Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

INVESTIGATION OF ORGANOALUMINUM β-DIKETONATES*

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(Received August 11th, 1970)

SUMMARY

A systematic study of the synthesis and chemistry of organoaluminum β-diketonates is reported. Variation of the chelate ligand as well as the substituents on aluminum leads to a dramatic change in stability and reactivity. Data obtained from chemical reactions and proton NMR data are correlated with the effect of changing the chemical environment of the aluminum atom.

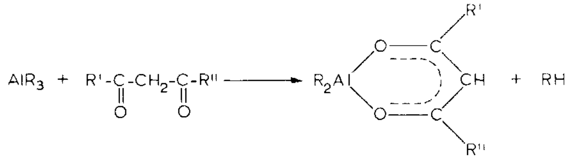
INTRODUCTION

Various routes to the synthesis of dialkylaluminum acetylacetonates [R_2Al-Acac (I)] have been reported recently[1]. Little is known about the chemistry and reactions of these compounds. In connection with a study of organoaluminum β-diketonates as cocatalysts in epoxide polymerizations[2] it became necessary to study the chemistry and to synthesize new representatives of these compounds. We wish to report the synthesis of several new compounds and our study of the chemistry of organoaluminum β-diketonates.

RESULTS AND DISCUSSION

I. Synthesis of dialkylaluminum β-diketonates

A. Protolysis reaction. The synthesis is carried out with an alkylaluminum compound and the free β-diketone, generally at ambient temperature in an inert diluent:



(1)

R=alkyl; R' and R'' can be CH_3,C_6H_5,CF_3

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[*] Parts of this paper were presented at the Fourth International Conference on Organometallic Chemistry, Bristol, England, 1969.

The reaction was performed with a variety of β-diketones. In addition to AlR_3, the chlorides, R_2AlCl and $RAlCl_2$ also were used as the organoaluminum component; in the latter case dichloroaluminum acetylacetonate (II) was obtained. Difficulties were encountered with the preparation of dialkylaluminium hexafluoroacetylacetonates (III) because of their thermal instability[3], so that in this case the reaction is preferentially carried out below 5°.

B. Redistribution reaction. The synthesis of several dialkylaluminum acetylacetonates (I) by the redistribution reaction has been recently described[1]. In contrast the dialkylaluminum hexafluoroacetylacetonates (III) could not be prepared by this route. Dichloroaluminum acetylacetonate (II) also was prepared from aluminum chloride and aluminum acetylacetonate[4]:

$$2\,AlCl_3 + Al(Acac)_3 \rightarrow 3\,Cl_2AlAcac \tag{2}$$

II. Properties and reactions of the complexes

A. General properties and H NMR correlations. The following complexes were isolated and characterized for the first time: dichloroaluminum acetylacetonate (II), dimethylaluminum hexafluoroacetylacetonate (III) and dimethylaluminum 1,3-diphenyl-1,3-propanedionate (IV). Compounds (II) and (IV) were found to be monomeric in benzene solution. The H NMR parameters of the new compounds are listed [together with those of (I), $R = CH_3$ for comparison] in Table 1.

TABLE 1

H NMR OF ORGANOALUMINUM β-DIKETONATES

β-Diketonate[a]	No.	CH-ring	CH_3-chelate	CH_3-Al
$Cl_2AlAcac$	(II)	4.93 (s)	1.40 (s)	
$(CH_3)ClAlAcac$	(V)	4.96 (s)	1.44 (s)	−0.19 (s)
$(CH_3)_2AlAcac$	(I), $R = CH_3$	5.04 (s)	1.58 (s)	−0.39 (s)
$(CH_3)_2Al(BA)$[b]	(VI)	5.76 (s)	1.60 (s)	−0.20 (s)
$(CH_3)_2Al(DBM)$	(IV)	6.61 (s)		−0.10 (s)
$(CH_3)_2Al(F_3A)$[b]	(VII)	5.34 (s)	1.27 (s)	−0.42 (s)
$(CH_3)_2Al(F_6A)$	(III), $R = CH_3$	5.90 (s)		−0.55 (s)

[a] δ values in ppm relative to internal TMS (60 MHz) in benzene solution at room temperature from solutions approx. 15% w/w in benzene. Shifts upfield from TMS shown negative; shifts downfield shown positive sign. Acac = acetylacetonate; BA = 1-phenyl-1,3-butanedionate; F_3A = 1,1,1-trifluoro-2,4-pentanedionate; F_6A = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; DBM = 1,3-diphenyl-1,3-propanedionate.
[b] These compounds were not isolated.

B. The effect of variation of ligands in organoaluminum β-diketonates. It has been reported[5] that β-diketones substituted with electron-withdrawing groups (*e.g.* trifluoromethyl groups) are less basic than those substituted with aromatic groups. Our results indicate that compound (IV) is thermally quite stable, whereas compounds of the type (III) are unstable even at ambient temperature. Directionally, the increase in basicity results in an increase in thermal stability. The tendency of trifluoromethyl groups to decrease the stability of the chelate has been well established[6−8]. In the case of a phenyl-substituted β-diketone, *e.g.* (IV), the stabilizing effect can be explained by the electron-releasing effect of the aromatic ring leading to a strengthening of the aluminum–oxygen bond.

Published data[7,9] indicate that a correlation between the stability (formation constant) of the chelate and the chemical shifts of the enolic proton for several β-diketones exists for metal complexes containing only chelate ligands as *e.g.* aluminum tris(acetylacetonate). In dimethylaluminum β-diketonates a change in the diketonate ligand should affect the magnetic environment of the aluminum and be reflected in the chemical shift of the methyl-aluminum protons. A plot of the values for the methyl-aluminum protons *vs.* those for the enolic proton of the free β-diketonate is shown in Fig. 1, where a linear relationship is obtained.

No formation constants are reported for the dimethylaluminum β-diketonates. The thermal instability of (III) has been mentioned earlier. Assuming that the previously mentioned correlation between formation constant and enolic proton chemical shifts applies the plot in Fig. 1 predicts (IV) to be the most stable of the compounds prepared.

The chemical shift of methyl groups attached to the chelate ring is less sensitive to change since they are further removed from the charged center. The chemical shift of the CH of the chelate ring is affected especially by the intramolecular electric field and thus very sensitive to changes in the chelate ligand (Table 1). Substitution of methyl in the chelate ring by phenyl produces a shift of the CH singlet. This shift is due to a ring-current effect, especially as the phenyl group can be nearly coplanar with the β-diketonate ligand. In a similar case a low-field effect has been observed[10] with aluminum tris-(β-diketonates) where the first phenyl substituent produced a change of 0.89 ppm, and the second 0.69 ppm to give a total change of 1.58 ppm. From Table 1 it can be seen that the introduction of the first phenyl group in our system contributed a change of 0.72 ppm *vs.* 0.85 ppm for the second. The total change is 1.57 ppm for the series of dimethylaluminum mono-β-diketonates *vs.* 1.58 ppm for the aluminum tris(β-diketonates).

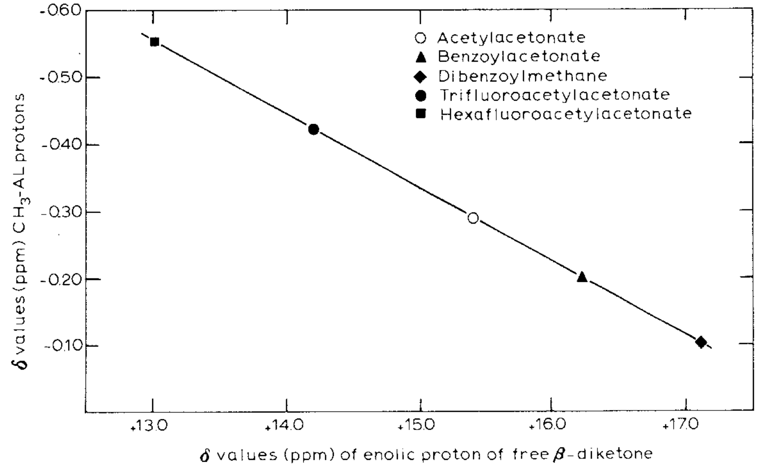

Fig. 1. Chemical shift of $(CH_3)_2Al$ β-diketonate *vs.* enolic proton of free ligand (TMS as internal standard).

An examination of the alkylmetal acetylacetonates of boron[11] and thallium[10] indicates that the chemical shift for CH and CH_3 of the chelate ring are approximately the same as for (I), suggesting that the chemical shift of the β-diketonate ligand is virtually independent of the metal.

The dialkylaluminum acetylacetonates (I) have little Lewis acidity, as evidenced by the lack of formation of stable complexes with Lewis bases, *e.g.* ether. No evidence for the formation of such derivatives could be found in H NMR experiments. Substitution of both alkyl groups by chlorine leads to (II) which has considerable Lewis acidity as evidenced by its formation of a stable complex with ether. In this case the difference in chemical behavior between (I) and (II) is not suggested by the H NMR data of the parent chelates.

C. Thermal stabilities. Compounds of type (I) can be distilled at elevated temperature without decomposition[1]. The dialkylaluminum hexafluoroacetylacetonates (III) are thermally unstable at room temperature and could only be distilled with decomposition. The decomposition products are higher boiling than (III), and give a different H NMR pattern than the pure compound. The detailed nature of the decomposition reaction has not yet been established*. Dichloroaluminum acetylacetonate (II) is thermally quite stable and can be distilled at temperatures above 90°. Dimethylaluminum 1,3-diphenyl-1,3-propanedionate (IV) is the most stable organoaluminum chelate we have encountered so far; even at about 150° no decomposition was observed.

D. Reactions of organoaluminum β-diketonates; redistribution and exchange reactions. Redistribution reactions between tin halides and *associated* organoaluminum compounds have been well documented[13]. It was of interest to see whether *monomeric* (I) would follow the same pattern. The results of these reactions are shown in eqns. (3) and (4).

$$(CH_3)_2AlAcac + SnCl_4 \rightarrow (CH_3)_2SnCl_2 + Cl_2AlAcac \tag{3}$$

$$2\,(CH_3)_2AlAcac + SnCl_4 \rightarrow Sn(CH_3)_4 + 2\,Cl_2AlAcac \tag{4}$$

A quantitative transfer of alkyls to the tin occurs accompanied by formation of (II).

A brief H NMR study of exchange reactions was carried out between dimethylaluminum acetylacetonate and other organoaluminum compounds. The results (Table 2) indicated no exchange on the NMR time scale at ambient temperature. All lines occur at the chemical shifts found for the pure compounds in benzene.

We believe exchange (A) does not proceed because of the strong association of the phenolate compound. No exchange was found in reaction (B) because of the stable

TABLE 2

H NMR EXCHANGE STUDIES WITH ORGANOALUMINUM β-DIKETONATES

Exchange reaction[a]	Exchange rate
(A) $(CH_3)_2AlAcac + (CH_3)_2AlOC_6H_5$	Slow or none
(B) $(CH_3)_2AlAcac + (CH_3)_3Al \cdot$ *p*-dioxane	Slow or none
(C) $(CH_3)_2AlAcac + (CH_3)_2Al(DBM)$	Slow or none

[a] In benzene at room temperature. DBM = 1,3-diphenyl-1,3-propanedionate.

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* It should be noted here that hexafluoroacetone reacts much more readily with Grignard compounds than does acetone itself. Thus the decomposition reaction of (III) could be related to a Grignard-type addition reaction of the organoaluminum reagent[12].

nature of the 1/1 etherate. Even the much more reactive trimethylaluminum does not exchange with this 1/1 adduct in benzene[14]. Reaction (C) offers the possibility for methyl and/or β-diketonate exchange but in studies up to 150° no exchange was observed.

This last reaction is of interest in connection with other redistribution reactions involving aluminum compounds in which β-diketonate groups and/or monodentate ligands are exchanged. Such exchange can involve the reaction between two different aluminum tris(β-diketonates)[15], or one aluminum tris(β-diketonate) and an aluminum compound with monodentate ligands as *e.g.* trialkylaluminums[1], or aluminum chloride (eqn. 2). A dissociation mechanism appears rather unlikely for such exchange reactions. Other mechanisms are being examined. Compounds of type (I), (II), (III) and (IV) are likely intermediates in such exchange reactions, consequently their behavior will give us valuable information on the transfer mechanism.

E. Complexing reactions. The low degree of Lewis acidity of compounds of the type (I), (III) and (IV) was indicated by their inability to form stable complexes with Lewis bases such as ether, tetrahydrofuran, phosphines, or tertiary amines. However, when (II) was treated with stoichiometric amounts or an excess of ether a stable, relatively insoluble 1/1 adduct was formed. No structural information about this adduct is yet available, but no stable adduct containing two moles of ether per aluminum could be detected.

EXPERIMENTAL

All reactions with organoaluminum compounds as well as with aluminum chloride and (II) were carried out in an atmosphere of dry nitrogen or argon. All solvents used in this study were dried and distilled under dry nitrogen or argon. The trialkylaluminums used were obtained from commercial sources (Texas Alkyls or Ethyl Corporation). Reagent grade aluminum chloride and tin tetrachloride were used in the redistribution reactions. The preparations of (I) ($R = CH_3$) and dimethylphenoxyaluminum were carried out as described previously[1]. The β-diketones were obtained from commercial sources and generally purified under a dry, inert atmosphere. Commercial aluminum tris(acetylacetonate) was purified by double recrystallization. All H NMR work was carried out with a Varian A-60 instrument. In general benzene or benzene-d_6 were used as solvents with TMS as an internal standard. NMR data are shown in Tables 1 and 3. The elementary analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Analytical results are collected in Table 4.

Preparation of (II)

Aluminum chloride (13.3 g) and aluminum acetylacetonate (16.2 g) together with 40 ml $CHCl_3$ were ballmilled for a period of 7 h. Insoluble matter was removed by centrifugation. After solvent removal the product was distilled. IR spectrum (Nujol mull, NaCl optics): 1615 (m), 1570 (s), 1535 (s), 1283 (m), 1260 (m), 1038 (sh), 1015 (m), 945 (m), 903 (m), 820 (w), 810 (sh), 650 (w), 639 (w), 610 (w). (s = strong; m = medium; w = weak; sh = shoulder)

(II) was also prepared by protolysis of methylaluminum dichloride with 2,4-pentanedione.

Preparation of dialkylaluminum hexafluoroacetylacetonates (III)

A typical preparation of this class of compounds is that for (III) ($R=CH_3$). A solution of 1,1,1,5,5,5-hexafluoro-1,3-pentanedione (20.4 g) in 100 ml pentane was slowly added to a cooled solution of trimethylaluminum (7.2 g) in 100 ml pentane at −40° over one hour. Subsequently the solvent was removed and the product distilled at reduced pressure. Considerable decomposition occurred in the distillation. H NMR analysis of (III) ($R=CH_3$) (yellow liquid) gave the correct ratio for protons. IR spectrum (CsBr/cyclohexane): 1645 (m); 1621 (m); 1568 (w); 1540 (w); 1455 (sh); 1430 (w); 1250 (s); 1220 (s); 1170 (s); 1140 (m); 1120 (w); 810 (w); 712 (m); 665 (w); 590 (w).

Similarly (III) ($R=C_2H_5$, i-C_4H_9) were prepared. The latter compound was not isolated. The diethyl derivative (III), $R=C_2H_5$, had a b.p. of 32°/9 mm.

TABLE 3

H NMR OF DIALKYLALUMINUM 1,1,1,5,5,5-HEXAFLUORO-2,4-PENTANEDIONATES (III) IN CHLOROBENZENE[a]

R	CH(ring)	CH_3-C	CH_2-Al	CH_3-Al
CH_3	6.23			−0.56
C_2H_5	6.23	1.02	+0.07	
i-C_4H_9	6.13	0.93	+0.18	

[a] Chemical shift data δ in ppm (60 MHz); TMS as int. standard.

Compounds (III) decompose at ambient temperature either pure or in solution and therefore must be stored cold. The decomposition products are generally higher boiling and have substantially different, more complex H NMR spectra.

Preparation of (IV)

A solution of 1,3-diphenyl-1,3-propanedione (23.7 g) in toluene (80 ml) was slowly added with stirring to trimethylaluminum (7.9 g) in 80 ml toluene at −5° over a period of 1 hour. H-NMR analysis of the solution indicated completion of the reac-

TABLE 4

SUMMARY OF ANALYTICAL DATA OF ISOLATED ORGANOALUMINUM β-DIKETONATES

Complex	Formula	Analysis found (calcd.) (%)			Mol. wt. found[a] (calcd.)	M.p. (°C) or b.p. [°C (mm)]
		Al	C	H		
(II)	$C_5H_7O_2Cl_2Al$[b]	13.61	30.48	3.75	211	79–81
		(13.71)	(30.46)	(3.55)	(197)	92 (0.001)
(III)	$C_7H_7O_2F_6Al$[c]	10.1				55 (153)
$R=CH_3$		(10.2)				
(IV)	$C_{17}H_{17}O_2Al$	9.37	72.22	6.17	288	126–129
		(9.64)	(72.86)	(6.07)	(280)	

[a] The molecular weights were determined cryoscopically in benzene. [b] Cl found 35.72%, calcd. 36.0%. [c] Compound is unstable at ambient temperature.

tion. Solvent removal gave a yellow solid (28 g) which was analysed after recrystallization from benzene; the ratio of protons agrees with (IV).

IR Spectrum: i. benzene (CsBr): 2930 (w); 1592 (s); 1540 (sh); 1523 (s); 1455 (s); 1443 (m); 1368 (s); 1330 (s); 1308 (m); 1231 (s); 1190 (s); 1160 (w); 1130 (w); 1109 (sh); 1075 (m); 1023 (m); 1002 (m); 948 (m); 820 (w); 792 (m); 768 (s); 720 (s); 622 (m); 558 (m); 470 (m); 320 (m). Decomposition test: (IV) was heated under argon to about 150° C. No discoloration or gas evolution were noted. The IR spectrum of the heated sample was essentially unchanged.

Preparation of other methylaluminum β-diketonates

The following new compounds were prepared *in situ* and not isolated (H NMR chemical shift Table 1): methylchloroaluminum acetylacetonate (V), dimethylaluminum 1-phenyl-1,3-butanedionate (VI), dimethylaluminum 1,1,1-trifluoro-2,4-pentanedionate (VII). These compounds were prepared by adding one ml of a one molar solution of the β-diketonate to one ml of a one molar solution of the methylaluminum compound with cooling and stirring. The gas evolution in each case was 92–96 % of the calculated amount of methane. The relative ratio of the different types of protons observed in the NMR spectra agreed with the theoretical values.

Redistribution reactions with $SnCl_4$

One molar solutions of (I) ($R = CH_3$) and $SnCl_4$ in benzene were mixed in 1/1 and 2/1 molar ratios. After several hours stirring at room temperature the product was analysed by H NMR. The H NMR spectra of tetramethyltin, trimethyltin chloride, dimethyltin dichloride and methyltin trichloride (obtained from M. & T. Chemicals Co. and Alfa Inorganics) were recorded using the same solvent and the same concentration as above. The H NMR analysis indicated quantitative alkylation (as shown in eqns. 3 and 4). The presence of tin–methyl species is easily recognized by the occurrence of satellite signals due to the isotopic distribution. The identification of the products was made by comparison of the H NMR chemical shift of the methyltin species in the product and the known methyltin compounds. The complete conversion was indicated by the disappearance of all aluminum-methyl groups (by H NMR).

Complexing reactions

The following dialkylaluminum β-diketonates were dissolved in dry ether: (I) ($R = CH_3$, C_2H_5, i-C_4H_9), (III) ($R = CH_3$), (IV) ($R = CH_3$). Subsequent vacuum stripping at ambient temperature gave the starting material. The H NMR spectra of (I), ($R = CH_3$) in benzene with or without the presence of stoichiometric amounts of Lewis base (ether, triethylamine, triphenylphosphine) were examined. No chemical shift change upon addition of the base was observed.

A solution of (II) in chloroform was reacted with excess ether. A precipitate was obtained which after drying (ambient temperature, 30 mm Hg) was shown to be a 1/1 adduct of ether and (II) by H NMR. Its chemical shift δ (in ppm) in $CHCl_3$ (int. TMS as standard) for chelate: CH, 5.92; CH_3, 2.16; for ether: CH_2, 3.83; for CH_3, 1.17. Upon heating the adduct to 90°/30 mm for 3 h some ether could be removed. NMR analysis at this point indicated the ratio of (II) to ether as 1/0.3. Complexes were also obtained between (II) and pyridine, 2,2′-bipyridine and tropolone, however their composition has not been further investigated.

ACKNOWLEDGEMENT

The valuable experimental assistance of Mrs. M. F. Lippin, Mrs. S. Pagnucco and Mr. W. Mykytka is gratefully acknowledged.

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