

NOTE

DIALKYLALUMINUM ACETYLACETONATES*

W. R. KROLL AND W. NAEGELE**

The Corporate Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036 (U.S.A.)

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INTRODUCTION

Alkylaluminum acetylacetonates $RAlAcac_2$ and $R_2AlAcac$ (Acac = acetylacetonate; R = alkyl) have not found much attention in the literature. Their stability and reactivity was not known. Brief mention of the dialkylaluminum acetylacetonates has been made recently^{1,2}. Alkyl-metal acetylacetonates with different metals have been described, *e.g.*, with boron³, with thallium^{4,5}, and tin⁶.

In the present paper several approaches are discussed for the synthesis of alkylaluminum acetylacetonates. New results are reported on the stability and the reactions of these compounds. Structural details for the dialkylaluminum acetylacetonates are presented for the first time.

RESULTS AND DISCUSSION

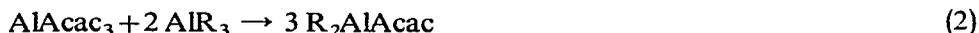
Synthesis of dialkylaluminum acetylacetonates

It has been reported that diisobutylaluminum acetylacetonate is prepared by reaction of 2,4-pentanedione with triisobutylaluminum¹ according to (1):



No characterization or structural proof were reported. In agreement with this result, we found that the method is general for the synthesis of above compounds.

We discovered another synthesis which gives the dialkylaluminum acetylacetonates in high yield without loss of a aluminum-carbon bond as in (1). This method uses the redistribution reaction (2):



The trialkylaluminum in solution is added to a solution of the aluminum

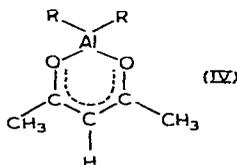
* Parts of this paper were presented at the 1967 International Symposium on Decomposition of Organometallic Compounds, Dayton, Ohio.

** Farbenfabriken Bayer A.G., Leverkusen.

acetylacetonate at ambient temperature. The exchange is fast and quantitative.

Properties and reactions of dialkylaluminum acetylacetonates

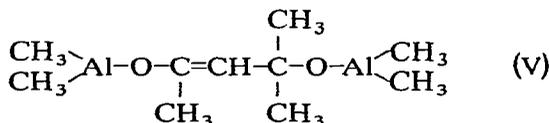
Dimethylaluminum acetylacetonate (I), diethylaluminum acetylacetonate (II), and diisobutylaluminum acetylacetonate (III) were prepared, isolated as stable compounds and identified by analysis. The NMR spectra for (I), (II) and (III) in benzene show a singlet for the ring proton and a singlet for the methyl groups of the chelate ring. These data are in full agreement with the assumption of a symmetrical chelate structure (IV).



Molecular weight determinations agree with a monomeric structure. This makes (IV) ideal model compounds for the study of their physical properties and their reactivity. All trialkylaluminums and compounds of the type R_2AlX (with few exceptions) are known to be strongly associated.

Compounds (I)–(III) are quite stable thermally. They do not disproportionate [reverse reaction of (2)] upon distillation. The hydrolytic stability of the alkylaluminum groups in (IV) is not much different from that of other alkylaluminum compounds.

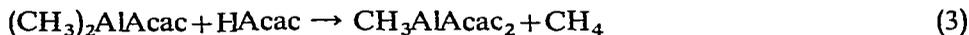
Subsequently, the stability of the chelate ligand of the dialkylaluminum acetylacetonates was investigated in reactions with various types of organoaluminum compounds. Trimethylaluminum and (I) in equimolar amounts reacted irreversibly at room temperature. By migration of a methyl group, a reaction product was formed for which following structure is proposed (V):



A similar reaction was obtained with dimethylaluminum monochloride, whereas dialkylaluminum monoalkoxides did not attack the chelate structure. This alkylation reaction can occur during the synthesis of (IV) unless the proper reaction conditions are followed. One can avoid such side reactions completely by using the Lewis base adduct instead of free AlR_3 or by using a Lewis base (*e.g.* ether) as solvent. Further studies are underway to establish the structure of the ring opening product (V).

Attempted synthesis of alkylaluminum bis(acetylacetonates)

The formation of alkylaluminum bis(acetylacetonates) was investigated. The reaction of (I) with equimolar amounts of 2,4-pentanedione should lead to the formation of methylaluminum bis(acetylacetonate) (VI):



The expected amount of methane was found, but (VI) could not be detected. Sub-

sequently it was tried to prepare (VI) using the redistribution reaction. Trimethylaluminum was reacted with aluminum acetylacetonate (VII) in a 1/2 molar ratio:



However, this approach also was unsuccessful. The analysis of the reaction products indicated formation of (VII) and (I) in equimolar ratio. It appears that if (VI) is formed, it is not stable and disproportionates readily:



Methylaluminum bis(acetylacetonate) should have the coordination number five which is not preferred for aluminum. In view of this fact an attempt was made to stabilize (VI) during its attempted preparation according to (4) by the presence of a Lewis base. However also this attempt failed as only the products of equation (5) could be observed.

EXPERIMENTAL

All reactions with aluminum organic compounds were carried out under dry argon or nitrogen. Trimethylaluminum, dimethylaluminum monochloride (Ethyl Corporation) and triisobutylaluminum (Texas Alkyls) were distilled. Dimethylphenoxyaluminum was prepared from trimethylaluminum and phenol in 1/1 molar ratio⁷. It was distilled and recrystallized several times. All solvents used in these studies were dried and distilled under dry argon or nitrogen.

Preparation of dialkylaluminum acetylacetonates

A. Preparation according to eqn. (1). A one molar solution of HACac is added under vigorous stirring and cooling to a one molar solution of the trialkylaluminum in benzene. The reaction is exothermic. After removal of the benzene, (IV) is distilled in vacuo. The yield of distilled, pure (IV) is usually above 60%.

B. Preparation according to eqn. (2). A solution of a trialkylaluminum (2–3 molar) is added at ambient temperature to a solution of (VII) in benzene (1 molar). Typically for the preparation of 1 mole of (I) the addition takes 1 h. Subsequently the solvent is removed in vacuo. The pure (IV) is distilled in vacuo, usually in yields above 75%.

TABLE I
CHEMICAL SHIFTS OF $\text{R}_2\text{AlAcac}^a$

R	$\delta(\text{Acac})$		$\delta(\text{R})$		
	CH	CH_3	CH	CH_3	CH_2
CH_3	+5.04(s)	+1.58(s)		-0.39	
C_2H_5	+5.00(s)	+1.57(s)		+1.38(t)	+0.25(q)
iso- C_4H_9	+5.00(s)	+1.55(s)	+2.18(m)	+1.19(d)	+0.38(d)

^a All spectra (60 MHz) obtained at room temperature from solutions ca. 15% w/w in benzene. The chemical shifts are given in ppm relative to internal tetramethylsilane (TMS). Shifts upfield from TMS negative, shifts downfield positive sign.

C. Properties of dialkylaluminum acetylacetonates. The NMR parameters are in Table 1. Quantitatively the ratio of the various types of protons agrees well with the calculated ratios.

The alcoholysis of (I) gave 95% of the calculated amount of methane. Other analytical data are in Table 2.

TABLE 2
ANALYTICAL DATA ON $R_2AlAcac$

R	Analysis found (calcd.)(%)			Mol. wt. found ^a (calcd.)	M.p. (°C)	B.p. [°C(mm)]
	Al	C	H			
CH ₃	17.0 (17.3)	53.93 (53.85)	8.66 (8.33)	166 (156)	28-29	82(15)
C ₂ H ₅	14.2 (14.6)	58.89 (58.69)	9.51 (9.24)			73(3.5)
iso-C ₄ H ₉	11.7 (11.3)	65.31 (65.00)	10.71 (10.41)	225 (240)		39(0.008)

^a The molecular weights were determined cryoscopically in benzene.

Table 3 shows characteristic IR bands of (I) and (VII) for comparison.

TABLE 3
IR ABSORPTION OF (I) AND (VII) (μ)

(I) ^a	6.3 s	6.54 s	7.25 s	7.73 m	8.38 m	9.7 m	10.65 m	12.78 m
(VII) ^b	6.32 s	6.56 s	7.25 s	7.8 m	8.36	9.7 m	10.7 m	12.85 m

^a In cyclohexane, comp. ^b 0.5% KBr pellet.

Attempted preparation of methylaluminum bis(acetylacetonate)

A. Reaction of trimethylaluminum with HAcac. At ambient temperature two mmoles of HAcac in benzene were added to one mmole trimethylaluminum in benzene (1 molar). Immediately two mmoles of methane were formed. Analysis by NMR indicated the presence of (VII) and (I). The same experiment was repeated on a larger scale using 50 mmoles trimethylaluminum and 100 mmoles HAcac. After completion of the reaction all volatile matter was distilled below 60° in vacuo. Analysis of the distillate showed only the presence of (I) besides the solvent. The residue was identified to be (VII).

B. Redistribution reaction. The reaction of trimethylaluminum with (VII) in 1/2 ratio did not give (VI) but only (I) and aluminum acetylacetonate. When the same reaction was carried out in presence of a Lewis base (*p*-dioxane) in stoichiometric amounts the same results were obtained.

Reactions of dimethylaluminum acetylacetonate with alkylaluminum compounds

Fifty ml of trimethylaluminum solution (1 molar in benzene) was added over

a period of 2 h to 50 ml of (I) in benzene (1 molar). After 26 h at ambient temperature, the reaction solution was hydrolyzed under cooling with dilute sulfuric acid under evolution of methane. The aqueous layer was extracted with ether and then combined with the organic layer. Analysis indicated diacetone alcohol as major product with a few percent mesityl oxide.

In analogous manner, dimethylaluminum monochloride (52 mmoles) in 60 ml of benzene were added to (I) (54 mmoles) in 100 ml of benzene. The reaction was completed by heating to 60° for several hours. Hydrolysis gave 3.7 l of methane. Workup similar to above gave diacetone alcohol as major product besides a small amount of mesityl oxide. If the above reactions are carried out in presence of a Lewis base, *e.g.* *p*-dioxane, no reaction occurs even after heating to 70° for several hours. When dimethylaluminum phenolate (1 mmole) was added to (I) (1 mmole) in benzene no reaction occurred even after heating to 55° for several hours.

ACKNOWLEDGEMENT

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