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Application of Mechanochemistry in Hydrometallation Reactions

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Abstract

The mechanochemical method of active aluminium preparation was developed. Also technique of preparation of aluminiumorganic derivatives from unsaturated hydrocarbons is fulfielled. Possibility of realization of hydroalumination under the conditions of mechanochemical activation in drums of planetary mills was demonstrated for the first time. Butillithium *via* reaction of a butenes mixture with a lithium hydride in conditions of a mechanochemical activation was synthesized.

INTRODUCTION

Various metal alkyls are used as co-catalysts of polymerization and reactants for fine organic synthesis. The most attractive methods for obtaining these metal alkyls are reactions of a metal with unsaturated hydrocarbons in hydrogen atmosphere, or reaction of hydrides with the same hydrocarbons [1, 2]. Such reactions are heterophasic and are complicated by mass transfer processes, inhibition by an oxide film and low reactivity of metals [3]. All these complications are easily removed by application of mechanochemical activation (MCA) [4].

The aim of this work is using mechanochemistry in reactions of hydrometallation to obtain the metalloorganic compounds.

EXPERIMENTAL

MCA was carred out in centrifugal planetary mill of AGO-2 type with steel balls 5 mm in diameter at drum rotation frequency of 17 s^{-1}. The mass of balls in a drum was 200 g.

The solid products were analyzed using X-rays diffraction. Diffraction patterns obtained were recorded with a DRON type diffractometer with CuK_a radiation with graphite monochromator on reflected beam. The solutions were analyzed by ^{13}C NMR, with a Bruker CXP-300 spectrometer and by chromatomass-spectrometry with GC/MS instrument. The GLC-analysis was carried out with LXM-8MD chromatograph equipped with a detector of thermal conductivity in isothermal mode and in temperature programming mode with linear programming 12 °C per minute. A 1000 ´ 2 mm column with PEG20M phase (0.4 %) on GTS. Column temperature 35–110 °C, detector temperature 240 °C, of hydrogen flow rate 50 ml/min.

Stage 1. Activation of aluminium

$Al + M$ ® $(AlM_x)^*$, M = Ni, Ti

The mixture of aluminium with nickel or titanium (5–10 and 1 %, respectively) was loaded into a drum, with a mass of grinding balls 200 g. The activation, lasting for 10 to 60 min, was performed in a centrifugal planetary mill. After that, the product was unloaded.

The degree of extraction of activated aluminium from a drum via various methods of extraction is shown in Table 1.

TABLE 1

The degree of extraction of activated aluminium (mass of Al − 1 g)

Mass of NaCl, g	t_{act}, min	Method of extraction	Extracted mass, g	Yield, %
4	15	In mill, 0.5 min in EtOH after activation	0.380	7.6
9	10	In mill, 18 min with NaCl after activation	3.920	39.2
14	10	Activation with NaCl	14.730	98.2

Note. t_{act} is time of acivation.

Stage 2. Alkene hydroalumination

$$3RCH = CH_2 + (AlM_x)^* + 3/2H_2 \xrightarrow{(iBu)_3Al} (RCH_2{-}CH_2)_3Al$$

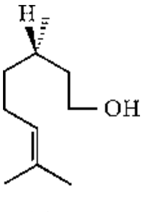
Version 1. Reaction in autoclave. Hydroalumination of alkenes in the reactor was performed under 40 atm pressure at 100−110 °C with pressure monitoring during reaction.

As a result of hydroalumination of heptene-1, styrene and dihydromyrcene, after oxidation and subsequent hydrolysis of aluminiumorganic derivatives, heptanol-1 with a yield of 30 %, 2-cyclohexylethanol with a yield of 21 % and citronellol (Scheme 1) with a yield of 65 % were obtained, respectively.

Version 2. Reaction under the conditions of mechanochemical activation. With the purpose of heating reactants, the mill AGO-2 was modified by replacing the water cooling system with a silicon oil heating system and thermostat. The modified planetary mill (Fig. 1) containing activated aluminium, prepared by a technique described above, was loaded with alkenes in a solvent. The process was carried out with monitoring of pressure after realization of activation.

Initial hydrogen pressure was 100 atm. Mechanochemical reaction was performed at 80−94 °C within 3 h. After this time, the pressure had fallen to 53 atm.

Yield of citronellol and heptanol-1 after oxidation and subsequent hydrolisis of aluminiumorganic derivatives, was 65 and 60 %, respectively. It is necessary to note, that mechanochemical reactions under similar conditions, apparently, are carried out for the first time.



Scheme 1

Stage 3. Oxidation and hydrolysis

$$(RCH_2{-}CH_2)_3Al \xrightarrow[2)\ HCl+H_2O]{1)\ O_2} RCH_2{-}CH_2{-}OH$$

For ascertainment the structure of metal alkyls thus obtained, they were oxidized and hydrolyzed. Oxidation by air was carried out in vessel with thermometer and reflux condenser with calcium chloride tube. Air passed with such a velocity that temperature did not exceed 60 °C. Hydrolysis was proceeded by dilute hydrochloric acid.

RESULTS AND DISCUSSION

Mechanochemical method of active aluminium preparation through mechanical alloying

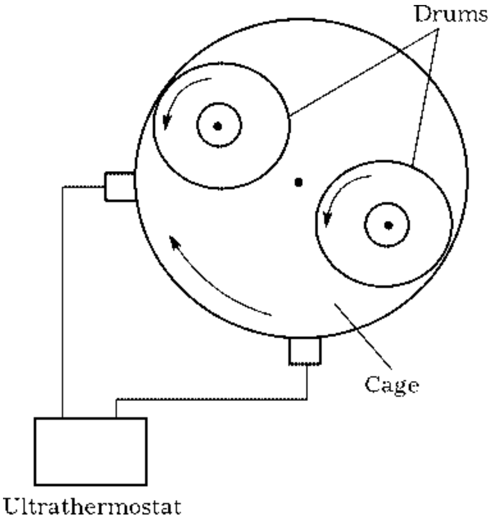


Fig 1. Scheme of device for hydroalumination on the basis of a planetary mill AGO-2.

of aluminium with other metals was developed in the present work. This method is alternative to existing methods giving pyrophoric materials.

To extract a product, the inert substances such as ethyl alcohol and sodium chloride were added to the activated powder. The proposed method of extraction by repeated processing of a sample in a mill in the presence of alcohol, as appeared, is ineffective in view of the extremely small amount of product separated using such a procedure. Slightly better results were obtained using sodium chloride as the separating agent, which was selected because of its chemical inertness.

In the third version, sodium chloride was added to a mixture of metals before MCA. Subsequent X-ray analysis has shown that it has not affected formation of solid solutions of aluminium with other metals. After MCA realized in such a way, it was possible to extract practically the whole product, as follows from the Table 1. Therefore, hereinafter, only this method was applied to obtain activated aluminium.

A technique of obtaining aluminiumorganic derivatives from heptene-1 and dihydromercene is mastered. The possibility of effective application of mechanical alloys of aluminium in this reaction was shown.

During the aluminium activation, doping by nickel and titanium was used to increase reactivity. These metals catalyze the reaction of aluminium with hydrogen. It is possible to assume that in atmosphere of hydrogen, the formation of aluminium hydride phase on metal surface, with the participation of nickel or titanium, takes place. These metals are capable of adsorbing and dissociating atomic hydrogen; this results in lowering of the activation energy of Al–H bond formation, which is necessary for hydroalumination.

The possibility of hydroalumination under the conditions of mechanochemical activation in drums of planetary mills was demonstrated for the first time.

The technique of oxidation and consequent hydrolysis of aluminiumorganic derivative of dihydromyrcene into citronellol and aluminiumorganic derivative of heptene-1 into heptanol-1 is mastered.

TABLE 2

Structure of initial and final mixtures of butenes with lithium hydride

Time of MCA, min	C_4H_{10}, %	C_4H_8-1, %	*cis-* and *trans-* C_4H_8-2, %
0	11.7	19.6	68.7
15	47.0	32.0	20.9
30	52.6	29.1	18.3

The results of this work can be used as a basis of industrial technology of deriving citronellol from components of turpentines.

Butyllithium was synthesized under reaction of butenes with lithium hydride during MCA. Structure of initial and final mixtures is shown in Table 2.

The obtained data show that under the conditions of MCA, hydrolithiation has passed, but the butyllithium derivative was hydrolyzed by water impurities in reactants, because no special attempts to remove water were made. At present, we investigate this reaction to obtain more strict proofs of Butyllithium formation and to check the possibility of using lithium hydride to obtain lithiumorganic compounds using MCA.

These methods can be used as common ones to obtain organometallic compounds, and can find industrial application.

Acknowledgement

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