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Organic Chemistry

Cp_2TiCl_2-Catalyzed hydroalkylation of α-olefins with $Bu^tBr—Et_3Al$

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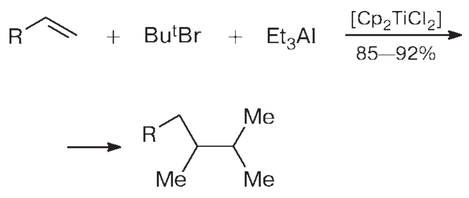
The reactions of olefins with alkyl halides and Et_3Al in the presence of catalytic amounts of Cp_2TiCl_2 were studied. Unbranched α-olefins of the aliphatic series underwent hydroalkylation under the action of *tert*-butyl bromide to form 2,3-dimethylalkanes.

Key words: hydroalkylation, olefins, organoaluminum compounds.

Hydroalkylation of olefins with alkyl halides catalyzed by palladium or rhodium salts is a convenient procedure for the construction of carbon—carbon bonds and the one-step synthesis of saturated hydrocarbons.[1] Examples are known of catalysts based on Group IVB metals, which show efficiency in these processes. Thus, aryl-substituted α-olefins have been recently subjected to Cp_2ZrCl_2-catalyzed hydroalkylation with alkyl bromides, tosylates, and sulfates in the presence of Bu^nMgCl.[2] However, the limited application of these reactions gave impetus to the closer examination of this process. Earlier,[3,4] we have demonstrated that an organoaluminum compound in the $Et_3Al—Cp_2TiCl_2$ system acts as an efficient H donor with respect to olefins and acetylenes. Hence, for the purpose of extending the field of application of Et_3Al as a hydrogenating agent and with the aim of developing new procedures for the construction of carbon—carbon bonds with the use of organoaluminum reagents, we investigated the reactions of olefins with alkyl halides in the presence of Et_3Al and catalytic amounts of Cp_2TiCl_2.

It was found that α-olefins of the aliphatic series underwent hydroalkylation under the action of Bu^tBr in the presence of Et_3Al and catalytic amounts of Cp_2TiCl_2 in hexane or CH_2Cl_2 to produce 2,3-dimethylalkanes **1** (Scheme 1). The reactions proceeded under mild condi-

Scheme 1



1a—d

R = n-C_5H_{11} (**a**), n-C_6H_{13} (**b**), n-C_9H_{19} (**c**), n-$C_{10}H_{21}$ (**d**)

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Table 1. Catalytic hydroalkylation of α-olefins

Olefin	Product	Yield (%)
Hept-1-ene	2,3-Dimethylnonane (**1a**)	85
Oct-1-ene	2,3-Dimethyldecane (**1b**)	92
Undec-1-ene	2,3-Dimethyltridecane (**1c**)	87
Dodec-1-ene	2,3-Dimethyltetradecane (**1d**)	85

tions (20—22 °C) for 12 h (Table 1). Under the above-mentioned conditions, primary and secondary alkyl halides (PrBr, BuI, or Pr^{i}Br) were not involved in these reactions.

Hence, aliphatic α-olefins can be subjected to hydroalkylation under the action of Et_3Al and Cp_2TiCl_2 in contrast to the known system[2] ($Bu^nMgCl—Cp_2ZrCl_2$). In these reactions, the addition of the *tert*-butyl radical was accompanied by the rearrangement, which was not observed in the case of the organomagnesium reagent.

Based on the experimental results and the published data,[4—8] we proposed the reaction scheme, which involves the following steps: the formation of the paramagnetic Ti^{III} complex;[6] the oxidative addition of *tert*-butyl bromide to the latter; carbotitanation of olefin through a radical mechanism; the double transfer of the radical center; alkylation at the Ti atom with Et_nAlBr_{3-n} (n = 1—3); the β-hydride transfer with regeneration of the catalytically active intermediate and the formation of the final product (Scheme 2).

The observed regiochemistry of the addition of the *tert*-butyl group to olefins is untypical of carbometallation proceeding by an ionic mechanism,[8] which is, apparently, indicative of the radical character of the reactions under consideration. The subsequent double transfer of the radical center occurs due to the electronic factors associated with the possibility of the most favorable delocalization of the unpaired electron. The final products are, presumably, formed through the transfer of the β-hydrogen atom from the ethyl ligand at the metal atom by a mono- or bimolecular[8] mechanism. According to the proposed scheme, the regeneration of the [Ti] intermediate occurs as a result of reductive elimination of ethylene from the [Ti]—C_2H_4 complex. Ethylene, in turn, undergoes polymerization because the system under study is similar in composition to Ziegler—Natta catalysts. Polymeric ethylene generated in the course of the reaction was identified by elemental analysis as a product of composition C_nH_{2n}. It should be noted that the proposed reaction scheme calls for the discussion and further investigations.

To summarize, we established that unbranched α-olefins of the aliphatic series undergo hydroalkylation under the action of Bu^{t}Br in the presence of Et_3Al and catalytic amounts of Cp_2TiCl_2. An efficient procedure was developed for the synthesis of 2,3-dimethylalkanes.

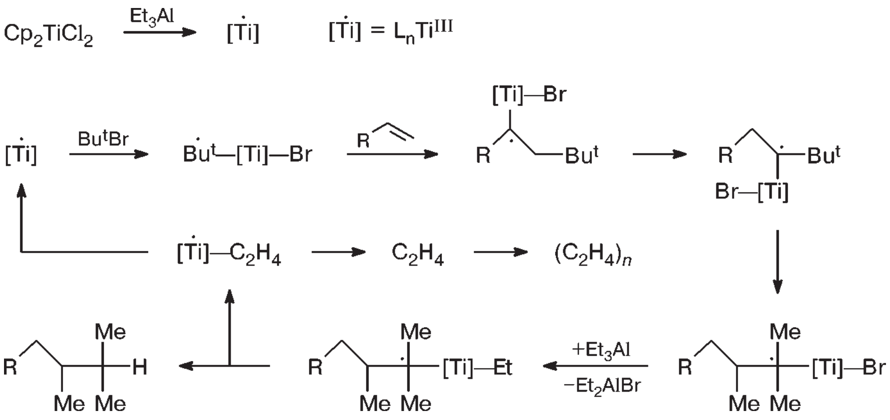
Experimental

The reactions were carried out under argon. All solvents were thoroughly dried before use. The reaction products were analyzed on a Carlo Erba chromatograph equipped with a 25 m × 0.2-mm Ultra-1 glass capillary column (Hewlett Packard) and a flame ionization detector (operating temperature 50—170 °C, helium as the carrier gas). The mass spectra were obtained on a Finnigan 4021 instrument; the energy of ionizing electrons was 70 eV; the temperature of the ionization chamber was 200 °C. The ^1H and ^{13}C NMR spectra were recorded on Jeol FX-90Q (22.5 MHz for ^{13}C and 90 MHz for ^1H) and Bruker AM-300 (75.46 MHz for ^{13}C and 300 MHz for ^1H) spectrometers. The ^1H and ^{13}C NMR spectra were measured with the use of $SiMe_4$ and $CDCl_3$, respectively, as the internal standard. The ^{13}C NMR spectra were recorded with full proton decoupling and with the use of the INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) procedure.

The yields of the products were determined by GLC with the use of nonane as the internal standard.

The assignments of the signals in the ^{13}C NMR spectra of compounds **1a—d** were made based on the Lindeman—Adams

Scheme 2



additive scheme[9] corrected for the magnetic nonequivalence of the methyl groups at the diastereotopic carbon atom.[10] The mass spectrum of compound **1a** was compared with the known data.[11]

Hydroalkylation of α-olefins (general procedure). Hexane (10 mL), olefin (4 mmol), Et_3Al (6 mmol), Bu^tBr (6 mmol), and Cp_2TiCl_2 (0.2 mmol) were successively charged under an atmosphere of inert gas into a 100-mL glass reactor, which was placed in an ice bath and put on a magnetic stirrer. Then the reaction mixture was stirred at 20—22 °C for 12 h. After completion of the reaction, the mixture was hydrolyzed with a 10% aqueous solution of HCl and the aqueous layer was extracted with diethyl ether. The extract was combined with the organic layer, kept over anhydrous $CaCl_2$, and concentrated *in vacuo*. The individual products were isolated by vacuum distillation.

2,3-Dimethylnonane (1a). B.p. 80 °C (20 Torr). Found (%): C, 84.79; H, 15.13. $C_{11}H_{24}$. Calculated (%): C, 84.52; H, 15.48. ^{13}C NMR ($CDCl_3$), δ: 20.39 (C(1)), 32.17 (C(2)), 38.73 (C(3)), 34.38 (C(4)), 27.74 (C(5)), 29.95 (C(6)), 32.17 (C(7)), 22.87 (C(8)), 14.22 (C(9)), 18.12 (C(10)), 15.45 (C(11)). ^1H NMR ($CDCl_3$), δ: 0.81 (t, 3 H, Me, $^3J_{C,H}$ = 5.13 Hz); 0.85 (d, 6 H, $C(1)H_3$, $C(10)H_3$, $^3J_{C,H}$ = 6.4 Hz); 0.87 (t, 3 H, Me, $^3J_{C,H}$ = 5.8 Hz); 1.10—1.54 (m, 12 H, C(2)H, C(3)H, $C(4)H_2$, $C(5)H_2$, $C(6)H_2$, $C(7)H_2$, $C(8)H_2$). MS, *m/z* (I_{rel} (%)): 156(1) M^+, 113(7) $[M - C_3H_7]^+$, 112 (19), 84 (5), 83 (7), 71 (73), 57 (98), 43 (100).

2,3-Dimethyldecane (1b). B.p. 90 °C (15 Torr). Found (%): C, 84.79; H, 15.13. $C_{12}H_{26}$. Calculated (%): C, 84.52; H, 15.48. ^{13}C NMR ($CDCl_3$), δ: 20.39 (C(1)), 32.17 (C(2)), 38.80 (C(3)), 34.38 (C(4)), 27.81 (C(5)), 30.28 (C(6)), 29.63 (C(7)), 32.17 (C(8)), 22.93 (C(9)), 14.22 (C(10)), 18.12 (C(11)), 15.45 (C(12)). ^1H NMR ($CDCl_3$), δ: 0.83 (t, 6 H, $C(10)H_3$, $C(12)H_3$, $^3J_{C,H}$ = 5.1 Hz); 0.86 (d, 6 H, $C(1)H_3$, $C(11)H_3$, $^3J_{C,H}$ = 6.4 Hz); 1.07—1.80 (m, 14 H, C(2)H, C(3)H, $C(4)H_2$, $C(5)H_2$, $C(6)H_2$, $C(7)H_2$, $C(8)H_2$, $C(9)H_2$). MS, *m/z* (I_{rel} (%)): 127 (6) $[M - C_3H_7]^+$, 126 (25), 98 (7), 97 (5), 85 (84), 71 (100).

2,3-Dimethyltridecane (1c). B.p. 110 °C (5 Torr). Found (%): C, 84.79; H, 15.13. $C_{15}H_{32}$. Calculated (%): C, 84.52; H, 15.48. ^{13}C NMR ($CDCl_3$), δ: 20.33 (C(1)), 32.10 (C(2)), 38.67 (C(3)), 34.31 (C(4)), 27.74 (C(5)), 30.21 (C(6)), 29.89 (C(7)), 29.89 (C(8)), 29.50 (C(9)), 29.50 (C(10)), 32.10 (C(11)), 22.80 (C(12)), 14.22 (C(13)), 18.05 (C(14)), 15.60 (C(15)). ^1H NMR ($CDCl_3$), δ: 0.81 (t, 6 H, $C(13)H_3$, $C(15)H_3$, $^3J_{C,H}$ = 5.1 Hz); 0.85 (d, 6 H, $C(1)H_3$, $C(14)H_3$, $^3J_{C,H}$ = 6.3 Hz); 1.07—1.75 (m, 20 H, C(2)H, C(3)H, $C(4)H_2$, $C(5)H_2$, $C(6)H_2$, $C(7)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$, $C(11)H_2$, $C(12)H_2$). MS, *m/z* (I_{rel} (%)): 171 (10) $[M - C_3H_7]^+$, 170 (15), 115 (7), 101 (9), 87 (10), 85 (7), 73 (69), 59 (100).

2,3-Dimethyltetradecane (1d). B.p. 93 °C (1 Torr). Found (%): C, 84.79; H, 15.13. $C_{16}H_{34}$. Calculated (%): C, 84.52; H, 15.48. ^{13}C NMR ($CDCl_3$), δ: 20.39 (C(1)), 32.04 (C(2)), 38.67 (C(3)), 34.25 (C(4)), 27.68 (C(5)), 30.21 (C(6)), 29.82 (C(7)), 29.82 (C(8)), 29.82 (C(9)), 29.50 (C(10)), 29.50 (C(11)), 32.04 (C(12)), 22.80 (C(13)), 14.22 (C(14)), 18.05 (C(15)), 15.45 (C(16)). ^1H NMR ($CDCl_3$), δ: 0.81 (t, 6 H, $C(14)H_3$, $C(16)H_3$, $^3J_{C,H}$ = 5.1 Hz); 0.85 (d, 6 H, $C(1)H_3$, $C(15)H_3$, $^3J_{C,H}$ = 6.35 Hz); 1.02—1.50 (m, 22 H, C(2)H, C(3)H, $C(4)H_2$, $C(5)H_2$, $C(6)H_2$, $C(7)H_2$, $C(8)H_2$, $C(9)H_2$, $C(10)H_2$, $C(11)H_2$, $C(12)H_2$, $C(13)H_2$). MS, *m/z* (I_{rel} (%)): 183 (7) $[M - C_3H_7]^+$, 182 (12), 127 (5), 113 (7), 99 (10), 97 (7), 85 (29), 71 (67), 57 (100).

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