

SYNTHESIS OF TRIMETHYLALUMINIUM

S. PASYNKIEWICZ AND M. BOLESŁAWSKI

Department of Organic Technology I, Institute of Technology (Politechnika), Warsaw (Poland)

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SUMMARY

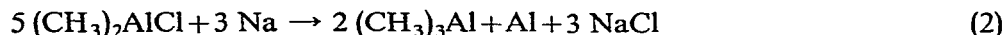
Trimethylaluminium has been synthesized from dimethylaluminium chloride and sodium/potassium melt in a solvent. The method gave trimethylaluminium in 70% yield.

The application of organoaluminium compounds as polymerization, copolymerization, and oligomerization catalysts and their commercial-scale production have given impetus to the rapidly expanding research programmes concerning the chemistry of these compounds.

The study of various reactions involving methylaluminium compounds (particularly trimethylaluminium) has been simplified because of their simple molecular structure, considerable stability, and easy interpretability of NMR and IR spectral data.

Several methods have been developed for preparing trimethylaluminium¹⁻⁴. The Grosse-Mavity method² has been most extensively used in both the industrial and laboratory scale preparation.

This method involves treating methylaluminium sesquichloride with sodium metal, *viz.*,



Trimethylaluminium can be isolated by vacuum distillation. Retreatment of the distillate with liquid sodium/potassium melt gives pure trimethylaluminium.

In an earlier work⁴ we studied the reaction of the sesqui compound with sodium in xylene at 90–100°. Trimethylaluminium was obtained in a low yield because of the deposition of a hard film of resulting sodium chloride and metallic aluminium on the surface of sodium metal. To prepare pure trimethylaluminium, it is necessary to carry out the reaction repeatedly or to use sodium in large excess.

There are numerous drawbacks to this route, which reduce the yield of the product. The sodium chloride and metallic aluminium by-products formed in considerable amounts impair the kinetic and diffusional conditions (mixing) and impede heat transfer. The less effective mixing in conjunction with the observed incomplete conversion^{3,4} of sodium on account of the products depositing on its

surface tends to decrease considerably the yield of trimethylaluminium and gives rise to contamination by chloro derivatives. The suggested⁴ repeated performance of the reaction or the use of sodium in considerable excess is not any better, either, because of the possible side reaction³:



This reaction reduces the concentration of trimethylaluminium and thus diminishes its final yield.

The reaction impediment due to product deposition on sodium is favourable to the building up of methylaluminium chloride compounds and thus leading to explosion hazards owing to the poor heat transfer in this highly exothermic reaction. This hazard increases as the scale of the reaction is raised.

In the present modification for the synthesis of trimethylaluminium, the above difficulties are overcome to a considerable degree by using a high-boiling solvent, carrying out the reaction at a high temperature, and employing a sodium/potassium melt.

The solvent used (n-decane, b.p. 173°) enables the alkali metals to become well dispersed and at the same time serves as a cooling medium. The high boiling point of n-decane also facilitates the distillation of pure trimethylaluminium.

Owing to the high temperature (150–170°) of reaction, the dimethylaluminium chloride added enters immediately into the reaction without any induction period. It avoids building up of the reactants in the system and thereby the vigorous course of the reaction, whereby the safety of the process is much enhanced.

The sodium/potassium (2/1) melt is much more reactive than pure sodium. Furthermore, it is fluid at room temperature and readily disperses in the solvent. Therefore, the resulting alkali metal chloride and metallic aluminium fail to deposit on the metal and thus permit its full conversion.

The present method allows to obtain pure trimethylaluminium, free of the chloro impurities, by using the alkali metals melt in a slight excess of 0.05–0.1 mole per mole Me_2AlCl .

The intensity of mixing has a great effect on the yield of the reaction. It affects the surface area of the reacting alkali metals (dispersion) and allows the surface to be renewed during the reaction.

The reaction between dimethylaluminium chloride and the potassium/sodium melt is highly exothermic; therefore, despite the presence of the solvent, the first portion of dimethylaluminium chloride should be added very slowly. Only after 50% of dimethylaluminium chloride has been added dropwise, the remaining portion can be introduced safely and rapidly.

EXPERIMENTAL

1. Materials

Dimethylaluminium chloride was prepared via the conventional procedure. The compound was at least 99% pure. The alkali metals, sodium and potassium (FOCh, Gliwice, Poland) were carefully deoxidated before use. n-Decane or decalin (VEB Laborchemie Apolda) was redistilled over sodium in a nitrogen atmosphere.

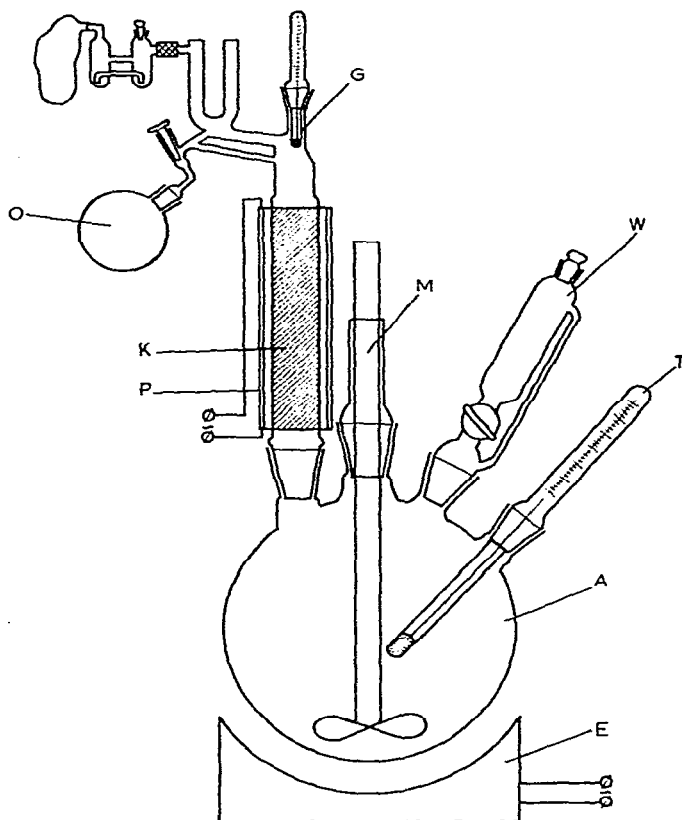


Fig. 1.

2. Apparatus

The reaction was carried out using the set-up presented in Fig. 1. It consisted of a four-necked 1-liter flask (A) equipped with a stirrer (M), thermometer (T), dropping funnel with a pressure equalizer (W), and a column (K) provided with a stillhead (G) and a receiver (O). The flask was heated on an electrical bath (E). The column used was 40 cm long and 3.5 cm across, packed with Fenske helices and was heated electrically using a heating mantle (P).

3. Synthesis

To the flask flushed out repeatedly with dry nitrogen were added n-decane (250 g), sodium (25 g, 1.087 mole), and potassium (20 g, 0.513 mole). The excess of the alkali metals over the amount demanded by the stoichiometry of the reaction was 0.141 mole. Dimethylaluminum chloride (135 g, 1.459 mole) was placed in the dropping funnel. The flask and its contents were heated to a temperature of 100–120°. The reactants were stirred vigorously (200–300 rpm) to disperse the sodium/potassium melt. The appropriate dispersion of the melt is recognizable by the contents turning deep-brown and no metal agglomerates visible any longer.

After the flask had been heated to a temperature of 150–155°, dimethylaluminum chloride was added dropwise. The first drops of dimethylaluminum chloride

added give rise to a rapid increase in the temperature of the reaction mixture to 173° (the b.p. of n-decane) and to deep darkening (black colour). The rate of addition of dimethylaluminium chloride was controlled so as to maintain the reaction mixture at moderately intense ebullition. In this first period of the reaction the heating rate of the flask should be reduced.

After about 50% of dimethylaluminium chloride had been added, the reaction mixture turned lighter owing to the formation of sodium chloride and potassium chloride and finally became pale-grey. In the course of addition of dimethylaluminium chloride the reaction becomes less and less exothermic and the heating rate of the flask must be increased. The boiling temperature of the mixture also diminishes from the original 173° for the pure solvent to 150–160° toward the end of the reaction. After all the dimethylaluminium chloride (about 1.5 h) had been added, stirring was continued together with heating for additional 5–6 h.

After the reaction had been completed, heating and stirring were discontinued to allow the solid products to settle. Then a sample of the supernatant liquid was withdrawn, hydrolyzed and analyzed for chlorine to check the extent of conversion of dimethylaluminium chloride.

If chlorine was present, the reaction mixture was stirred and heated at 155° for several hours again. When chlorine was absent, which is usually the case, pure trimethylaluminium was isolated from the reaction mixture. For this purpose the contents of the flask were heated. Cooled toluene or xylene was passed through the stillhead cooler. Distillation was continued to collect the fraction boiling at 124–126°.

Trimethylaluminium collected was analyzed. The fraction collected, 49 g, b.p. 124–126°, was 98.2% of trimethylaluminium and 1.8% of n-decane. No chlorine was detected. The yield was 68.4% of the theoretical.

4. Analysis

Chlorine, aluminium, and methyl groups were determined in the product. The analytical data were used for calculation of the content of trimethylaluminium in the distillate. After the sample had been decomposed, methyl groups and aluminium were determined by the procedure developed by Dahlig and Pasynkiewicz⁴.

Qualitative tests were made for chlorine during the course of the reaction. The reaction solution was sampled by means of a hypodermic syringe, about 2 ml, decomposed with distilled water and treated with 0.5 N silver nitrate to observe whether turbidity appeared.

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