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Zirconium-Catalyzed Reaction of Terminal Alkenes with Triethylindium

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Abstract—Terminal alkenes (undec-1-ene, oct-1-ene, and allylbenzene) reacted with triethylindium in the presence of a catalytic amount of Cp_2ZrCl_2 in hexane to give mixtures of three organoindium compounds whose hydrolysis in D_2O afforded 2-substituted 1,4-dideuterobutane containing minor amounts of 2-substituted 1- and 4-deuterobutanes.

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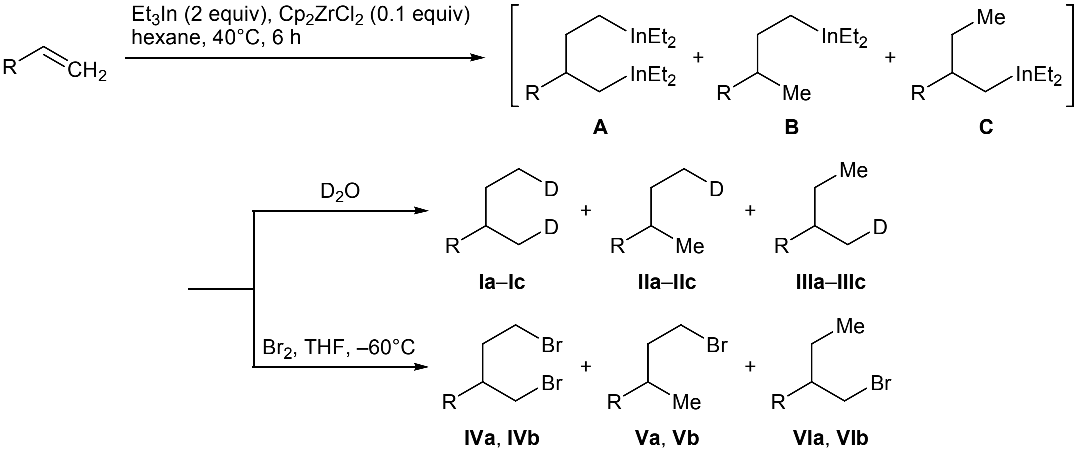
Carbometalation of olefins and acetylenes provides a convenient method for building up carbon–carbon bonds. Catalytic carbomagnesation and carboalumination have found wide application in practical organic synthesis [1, 2]. Zirconium-catalyzed reactions of olefins and acetylenes with alkylmagnesiums and alkylaluminums follow a complicated pattern. Depending on the conditions, solvent, and organometallic reagent nature, these reactions can occur as carbometalation, cyclometalation, or hydrometalation. As a rule, cyclometalation is promoted by ethyl derivatives of aluminum and magnesium. Cycloalumination by the action of triethylaluminum was reported for the first time in 1989 [3], and catalytic cyclomagnesation of terminal alkenes with Et_2Mg was described later [4, 5]. On the other hand, Cp_2ZrCl_2-catalyzed reaction of Et_2Zn with terminal alkenes (α-olefins) afforded only carbometalation products [6]. Thus, the role of the metal nature is important in this reaction. Organoindium reagents turned out to be efficient in cross-couplings with various aryl halides [7]; therefore, the synthesis of indiacyclopentanes and their subsequent functionalization seem to be an important problem. With a view to develop new methods of synthesis of organoindium compounds and elucidate the effect of the metal nature on the ratio of carbo- and cyclometalation products, in the present work we examined reactions of Et_3In with α-olefins in the presence of a catalytic amount of Cp_2ZrCl_2.

Undec-1-ene reacted with 2 equiv of Et_3In in the presence of Cp_2ZrCl_2 (10 mol % with respect to the unsaturated substrate) in hexane at 40°C (reaction time 6 h), and the subsequent hydrolysis in D_2O afforded 1-deutero-3-(deuteromethyl)dodecane (**Ia**) containing D–H exchange products as impurities (Scheme 1). The overall yield was 84%. According to the ^{13}C NMR data, the degree of deuteration of C^1 was 66%, and of C^{13}, 80%. Presumably, the reaction mixture obtained after deuterolysis contained dideutero derivative **Ia** together with monodeutero derivatives **IIa** and **IIIa** and 3-methyldodecane; a mixture of the latter three products at a definite ratio is characterized by the observed deuterium distribution. The ^{13}C NMR spectrum of **Ia** with impurities of products of deuterium replacement by hydrogen coincided with the spectrum of the deuterolysis product of aluminacyclopentane derived from undec-1-ene [3], but two additional signals were present due to terminal carbon atom of the ethyl group and methyl carbon atom. The molecular ion peak in the mass spectrum of the deuterolysis products had an *m*/*z* value of 186, which unambiguously confirmed structure **Ia**.

Thus, the Cp_2ZrCl_2-catalyzed reaction of undec-1-ene with Et_3In gives rise to a mixture of organoindium compounds **A**–**C** and 3-methyldodecane. To determine the product ratio, the reaction mixture obtained by Cp_2ZrCl_2-catalyzed reaction of undec-1-ene with Et_3In was subjected to bromination with Br_2 in THF at –60°C. According to the ^1H NMR data, the ratio of the resulting bromoalkanes **IVa**, **Va**, and **VIa** was ~5 : 2 : 3. GLC analysis showed the absence of 3-methyldodecane among the products, which indicated formation

Scheme 1.



R = n-C_9H_{19} (**a**), n-C_6H_{13} (**b**), $PhCH_2$ (**c**).

of a mixture of compounds **Ia**, **IIa**, and **IIIa** after deuterolysis. The ratio of bromoalkanes **IVa**, **Va**, and **VIa** was fairly consistent with the observed degree of deuteration. However, the NMR spectra of the mixture obtained by catalytic reaction of Et_3In with undec-1-ene did not allow us to unambiguously determine the structure of organoindium compounds **A**–**C**.

Oct-1-ene and allylbenzene reacted with triethylindium in a similar way. The degree of deuteration of compounds **Ib** and **Ic** ranged from 55 to 84% (**Ib**: 62% at C^1 and 84% at C^{10}; **Ic**: 55% at C^1 and 81% at C^{11}). Dideutero derivatives **Ib** and **Ic** were identified by comparing their ^{13}C NMR spectra with those of 1-deutero-3-(deuteromethyl)nonane [3] and 1-[4-deutero-2-(deuteromethyl)butyl]benzene [8] which were synthesized previously by deuterolysis of the cycloalumination products of oct-1-ene and allylbenzene. The reaction mixture obtained from oct-1-ene was subjected to bromination as described above for the reaction with undec-1-ene. The yield of dibromo derivative **IVb** was 40%, and 45% of a mixture of bromoalkanes **Vb** and **VIb** at a ratio of ~2:5 was also isolated. The ratio of bromo derivatives **IVb**, **Vb**, and **VIb** corresponded to the degree of deuteration of compound **Ib**.

We can conclude that one of the main products in the reactions under study is organoindium compound **A**. It is likely to be formed according to a mechanism analogous to that proposed for the cycloalumination of α-olefins with Et_3Al. In addition, considerable amounts of organoindium compounds **B** and **C** are formed. The latter can formally be regarded as carboindation product; however, simultaneous formation of compound **C** suggests a more complicated mechanism of the reaction under study.

It should be noted that the mechanism of Cp_2ZrCl_2-catalyzed reaction of α-olefins with ethyl derivatives of transition metals (Al, Mg, Zn, In) depends on the nature of the organometallic reagent. The reactions with Et_3Al generally follow the cycloalumination path, and hydrolysis of the reaction mixture with D_2O yields dideutero derivatives with a degree of deuteration of more than 95%. The catalytic reaction of Et_2Zn with α-olefins gives exclusively carbometalation products. The results of the present work showed that the Cp_2ZrCl_2-catalyzed reaction of terminal alkenes with Et_3In involves both carboindation and other processes which will be the subject of our further studies.

EXPERIMENTAL

All reactions were carried out under argon with commercially available reagents. Hexane was preliminarily distilled over (i-Bu)$_3$Al. Triethylindium was prepared by transalkylation of $InCl_3$ with triethylaluminum in the presence of KCl [9] and subsequent distillation. Its purity was checked by ^1H and ^{13}C NMR spectroscopy. The reaction mixtures and products were analyzed by GLC on a Carlo Erba chromatograph equipped with a flame ionization detector and a 25-m× 0.2-mm Ultra-1 glass capillary column (Hewlett Packard); oven temperature 50–170°C; carrier gas helium. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan 4021 instrument (ion source temperature 200°C). The elemental compositions were determined on a Carlo Erba 1106 analyzer. The bromine content was determined according to Schöniger [10]. The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400.13 MHz for

^{1}H and 100.62 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane as reference. The degree of deuteration at particular carbon atoms was estimated by comparing the intensities of signals in the ^{13}C NMR spectra of the hydrolysis products, recorded under similar conditions (probe temperature, solvent concentration, magnetic field parameters, and pulse sequence parameters).

Typical procedure for the Cp_2ZrCl_2-catalyzed reaction of terminal alkenes with triethylindium. A reactor was filled with argon and charged in succession with 1 mmol of undec-1-ene, oct-1-ene, or allylbenzene, 0.1 mmol (0.029 g) of Cp_2ZrCl_2, 5 ml of hexane, and 2 mmol of Et_3In, and the mixture was stirred for 6 h at 40°C. The mixture was then diluted with 5 ml of hexane and cooled to 0°C, 3 ml of D_2O was added dropwise, and the precipitate was filtered off. The organic phase was separated, the aqueous phase was extracted with diethyl ether, and the extract was combined with the organic phase, dried over $CaCl_2$, and concentrated under reduced pressure. The products were isolated by distillation under reduced pressure.

(1-^{2}H$_{1}$)-3-[(^{2}H$_{1}$)Methyl]dodecane (Ia). Overall yield of **Ia**, **IIa**, and **IIIa** 84%, ratio 46 : 20 : 34. bp 100–103°C (10 mm). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, $C^{12}H_3$, $J = 7.0$ Hz), 0.80–0.95 m (4H, 1-H, 13-H), 1.00–1.40 m (18H, 2-H–11-H), 1.40–1.45 m (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.12 t (C^1, $^{1}J_{CD} = 19$ Hz), 18.91 t (C^{13}, $^{1}J_{CD} = 19$ Hz), 14.14 (C^{12}), 22.70 (C^{11}), 27.13 (C^5), 29.49 (C^2), 29.38 (C^7), 29.75 (C^6), 29.68 (C^8), 30.05 (C^9), 31.94 (C^{10}), 34.31 (C^3), 36.66 (C^4). Mass spectrum: *m/z* 186 $[M]^+$. Found, %: C 83.69. $C_{13}H_{26}D_2$. Calculated, %: C 83.78. *M* 186.37.

(1-^{2}H$_{1}$)-3-[(^{2}H$_{1}$)Methyl]nonane (Ib). Overall yield of **Ib**, **IIb**, and **IIIb** 67%, ratio 46 : 16 : 38. bp 55–58°C (15 mm). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, C^9H_3, $J = 6.8$ Hz), 0.80–0.85 m (4H, 1-H, 10-H), 1.00–1.40 m (12H, 2-H–8-H), 1.40–1.50 m (1H, 3-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.10 t (C^1, $^{1}J_{CD} = 18$ Hz), 18.91 t (C^{10}, $^{1}J_{CD} = 19$ Hz), 14.14 (C^9), 22.71 (C^8), 27.15 (C^5), 29.45 (C^2), 29.80 (C^6), 31.66 (C^7), 34.51 (C^3), 36.79 (C^4). Found, %: C 83.11. $C_{10}H_{20}D_2$. Calculated, %: C 83.24.

{(4-^{2}H$_{1}$)-2-[(^{2}H$_{1}$)Methyl]butyl}benzene (Ic). Overall yield of **Ic**, **IIc**, and **IIIc** 81%, ratio 36 : 19 : 45. bp 70–73°C (10 mm). ^{1}H NMR spectrum, δ, ppm: 0.80–1.10 m (4H, 1-H, 11-H), 1.12–1.32 m (2H, 2-H), 1.60–1.70 m (1H, 3-H), 2.35–2.45 m and 2.60–2.70 m (1H each, 4-H), 7.10–7.25 m (4H, 6-H, 7-H, 9-H, 10-H), 7.25–7.35 m (1H, 8-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.19 t (C^1, $^{1}J_{CD} = 19.00$ Hz), 18.64 t (C^{11}, $^{1}J_{CD} = 19.00$ Hz), 29.71 (C^2), 31.94 (C^3), 43.33 (C^4), 125.55 (C^8), 128.05 (C^7, C^9), 129.18 (C^6, C^{10}), 141.73 (C^5). Found, %: C 88.17. $C_{11}H_{14}D_2$. Calculated, %: C 87.93.

Typical bromination procedure. Zirconium-catalyzed reaction of α-olefins with Et_3In was carried out as described above, except for deuterolysis. Diethyl ether, 5 ml, and pyridine, 1 ml, were added to the reaction mixture, the mixture was cooled to –60°C, and a solution of 6 mmol (0.31 ml) of bromine in 4 ml of tetrahydrofuran was added dropwise. The mixture was stirred for 15 min at –60°C and slowly poured into a mixture of ice with 5% aqueous HCl. The organic phase was separated, the aqueous phase was extracted with diethyl ether, and the extract was combined with the organic phase, dried over $CaCl_2$, and concentrated under reduced pressure. The products were isolated by distillation under reduced pressure.

1-Bromo-3-(bromomethyl)dodecane (IVa). Yield 47%, bp 143–144°C (3 mm). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, $C^{12}H_3$), 1.20–1.50 m (16H, 4-H–11-H), 1.50–1.60 m (2H, 2-H), 1.85–2.10 m (1H, 3-H), 3.40–3.55 m (4H, 1-H, 13-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.12 (C^{12}), 22.68 (C^{11}), 26.62 (C^5); 29.32, 29.56, 29.60, 29.64 (C^6, C^7, C^8, C^9); 31.90 (C^{10}), 32.02 (C^1), 32.20 (C^4), 34.89 (C^3), 37.44 (C^2), 40.07 (C^{13}). Found, %: C 45.80; H 7.53; Br 48.1. $C_{13}H_{26}Br_2$. Calculated, %: C 45.63; H 7.66; Br 46.71.

1-Bromo-3-methyldodecane (Va) and 1-bromo-2-ethylundecane (VIa). Overall yield 45%, ratio ~1 : 2, bp 101–106°C (1 mm). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.98 ($C^{13'}$), 14.15 (C^{12}, $C^{11'}$), 19.35 (C^{13}), 22.71 (C^{11}, $C^{10'}$), 25.73 ($C^{12'}$), 26.12 (C^5), 26.55 ($C^{4'}$); 29.30, 29.51, 29.58, 29.60 (C^6, C^7, C^8, C^9, $C^{5'}$, $C^{6'}$, $C^{7'}$, $C^{8'}$); 30.88 (C^4), 31.18 ($C^{3'}$), 31.52 (C^2), 31.95 (C^{10}, $C^{9'}$), 35.54 (C^3), 36.62 ($C^{2'}$), 38.29 ($C^{1'}$), 40.13 (C^1). Found, %: C 58.73; H 10.15; Br 32.2. $C_{13}H_{27}Br$. Calculated, %: C 59.31; H 10.34; Br 30.35.

1-Bromo-3-(bromomethyl)nonane (IVb). Yield 40%, bp 127–129°C (3 mm). ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, C^9H_3, $J = 10$ Hz), 1.20–1.50 m (10H, 4-H–8-H), 1.80–2.20 m (3H, 2-H, 3-H), 3.35–3.50 m (1-H, 10-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.13 t (C^9), 22.68 (C^8), 26.64 (C^5), 28.43 (C^6), 31.79 (C^7), 32.09 (C^1), 32.97 (C^4), 34.18 (C^3), 35.67 (C^2), 40.14 (C^{10}). Found, %: C 40.57; H 6.65; Br 54.9. $C_{10}H_{20}Br_2$. Calculated, %: C 40.03; H 6.72; Br 53.26.

1-Bromo-3-methylnonane (Vb) and 1-bromo-2-ethyloctane (VIb). Overall yield 45%, ratio ~2 : 5, bp 108–112°C (10 mm). ^{13}C NMR spectrum (CDCl$_3$), δ_C, ppm: 11.90 (C$^{10'}$), 14.10 (C^9, C$^{8'}$), 19.44 (C^{10}), 22.65 (C^8, C$^{7'}$), 25.64 and 25.71 (C^5, C$^{4'}$), 26.03 (C$^{9'}$), 26.50 (C^7, C$^{5'}$), 30.98 (C^6), 31.04 (C$^{3'}$), 31.83 (C$^{6'}$), 35.17 (C^3), 36.51 (C^4), 40.52 (C$^{2'}$), 31.41 (C^2), 38.34 (C$^{1'}$), 40.94 (C^1). Found, %: C 53.66; H 9.37; Br 39.0. $C_{10}H_{21}Br$. Calculated, %: C 54.30; H 9.57; Br 36.13.

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