One-step synthesis of trialkylaluminum derivatives and dialkylaluminum hydrides by the reaction of alkaline metal aluminum hydrides with α-olefins and alkylaluminum chlorides

V. V. Gavrilenko

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: bre@ineos.ac.ru

A simple method for one-step preparation of the organoaluminum compounds R_3Al, R_2AlH, $R_2R'Al$, and $RR'AlH$ by the reaction of $MAlH_4$ (M = Li, Na) with R_2AlHal (Hal = Cl, Br) and α-olefins (3-methylbut-1-ene, hex-1-ene, oct-1-ene, dec-1-ene) was proposed.

Key words: organoaluminum compounds, trialkylaluminum derivatives, dialkylaluminum hydrides, mixed alkylaluminum hydrides, mechanochemical activation.

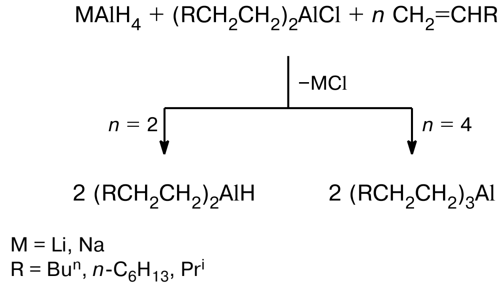
Hydroalumination of olefins discovered by K. Ziegler and co-authors in 1954 is one of the most important reactions in the synthesis of organoaluminum compounds (OAC). The industrial production of OAC is based on the direct synthesis of alkylaluminum derivatives from Al, H_2, and α-olefins.[1,2] We have previously[3,4] shown that the reaction of non-solvated aluminum hydride with α-olefins affords pure R_3Al in the individual state. Taking into account that AlH_3 is insufficiently accessible, we continued to synthesize R_3Al from more available reagents, *viz.*, $MAlH_4$ (M = Li, Na), α-olefins, and R_2AlX (X = Cl, Br). The most of them are commercial reagents or can easily be prepared in ~100% yield by the classical reactions[1] and used without additional purification. We showed that all the reactants do not react upon mixing and heating for 8 h at 60—100 °C. However, the reaction occurred readily under mechanochemical activation (high-speed stirrer or ball mill) both without solvent and in aliphatic or aromatic hydrocarbons to produce OAC within 1—2 h in ~100% yield (monitored by the absence of halide in solution after HNO_3 hydrolysis). This reaction seems to be general and occurs with all the α-olefins studied (3-methylbut-1-ene, hex-1-ene, oct-1-ene, dec-1-ene) by Scheme 1. Monoalkyl dichlorides $RAlCl_2$ also react readily with $MAlH_4$ (2 mol) and olefins to form the same products.

This reaction can be attributed to general methods for the synthesis of the R_2AlH and R_3Al OACs.

When R_2AlCl and α-olefin contain different R radicals, mixed OACs like $RR'AlH$ and $R_2R'Al$ form.

The reaction with $Bu^i{}_2AlCl$ at first affords R_2Bu^iAl, which is transformed (in an α-olefin excess) into R_3Al with the displacement of isobutylene. In an $MAlH_4$ excess, admixtures of complexes of the $MAlR_4 \cdot AlH_3$ type and others can be found in the reaction mixture along with R_3Al and R_2AlH. These admixtures can easily be removed by treatment of the solution with $AlCl_3$ in amounts equivalent to the metal content.

Scheme 1



The further study of the reaction showed that it can occur without mechanical activation. With this purpose, $MAlH_4$ should be treated (before the reaction) with a minor amount of the preliminarily prepared R_3Al, the mixture should be heated to 100 °C, and only then R_2AlCl and olefin should be added. In this case, R_2AlCl reacts with the $MAlH_4 \cdot R_3Al$ complex formed at the first step and soluble in hydrocarbons, *i.e.*, the process occurs under homogeneous conditions. As the binuclear complex is consumed, the aluminum hydride is gradually dissolved to react with R_3Al, and to drive the reaction to completion. Such a procedure is 1.5—2 times longer than that using mechanochemical activation but gives the same results.

Thus, we developed the new preparative method for the synthesis of non-solvated OAC, *viz.*, R_3Al, R_2AlH,

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$R_2R'Al$, and $RR'AlH$, based on alkaline metal aluminum hydrides, α-olefins, and alkylaluminum chlorides. The method provides new challenges of using OAC in synthesis and catalysis.

Experimental

Purity of lithium and sodium aluminum hydrides after recrystallization from ether—toluene and THF—toluene mixtures was 98.5 and 99.5%, respectively. Commercial α-olefins were additionally dried over $MgSO_4$ and distilled in the presence of $NaAlEt_4$ (chromatographic purity was 95—98%, endo-olefins were admixtures). GLC analyses were performed on an LKhM-8MD instrument (column 2 m × 0.4 mm, 5% SE-30 on Chromaton N-AW washed with acid, particle size 0.2 mm). Alkylaluminum chlorides R_2AlCl and $RAlCl_2$ were prepared from pure R_3Al and freshly sublimed $AlCl_3$.[1] All reagents were stored under argon. The content of aluminum in samples was determined by trilonometry.[5] The content of hydride hydrogen in R_2AlH was determined using gas-volumetry by the decomposition of a weighted sample of the substance in Et_2NH [1,2] followed by freezing out gaseous products in a trap with liquid nitrogen.

Synthesis of R_3Al or R_2AlH from $MAlH_4$, α-olefins, and R_2AlCl (general procedure). The specified amount of $MAlH_4$ was loaded in a vertical-type[6] ball mill with a 100-mL glass (steel balls 2—4 mm in diameter) under argon or nitrogen, a solvent (heptane or toluene) was added, and the mixture was agitated for 15 min at 70—90 °C. A mixture of α-olefin with R_2AlCl (4 : 1 or 2 : 1) was gradually introduced into the reactor from a dropping funnel. The reaction is accompanied by heat release. The flow rate was controlled in such a way that the temperature would not exceed 90—100 °C. The reaction completed for 1—2 h. The reaction mixture was cooled and filtered, and the solvent was removed *in vacuo*. The residue was analyzed for Cl.

Trihexylaluminum was prepared using the general procedure. The reactor was loaded with $LiAlH_4$ (2.09 g) in heptane (40 mL), the mixture was agitated for 15 min at 70 °C, and a mixture of $(C_6H_{13})_2AlCl$ (11.6 g) with hex-1-ene (18.5 g) (molar ratio $LiAlH_4 : (C_6H_{13})_2AlCl$: hex-1-ene = 1.1 : 1.0 : 4.5) was gradually added from a dropping funnel. The resulting mixture was agitated for 1.5 h at 90 °C. The product was cooled down and filtered through a glass filter No. 4 under argon. The solvent and olefin excess were removed *in vacuo* (10 Torr) at 60—70 °C to a constant weight of the residue. The yield was 26.8 g (95%) based on $(C_6H_{13})_2AlCl$. Found (%): Al, 9.15. $C_{18}H_{39}Al$. Calculated (%): Al, 9.55.

Dihexylaluminum hydride was synthesized similarly from $LiAlH_4$ (2.1 g) in heptane (30 mL) and a mixture of $(C_6H_{13})_2AlCl$ (11.6 g) and hex-1-ene (8.2 g) (molar ratio $LiAlH_4 : (C_6H_{13})_2AlCl$: hex-1-ene = 1.1 : 1.0 : 1.95). The reaction proceeded to completion for 2.5 h at 70—100 °C. The transparent product (18.8 g) was obtained. Found (%): Al, 13.04; H^-, 0.486. $C_{12}H_{27}Al$. Calculated (%): Al, 13.60; H^-, 0.501.

Diisoamylethylaluminum. According to the general procedure, $NaAlH_4$ (2.8 g) and toluene (30 mL) were loaded in a ball mill equipped with a reflux condenser. The mixture was heated to 70 °C and agitated for 10 min, and a mixture of Et_2AlCl (6.0 g) and 3-methylbut-1-ene (15.9 g) (molar ratio $NaAlH_4 : Et_2AlCl : Me{-}CH(Me){-}CH{=}CH_2$ = 1.04 : 1.0 : 4.5) was added from a dropping funnel. The reaction was performed for 1.5 h and ceased at 100 °C. The suspension was filtered off, and toluene was distilled off *in vacuo*. The product was obtained in 93% yield (18.4 g). Found (%): Al, 13.04. $C_{12}H_{27}Al$. Calculated (%): Al, 13.60.

Isoamylethylaluminum hydride was prepared similarly to the previous synthesis from $NaAlH_4$ (2.8 g), Et_2AlCl (6.0 g), and 3-methylbut-1-ene (7.0 g) (reactant ratio 1.04 : 1.00 : 1.98). The product was obtained in 92.2% yield (13.7 g). Found (%): Al, 22.41; H^-, 0.82. $C_7H_{17}Al$. Calculated (%): Al, 22.63; H^-, 0.846.

Trioctylaluminum. A ball mill was loaded with $LiAlH_4$ (1.95 g) and oct-1-ene (24 g), and the mixture was heated to 75 °C with agitation for 20 min. Then $(C_8H_{17})_2AlCl$ (14.4 g) was added from a dropping funnel for 0.5 h, and the mixture was agitated for 1 h at 95—100 °C (reactant ratio 1 : 4.28 : 1, respectively). The precipitate was filtered off, and an octene excess was distilled off *in vacuo* (1 Torr) at 80—90 °C. The product was obtained in 98% yield (35.8 g) as a transparent viscous liquid. Found (%): Al, 7.07. $C_{24}H_{51}Al$. Calculated (%): Al, 7.36.

Dioctylaluminum hydride was prepared similarly to the previous synthesis from $LiAlH_4$ (1.95 g), oct-1-ene (11.0 g), and $(C_8H_{17})_2AlCl$ (14.4 g) (molar ratio 1.03 : 1.96 : 1.00, respectively). The product $(C_8H_{17})_2AlH$ was obtained in 94% yield (28.0 g). Found (%): Al, 11.76; H^-, 0.41. $C_{16}H_{35}Al$. Calculated (%): Al, 11.95; H^-, 0.446.

Tridecylaluminum. Sodium aluminum hydride (3.0 g, 0.056 mol) and dec-1-ene (45 g, 0.32 mol) were agitated for 10 min at 70 °C, and $Bu^i{}_2AlCl$ (7.4 g, 0.042 mol) was added for 0.5 h to the reaction mixture. The mixture was stored for 1.5 h at 95—100 °C. Isobutylene (~4 mL) was collected in a trap cooled with liquid nitrogen. After the precipitate was separated, the filtrate was heated for 1 h at 80 °C (1 Torr). The product was obtained in 97% yield (43.2 g) as a transparent viscous liquid. Found (%): Al, 5.71. $C_{30}H_{63}Al$. Calculated (%): Al, 5.98. According to the GLC data, after hydrolysis the content of decane was 98%, that of decene was ~1%, and other admixtures amounted to ~1%.

References

1. H. Lehmkuhl and K. Ziegler, *Methoden zur Herstellung und Umwandlung von organischen Aluminium-Verbindungen*, in Houben-Weyl, *Methoden der organische Chemie. Band XIII/4. Metallorganische Verbindungen*, Georg Thieme Verlag, Stuttgart, 1970, 314.
2. *Justis Liebigs Ann. Chem.*, **B629**, 1960.
3. V. V. Gavrilenko, *Abstr. of XIIth Fechem Conf. of Organomet. Chem. (August 31—September 5, 1997)*, Prague, 1997, Pos. 97.
4. V. V. Gavrilenko, *Izv. Akad. Nauk*, *Ser. Khim.*, 1997, 1709 [*Russ. Chem. Bull.*, 1997, **46**, 1630 (Engl. Transl.)].
5. G. Schwarzenbach, *Die chemische Analyse, Bd. 45 (Die Komlexometrische Titration)*, Ferdinand Enke, Stuttgart, 1955, 73.
6. H. Clasen, *Angew. Chem.*, 1961, **73**, 322.

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