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REACTION OF ALUMINIUM DIMETHYLACETYLACETONATE WITH METHYLALUMINIUM COMPOUNDS

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Summary

The C-methylation reaction of aluminium dimethylacetylacetonate under the influence of trimethylaluminium and dimethylaluminium chloride has been ascertained. Methylalumium dichloride does not methylate aluminium dimethylacetylacetonate. Aluminium methylchloroacetylacetonate and aluminium dichloroacetylacetonate do not undergo a C-methylation reaction under the influence of the studied methylaluminium compounds.

Introduction

Kroll and Naegele [1] ascertained the course of C-methylation reaction of aluminium dimethylacetylacetonate by trimethylaluminium. On the basis of the hydrolysis products the authors proposed a structure of the non-isolated reaction product. Studies on the isolated product in the reaction of equimolar quantities of aluminium dimethylacetylacetonate and trimethylaluminium that were carried out by us prove that opening of the chelate ring occurs.

Results and discussion

Reactions of aluminium dimethylacetylacetonate ($Me_2Alacac$) with methylaluminium compounds

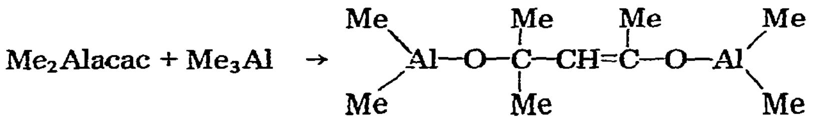
The reaction of aluminium dimethylacetylacetonate with an equimolar quantity of trimethylaluminium was carried out in toluene at room temperature. After refluxing the solution 24 h after the reaction was completed a product (b.p. 135°/5mm Hg) was obtained, which is a solid at room temperature. On the basis of results shown later in this paper, structure I is proposed.

TABLE

CHEMICAL SHIFTS IN THE PMR SPECTRA OF Me_3Al, $Me_2Alacac$ AND COMPOUND I

Compound	Chemical shifts (ppm)[a]		
	—CH—	CH_3—	CH_3—Al
Me_3Al			10.12
$Me_2Alacac$	4.75	8.18	10.31
Compound I	5.83	8.12, 8.48	10.16, 10.22

[a] Spectra were run in toluene, chemical shifts were measured from the signal of protons of the toluene methyl group (τ 7.66 ppm).



$$Me_2Alacac + Me_3Al \rightarrow Me_2Al{-}O{-}C(Me)_2{-}CH{=}C(Me){-}O{-}AlMe_2 \quad (1)$$

(I)

Chemical shifts of signals occurring in PMR spectra of substrates and products of reaction 1 are shown in Table 1. The signals of protons of methyl groups bonded with aluminium in compound I have an equal intensity. The signal with the chemical shift τ 8.48 ppm has an intensity twice as high as the signal τ 8.12 ppm. The intensity ratio of the individual signals are consistent with the proposed structure (Fig. 1). From literature data it results [2] that the signal at τ 8.48 ppm is the signal of protons of a methyl group bonded with carbon of sp^3 hybridization, however, in the chelate ring of acetylacetonates carbon is sp^2 hybridized. The transition to sp^3 hybridization is possible after the addition of an acetylacetonate ligand to one of the carbon atoms.

The percentage of aluminium and hydrolyzable methyl groups in compound I is shown in Table 2. The molecular weight determined in benzene by cryoscopic method is 386, the calculated value is 288. This indicates that the degree of association in compound I is 1.7.

As a result of hydrolysis of compound I methane, an inorganic precipitate and diacetone alcohol (identified by IR spectrum) were obtained. The presence of 4-hydroxy-4-methyl-2-pentone as a hydrolysis product confirms the course of the C-methylation reaction.

The reactions of aluminium dimethylacetylacetonate with trimethylaluminium, like most reactions of organoaluminium compounds, probably proceeds via a donor—acceptor complex formation stage. In the enol form ring of acetyl-

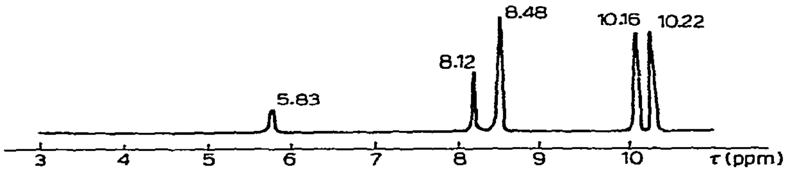
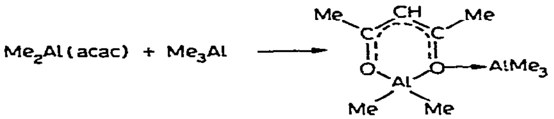


Fig. 1. The NMR spectrum of compound I in toluene solution.

TABLE 2

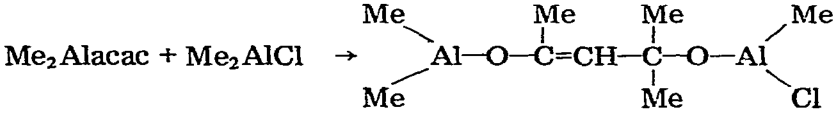
PERCENTAGE OF ALUMINIUM AND HYDROLYZABLE METHYL GROUPS IN COMPOUND I

Compound	Analysis found (calcd.) (%)	
	Al	CH_3—Al
I	23.4 (23.6)	24.6 (26.3)



acetone the carbon substituted by a methyl group has a partial positive charge and the methine carbon a partial negative charge. The formation of a complex causes a change of the chelate ring charge configuration. The partial positive charge of the carbon atom substituted by a methyl group and bonded with oxygen (electron donor) increases. As a result of increasing electron density on the aluminium atom a complexed trimethylaluminium molecule becomes a stronger alkylation agent. Stabilization of the complex is possible by methyl group transfer from the aluminium atom to the carbon atom and formation of a new aluminium—oxygen bond. This leads to formation of the proposed linear structure of compound I.

On the basis of PMR spectra a C-methylation reaction of aluminium dimethylacetylacetonate under the influence of dimethylaluminium chloride has been ascertained (eqn. 2). The presence of a signal with the chemical shift τ 8.5 ppm in the PMR spectrum (Table 3) confirms the course of the methyl group addition reaction. The intensity ratios of signals in the PMR spectrum of a solution containing equimolar quantities of Me_2Alacac and Me_2AlCl are in accordance with the proposed structure of compound II (Fig. 2).



$$Me_2\text{Alacac} + Me_2AlCl \rightarrow (Me)_2Al\text{—}O\text{—}\overset{Me}{C}\text{=}CH\text{—}\underset{Me}{\overset{Me}{C}}\text{—}O\text{—}Al(Me)(Cl) \qquad (2)$$

(II)

TABLE 3

CHEMICAL SHIFTS OF SIGNALS IN PMR SPECTRA OF: Me_2AlCl, $MeAlCl_2$, COMPOUND II AND Me_2Alacac + $MeAlCl_2$ SOLUTIONS

	Chemical shifts (ppm)		
	CH_3—	—CH—	CH_3—Al
Me_2AlCl			10.18
$MeAlCl_2$			10.11
Me_2Alacac	4.75	8.18	10.31
Compound II	5.85	8.2, 8.5	10.16, 10.27
Me_2Alacac + $MeAlCl_2$	4.77	8.22	10.07

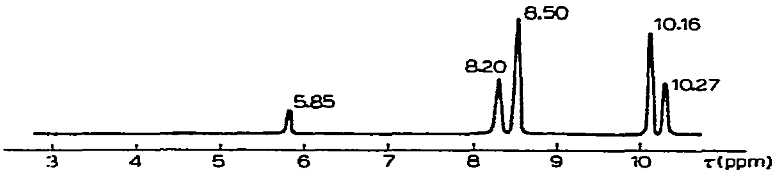


Fig. 2. The NMR spectrum of the mixture Me_2Alacac + Me_2AlCl in toluene solution.

The values of chemical shifts of signals that occur in the PMR spectrum of equimolar quantities of aluminium dimethylacetylacetonate and methylaluminium dichloride are shown in Table 3. The signals of protons of methyl groups (τ 8.22 ppm) and methine groups (τ 4.77 ppm) have chemical shifts almost unchanged when compared with those of aluminium dimethylacetylacetonate. This confirms that the chelate structure of aluminium dimethylacetylacetonate is retained. One signal for protons of the methyl groups bonded with aluminium (τ 10.07 ppm) occurs in the spectrum. This confirms a quick exchange of methyl groups bonded with aluminium in aluminium dimethylacetylacetonate and methylaluminium dichloride. Probably due to considerably lower alkylation properties of $MeAlCl_2$ no C-methylation reaction is observed.

Reactions of aluminium methylchloroacetylacetonate and aluminium dichloroacetylacetonate with methylaluminium compounds

The PMR studies show that the C-methylation reaction of the acetylacetonate ligand does not occur when aluminium methylchloroacetylacetonate is heated with equimolar quantities of dimethylaluminium chloride and methylaluminium dichloride; or when aluminium dichloroacetylacetonate is treated with equimolar proportions of trimethylaluminium, dimethylaluminium chloride and methylaluminium dichloride. The signal of protons of methyl groups bonded with sp^3 hybridized carbon is not observed in the PMR spectrum of mixed products. The chlorine electron acceptor substituents bonded with aluminium causes a change of charge value in the chelate ring. Consequently, the partial negative charge of the oxygen atom and also its donor properties decrease. Due to this the formation of sufficiently strong donor—acceptor complexes with methylaluminium compounds is impossible. The formation of a complex in which the partial positive charge on the carbon atom bonded with the donor oxygen atom increases is probably decisive for the C-methylation reaction.

Experimental

Materials

Methylaluminium compounds were obtained by known methods. Trimethylaluminium and dimethylaluminium chloride were purified by distillation, and methylaluminium dichloride by crystallization from n-heptane. Aluminium acetylacetonates were obtained in the reaction of acetylacetone with corresponding methylaluminium compounds and purified by distillation. Toluene was dried over $CaCl_2$, distilled in a pure nitrogen atmosphere from sodium and then stored over molecular sieves 4A.

Method

The reactions of aluminium acetylacetonates with organoaluminium compounds were carried out at room temperature by adding to aluminium acetylacetonate in toluene a toluene solution of a methylaluminium compound and stirring the mixture for two to five hours depending on the quantity of the initial reactants.

Analysis

PMR spectra were recorded on a JEOL-C-60H (60 MHz) apparatus in toluene. Aluminium was determined by sodium versenate, and hydrolyzable methyl groups by volumetric gas analysis of the evolved methane.

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