$

terminal methylene. Of various solvents DCE was found best. In ether or hexane solvent or with Me_3Ga instead of Me_3Al, the reaction did not proceed at all. Double carbometallation was not observed even under forcing conditions: large excess Me_3Al and 1 equiv Zr catalyst gave **2a** only (66% yield). Best yield 75% was achieved with the Zr-catalyst (19 mol%) at 40-45 °C, 10 h. Cp_2TiCl_2 catalyst gave a complex mixture of products, whereas Cp_2VCl_2 catalyst (5.7 mol%) gave (Z)-**3**$^{3)}$ (27% yield) in one step.

The stereochemistry of the carbometallation is worthy of note. The trans-fashion may be ascribed to a facile cis→trans isomerization of an initially produced (Z)-alkenylaluminium species$^{2,8)}$ to (E)-isomer (**A**) thanks to the intramolecular coordination effect of the nearby acetylenic bond to aluminium.$^{9)}$ Under vanadium catalysis, the reductive elimination seems to be faster than the configurational isomerization.

The reaction of **A** with other electrophiles such as D_2O, N-bromosuccinimide (NBS), N-chlorosuccinimide (NCS), and AcCl, afforded the corresponding substituted products **2b**-**e**$^{3)}$ in 60, 47, 47, and 44% yields respectively. Addition of excess CuCl to the intermediate **A** at room temperature promoted reductive elimination to give (E)-**3**$^{3)}$ in 67% yield. Oxidation of **A** with $CuCl_2$ induced dimerization of the alkenyl group and gave (E,E)-**4**$^{3)}$ (48% yield) along with (E)-**3** (12%). The products **2**, **3**, and **4** are expectedly useful synthetic building blocks.

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