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SHORT COMMUNICATIONS

Cp_2TiCl_2-Catalyzed Hydroalkylation of Cycloalkenes with *t*-BuBr–Et_3Al

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We previously studied reactions of α-olefins with various alkyl halides in the presence of triethylaluminum and a catalytic amount of Cp_2TiCl_2 or Cp_2ZrCl_2 and found that the system *t*-BuBr–Et_3Al–Cp_2TiCl_2 ensures successful hydroalkylation of aliphatic α-olefins with formation of the corresponding 2,3-dimethylalkanes in high yield [1]. Our further studies showed that cyclic olefins can also be involved in analogous reactions which lead to the formation of mixtures of isomers and that the character of their transformations depends on the ring size and olefin nature.

Cyclopentene was thus converted into compounds **Ia** and **IIIa** at a ratio of ~1:2 (overall yield 83%), from cyclohexene we obtained a mixture of compounds **Ib** and **IIb** at a ratio of ~1:3 (overall yield 89%), and the major products in the reactions with cycloheptene and cyclooctene were the corresponding *tert*-butylcycloalkanes **Ic** and **Id** whose yield reached 50–70% (Scheme 1). Cyclic olefins having a tertiary carbon atom, such as norbornene, norbornadiene, and 4-vinylcyclohex-1-ene, underwent isomerization, while no products of addition of *tert*-butyl group were formed. Primary and secondary alkyl halides (isopropyl bromide, butyl iodide, and ethyl chloride) failed to react under these conditions.

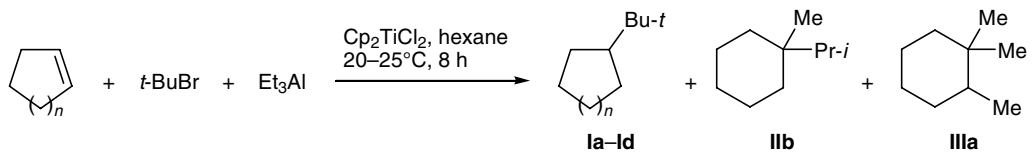
Compounds **Ia/IIIa** and **Ib/IIb** were analyzed as mixtures. Signals in the ^{13}C NMR spectra of **Ia** and **IIb** were assigned taking into account published data for compound **IIIa** [2] and **Ib** [3] and using the additivity scheme [4, 5]. The mass spectra of **Ia**, **Ib**, and **IIIa** were compared with those reported in [3].

The addition of a *tert*-butyl group to cycloheptene and cyclooctene follows from the presence of a strong signal at δ_C 26.96 and 27.16 ppm in the ^{13}C NMR spectra of compounds **Ic** and **Id**, respectively, and of a singlet at δ 0.8 ppm in the ^1H NMR spectra. The mass spectra of these compounds contained a ion peak belonging to isobutylene. The ^{13}C NMR signals were assigned using the additivity scheme [4, 5].

Treatment of the reaction mixtures with D_2O gave no hydrocarbons containing deuterium atoms (according to the mass spectral data). On the basis of the mechanism proposed in [1] for hydroalkylation of α-olefins, the observed transformations may be rationalized as shown in Scheme 2.

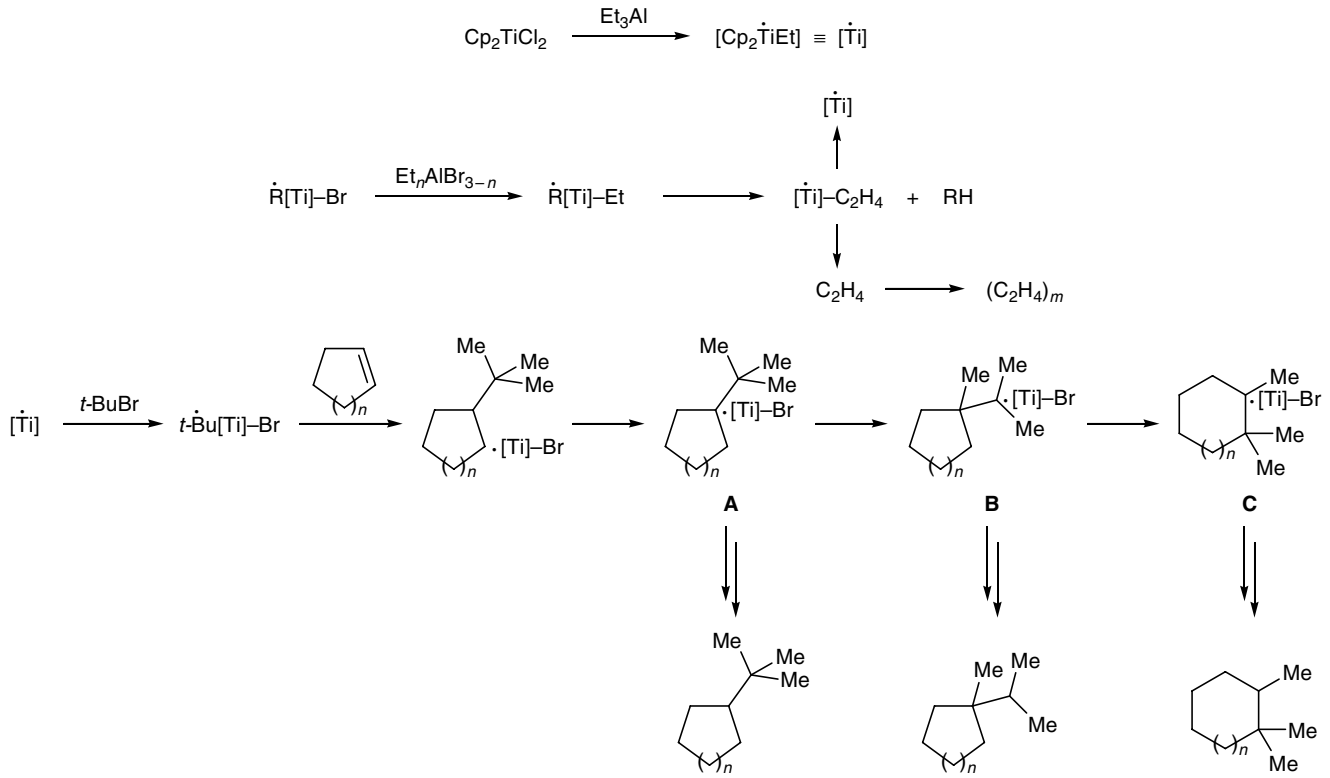
The absence of methylisopropylcyclopentane among the products obtained from cyclopentene (n = 3) may be explained assuming that the rearrangement (ring expansion) of intermediate **B** into **C** is energetically favorable. The reason for the low selectivity of hydroalkylation of cyclic olefins as compared to α-olefins may be that the radical center in intermediate **A** resides at the tertiary carbon atom; there-

Scheme 1.



n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**).

Scheme 2.



fore, stabilization of intermediate **A** favors increased fraction of *tert*-butyl-substituted products. Cyclic olefins with a tertiary carbon atom are likely to react via hydrogen abstraction from that carbon atom, followed by skeletal isomerization.

General procedure for hydroalkylation of cycloalkenes. A reactor was immersed into an ice bath, filled with argon, and charged in succession with 50 ml of hexane, 10 mmol of cycloalkene, 20 mmol of Et_3Al, 20 mmol of *tert*-butyl bromide, and 0.05 mmol of Cp_2TiCl_2. The mixture was stirred for 8 h at 20–25°C and treated with 10% hydrochloric acid, the organic phase was separated, the aqueous phase was extracted with diethyl ether, and the extract was combined with the organic phase, dried over anhydrous calcium chloride, and concentrated under reduced pressure. The products were isolated by vacuum distillation.

***tert*-Butylcyclopentane (Ia).** Yield 29%, bp 51°C (30 mm). ^{1}H NMR spectrum, δ, ppm: 0.77 s [9H, $(CH_3)_3C$], 1.17–1.97 m (9H, CH, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 23.32 t (C^3, C^4), 29.04 q [(**C**$H_3)_3C$], 35.55 t (C^2, C^5), 40.94 s (**C**Me_3), 47.64 s (C^1). Mass spectrum, *m/z* (I_{rel}, %): 111 [M – CH_3]$^+$ (12), 69 [M – C_4H_9]$^+$ (30), 68 $[C_5H_8]^+$ (24), 57 [*t*-Bu]$^+$ (84), 56 $[C_4H_8]^+$ (100).

1,1,2-Trimethylcyclohexane (IIIa). Yield 54%, bp 51°C (30 mm). ^{1}H NMR spectrum, δ, ppm: 0.88 br.s (9H, CH_3), 1.17–1.97 m (9H, CH, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 16.23 q (2-CH_3), 18.96 q (1-CH_3, ax.), 22.67 t (C^5), 26.70 t (C^4), 30.47 q (1-CH_3, eq.), 31.12 t (C^3), 33.01 s (C^1), 40.94 s (C^2). Mass spectrum, *m/z* (I_{rel}, %): 126 [M]$^+$ (21), 111 [M – CH_3]$^+$ (52), 98 [M – C_2H_4]$^+$ (8), 69 $[C_5H_8]^+$ (100), 56 $[C_4H_8]^+$ (71), 55 $[C_4H_8 – H]^+$ (65).

***tert*-Butylcyclohexane (Ib).** Yield 20%, bp 67°C (25 mm). ^{1}H NMR spectrum, δ, ppm: 0.74 s [9H, $(CH_3)_3C$], 1.10–1.58 m (11H, CH, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 27.03 t (C^4), 27.55 t (C^3, C^5), 27.68 q [(**C**$H_3)_3$**C**], 27.87 t (C^2, C^6), 31.90 s [$(CH_3)_3$**C**], 48.68 d (C^1). Mass spectrum, *m/z* (I_{rel}, %): 140 [M]$^+$ (2), 125 [M – CH_3]$^+$ (2), 82 [M – C_4H_9]$^+$ (12), 57 $[C_4H_9]^+$ (64), 56 $[C_4H_8]^+$ (100).

1-Isopropyl-1-methylcyclohexane (IIb). Yield 69%, bp 67°C (25 mm). ^{1}H NMR spectrum, δ, ppm: 0.85 d [6H, (C**H**$_3)_2$CH, $^3J_{CH}$ = 6.13 Hz], 0.86 s (3H, 1-CH_3), 1.07–1.67 m [11H, $(CH_3)_2$C**H**, CH_2]. ^{13}C NMR spectrum, δ_C, ppm: 16.95 q [(**C**$H_3)_2$CH], 18.96 q (1-CH_3), 22.28 t (C^3, C^5), 26.83 t (C^4), 27.68 d [**C**H$(CH_3)_2$], 29.68 (C^4), 34.96 (C^1), 36.33 (C^2, C^6). Mass spectrum, *m/z* (I_{rel}, %): 125 [M – CH_3]$^+$ (1), 97 (79), 81 (17), 69 (16), 55 (100).

***tert*-Butylcycloheptane (Ic).** Yield 53%, bp 69°C (22 mm). ^{1}H NMR spectrum, δ, ppm: 0.83 s [9H, $(CH_3)_3C$], 0.95–1.72 m (13H, CH, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 49.46 d (C^1), 28.20 t (C^2, C^7), 27.55 t (C^3, C^6), 27.55 t (C^4, C^5), 26.96 q [$(\mathbf{C}H_3)_3C$], 32.04 s [$(CH_3)_3\mathbf{C}$]. Mass spectrum, *m*/*z* (I_{rel}, %): 154 $[M]^+$ (1), 139 $[M - CH_3]^+$ (2), 96 $[M - C_4H_9]^+$ (10), 57 $[C_4H_9]^+$ (52), 56 $[C_4H_8]^+$ (100). Found, %: C 86.31; H 13.99. $C_{11}H_{22}$. Calculated, %: C 85.63; N 14.37.

***tert*-Butylcyclooctane (Id).** Yield 67%, bp 75°C (30 mm). ^{1}H NMR spectrum, δ, ppm: 0.84 s [9H, $(CH_3)_3C$], 1.17–1.41 m (15H, CH, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 43.87 d (C^1), 28.72 t (C^2, C^8), 26.56 t (C^3, C^7), 30.93 t (C^4, C^6), 29.76 t (C^5), 27.16 q [$(\mathbf{C}H_3)_3C$], 32.23 s [$(CH_3)_3\mathbf{C}$]. Mass spectrum, *m*/*z* (I_{rel}, %): 168 $[M]^+$ (1), 153 $[M - CH_3]^+$ (2), 110 $[M - C_4H_9]^+$ (9), 57 $[C_4H_9]^+$ (41), 56 $[C_4H_8]^+$ (100). Found, %: C 85.75; H 13.87. $C_{12}H_{24}$. Calculated, %: C 85.63; N 14.37.

Hexane and *tert*-butyl bromide were thoroughly purified prior to use. The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol FX-90Q spectrometer at 90 and 22.5 MHz, respectively, using $CDCl_3$ as solvent and TMS as internal reference. The ^{13}C NMR spectra were measured with complete decoupling from protons and in the INEPT mode (Insensitive Nuclei Enhanced by Polarization Transfer). The products were analyzed by GLC on a Carlo Erba chromatograph equipped with a flame-ionization detector and an HP-Ultra-1 column, 25 m×0.2 mm; 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 yields were determined by GLC using nonane or undecane as internal standard.

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