ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 8, pp. 1254–1256. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © R.G. Bulgakov, D.S. Karamzina, S.P. Kuleshov, U.M. Dzhemilev, 2010, published in Zhurnal Organicheskoi Khimii, 2010, Vol. 46, No. 8, pp. 1252–1254.

SHORT COMMUNICATIONS

Hydrogenolysis of Cycloalkanes over $TbCl_3 \cdot 3H_2O \cdot 3(RO)_2AlOH$

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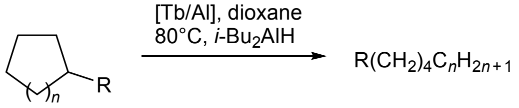
Received June 10, 2009

DOI: 10.1134/S1070428010080233

We previously demonstrated the possibility for mild activation and cleavage of C–C bonds in cyclohexane, cycloheptane, and cyclooctane using a new catalyst, $LnCl_3 \cdot 3H_2O \cdot 3(RO)_2AlOH$ (R = Et, *i*-Bu) in combination with $(i\text{-Bu})_2AlH$ [1]. The synthesis of $LnCl_3 \cdot 3H_2O \cdot 3(RO)_2AlOH$ (hereinafter referred to as Ln/Al) by reaction of $LnCl_3 \cdot 6H_2O$ with $Al(OR)_3$ was described in [2]. One-pot hydrogenolysis of cycloalkanes over Ln/Al ensures selective preparation of the corresponding linear alkanes (hexane, heptane, and octane) under considerably milder conditions (80°C, 1 atm) [1] than those reported in [3] for the hydrogenolysis of the same cycloalkanes over such metal complex catalysts as $Re_2(CO)_{10}$, $Re_3H_3(CO)_{12}$, and $Re_4H_4(CO)_{12}$ in combination with $(i\text{-Bu})_2AlH$ (150–180°C, hydrogen pressure 50 atm).

In the present work hydrogenolysis of cyclohexane was used as model reaction to estimate the effect of a number of experimental factors on the catalytic activity of Ln/Al. This factors included the nature of anion (Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}) linked to Ln^{3+} ion in the initial $LnX_3 \cdot 6H_2O$ salt, radical R (R = Et, *i*-Bu), and solvent (dioxane, toluene, benzene), the presence of a substituent (CH_3) in cycloalkane molecule, temperature, order of mixing of the reactants, and reactant ratio. In addition, the relation between the efficiency of hydrogenolysis and strain energy in initial cycloalkanes (cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclodecane) was analyzed.

The hydrogenolysis was performed according to one-pot procedure: a reactor was charged in succession with 0.08 mmol of $LnCl_3 \cdot 6H_2O$ and 0.24 mmol of $Al(OR)_3$ in dioxane, the mixture was kept for 4 h at 25°C to generate Ln/Al *in situ*, and the other reagents were then added (overall reaction time 10 h). The efficiency of Ln/Al as catalyst was estimated by the conversion of cycloalkanes; the only hydrogenolysis product was the corresponding linear alkane.



R = H, *n* = 1, 3, 4, 6; R = Me, *n* = 2.

As we showed previously [1], the conversion (%) of cyclohexane decreases in the lanthanide series Tb (67) > Eu (52) > Nd (40) > Ce (38), which coincides with the known complexing power series of lanthanide ions. Taking these data into account, the effect of the anion nature in the catalyst Ln/Al was studied in the reactions performed in the presence of the most effective terbium catalyst Tb/Al. The anion nature in the initial crystal hydrate appreciably affected the efficiency of hydrogenolysis. The Tb/Al catalyst prepared by reaction of $TbCl_3 \cdot 6H_2O$ with $Al(OEt)_3$ was more effective than that obtained from $Tb(NO_3)_3 \cdot 6H_2O$ and $Al(OEt)_3$. We have encountered with some difficulties while attempting to obtain catalysts by reactions of $Al(OEt)_3$ with $Tb_2(SO_4)_3 \cdot 8H_2O$ and $Tb_2(CO_3)_3 \cdot 6H_2O$. In the reactions of $Al(OEt)_3$ with $TbCl_3 \cdot 6H_2O$ and $Tb(NO_3)_3 \cdot 6H_2O$, the solid phase disappeared in 4 h at 25°C to produce a homogeneous (visually) and catalytically active solution, whereas in the reactions of $Al(OEt)_3$ with $Tb_2(SO_4)_3 \cdot 8H_2O$ and $Tb_2(CO_3)_3 \cdot 6H_2O$ the solid phase was retained under analogous conditions, and such systems (including both liquid and solid phases) showed no catalytic activity in the hydrogenolysis of cyclohexane. Thus variation of the catalytic activity (%) of initial crystal hydrates with different anions conforms to the following series:

$$TbCl_3 \cdot 6H_2O\ (67) > Tb(NO_3)_3 \cdot 6H_2O\ (14)$$
$$> Tb_2(SO_4)_3 \cdot 8H_2O\ (0) = Tb_2(CO_3)_3 \cdot 6H_2O\ (0).$$

Considerably lower catalytic activity of terbium(III) nitrate compared to chloride may be understood taking into account that NO_3^- is a bulkier anion which hampers formation of catalytically active hydrogenolysis centers as a result of change of coordination environment of Tb^{3+} ion. The nature of the R radical (R = Et, *i*-Bu) in the akoxy fragment (RO) of Tb/Al did not affect the conversion of cyclohexane. The conversion of cyclohexane decreased in going from dioxane (67%) to aromatic solvents, toluene (11%) and benzene (9%). Presumably, higher efficiency of hydrogenolysis in dioxane is related to enhanced mobility of the hydrogen atom in $(i\text{-}Bu)_2AlH$ due to hydrogen bonding with oxygen atom in dioxane molecule. Higher efficiency of dehalogenation of halogenated hydrocarbons by the action of $(i\text{-}Bu)_2AlH$ in ether solvents in the presence of a number of metal complex catalysts was rationalized in a similar way [4].

The effect of temperature was studied in the range from 25 to 80°C. No hydrogenolysis occurred below 40°C, and the conversion of cyclohexane at 60 and 80°C was 30 and 67%, respectively. In the absence of $(i\text{-}Bu)_2AlH$ thermal cracking of cyclohexane did not observed even under pressure at 180°C (6 h).

The conversion of cyclohexane strongly depended on the reactant ratio and order of their addition. At Ln^{3+}–cyclohexane–$(i\text{-}Bu)_2AlH$ molar ratios of 1:60:90 and 1:60:60 the conversions of cyclohexane were 67 and 43%, respectively. If cyclohexane was added prior to $(i\text{-}Bu)_2AlH$, its conversion was 67%, and it decreased to 40% when cyclohexane was added after $(i\text{-}Bu)_2AlH$ (in both cases, the reactants were added after generation of the Ln/Al catalyst). The lower conversion of cyclohexane in the latter case is likely to result from dehydration of Tb^{3+} ion due to reaction of crystallization water in the catalyst with $(i\text{-}Bu)_2AlH$; ion Tb^{3+} thus becomes coordinately unsaturated and gives rise to catalytically inactive Tb–Cl–Tb(Al) units. Addition of $(i\text{-}Bu)_2AlH$ to Tb/Al leads to appreciable shortening of the photoluminescence lifetime of terbium ion $\tau(Tb^{3+}*)$ from 1000 to 15 μs. The formation of Tb–Cl–Tb(Al) units was observed by us previously [5] in the reaction of $TbCl_3 \cdot 6H_2O$ with $(i\text{-}Bu)_3Al$, which was also accompanied by reduction of $\tau(Tb^{3+}*)$ from 420 to <15 μs.

In keeping with the above stated, higher efficiency of catalytic hydrogenolysis of cyclohexane added before $(i\text{-}Bu)_2AlH$ may be rationalized on the assumption that cyclohexane is coordinated to Tb^{3+} ion thus hampering formation of Tb–Cl–Tb(Al) after dehydration of terbium ion [reaction of crystallization water with $(i\text{-}Bu)_2AlH$]. In this case catalytically active centers are formed before Tb–Cl–Tb(Al).

The conversion of cycloalkanes increased with rise in the strain energy in the ring.

Catalytic hydrogenolysis of alkyl-substituted cyclohexane over Tb/Al occurred more readily than analogous reaction with unsubstituted cyclohexane; the conversion was 75 and 67%, respectively. The only hydrogenolysis product obtained from methylcyclohexane was *n*-heptane. This means that the reaction with methylcyclohexane involves cleavage of the C–C bond at the carbon atom linked to the methyl group $[(H_3C)C–CH_2]$ rather than cleavage of $H_2C–CH_2$ bond. Higher efficiency of hydrogenolysis of methylcyclohexane is determined by lower strength of the $(H_3C)C–CH_2$ bond. This is confirmed by the results of RI-MP2/L2 quantum-chemical calculations (PRIRODA program) of the energies of the $(H_3C)C–CH_2$ and $H_2C–CH_2$ bonds (396 and 410 kJ/mol, respectively). These results are consistent with the data of [6], according to which the apparent energies of activation for hydrogenolysis of methylcyclohexane and cyclohexane over Ru/C are equal to 59 and 67 kJ/mol, respectively.

Hydrogenolysis of cycloalkanes (*general procedure*). A glass reactor was charged with 0.08 mmol of $LnCl_3 \cdot 6H_2O$, 0.24 mmol of $Al(OR)_3$ in 12.5 ml of dioxane was added, and the mixture was stirred until $LnCl_3 \cdot 6H_2O$ disappeared and a homogeneous solution was formed (25°C, 4 h). The corresponding cycloalkane, 4.8 mmol, was added, the mixture was purged with argon over a period of 10 min, 7.2 mmol of $(i\text{-}Bu)_2AlH$ was 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 sodium sulfate, and the solvent was distilled off.

Pentane. Conversion of cyclopentane 77%, n_D^{20} = 1.3582 (1.3580 [7]). ^1H NMR spectrum, δ, ppm: 0.80 t (6H, CH_3), 1.33 br.s (6H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 13.73 q (C^1, C^5), 22.93 t (C^2, C^4), 34.58 t (C^3).

Hexane. Conversion of cyclohexane 67%, n_D^{20} = 1.3752 (1.3751 [7]). ^1H 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. *a*. Conversion of cycloheptane 72%.

b. Conversion of methylcyclohexane 75%, n_D^{20} = 1.3879 (1.3878 [7]). ^{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. Conversion of cyclooctane 75%, n_D^{20} = 1.3976 (1.3974 [7]). ^{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).

Decane. Conversion of cyclodecane 77%, n_D^{20} = 1.4108 (1.4110 [7]). ^{1}H NMR spectrum, δ, ppm: 0.91 t (6H, CH_3), 1.25 br.s (16H, CH_2). ^{13}C NMR spectrum, δ_C, ppm: 14.00 q (C^1, C^{10}), 22.80 t (C^2, C^9), 28.66 t (C^5, C^6), 31.57 t (C^3, C^8), 29.15 t (C^4, C^7).

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 $CDCl_3$ as solvent and tetramethylsilane as internal reference. The hydrogenolysis products were analyzed by GLC on a Tsvet 500M chromatograph equipped with a flame ionization detector and a steel column, 2000 × 3 mm, packed with 30.5% of SE on Chromaton N-AW-HMDS; oven temperature programming from 50 to 270°C at a rate of 8 deg/min.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 08-03-00278-a). The authors thank D.Sh. Sabirov (Institute of Petroleum Chemistry and Catalysis, Russian Academy of Sciences) for his help in performing quantum-chemical calculations.

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