

ALUMINIUM-CARBON BOND REACTIVITY IN GEMINAL ORGANODIALUMINIUM COMPOUNDS

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(Received September 30th, 1986)

Summary

The reactions of 1,1-bis(diisobutylaluminium)hexane (1) with diethylamine, *N*-methylaniline, methanol and *m*-cresol have been studied. During partial protolysis both the aluminium-*i*-butyl bond and the aluminium-carbon bond in the aluminium-carbon-aluminium bridge undergo cleavage. The route of protolysis mainly depends on the protolytic agent used. The reaction of (1) with acetone has also been studied. Acetone was reduced to *i*-butanol with a 95% yield. The ratio of the *i*-butyl to hexylidene groups from β -hydride elimination is 2 : 1.

Introduction

In a geminal organoaluminium compound each aluminium atom is attached to two alkyl groups and to the bridging alkylidene group. Therefore two different pathways of the reaction, in which organic groups bonded to aluminium take part, are possible.

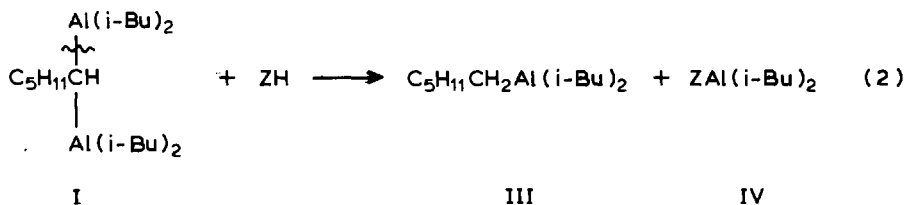
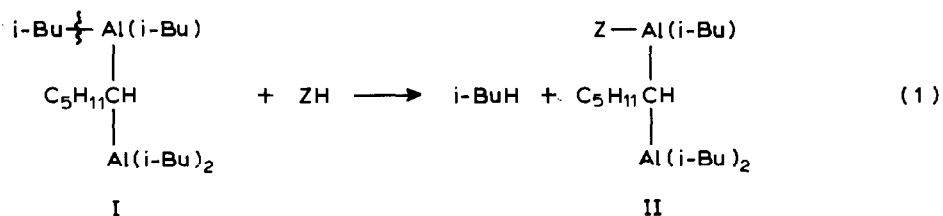
Two examples of such reactions have been studied - the partial protolysis of 1,1-bis(diisobutylaluminium)hexane, and its reaction with acetone.

Results and discussion

Partial protolysis

Organoaluminium compounds readily react with substances containing an acidic hydrogen [1-5]. Partial hydrolysis, alcoholysis and generally protolysis of aluminium alkyls give the possibility of substituting various groups for aluminium attached alkyls, thus leading to other organoaluminium compounds [6-10].

The course of reactions in the partial protolysis of organoaluminium compounds with all-identical Al-C bonds is well known [5,8-10]. In this work the splitting of the aluminium-carbon bond (eq. 1) and the aluminium-carbon-aluminium bridge (eq. 2) in the protolysis of geminal organoaluminium compounds have been investigated:



Reactions 1 and 2 can be distinguished from one another because of the evolution of isobutane (in eq. 1) and the different deuterolysis products of the post-reaction mixtures. Complete deuterolysis of I and II leads to hexane- d_2 , whereas in the deuterolysis of III, hexane- d_1 is formed:



The relative reactivity of the two unequivalent aluminium-carbon bonds during protolysis have been investigated for reagents of differing acidity. Diethylamine, *N*-methylamine, methanol and *m*-cresol have been chosen as model compounds. It has been found that depending on the protolytic agent used both aluminium-carbon bonds can undergo splitting during protolysis at a 1:1 molar ratio of reactants.

The progress of the protolysis reactions with the various acidic reactants was monitored by IR spectroscopy. The reaction mixtures were heated until the bonds corresponding to the N-H or O-H stretching vibrations of the protolytic agent disappeared. The reaction mixtures were then deuterolyzed and analyzed by means of GLC/MS and the degree of bridge-splitting calculated (Table 1).

The proportion of aluminium-carbon-aluminium bridges cleaved (eq. 2) as a result of protolysis increases in the order $m\text{-CH}_3\text{C}_6\text{H}_4\text{OH} < \text{CH}_3\text{OH} < \text{MePhNH} < \text{Et}_2\text{NH}$.

This is confirmed by a decrease in the volume of isobutane evolved, and corresponds well with the decreasing acidity of the protolytic agents.

Diethylamine - a reagent of the lowest acidity - reacts with I only at elevated temperatures. The IR and ^1H NMR spectra change characteristically when an

TABLE 1
PARTIAL PROTOLYSIS OF 1,1-BIS(DIISOBUTYLALUMINIUM)HEXANE

Protolytic agent ^a	Solvent	Temperature (°C)	Amt. of isobutene evolved mole/mole ^b	Degree of bridge-splitting %
diethylamine	xylene	130	0	84
<i>N</i> -methylaniline	toluene	45	0.03	62
methanol	toluene	room	0.3	15
<i>m</i> -cresol	toluene	room	0.4	8

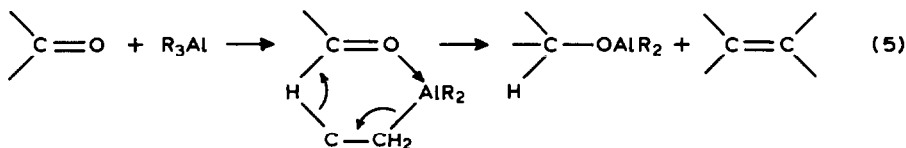
^a Molar ratio of the reagents 1 : 1. ^b Moles of isobutene per 1 mole of 1,1-bis(diisobutylaluminium)hexane.

equimolar mixture of I and diethylamine is heated at 130°C. Both the N–H stretching band (3270 cm⁻¹) and the doublet assigned to the methylene protons of the isobutyl group of the complex (i-Bu₂Al)₂CHC₅H₁₁ · HNet₂ (δ -0.15 ppm) disappear.

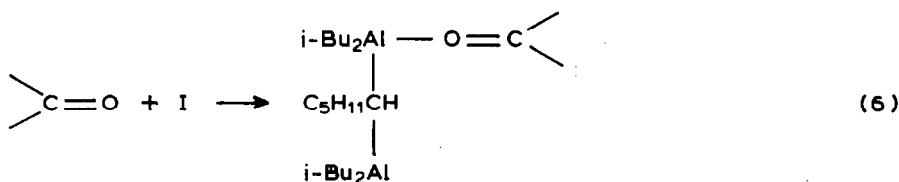
It is worth noting that *m*-cresol (a relatively strong acid) does not cause significant splitting of the aluminium–carbon bonds but mainly splits the Al–i-Bu bond and the aluminium–carbon-bridge only slightly. In contrast, a very weak acid – diethylamine – mainly splits the bridge. This cannot be satisfactorily explained as yet – further investigations on the mechanism of this process are required.

Reactions with acetone

Organoaluminium compounds react with ketones to give reduction, alkylation, and enolization products [11–15]. The reduction of ketones by an alkylaluminium compound consists of the transfer of a β-hydrogen from the aluminium-bonded alkyl group to the carbonyl carbon. This transfer takes place via a six-membered transition-state in a donor-acceptor complex [12,14] (eq. 5).

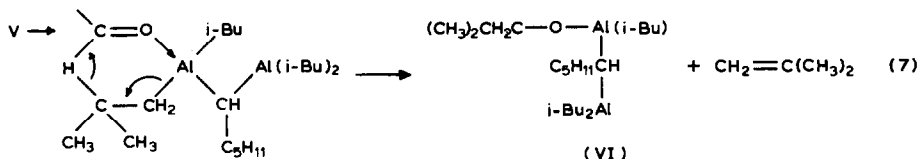


1,1-Bis(diisobutylaluminium)hexane reacts with acetone yielding only the ketonic reduction product. Isopropanol was found to be present after hydrolysis of the post-reaction mixture, whereas neither alkylation nor enolization products were present. The formation of the complex between I and acetone is undoubtedly the initial step of the process (eq. 6).

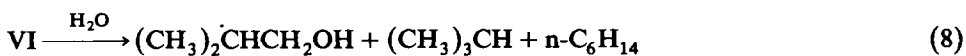


Both hexylidene and isobutyl groups may be involved in the reaction with the carbon atom of the carbonyl group. The transfer of β-hydrogen from the isobutyl

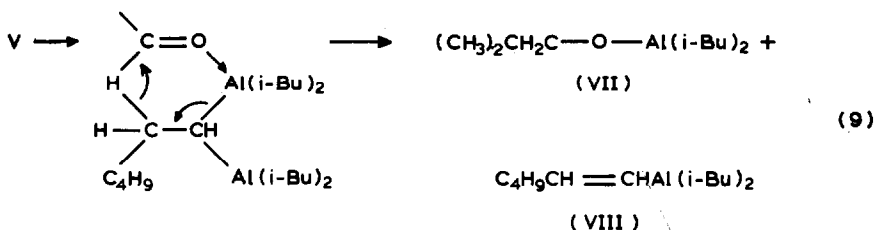
group causes the formation of isobutene and the product (VI) (eq. 7).



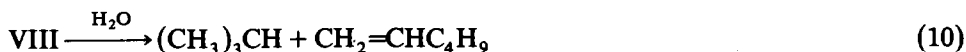
The hydrolysis of VI yields i-butanol, i-butane, and n-hexane eq. 8.



If the β -hydrogen transfer from the hexylidene group to the carbon atom of the carbonyl group takes place, then di(i-butyl)aluminium-i-propoxide (VII) and di(i-butyl)1-hexenylaluminium (VIII) [9] are formed.



The hydrolysis of (VII) gives i-butanol and i-butane and that of (VIII) gives i-butane and 1-hexane eq. 10.



From the results obtained after hydrolysis of the products of reaction [6] it appears that from 1 mol of I 0.65 mol of hexane and 0.35 mol of 1-hexene are formed.

A comparison of the amount of n-hexene evolved in reaction 8 and 1-hexene in reaction [10] indicates that the i-butyl and hexylidene groups take part in the β -hydrogen elimination. The mutual reactivity ratio of both groups is almost exactly 2 : 1. The yield of i-propanol after hydrolysis of the products of reactions 7 and 9 is 95%.

Experimental

All operations were performed in a purified dry nitrogen atmosphere. All the reagents purchased were dried and distilled before use.

1,1-Bis(diisobutylaluminium)hexane [1] was synthesized according to a published method [5].

Partial protolysis

A solution of 1,1-bis(diisobutylaluminium)hexane (1.83 g, 5 mmol) in 5 cm³ of solvent was cooled to -70°C and 5 mmol of the protolytic agent was added as

slowly as possible. The mixture was then allowed to warm up slowly to room temperature. The mixture was heated when necessary until the $\nu(\text{NH})$ or $\nu(\text{OH})$ stretching band in the IR spectrum of a sample of the reaction mixture disappeared (Table 1). The volume of gas evolved was measured in a gas burette, then analyzed by means of GLC.

A 0.5 cm³ sample of the post-reaction mixture was diluted with 0.5 cm³ of toluene and deuterolyzed using D₂O followed by 10% DCl in D₂O. The organic layer was collected and analyzed by means of GLC/MS. The degree to which bridges had been split was calculated by a comparison with the contents of hexane-*d*₂ (in total hexane) obtained under the same deuterolysis conditions from the parent substance I and from the post-reaction mixture. The results are shown in Table 1.

Reaction with acetone

To a solution of I (3.46 g, 9.44 mmol) in 15 cm³ of pentane, dropwise was added 0.549 g (9.45 mmol) of acetone at -75°C. The reaction mixture was then allowed to warm up to room temperature and refluxed for 30 min. The gas evolved was collected in a gas burette (GLC analysis: isobutene). The solvent was distilled off and the residue hydrolyzed. The products of hydrolysis were extracted four times from the water layer with small amounts of ether. GLC analysis: i-propanol, 0.539 g (8.97 mmol, 95%); hexane, 0.485 g; 1-hexene, 0.255 g; molar ratio of hexane:1-hexene = 0.65:0.35.

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