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REACTIONS OF ACETYLACETONE AND ALUMINIUM TRIS(ACETYLACETONATE) WITH METHYLALUMINIUM COMPOUNDS

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SUMMARY

The reactions of acetylacetone with trimethylaluminium and methylaluminium chloride compounds have been investigated. At 1/1 molar ratios of reagents, dimethylaluminium acetylacetonate, methylaluminium chloride acetylacetonate and aluminium dichloride acetylacetonate were obtained at −70°. At a ratio of 1/3 (acetylacetone in excess) aluminium tris(acetylacetonate) was the only product formed in the reactions. The reaction mechanisms are discussed in terms of the data obtained.

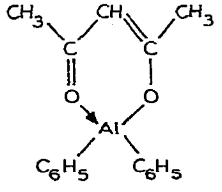
INTRODUCTION

Transition metal acetylacetonates have often been used for preparing active catalytic systems. Treatment of suitable acetylacetonates with organoaluminium compounds can afford compounds which are catalytically active in the oligomerization or cyclo-oligomerization of olefins and dienes.

The mechanisms of the reactions of organoaluminium compounds with transition metal acetylacetonates have not yet been elucidated. Since these reactions follow complex courses, it was deemed advisable to begin the study by exploring simple systems, *i.e.*, to examine initially the course of the reactions of organoaluminium compounds with acetylacetone.

In this work, reactions of acetylacetone with trimethylaluminium and methylaluminium chloride compounds have been studied in an attempt to identify the products forming at various reagent mole ratios and to consider the mechanisms of the reactions.

Costa and Calcinari[1] investigated the reaction of acetylacetone with triphenylaluminium and postulated, on the grounds of pertinent IR spectral evidence, the existence of an unisolated diphenylaluminium acetylacetonate (I). Bogdanović[2] has



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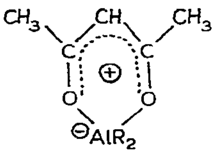


(II)

prepared diphenylaluminium acetylacetonate and diisobutylaluminium acetylacetonate ((II); R = Ph, i-Bu) by pyrolysis methods.

Kroll and Naegele[3] have described the preparation of dialkylaluminium acetylacetonates from acetylacetone and aluminium acetylacetonate.

RESULTS

Reactions of acetylacetone with methylaluminium compounds

In the present study, the reactions of trimethylaluminium and methylaluminium chloride compounds with acetylacetone (AcacH) have been investigated in relation to reagent mole ratio, the sequence of reagent addition and temperature.

At a ratio of Me_3Al/AcacH 1/1 (by moles), trimethylaluminium reacted with acetylacetone at − 70° to yield dimethylaluminium acetylacetonate ($Me_2AlAcac$) as the only major product together with methane (reaction 1). The yield of reaction (1) was found to be unaffected by the sequence in which the reagents were added.

$$Me_3Al + AcacH \rightarrow Me_2AlAcac + MeH \tag{1}$$

At a ratio of 1/2 (acetylacetone in excess), reaction (2) afforded, in addition to Me_2Al-Acac, aluminium tris(acetylacetonate), $AlAcac_3$:

$$2\,Me_3Al + 4\,AcacH \rightarrow Me_2AlAcac + AlAcac_3 + 4\,MeH \tag{2}$$

Reaction (2) gives two moles of methane; the first mole of methane is liberated at −70° and, in agreement with eqn. (1), dimethylaluminium acetylacetonate is then formed. The addition of a second mole of acetylacetone causes no further liberation of methane at −70°. At temperatures between −40 and 0°, methane is evolved at a slow rate. Liberation of the second mole of methane in quantitative yield occurs only at temperatures higher than 0°C as a result of the reaction of dimethylaluminium acetylacetonate with acetylacetone. This delay in the evolution of methane in reaction (2) suggests that dimethylaluminium acetylacetonate is less reactive toward acetylacetone than is trimethylaluminium.

TABLE 1

CHEMICAL SHIFTS OF PROTONS OF ALUMINIUM ACETYLACETONATES (ROOM TEMPERATURE)

Compound	*Chemical shift τ (ppm)*[a]		
	CH_3	*-CH-*	*CH_3-Al*
$AlAcac_3$	8.05	4.56	
$Me_2AlAcac$	8.18	4.75	10.31
MeClAlAcac	8.23	4.67	10.08
$Cl_2AlAcac$	8.13	4.41	
$Me_3Al + 2\,AcacH$[b]	8.075, 8.18	4.56, 4.75	10.31

[a] The shift was measured by taking τ 7.66 for the signal due to the toluene methyl-hydrogens. [b] Signals occurring in the spectrum of the products of reaction (2).

The composition of the reaction mixture resulting from reaction (2) was identified on the basis of the NMR spectrum of the solution after completion of the synthesis. In addition to signals due to $Me_2AlAcac$, signals were also present which were attributable to $AlAcac_3$ (Table 1).

At a ratio of 1/3 (*i.e.* excesss acetylacetone present), trimethylaluminium reacted to yield aluminium tris(acetylacetonate) exclusively [reaction (3)]. Quantitative evolution of methane following the addition of a second and a third mole of acetylacetone occurred at temperatures higher than 0°.

$$Me_3Al + 3\ AcacH \rightarrow AlAcac_3 + 3\ MeH \qquad (3)$$

In the reaction of dimethylaluminium chloride with acetylacetone, with the reagents present in a mole ratio of 1/1, methylaluminium chloride acetylacetonate was formed at −65° (reaction 4).

$$Me_2AlCl + AcacH \rightarrow MeClAlAcac + MeH \qquad (4)$$

In the reaction of dimethylaluminium chloride with acetylacetone at a mole ratio of 1/3 (acetylacetone in excess), the products shown in eqn. (5), were obtained.

$$Me_2AlCl + 3\ AcacH \rightarrow AlAcac_3 + 2\ MeH + HCl \qquad (5)$$

In this reaction the first mole of methane is evolved at −65°, whereas the second mole of methane and hydrogen chloride are evolved only at temperatures higher than 0°.

According to the reagent mole ratio employed, reactions of methylaluminium dichloride with acetylacetone afford the products shown in eqns. (6)–(8).

$$MeAlCl_2 + AcacH \rightarrow Cl_2AlAcac + MeH \qquad (6)$$

$$2\ MeAlCl_2 + 4\ AcacH \rightarrow AlAcac_3 + Cl_2AlAcac + 2\ MeH + 2\ HCl \qquad (7)$$

$$MeAlCl_2 + 3\ AcacH \rightarrow AlAcac_3 + MeH + 2\ HCl \qquad (8)$$

In reactions (6)–(8), evolution of a mole of methane occurs at −60°.

Table 1 lists the chemical shifts of the protons of aluminium acetylacetonates.

Reactions of aluminium tris(acetylacetonate) with methylaluminium chloride compounds

According to Kroll[3], an exchange of ligands occurs in the reaction of aluminium tris(acetylacetonate) with trimethylaluminium [reaction (9)].

$$AlAcac_3 + 2\ Me_3Al \rightarrow 3\ Me_2AlAcac \qquad (9)$$

NMR studies showed that a similar ligand exchange takes place in the reaction of aluminium tris(acetylacetonate) with methylaluminium chloride compounds [reactions (10) and (11)].

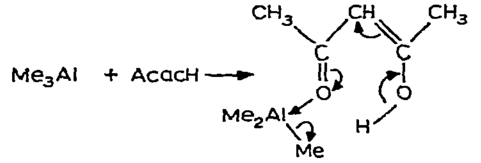
$$AlAcac_3 + 2\ Me_2AlCl \rightarrow Me_2AlAcac + 2\ MeClAlAcac \qquad (10)$$

$$AlAcac_3 + 2\ MeAlCl_2 \rightarrow 2\ MeClAlAcac + Cl_2AlAcac \qquad (11)$$

As is shown in Table 1, aluminium acetylacetonates exhibit different proton chemical shifts, thus enabling the identification of the products of reactions (10) and (11) on the basis of NMR spectra. The quantitative proportions of the resulting acetylacetonates were evaluated from the observed intensities of the signals.

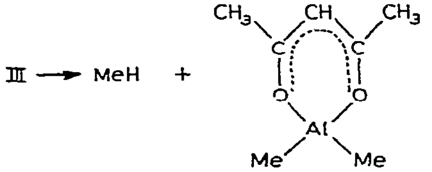
DISCUSSION

Since methylaluminium compounds react with acetylacetone in a non-polar solvent (toluene), the reaction is hardly likely to proceed by an ionic mechanism. Furthermore, if the reaction were to proceed via attack of the enol proton, the reactivities of trimethylaluminium and dimethylaluminium acetylacetonate would be similar. The observed decreased reactivity of the latter compound rules out an ionic mechanism involving the participation of a free CH_3^- anion. It must therefore be assumed that the first stage in the reaction involves the formation of a donor–acceptor complex between trimethylaluminium and acetylacetone [reaction (12)]. For the sake of simplicity, trimethylaluminium is presented as the monomer in this equation rather than as the dimer. The electron accepting properties of the aluminium atom in the resulting complex (III) give rise to a synchronous displacement of electrons whereby the O–H and Al–Me bonds become weakened and new bonds are formed. As a result, methane is formed and the dimethylaluminium acetylacetonate ring is closed [reaction (13)]. In dimethylaluminium acetylacetonate, the tetracoordinate aluminium atom is more negatively charged than the similarly tetracoordinate aluminium atom in dimeric trimethylaluminium. NMR studies confirm this suggestion since the signals attributable to the protons of the methyl groups attached to the aluminium atom in dimethylaluminium acetylacetonate are shifted upfield in comparison with those due to the protons of the methyl groups in trimethylaluminium (~0.2 ppm). Hence, dimethylaluminium acetylacetonate is a weaker Lewis acid than trimethylaluminium. Presumably this property, and the increased steric hindrance due to the bulky acetylacetonate group, are responsible for the lower reactivity of dimethylaluminium acetylacetonate towards acetylacetone.



(III)

(12)



(13)

NMR studies carried out at −70° support the suggestion that the first stage of the reaction of dimethylaluminium acetylacetonate with acetylacetone involves the formation of a complex for, at this temperature, no reaction involving the evolution of methane takes place. Data are listed in Table 2.

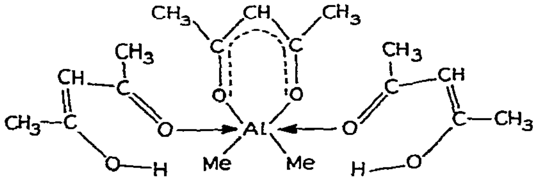
As is evident from the τ-values presented in Table 2, a product mixture consisting of $Me_2AlAcac$ and 2 AcacH produces no signal attributable to free acetylacetone. It is therefore likely that two molecules of the enol form of acetylacetone are

TABLE 2

CHEMICAL SHIFTS OF PROTONS OF DIMETHYLALUMINIUM ACETYLACETONATE AND ACETYLACETONE AT −70°

Compound	*Chemical shift τ (ppm)*		
	CH_3	*-CH-*	*CH_3-Al*
Me_2AlAcac	8.36	5.13	9.95
AcacH	8.08, 7.95	4.7, 6.63	
Me_2AlAcac + 2 AcacH[a]	8.36, 8.19	5.13, 5.0	9.95

[a] The mixture was obtained by adding AcacH to a solution of Me_2AlAcac in toluene at −70°.



(IV)

combined in a complex with dimethylaluminium acetylacetonate. This complex may well possess structure (IV), containing a hexacoordinate aluminium atom. The later stages of the reaction involve the evolution of methane and the formation of aluminium tris(acetylacetonate). A similar mechanism is also believed to apply for the reaction of methylaluminium chloride compounds.

EXPERIMENTAL

1. *Materials*

Pure-grade acetylacetone (VEB Laborchemie, D.D.R.) was dried and used after re-distillation in a nitrogen atmosphere.

Methylaluminium compounds were prepared by conventional methods. Trimethylaluminium and dimethylaluminium chloride were purified by distillation and methylaluminium dichloride was purified by crystallization from n-heptane.

Aluminium tris(acetylacetonate) was prepared by the method described in this paper and purified by crystallization from ethanol.

Commercial, pure-grade toluene was dried over calcium chloride, distilled from sodium in a nitrogen atmosphere, and stored over type 4A molecular sieves.

2. *Method*

Reactions of acetylacetone with methylaluminium compounds were carried out in a four-necked round-bottomed 100 ml flask equipped with stirrer, thermometer, cold trap and dropping funnel. Before the start of a particular reaction, the apparatus was repeatedly evacuated and filled with nitrogen. Toluene and an organoaluminium compound were injected by means of a hypodermic syringe. After the stirrer had been started, the system was cooled down to −70° (in an acetone/Dry-Ice cooling bath) and a solution of acetylacetone in toluene was added in a dropwise manner. The volume of gas evolved was measured in terms of the volume of displaced brine (the brine bottle was 2 l in capacity).

Aluminium acetylacetonates were isolated by distillation under reduced pressure.

Reactions of aluminium tris(acetylacetonate) were carried out at room temperature. To a solution of aluminium tris(acetylacetonate) in toluene, a methylaluminium compound dissolved in toluene was added by the use of a hypodermic syringe. All operations were performed in a nitrogen atmosphere.

3. *Analysis*

NMR spectra were recorded on a JEOL-C-60H (60 MHz) spectrometer. All spectra were run in toluene as solvent. The spectra were recorded at room temperature (Table 1) and at −70° (Table 2).

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