SHORT COMMUNICATIONS

Mild C–C Bond Cleavage in Cycloalkanes by the Action of New Lanthanide Catalysts LnCl₃·3H₂O·3(EtO)₂AlOH

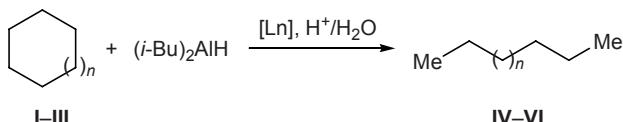**R. G. Bulgakov, D. S. Karamzina, S. P. Kuleshov, and U. M. Dzhemilev**

*Institute of Petroleum Chemistry and Catalysis, Russian Academy of Sciences,
pr. Oktyabrya 141, Ufa, 450075 Bashkortostan, Russia
e-mail: ink@anrb.ru*

Different ways of hydrocarbon processing (cracking, hydrogen cracking, skeletal isomerization, reforming) involve transformations of saturated hydrocarbons through activation and cleavage of carbon–carbon bonds. Therefore, an important relevant problem is search for new methods for activation of thermodynamically stable nonpolar C–C bonds. Noncatalytic dissociation of C–C bonds in alkanes and unstrained cycloalkanes requires fairly severe conditions: high temperature (300–1000°C) and pressure (more than 50 atm) [1]. Various transition metal compounds, especially those derived from VI–VIII Group elements, in combination with organoaluminums make it possible to perform such reactions at 150–180°C. Superacids and superelectrophilic reagents based on polyhalomethanes activate C–C bonds under even milder conditions (20–200°C) [2]. However, wide application of superacids in practice is strongly limited because of their corrosion activity and high cost.

In the present communication we report on the first example of using lanthanide complexes as catalysts for low-temperature activation of C–C bonds in hydrogenolysis of cycloalkanes. The catalysts, LnCl₃·3H₂O·3(EtO)₂AlOH complexes ([Ln], Ln = Ce, Nd, Eu, Tb), were generated *in situ* according to the procedure described in [3], i.e., by reaction of LnCl₃·6H₂O with Al(OEt)₃. As hydrogenating agents we used LiAlH₄,

NaBH₄, [Bu₄N][Pr(BH₄)₄·DME] (where DME stands for 1,2-dimethoxyethane), and molecular hydrogen (bubbling at a flow rate of 0.4 ml/s). The reactions were performed under mild conditions: 80°C, 760 mm, 6 h. Experiments with molecular hydrogen were carried out under more drastic conditions: a high-pressure reactor was continuously shaken over a period of 5 h at 215°C and a hydrogen pressure of 16 atm.

We found that [Ln] in combination with (*i*-Bu)₂AlH is a highly selective and fairly efficient catalyst (see table). The conversion of cyclohexane (strain energy $E_s = 0$ kJ/mol) over [Tb] was 67%, while the known catalyst Re₂(CO)₁₀–(*i*-Bu)₂AlH ensured only 22% conversion [1]. The conversions of cycloheptane and cyclooctane ($E_s = 3.7$ and 5.1 kJ/mol, respectively) were 72 and 78%. In the reactions with other hydrogenating agents, the conversion of cyclohexane over [Tb] did not exceed 10%.

The examined lanthanides rank as follows with respect to the conversion of cyclohexane (%): Ce (38) < Nd (40) < Eu (52) < Tb (67). This series coincides with the known series of complexing power of lanthanide ions [4].

The conversion of cyclohexane in the presence of simpler lanthanide compounds, such as LnCl₃, LnCl₃·6H₂O, LnCl₃·3TBP (TBP is tributyl phthalate), and aluminum alkoxides Al(OR)₃ (R = Et, *i*-Bu), was considerably lower (15%). Our results led us to presume that the catalytically active center in the hydrogenolysis process includes both metal ions, lanthanide and aluminum.

Typical procedure for hydrogenolysis of cycloalkanes. A solution of 0.24 mmol of Al(OEt)₃ in

[Ln] = LnCl₃·3H₂O·3(EtO)₂AlOH; Ln = Ce, Nd, Eu, Tb;
I, **IV**, *n* = 1; **II**, **V**, *n* = 2; **III**, **VI**, *n* = 3.

12.5 ml of dioxane was added under argon to 0.08 mmol of $LnCl_3 \cdot 6H_2O$, and the mixture was stirred until it became homogeneous and $LnCl_3 \cdot 6H_2O$ disappeared. Cycloalkane **I–III**, 4.8 mmol, and $(i\text{-Bu})_2AlH$, 7.2 mmol, were added, and the mixture was heated for 6 h at 80°C. The mixture was then cooled to 10°C, treated with 15 ml of 10% hydrochloric acid, and extracted with diethyl ether, The extract was dried over Na_2SO_4, and the solvent was distilled off.

Hexane (**IV**). n_D^{20} = 1.3752 (1.3751 [5]). ^{1}H NMR spectrum, δ, ppm: 0.96 t (6H, CH_3), 1.35 br.s (8H, CH_2). ^{13}C NMR spectrum, $δ_C$, ppm: 14.03 q (C^1, C^6), 23.04 t (C^2, C^5), 32.13 t (C^3, C^4).

Heptane (**V**). n_D^{20} = 1.3879 (1.3878 [5]). ^{1}H NMR spectrum, δ, ppm: 1.02 t (6H, CH_3), 1.42 br.s (10H, CH_2). ^{13}C NMR spectrum, $δ_C$, ppm: 14.09 q (C^1, C^7), 23.18 t (C^2, C^6), 29.43 t (C^4), 32.29 t (C^3, C^5).

Octane (**VI**). n_D^{20} = 1.3976 (1.3974 [5]). ^{1}H NMR spectrum, δ, ppm: 0.92 t (6H, CH_3), 1.45 br.s (12H, CH_2). ^{13}C NMR spectrum, $δ_C$, ppm: 14.19 q (C^1, C^8), 22.90 t (C^2, C^7), 29.45 t (C^4, C^5), 32.30 t (C^3, C^6).

The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q spectrometer at 89.5 and 22.5 MHz, respectively, using tetramethylsilane as internal reference and chloroform-d as solvent. The products were analyzed by GLC on a Tsvet 500M chromatograph equipped with a flame ionization detector and a steel column, 2 m×3 mm (stationary phase 30.5% of SE on Chromaton N-AW-HMDS; oven temperature programming from 50 to 270°C at a rate of 8 deg/min).

Hydrogenolysis of cycloalkanes with the system $LnCl_3 \cdot 3H_2O \cdot 3(EtO)_2AlOH–(i\text{-Bu})_2AlH$ in dioxane

Initial compound no.	Ln	Conversion, %	Product
I	Tb	67	**IV**
I	Eu	52	**IV**
I	Nd	40	**IV**
I	Ce	38	**IV**
II	Tb	72	**V**
III	Tb	78	**VI**

REFERENCES

1. Akhrem, I.S. and Vol'pin, M.E., *Usp. Khim.*, 1990, vol. 59, p. 1906.

2. Zhorov, Yu.M., *Termodinamika khimicheskikh protsessov* (Thermodynamics of Chemical Processes), Moscow: Khimiya, 1985, p. 135.

3. Bulgakov, R.G., Kuleshov, S.P., Karamzina, D.S., Makhmutov, A.R., Vafin, R.R., Shestopal, Ya.L., Mullagaliev, I.R., Monakov, Yu.B., and Dzhemilev, U.M., *Kinet. Katal.*, 2006, vol. 47, p. 760.

4. Yatsimirskii, B.K., Kostromina, N.A., Sheka, Z.A., Davidenko, N.K., Kriss, E.E., and Ermolenko, V.I., *Khimiya kompleksnykh soedinenii redkozemel'nykh elementov* (Chemistry of Rare-Earth Coordination Compounds), Kiev: Naukova Dumka, 1966, p. 493.

5. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.