

단 신

지르코늄을 촉매로 한 올레핀의 위치 선택성 수소화 알루미늄 첨가반응

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Zr-Catalyzed Regioselective Hydroalumination of Olefins

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The hydrometalation of a carbon-carbon multiple bond is one of the most fundamental and straightforward methodologies for the preparation of new organometallics.^{1,2} Although hydroboration proceeds without any activators, most hydrometalations are promoted by transition metal catalysts.^{1,3} The hydroalumination of olefins catalyzed by titanium or zirconium compounds has been developed as a convenient route to a variety of alkylaluminum compounds, but most of these reactions require long reaction time or elevated temperature.^{4,5} In particular, $TiCl_4$, $ZrCl_4$, and UCl_4 are effective catalysts for the addition of lithium aluminum hydride or alane to olefinic double bonds to afford the corresponding organoaluminate or organoalane, respectively. These reactions are not restricted to terminal olefins, but internal olefins also react with $LiAlH_4$.⁶ It was recently reported that $ZrCl_4$ -catalyzed hydrostannation of alkynes with Bu_3SnH enables to produce the *trans* hydrostannation product with high regio- and stereoselectivity,⁷ and that the allylstannation of alkynes proceeds in the presence of catalytic amounts of $ZrCl_4$ or $EtAlCl_2$ in the *trans* addition manner.⁸ We have directed our attention to the selective reactions of unsaturated hydrocarbons

by using titanium compounds.⁹ We describe here a rapid and convenient procedure for the regioselective hydroalumination of olefins with $LiAlH_4$ in the presence of $[C_5(CH_3)_5]_2ZrCl_2$, and an efficiency of the reaction was evaluated by converting the olefins to the alkylaluminates under mild conditions.

EXPERIMENTAL SECTION

All glassware used was predried in an oven, assembled hot and cooled with a stream of argon in glove box. All reactions were carried out under argon atmosphere. THF was distilled from sodium benzophenone ketyl prior to use. All other solvents were distilled and stored over an appropriate drying agent. $[C_5(CH_3)_5]_2ZrCl_2$, $LiAlH_4$, and $LiAlD_4$ were purchased from Strem Co., and used without further purification. All olefins were purified before use. 1H NMR spectra were recorded in $CDCl_3$ on Varian Gemini-200 spectrometer with tetramethylsilane as an internal standard. Infrared spectra were measured in a KBr pellet with a Matterson Genesis II FT-IR spectrophotometer.

GC analyses were carried out with a Younglin

GC-600D gas chromatograph equipped with HP-5 (Hewlett Packard, 0.32 mm, 30 m) or BP-5 (SGE, 0.32 mm, 60 m) capillary columns. Mass spectra were obtained using a Shimadzu GC/MS QP-5000.

Typical procedure for hydroalumination. The mixture of $[\text{C}_5(\text{CH}_3)_2]_2\text{ZrCl}_2$ (0.112 g, 0.26 mmol), LiAlH_4 (0.191 g, 5.03 mmol), and THF (15 mL) were placed in a vessel under argon. After stirring for 1 h, and allylbenzene (1.182 g, 10.0 mmol) were slowly introduced to the mixture at 0 °C. The complete reaction was confirmed by GC, and the mixture was treated with dilute hydrochloric acid (10 mL) and extracted with *n*-pentane. The organic layer was dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on alumina (*n*-pentane), and *n*-pentane was removed to yield the propylbenzene (0.998 g, 83%). $^1\text{H NMR}$ (CDCl_3): δ 7.12~7.27 (m, 5H, C_6H_5), 2.55 (t, 2H, CH_2), 1.65 (m, 2H, CH_2), 0.92 (t, 3H, CH_3). IR (cm^{-1}): 3026, 2870, 1608, 1475, 1375, 753, 697.

Preparation of (2-Bromoethyl)benzene. To a solution of LiAlH_4 (0.380 g, 10.0 mmol) and $[\text{C}_5(\text{CH}_3)_2]_2\text{ZrCl}_2$ (0.216 g, 0.5 mmol) in THF (20 mL) was added styrene (2.088 g, 20.0 mmol). The reaction mixture was stirred at 0 °C for 3 h. Bromine (7.680 g, 48 mmol) in diethyl ether (40 mL) was added dropwise at 0 °C. After completion of bromine addition, the reaction mixture was allowed to remain 0.5 h at room temperature. Then the mixture was washed with 10% sodium thiosulfate solution, and saturated sodium chloride solution. The organic layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with *n*-hexane as an eluent. The product was obtained (2.96 g, 80%). $^1\text{H NMR}$: δ 7.17~7.31 (m, 5H C_6H_5), 3.54 (t, 2H, CH_2), 3.14 (t, 2H, CH_2). IR (cm^{-1}): 3062, 3028, 2964, 1602, 1453, 1262, 749, 698. Mass m/e 184 (M^+), 186 ($M^+ + 2$). The products are known and were characterized by comparison with authentic samples using GC and spectral data.

RESULTS AND DISCUSSION

The reaction dependence on LiAlH_4 /olefin ratio was examined with 1-octene in the presence of catalytic amounts of $[\text{C}_5(\text{CH}_3)_2]_2\text{ZrCl}_2$. The reactions of LiAlH_4 with 1-octene in the ratios 1/1 and 1/2 readily proceeded at 0 °C for 1 h, respectively, but the reactions in the ratios 1/3 and 1/4, respectively, were relatively slow under the same conditions (up to 24 h). It was found that up to four equivalents of olefin can react with one equivalent of LiAlH_4 to give the alkylaluminates at 65 °C for 5 h.⁶ We have studied the hydroalumination of various representative olefins with LiAlH_4 in the presence of catalytic amounts of $[\text{C}_5(\text{CH}_3)_2]_2\text{ZrCl}_2$ in THF at 0 °C, the reaction mixture was hydrolyzed (Table 1). As shown there, the reaction of monosubstituted olefins such as 1-octene, styrene, and 3-phenyl-1-propene occurred at 0 °C in excellent yields (runs 1, 3, and 4). Monosubstituted olefins have been hydroaluminated quantitatively without affecting aliphatic and aromatic functionalities. We examined the reaction of 1,1-disubstituted and 1,2-disubstituted olefins, such as 2-octene, 2-phenyl-2-propene, and cyclohexene, but these olefins were not hydroaluminated at 0 °C even after 5 h (runs 2, 5, and 6). To examine the regioselectivity of this system, the hydroalumination of diolefins such as 4-vinyl-1-cyclohexene, 7-methyl-1,6-octadiene, and myrcene was carried out, corresponding products such as 4-ethyl-1-cyclohexene, 2-methyl-2-octene, and 2-ethyl-6-methyl-1,5-heptadiene were obtained in good to excellent yields, respectively (runs 7~10). The reaction permits the selective addition of LiAlH_4 to the monosubstituted double bond of di- and triolefins. Table 2 shows the results obtained by bromination of alkylhydroaluminated products of 1-octene and styrene. The reaction of 1-octene and styrene gave the 1-bromooctane (95%) and (2-bromoethyl)benzene (96%) in excellent yields, respectively. The bromination results demonstrate that the reaction proceeds specifically to place the aluminum at the terminal carbon atom. This finding was also supported by isolation of deuterated product after addition of bromine following hydroalumination of styrene with LiAlD_4 .

Table 1. The hydroalumination-hydrolysis of olefins^a

Run	Olefin	Time(h)	Product	Yield (%) ^b
1		1		99
2		1		trace
		5		< 5
3		1		85
		3		95
4		1		96
		3		99
5		1		trace
		5		trace
6		1		trace
		5		trace
7		1		77
		5		84
8		5		49
		18 ^c		78
9		1		90
		3		99

^aReaction conditions: $[C_3(CH_3)_2ZrCl_2]$ (0.26 mmol), $LiAlH_4$ (5 mmol), olefin (10 mmol), THF 15 mL, 0 °C. ^bGC yields. ^cAt 30 °C.

Table 2. The hydroalumination-bromination of olefins^a

Run	Olefin	$LiAlH_4$ ($LiAlD_4$)	Time (h)	Products	Yield (%) ^b
1		$LiAlH_4$	1		95
					trace
2		$LiAlH_4$	3		93
					trace
3		$LiAlD_4$	3		93
					trace

^aReaction conditions: $[C_3(CH_3)_2ZrCl_2]$ (0.5 mmol), $LiAlH_4$ (or $LiAlD_4$) (10 mmol), olefin (20 mmol), Br_2 (1 mL), 0 °C. ^bGC yields.

In summary, we have demonstrated that mono-substituted olefins can be hydroaluminated with $LiAlH_4$ in the presence of catalytic amounts of the $[C_3(CH_3)_2ZrCl_2]$ under mild conditions. This reaction is rapid, and gives higher regioselectivity in excellent yields, and involves anti-Markovnikov addition. Further investigations of more useful applications are in progress.

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