ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 10, pp. 1570–1572. © Pleiades Publishing, Inc., 2006.
Original Russian Text © R.G. Bulgakov, S.P. Kuleshov, D.S. Karamzina, U.M. Dzhemilev, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 10, pp. 1581–1582.

SHORT COMMUNICATIONS

Reduction of Halogen-Containing Hydrocarbons with Diisobutylaluminum Hydride, Catalyzed by $LnCl_3 \cdot 3H_2O \cdot 3(EtO)_2AlOH$ Complexes

R. G. Bulgakov, S. P. Kuleshov, D. S. Karamzina, 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

Received May 31, 2006

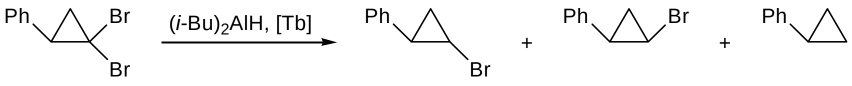
DOI: 10.1134/S1070428006100290

The problem of reductive dehalogenation of halogenated hydrocarbons can be divided into two main parts. The first of these is concerned with complete dehalogenation via catalytic hydrogenation [1], which is important for utilization of organohalogen wastes. The second part includes partial dehalogenation to obtain commercially valuable products, for example, reduction of dihalocyclopropanes to monohalocyclopropanes which are used in the synthesis of multipurpose cyclopropenes [2]. An effective dehalogenation procedure is based on the reduction of aryl or alkyl halides with accessible diisobutylaluminum hydride in the presence of transition metal complexes (Ti, V, Mn, Fe, Co, Ni, Zr, Mo, Ru, Rh, Pd, Hf, W) [3–5]. The catalytic activity of lanthanide compounds in the dehalogenation processes was not studied previously [1, 6].

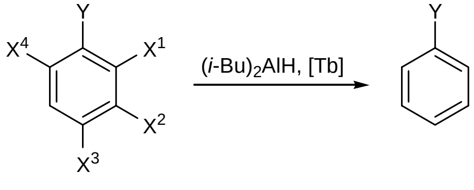
The present communication reports for the first time on the efficiency of lanthanide catalysts in the reductive dehalogenation of halocyclopropanes and aryl halides with $(i\text{-}Bu)_2AlH$. As catalysts we used lanthanide complexes of the general formula $LnCl_3 \cdot 3H_2O \cdot 3(EtO)_2AlOH$ (where Ln = Ce, Nd, Eu, Tb, Ho; hereinafter referred to as [Ln]); their preparation by reaction of $LnCl_3 \cdot 6H_2O$ with $Al(OEt)_3$ was described in [7].

The examined [Ln] catalysts turned out to be highly selective and fairly effective (see table). Thus the conversion of chlorobenzene over [Tb] was 60%, while the known catalyst, $(BuO)_4Ti$, ensured only 35% conversion [3]. Using bromobenzene as model substrate, we examined how the conversion (%) depends on the lanthanide nature and obtained the following series: Ce (16) < Nd (42) < Tb (80) > Eu (28) > Ho (26). The maximal conversion was observed in the presence of the terbium catalyst [Tb]; it increased according to the known C–Hlg bond energy series: Cl > Br > I.

In the reduction of chloro- and bromobenzenes, the reaction mixture contained hexane in addition to benzene as the major product (see table). This result was



I **II** **III**



IVa–IVd **Va–Vd**

X^1 = Cl, Br, I, $X^2 = X^3 = X^4$ = Y = H (**a**); $X^1 = X^2 = X^3 = X^4$ = Cl, Y = OH (**b**); Y = BrC_6H_4, X^3 = Br, $X^1 = X^2 = X^4$ = H (**c**); Y = Ph, X^3 = Br, $X^1 = X^2 = X^4$ = H (**d**).

unexpected, for opening of carbocycles in catalytic hydrogenation usually occurs at higher temperature (150–180°C) [8]. We presumed that hexane is formed through a series of consecutive transformations by the action of [Tb] and $(i\text{-Bu})_2AlH$: halobenzene → benzene → cyclohexane → hexane. In fact, cyclohexane was found to react with the system [Tb]–$(i\text{-Bu})_2AlH$ under relatively mild conditions (80°C) to give hexane with a conversion of 67%.

In the dehalogenation of 1,1-dibromo-2-phenylcyclopropane, [Tb] was less active (conversion 64%) than the most efficient catalyst $(BuO)_4Ti$ (conversion 98%). On the other hand, [Tb] was more selective: the ratio of the most important products, *cis*- and *trans*-1-bromo-2-phenylcyclopropanes, to phenylcyclopropane was 3.5:1 against 1:3 in the presence of $(BuO)_4Ti$.

Simpler salts like $LnCl_3$ and $LnCl_3 \cdot 6H_2O$, complexes $LnCl_3 \cdot 3TBP$, and aluminum alkoxides $Al(OR)_3$ (R = Et, *i*-Bu) showed poor catalytic activity in the dehalogenation of bromobenzene (conversion ≤15%). Therefore, we presumed that the most active catalysts in the dehalogenation process, as well as in the polymerization of dienes [9], are those possessing two different metal ions (i.e., Ln and Al) as catalytically active centers.

Complex $LnCl_3 \cdot 3H_2O \cdot 3(EtO)_2AlOH$. A solution of 0.75 mmol of $Al(OEt)_3$ in 5 ml of dioxane was added under argon to 0.25 mmol of $LnCl_3 \cdot 6H_2O$, and the mixture was stirred until the crystals of $LnCl_3 \cdot 6H_2O$ disappeared (the mixture turned visually homogeneous). Separation of the mixture in a centrifuge gave a gel which was washed with dioxane and dried under reduced pressure (10 mm) for 20 min (until a free-flowing powder was obtained). Found, %: C 20.44; H 5.62; Al 11.05; Cl 14.28; Tb 21.87. $C_{12}H_{39}Al_3Cl_3O_{12}Tb$. Calculated, %: C 19.96; H 5.40; Al 11.23; Cl 14.76; Tb 22.03.

Reduction of halogenated hydrocarbons (*typical procedure*). A solution of 0.24 mmol of $Al(OEt)_3$ in 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. Halogenated hydrocarbon, 4.8 mmol, and $(i\text{-Bu})_2AlH$, 7.2 mmol (28.8 mmol in the reduction of tetrachlorophenol), were added, and the mixture was heated for 6 h at 80°C, cooled to 10°C, decomposed by treatment with 15 ml of 10% hydrochloric acid, and extracted with diethyl ether. The extract was dried over Na_2SO_4.

***cis*-1-Bromo-2-phenylcyclopropane.** ^1H NMR spectrum, δ, ppm: 3.23 m (1H, CH), 1.27 m (2H, CH), 2.16 m (3H, CH_2), 7.01 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.15 t (C^3), 22.04 d (C^2), 23.99 d (C^1), 125.89 d (C^5, C^9), 126.71 d (C^7), 128.47 d (C^6, C^8), 137.05 s (C^4).

Reduction of halogenated hydrocarbons with $(i\text{-Bu})_2AlH$ in the presence of $TbCl_3 \cdot 3H_2O \cdot 3(EtO)_2AlOH$ in dioxane

Initial compound	Conversion, %	Reduction products
C_6H_5Cl	60	C_6H_6 + hexane, 4:1
C_6H_5Br	80	C_6H_6 + hexane, 3:1
C_6H_5I	100	C_6H_6
2,3,4,6-Tetrachlorophenol	53	C_6H_5OH
1,1-Dibromo-2-phenylcyclopropane	64	**II** + **I** + **III**, 2:1.5:1
p-$BrC_6H_4C_6H_4Br$	100	*p*-$C_6H_5C_6H_4Br$
p-$C_6H_5C_6H_4Br$	5	$C_6H_5C_6H_5$

***trans*-1-Bromo-2-phenylcyclopropane.** ^1H NMR spectrum, δ, ppm: 2.93 m (1H, CH), 1.66 m (2H, CH), 2.48 m (3H, CH_2), 7.41 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 18.88 t (C^3), 21.59 d (C^2), 26.83 d (C^1), 126.45 d (C^7), 127.86 d (C^5, C^9), 128.47 d (C^6, C^8), 139.72 s (C^4).

The ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q spectrometer using $CDCl_3$ as solvent and TMS as internal reference. GLC analysis was performed on a Tsvet 500M chromatograph equipped with a flame-ionization detector and a steel column, 2 m× 3 mm, packed with 5% of SE-30 on Chromaton N-AW-HMDS; oven temperature programming from 50 to 270°C at a rate of 8 deg/min. The concentration of Ln^{3+} was determined by spectrofluorimetry [10, 11], the concentration of Al^{3+}, by complexometry [12], and that of water, according to Fischer.

REFERENCES

1. Zanaveskin, L.N., Aver'yanov, V.A., and Treger, Yu.A., *Usp. Khim.*, 1996, vol. 65, p. 667.
2. Yanovskaya, L.A., Dombrovskii, V.A., and Khusid, A.Kh., *Tsiklopropany s funktsional'nymi gruppami* (Functionalized Cyclopropanes), Moscow: Nauka, 1980, p. 223.
3. Dzhemilev, U.M. and Gaisin, R.L., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, p. 2332.
4. Dzhemilev, U.M., Gaisin, R.L., Turchin, A.A., Khalikova, N.R., Baikova, I.P., and Tolstikov, G.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, p. 1080.
5. Dzhemilev, U.M., Gaisin, R.L., Turchin, A.A., and Tolstikov, G.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, p. 2084.

6. Lunin, V.V. and Lokteva, E.S., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1996, p. 1609.
7. 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.
8. Vol'pin, M.E., Akhrem, I.S., Reznichenko, S.V., and Grushin, V.V., *J. Organomet. Chem.*, 1987, p. 109.
9. Monakov, Yu.B. and Tolstikov, G.A., *Kataliticheskaya polimerizatsiya 1,3-dienov* (Catalytic Polymerization of 1,3-Dienes), Moscow: Nauka, 1990, p. 104.
10. Panyushin, V.T., Afanas'ev, Yu.A., Khanaev, E.I., and Garnovskii, A.D., *Lantanoidy. Prostye i kompleksnye soedineniya* (Lanthanides. Simple and Coordination Compounds), Rostov-on-Don: Rostov. Gos. Univ., 1980, p. 296.
11. Bulgakov, R.G., Kuleshov, S.P., Zuzlov, A.N., Mullagaleev, I.R., Khalilov, L.M., and Dzhemilev, U.M., *J. Organomet. Chem.*, 2001, p. 56.
12. Charlot, G., *Les Méthodes de la Chimie Analytique. Analyse Quantitative Minérale*, Paris: Masson, 1961, 4th ed., p. 965.