

Synthesis of trialkylaluminum derivatives by the reaction of non-solvated aluminum hydride with α -olefins

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Hydroalumination of α -olefins by non-solvated polymeric aluminum hydride $(\text{AlH}_3)_n$ occurs at 120–140 °C. Mechanochemical activation accelerates this reaction. The addition of catalytic amounts of the prepared R_3Al forms to the reaction system decreases the temperature of the process to 90–100 °C. The greatest initiation effect is observed when *ate*-complexes of the MAIR_4 type ($\text{M} = \text{Li}, \text{Na}$) are used: the reaction occurs with a higher rate already at 60–90 °C affording R_3Al free of admixtures of carbalumination products and dimers of α -olefins.

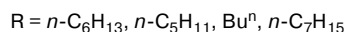
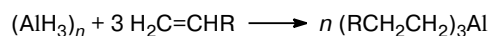
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Hydroalumination of α -olefins is one of the most important reactions in the synthesis of organoaluminum compounds. Lithium aluminum hydride and aluminum hydride (AH) in the form of the $(\text{AlH}_3)_3 \cdot \text{OEt}_2$ solvate have first been prepared by Schlesinger.¹ Later² the reaction of these hydrides with α -olefins at 100–110 °C was studied. This reaction affords organoaluminum compounds of the LiAlR_4 and LiR_3AlH type (for β -branched olefins). The use of the AH solvate gives a mixture of R_3Al and $\text{R}_3\text{Al} \cdot \text{OEt}_2$ (2 : 1). It is known that the elimination of Et_2O from the R_3Al etherate poses a certain problem, which impedes the synthesis of individual trialkylaluminum derivatives.

Non-solvated AH in the form of a solid polymeric substance was prepared³ in 1976 by crystallization from a mixed solvent (ether–benzene) in the presence of additives (LiAlH_4 and LiBH_4 , 5 mol.% each). Aluminum hydride is insoluble in many inorganic and most part of organic solvents and is inert toward α -olefins under standard conditions. In this work, we studied the reaction of α -olefins with AH to develop preparative methods for the synthesis of R_3Al .

We found that heating of AH to 150–200 °C in a sealed ampule resulted in its decomposition and formation of the aluminum mirror. The corresponding R_3Al were observed in the presence of olefins (Scheme 1). The noncatalytic addition of AH to olefins begins in any case at 120–140 °C simultaneously with the fast thermal decomposition of AH. This is confirmed by the kinetic studies of the thermal decomposition of AH⁴ and analysis of the mass spectra of its thermolysis products containing the Al^+ , AlH^+ , AlH_2^+ , AlH_3^+ , AlH_4^+ , and Al_2H_6^+ species.⁵

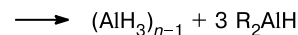
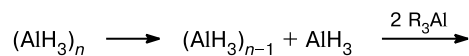
Scheme 1



Mechanical activation accelerates the process.

Further it turned out that the prepared R_3Al forms added to the reaction mixture (AH + olefin) decreased the temperature of the process to 100–110 °C and even to 80–90 °C under mechanochemical activation.^{6,7} The role of the R_3Al additives in this reaction is the destruction of the crystalline lattice of AH and alkyl-hydride exchange according to Scheme 2.

Scheme 2

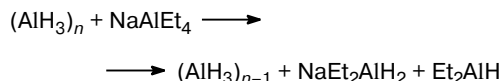


The R_2AlH formed in this reaction readily reacts with α -olefins already at 60–100 °C. Using the reactions of AH with isobutylene, hex-1-ene, and dec-1-ene^{6,7} as examples, the corresponding R_3Al were obtained from hept-1-ene, oct-1-ene, and non-1-ene. Side processes can occur at the reaction temperature >100 °C: elimination of α -olefins and their dimerization.

Another route of activation of the reaction of AH with olefins, which simultaneously decreases the temperature of the process, is associated with the use of catalytic addi-

tives of the MAIR₄-type complexes. They are easily synthesized by the reaction of alkaline metals with R₃Al. In fact, it turned out that in the presence of NaAlEt₄ (5 mol.%) AH readily reacts with hex-1-ene already at 60–70 °C. This can be explained by the fact that NaAlEt₄ reacts with AH to form Et₂AlH and NaEt₂AlH₂ (Scheme 3) likely through the intermediate complex NaAlEt₄·AlH₃.

Scheme 3



The products of this reaction (see Scheme 3) are further added to α -olefins to form NaAlR₄ and R₃Al. Then the cycle repeats but with a sharp increase in the reaction rate, because both catalysts, *viz.*, R₃Al and NaAlR₄, begin to work. This results in the evolution of a great amount of heat, which should be removed by cooling or controlling the rate of olefin addition to the reaction mixture in order to prevent the "thermal explosion." The MR₃AlH complexes easily obtained from the corresponding metal hydrides and R₃Al can be used instead of MAIR₄ for the initiation of olefin hydroalumination. In a separate experiment on the reaction of (AlH₃)_n with NaAlEt₄ at 100–125 °C, we detected 64% Et₃Al and 36% Et₂AlH in the liquid reaction products after they were distilled *in vacuo*. The extraction of the solid residue with toluene and THF produced NaEt₂AlH₂ and NaAlH₄ (60 : 40), which confirms the scheme proposed for the process.

It should be mentioned that the LiAlH₄ additives (5–10%) can be used instead of NaAlR₄ as the catalyst of the process. These additives react with α -olefins already at 100–120 °C² to form LiAlR₄, after which the reaction smoothly ceases at 60–100 °C. Mixtures of NaAlH₄ and R₃Al, which readily form a mixture of NaR₂AlH₂ and R₂AlH, are also efficient as the catalyst of this process.

Thus, the methods developed for the synthesis of R₃Al from non-solvated AH and α -olefins in the presence of MAIR₄, MR₃AlH, and R₃Al produce individual trialkylaluminum derivatives free of admixtures of R₂AlH, olefin dimers, and carbalumination products. The MAIR₄ catalyst, which remained in the reaction mixture, can easily be transformed into R₃Al by the addition of the calculated amount of aluminum halides.

Experimental

All experiments were carried out in an inert atmosphere (nitrogen or argon). Hydrocarbon solvents and ethers were dried over hydrides (NaH, LiAlH₄), distilled, and stored over Na or Ca. Commercially available olefins were stored over anhydrous Na₂SO₄ and distilled with the NaAlEt₄ additive (1–5%).

LiAlH₄ used for the synthesis of AlH₃ was recrystallized from an ether–toluene mixture. Technical AlCl₃ (purity 98–99%) was purified by heating to 180 °C with addition of 10–15% Al powder (trade mark A-1) and 1–8% Mg powder Mg (MPF-4) and sublimation *in vacuo*. Aluminum hydride was synthesized according to a known procedure³ (purity of the product was 95–98%); NaAlEt₄ was prepared by the reaction of Et₃Al with metallic Na⁸ and recrystallized from toluene. Aluminum was analyzed by complexometric titration (using eriochrome as an indicator⁹) and gravimetrically (precipitation with hydroxyquinoline). Hydride hydrogen was determined by the gas volumetric method. Purity of olefins and paraffins after R₃Al hydrolysis was monitored by GLC on an LKhM-8MD instrument (2 m × 4 mm, 5% SE-30 on Chromaton (acid washed) with a particle size of 0.2 mm).

The syntheses of Buⁱ₃Al, (C₆H₁₃)₃Al and (C₁₀H₂₁)₃Al from (AlH₃)_n and olefins have been described previously.⁷

Tri(*n*-octyl)aluminum. A (synthesis without promoters). A 100-mL three-necked flask equipped with a reflux condenser, a dropping funnel, and a thermometer was loaded with (AlH₃)_n (1.65 g, 0.055 mol, calculated for 100% purity) suspended in octane (30 mL), and the mixture was heated to 120 °C. At first, a portion of olefin (33%) was added from the dropping funnel containing oct-1-ene (19.3 g, 0.173 mol, ~10% excess). After 30 min, the temperature of the mixture raised to 125 °C (reflux). Then the temperature was decreased to 100–110 °C, and the remained olefin was added during 3–4 h. The mixture was kept for 1 h at 90–100 °C, cooled, and filtered through a glass filter no. 4. Octane and excess octene were distilled off *in vacuo* below 80 °C (7 Torr). A light liquid product was obtained (14.3 g, 91%). Found (%): Al, 7.08. C₂₄H₅₁Al. Calculated (%): Al, 7.36. The obtained product (13.1 g) was oxidized with dry air in heptane (50 mL), hydrolyzed, dried above Na₂SO₄, and distilled at 82–83 °C (7 Torr). *n*-Octyl alcohol (12.0 g) was isolated, *n*_D²⁰ 1.4292 (*cf.* Ref. 10: b.p. 196 °C, *n*_D²⁰ 1.4303).

B (synthesis with the activation of the process by adding R₃Al in a ball mill). A vertical ball mill¹¹ (capacity 150 mL, 70 g of balls 3–4 mm in diameter) was loaded with (AlH₃)_n (1.10 g, 0.036 mol), octane (30 mL), Buⁱ₃Al (1 g, 0.005 mol), and oct-1-ene (19.5 g, 0.174 mol). The reaction mixture was gradually heated to 100 °C with permanent stirring (temperature jump to 115 °C), cooled, and stored for 2 h at 90–100 °C. The balls and blend were separated, and the residue was washed with octane (2 × 20 mL). A light filtrate was evaporated at 80–90 °C (7 Torr) to a constant weight. The target product was obtained in 88.6% yield (16.9 g). Found (%): Al, 7.11. C₂₄H₅₁Al. Calculated (%): Al, 7.36.

C (synthesis with activation by NaBuⁱ₃AlH). A mixture of (AlH₃)_n (1.65 g, 0.055 mol), NaBuⁱ₃AlH (2.25 g, 0.013 mol), and octane (30 mL) were heated to 80 °C for 1 h, and oct-1-ene (9.7 g) was added. The temperature spontaneously raised to 100 °C for 20 min. The reaction mixture was cooled, and oct-1-ene (15 g) was additionally added (totally 24.7 g) from a dropping funnel at 90 °C for 0.5–1 h. A light product, *viz.*, (C₈H₁₇)₃Al + NaAl(C₈H₁₇)₄ mixture (27.1 g), was obtained after standard treatment. Found (%): Al, 7.02. C₂₄H₅₁Al. Calculated (%): Al, 7.36.

D (synthesis with activation by LiAlH₄). A known procedure³ was used to obtain γ -AlH₃ in a mixture with excess LiAlH₄ (without washing off LiAlH₄ with ether). This mixture (1.60 g, 1.2 g of AlH₃ + 0.4 g of LiAlH₄), octane (30 mL), and oct-1-ene

(8 g) were used for the reaction. The reaction mixture was heated to 100–110 °C for 1 h, and oct-1-ene (12 g) was added for 2 h at 90–100 °C. Then the mixture was filtered. Excess octene and octane were removed *in vacuo* at 60–70 °C (1 Torr), and AlCl_3 (0.45 g) was added to the residue. The mixture was heated at 80 °C, and LiCl was filtered off. Compound $(\text{C}_8\text{H}_{17})_3\text{Al}$ was obtained in 89% (14.3 g). Found (%): Al, 7.12. $\text{C}_{24}\text{H}_{51}\text{Al}$. Calculated (%): Al, 7.36.

Tri(*n*-heptyl)aluminum. A ball mill (150 mL, 70 g of balls 3–4 mm in diameter) was loaded with $(\text{AlH}_3)_n$ (1.65 g, 0.055 mol), heptane (25 mL), hept-1-ene (18.0 g, 0.183 mol), and Bu^i_3Al (1 g, 0.005 mol), and the mixture was stirred for 3 h at 90–100 °C. The reaction product was filtered off, and a precipitate was washed with heptane (10 mL). Heptane and excess heptene were removed *in vacuo*. A light liquid product (16.1 g, 91.0%) was obtained. Found (%): Al, 8.18. $\text{C}_{21}\text{H}_{45}\text{Al}$. Calculated (%): Al, 8.32. This product (14.0 g) in heptane (30 mL) was oxidized with dry air followed by hydrolysis to afford *n*-heptyl alcohol (14.3 g), b.p. 174–175 °C, n_D^{20} 1.4223 (*cf.* Ref. 10: b.p. 175 °C, n_D^{20} 1.4231).

Tri(*n*-hexyl)aluminum. A mixture of AlH_3 (1.65 g, 0.055 mol), toluene (10 mL), NaAlEt_4 (0.98 g), and hex-1-ene (16.8 g, 0.21 mol) was heated in a flask equipped with a reflux condenser and a thermometer at the reflux temperature of the mixture. After 20 min, the temperature raised from 80 to 100 °C and then gradually decreased to 70–80 °C. After 2 h, the reaction mixture was cooled and filtered off, and a precipitate was washed with hexane (10 mL). The solvents and excess hexene were removed *in vacuo* at 60–80 °C (7 Torr), and 15.1 g of the product were obtained. Found (%): Al, 9.41. $\text{C}_{18}\text{H}_{39}\text{Al}$. Calculated (%): Al, 9.55.

Tri(*n*-nonyl)aluminum. A mixture of $(\text{AlH}_3)_n$ (1.53 g, 0.051 mol), $\text{NaBu}^i_2\text{AlH}_2$ (1.7 g, 0.01 mol), and non-1-ene (32.0 g, 0.253 mol) was heated in a ball mill to 100 °C and then stored for 1.5 h at 90–100 °C. After separation of the balls and filtration, residues of nonene were removed *in vacuo*. A transparent product (18.5 g) was obtained. Powdered AlCl_3 (0.35 g, 0.026 mol) was added to the product, and the mixture was heated with stirring for 1.5 h at 80–90 °C. The formed NaCl was separated by filtration. The probe of the hydrolysis product for halogen (AgNO_3) was negative. Found (%): Al, 6.22. $\text{C}_{27}\text{H}_{57}\text{Al}$. Calculated (%): Al, 6.61.

Reaction of $(\text{AlH}_3)_n$ with NaAlEt_4 . A three-necked flask was loaded with $(\text{AlH}_3)_n$ (3.1 g) and NaAlEt_4 (9.8 g). The mixture was heated to 125 °C for 1 h (to the homogeneous state) and then stored for 2 h at 100 °C. Liquid products (5.8 g) were

distilled off *in vacuo* (1 Torr) at 70–80 °C. Their composition after hydrolysis and determination of the amounts of ethane and hydrogen (7.5 : 1.0) corresponded to the ratio $\text{Et}_3\text{Al} : \text{Et}_2\text{AlH} = 1.76 : 1.00$. The extraction of a solid residue with toluene gave $\text{NaEt}_2\text{AlH}_2$ (3.1 g), m.p. 83–85 °C (*cf.* Ref. 12: 84–88 °C) and then, after the treatment with THF, NaAlH_4 was extracted (2 g). Found (%): H, 7.25. NaAlH_4 . Calculated (%): H, 7.41.

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