Journal of Organometallic Chemistry, 309 (1986) C1–C3
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

HYDROALUMINATION OF OLEFINS BY THE $LiAlH_4/UCl_4$ SYSTEM

JEAN-FRANÇOIS LE MARECHAL, MICHEL EPHRITIKHINE and GÉRARD FOLCHER
Service de Chimie Moléculaire, IRDI/DESICP/DPC-UA 331, CEA-CEN/Saclay 91191
Gif-sur-Yvette Cédex (France)

(Received April 3rd, 1986)

Summary

$LiAlH_4$ reacts with olefins in the presence of a catalytic amount of UCl_4 or UCl_3 to give alkylaluminate compounds. The active species in these reactions is thought to be $U(AlH_4)_3$.

A few transition metal systems catalyse the addition of lithium aluminium hydride or alanes to alkenes under mild conditions and on the bench scale to give the corresponding organoaluminium derivatives [1,2,3], which are versatile reagents in organic synthesis [4]. In particular, $TiCl_4$ and $ZrCl_4$ are very effective catalysts for the preparation of organoaluminates from mono- or di-olefins and $LiAlH_4$ [3]. We describe here a study of the hydroalumination of olefins by the $LiAlH_4/UCl_4$ system, which involves comparison of the catalytic properties of 5*f* and *d* block transition metal chlorides and provides new insight into the mechanism of these reactions.

Terminal olefins reacted with $LiAlH_4$ at room temperature in dry tetrahydrofuran (THF) in the presence of a catalytic amount (1%) of UCl_3 (made by treatment of UCl_4 with 0.25 equivalents of $LiAlH_4$ in THF) to give pale brown solutions. After complete reaction of the alkene (up to 24 h, depending on the alkene/$LiAlH_4$ ratio), hydrolysis gave the corresponding n-alkane in quantitative yields (GC analysis) [5]. It was found that up to 4 equivalents of olefin can react with 1 equivalent of $LiAlH_4$ to give the alkylaluminates (I) * (eq. 1). The olefin hydroalumination is regiospecific, and involves anti-Markovnikov addition **.

$$x\ RCH{=}CH_2 + LiAlH_4 \xrightarrow{UCl_3} \underset{(I)}{(RCH_2CH_2)_xAlH_{4-x}Li} \xrightarrow{H_2O} RCH_2CH_3 \qquad (1)$$

($R = H$ or a linear alkyl group C_nH_{2n+1} ($n = 1$–6), $x \leqslant 4$)

---

* Compounds I were not isolated but were used in situ.

** Reaction of the propyl- and the butyl-aluminates with D_2O gave, respectively, propane and butane deuterated exclusively at the terminal position (500 MHz NMR analysis). See also the reactions mentioned in the next footnote.

0022-328X/86/$03.50

Under the same conditions *cis*-2-butene and *cis*-2-pentene underwent hydroalumination in 20% yield. Reactions of these olefins with the $LiAlH_4/UCl_4$ system in diglyme, followed after 6 h hydrolysis, gave the corresponding alkanes (70%) and the *trans* olefins (30%), which were found to be unreactive. Bromolysis of the butylaluminates obtained from 2-butene gave 1-bromo- and 2-bromo-butane in 28 and 42% yield, respectively (GC-MS analysis). This result shows that alkylaluminates are less readily isomerised in these reactions than in those involving the $LiAlH_4/TiCl_4$ system [3].

The results show that for olefin hydroalumination the $UCl_4/LiAlH_4$ mixture is an attractive alternative to the titanium reagent developed by Sato et al. [3]. The alkylaluminate products are useful intermediates in organic synthesis [2–4] *.

We turned our attention to the identification of active species in these reactions. As stated in a recent paper [6]: "... nothing is known about the detailed mechanism of these transition metal assisted hydride reduction" and it is necessary to "report crucial experimental details about precipitate formation or gas evolution...". Addition of excess $LiAlH_4$ at $-30°C$ to a purple solution of UCl_3 [7] gave a grey precipitate, which was found to come from the reaction of 3 equivalents of $LiAlH_4$ with 1 equivalent of UCl_3. This pyrophoric and poorly soluble uranium compound (10^{-3} M l^{-1}) was stable at low temperature but decomposed above $-20°C$ with evolution of hydrogen and formation of Al metal (X-ray powder analysis) and an unidentified insoluble uranium-containing species. The stoichiometry of formation and the reactions [8] of the precipitate indicate that it must be the uranium(III) aluminohydride $U(AlH_4)_3$ (II). It is probable that II contains U–H–Al bridging bonds, analogous to the bridges in the recently reported titanium [9] and yttrium [10] aluminohydrides.

Addition of a THF solution containing $LiAlH_4$ and 1-butene or 1-pentene ($olefin/LiAlH_4 = 2$) to II at $-30°C$ followed by warming at 20°C gave a pale brown solution which was hydrolysed after 4 h to give quantitative yield of the corresponding alkane. A similar reaction with the mother liquor from which II had separated was complete only after 48 h. These results clearly indicate that II is an active species in the catalytic hydroalumination of olefins; we think that it reacts with alkene $RCH{=}CH_2$ to give the intermediate $U(AlH_4)_2(AlH_3CH_2CH_2R)$ (III), in which the alkyl group may be bridging. This reaction would be favoured by initial coordination of olefin to the uranium atom in the bimetallic complex II, before insertion into a metal–hydrogen bond. Reaction of III with lithium aluminate would then give the product I and regenerate II.

References

1 E. Negishi and T. Yoshida, Tetrahedron Lett., 21 (1980) 1501.
2 K. Isagawa, K. Tatsumi and Y. Otsuji, Chemistry Lett., (1976) 1145 and (1977) 1117.
3 F. Sato, S. Sato, H. Kodama and M. Sato, J. Organomet. Chem., 142 (1977) 71.
4 R. Zietz, G.C. Robinson and K.L. Lindsay, in G. Wilkinson (Ed.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, vol 7, p. 365.

---

* Iodolysis of compounds I ($R = n\text{-}C_5H_{11}$, $n\text{-}C_6H_{13}$) gave the corresponding 1-iodoalkanes. Treatment of I ($R = n\text{-}C_2H_5$, $n\text{-}C_3H_7$ and $n\text{-}C_4H_9$) with formaldehyde gave the corresponding RCH_2OH alcohols, in yields, (based on olefin taken and determined by GC) in the range 45–50%.

5 G. Folcher, J.F. Le Marechal and H. Marquet-Ellis, J. Chem. Soc., Chem. Commun., (1982) 323. This communication reported the hydrogenation of olefins by $LiAlH_4$ in the presence of UCl_4. It is clear that these reactions involved alkylaluminate intermediates which were hydrolysed by not thoroughly dried solvant.
6 J.O. Osby, S.W. Heinzman and B. Ganem, J. Am. Chem. Soc., 108 (1986) 67.
7 D.C. Moody and J.D. Odom, J. Inorg. Nucl. Chem., 41 (1979) 533.
8 G.L. Soloveichik and B.M. Bulychev, Russian Chem. Rev., 52 (1983) 43.
9 E.B. Lobkovskii, G.L. Soloveichik, A.I. Sisov, B.M. Bulychev, A.I. Gusev and N.I. Kirillova, J. Organomet. Chem., 265 (1984) 167.
10 V.K. Belsky, A.B. Erofeev, B.M. Bulychev and G.L. Soloveichik, J. Organomet. Chem., 265 (1984) 123.