

PHENOXYALUMINIUM COMPOUNDS

VII *. REACTIONS OF ORGANOALUMINIUM COMPOUNDS WITH HINDERED PHENOLS

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(Received May 22nd, 1978)

Summary

Reactions of Me_3Al , $i\text{-Bu}_3\text{Al}$, Me_2AlCl and $\text{Me}_2\text{AlC}\equiv\text{CMe}$ with 2,6-di-*t*-butyl-4-methylphenol have been studied at different molar ratios of the reactants.

It is found that in the reaction with the phenol, trimethylaluminium forms monomeric methylaluminium diphenoxide; triisobutylaluminium gives both monomeric mono- and di-phenoxyaluminium (depending on molar ratios of the reactants) and dimethylchloroaluminium forms dimeric methylphenoxyaluminium chloride.

It is found that methylpropynylaluminium phenoxide is unstable and disproportionates in hydrocarbon solutions.

The mechanisms of some of these reactions are suggested.

Introduction

Simple alcohols or phenols when mixed with organoaluminium compounds form strongly associated aluminium alkoxides or phenoxides. The formation of mono-, di- or tri-alkoxides or phenoxides depends upon the molar ratio of the reactants. Mono-alkoxides or -phenoxides neither disproportionate upon heating nor when stored in hydrocarbon solutions [1]. It was stated however that dimethylaluminium methoxide disproportionates in the presence of a base [2]. We reported previously [3] the formation of monomeric phenoxyaluminium compounds. More detailed results concerning these reactions and the reactions of

* For part VI see ref. 5.

(DBMP*)H with $(\text{Me}_2\text{AlCl})_2$ and $(\text{Me}_2\text{AlC}\equiv\text{CMe})_2$ are the subject of this work.

Results and discussion

I. Reactions of trialkylaluminium with (DBMP)H

It was reported previously [3] that trimethylaluminium reacts with (DBMP)H to form $\text{MeAl}(\text{DBMP})_2$ independent of the molar ratio of reactants. The ^1H NMR spectrum of the toluene reaction mixture at 1 : 1 ** molar ratio of Me_3Al to (DBMP)H shows in the region of Me—Al protons a singlet at $\tau = 10.62$ ppm, which at -78°C splits into three peaks at $\tau = 9.75$, 10.02 and 10.37 ppm. The peaks at 9.75 and 10.37 correspond closely to those of the Me_3Al dimer. Indeed after evaporation of the solvent Me_3Al was found in the distillate. In the PMR spectrum of the toluene solution of the white residue (or the product of its crystallization from cyclohexane) the peaks at τ 7.50, 8.19 and 10.02 ppm (intensity ratio 2/12/1) (Table 1) were found. The same spectral phenomena were observed for the product of the reaction when $\text{Me}_3\text{Al}/(\text{DBMP})\text{H}$ 1/2. This fact, together with elementary analysis and molecular weight determination, proved that the compound obtained is $\text{MeAl}(\text{DBMP})_2$ monomer.

Reaction of $i\text{-Bu}_3\text{Al}$ with (DBMP)H in molar ratio 1/1 forms the liquid monomer $i\text{-Bu}_2\text{Al}(\text{DBMP})$ (Table 2) which undergoes disproportionation when heated to 110°C under a vacuum of 10^{-4} Torr. $i\text{-Bu}_3\text{Al}$ formed during this process distills off and the white residue, which dissolves in toluene, is identical with that of the product of the reaction of $i\text{-Bu}_3\text{Al} : (\text{DBMP})\text{H}$ 1 : 2 (Table 1). This indicates that the product of disproportionation is $i\text{-BuAl}(\text{DBMP})_2$. The compound forms monomeric species of molecular weight 541 (Table 2) as was shown by a cryoscopic determination.

On the basis of the above results it can be suggested that the reaction of (DBMP)H with Me_3Al proceeds similarly for $i\text{-Bu}_3\text{Al}$, via dialkylaluminium phenoxide which under the reaction conditions disproportionates with formation of diphenoxide (Scheme 1). It can be suggested that the driving force of the disproportionation is the enthalpy of trimethylaluminium dimerization (in contrast to triisobutylaluminium which exists predominantly as a monomer).

II. Reaction of Me_2AlCl with (DBMP)H

The reaction of Me_2AlCl with (DBMP)H proceeds with evolution of not more than 1 mole of methane per mole of Me_2AlCl with or without an excess of the phenol. The crystalline white solid was obtained and identified as a $\text{Me}(\text{DBMP})\text{-AlCl}$ by means of PMR spectra (Table 1) and elemental analysis (Table 3). Its molecular weight corresponds closely to a dimeric species (Table 2).

These facts lead us to propose that the reaction between Me_2AlCl dimer and (DBMP)H proceeds via unsplit or partially split dimer according to Scheme 2.

III. Reaction of $\text{Me}_2\text{AlC}\equiv\text{CMe}$ with (DBMP)H

The reactions of $\text{Me}_2\text{AlC}\equiv\text{CMe}$ with (DBMP)H were performed at molar ratios 1/1, 1/2 and 1/5. Independent of an excess of (DBMP)H not more than two

* DBMP = 2,6-di-*t*-butyl-4-methylphenoxy.

** All molar ratios are given relative to organoaluminium compounds in monomeric form.

TABLE 1

CHEMICAL SHIFTS OF PROTONS IN PMR SPECTRA OF TOLUENE SOLUTION OF 2,6-di-t-BUTYL-4-METHYLPHENOXYALUMINIUM COMPOUNDS

Compound	τ (ppm) (intensity)			
	$\text{CH}_3\text{-C}_\text{AR}$	$(\text{CH}_3)_3\text{-}$	$(\text{CH}_3)_2\text{-CH-}$	$\text{-CH}_x\text{-Al}$
$\text{MeAl}(\text{DBMP})_2$	7.50 s (2)	8.19 s (12)	—	10.02 s (1)
$\text{i-Bu}_2\text{Al}(\text{DBMP})$	7.32 s (3)	8.20 s (18)	8.67 d (12)	9.49 d (4)
$\text{i-BuAl}(\text{DBMP})_2$	7.58 s (3)	8.20 s (18)	8.96 d (3)	9.25 d (1)
$\text{Me}(\text{DBMP})\text{AlCl}$	7.59 s (1)	8.30 s (6)	—	9.88 s (1)

TABLE 2

MOLECULAR WEIGHTS OF 2,6-di-t-BUTYL-4-METHYLPHENOXYALUMINIUM COMPOUNDS DETERMINED CRYOSCOPICALLY IN BENZENE

Compound	Molecular weight		Degree of association
	Calculated for monomer	Found	
$\text{MeAl}(\text{DBMP})_2$	480	494	1.0
$\text{i-Bu}_2\text{Al}(\text{DBMP})$	360	395	1.1
$\text{i-BuAl}(\text{DBMP})_2$	522	541	1.0
$\text{Me}(\text{DBMP})\text{AlCl}$	297.5	600	2.0

SCHEME 1

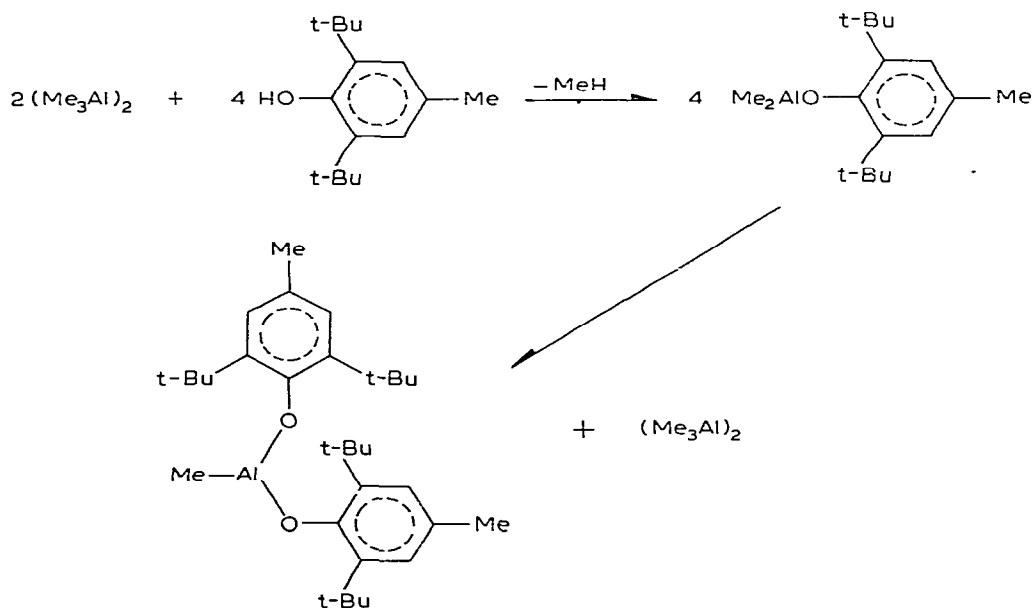


TABLE 3
ELEMENTAL ANALYSIS DATA

Compound	Al(%)		Cl(%)	
	Calcd.	Found	Calcd.	Found
MeAl(DBMP) ₂	5.63	5.4	—	—
i-Bu ₂ Al(DBMP)	7.50	7.6	—	—
i-BuAl(DBMP) ₂	5.31	5.2	—	—
Me(DBMP)AlCl	10.92	10.6	11.97	12.2

moles of gaseous products were evolved, similar to the analogous reaction with trialkylaluminiums. Whereas at the beginning of the addition of phenol a great excess of methane was observed, at the end of the reaction nearly equimolar amounts of methane and methylacetylene were found in gaseous products (Table 4).

In the region of Me—Al protons of the PMR spectrum of the reaction mixture, at molar ratio of Me₂AlC≡CMe : (DBMP)H lower than 1/2, four signals are always observed. This fact suggests the formation of a mixture of methylaluminium pro-

SCHEME 2

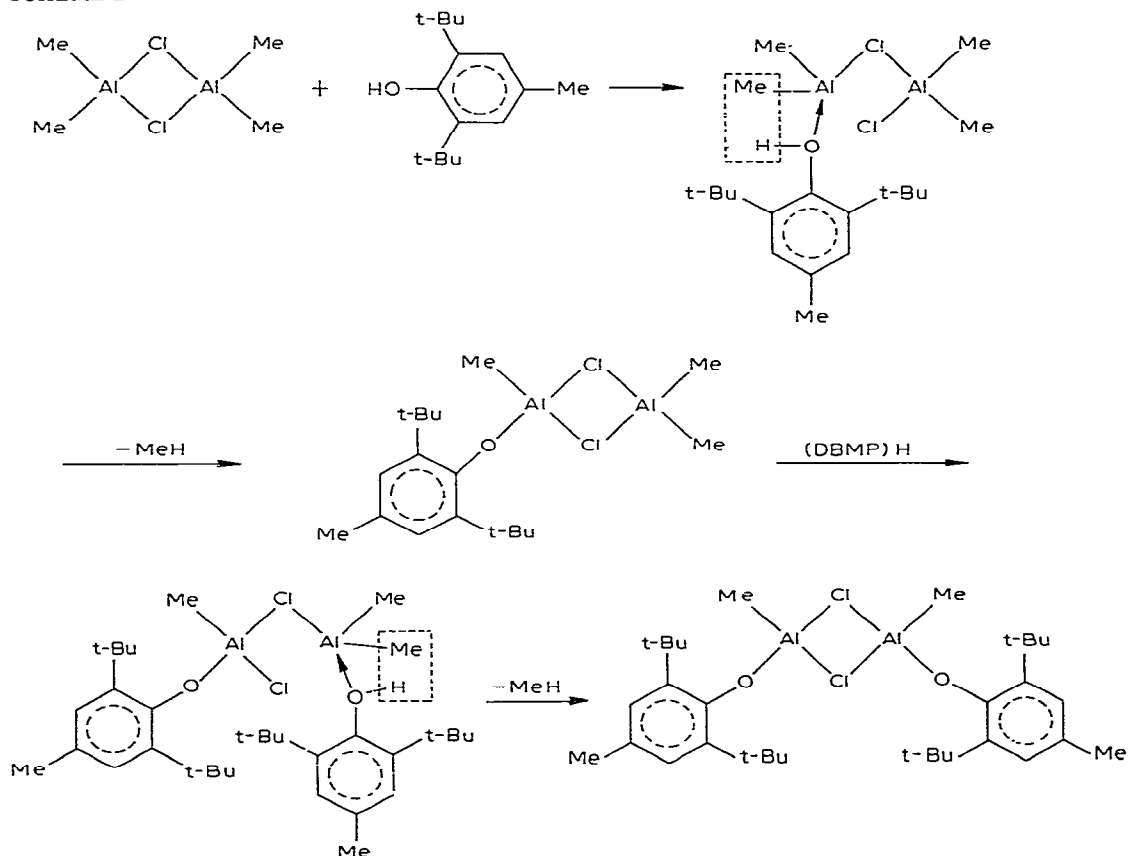


TABLE 4

MOLAR RATIOS OF METHANE TO METHYLACETYLENE ELIMINATED IN THE REACTION $\text{Me}_2\text{AlC}\equiv\text{CMe}$ WITH $(\text{DBMP})\text{H}$ WITH VARIATION OF THE AMOUNT OF PHENOL PER MOL OF $\text{Me}_2\text{AlC}\equiv\text{CMe}$

$(\text{DBMP})\text{H}$ (mol)	0.25	0.5	1	1.5	2
Molar ratio $\text{MeH}/\text{MeC}\equiv\text{CH}$	5	3	2.8	1.6	0.6

ducts. The PMR spectrum of the $\text{Me}_2\text{AlC}\equiv\text{CMe} : (\text{DBMP})\text{H}$ 1/2 has signals at τ 10.02 ppm, 8.34 ppm, 8.19 ppm and 7.50 ppm. The spectrum (Fig. 1) is nearly identical with the spectrum of $\text{MeAl}(\text{DBMP})_2$ (Table 1). Moreover, during hydrolysis of the crystals obtained in the reaction of $\text{Me}_2\text{AlC}\equiv\text{CMe}$ with $(\text{DBMP})\text{H}$ at molar ratio 1/2 nearly 10 molar % of $\text{MeC}\equiv\text{CH}$ was evolved. This suggests that for molar ratio $\text{Me}_2\text{AlC}\equiv\text{CMe}/(\text{DBMP})\text{H}$ 1/2, $\text{MeAl}(\text{DBMP})_2$ is formed contaminated with a small amount of $\text{MeC}\equiv\text{CAl}(\text{DBMP})_2$.

The rather complex PMR spectrum of reaction products for molar ratio $\text{Me}_2\text{AlC}\equiv\text{CMe} : (\text{DBMP})\text{H}$ 1 : 1 (Fig. 2a) indicates the presence of several compounds in the mixture. The following experiments were carried out to find the components of the mixture:

(1). The positions of the signals τ 7.50 and 10.02 ppm correspond closely to those of $\text{MeAl}(\text{DBMP})_2$. The addition of pure $\text{MeAl}(\text{DBMP})_2$ to the mixture of the products causes the apparent increase in the intensities of these two peaks. This confirms the presence of $\text{MeAl}(\text{DBMP})_2$ in the mixture.

(2). After evaporation of solvent, $\text{Me}_2\text{AlC}\equiv\text{CMe}$ was found in the distillate. In the PMR spectrum a simultaneous decrease in the intensity of the signal at τ

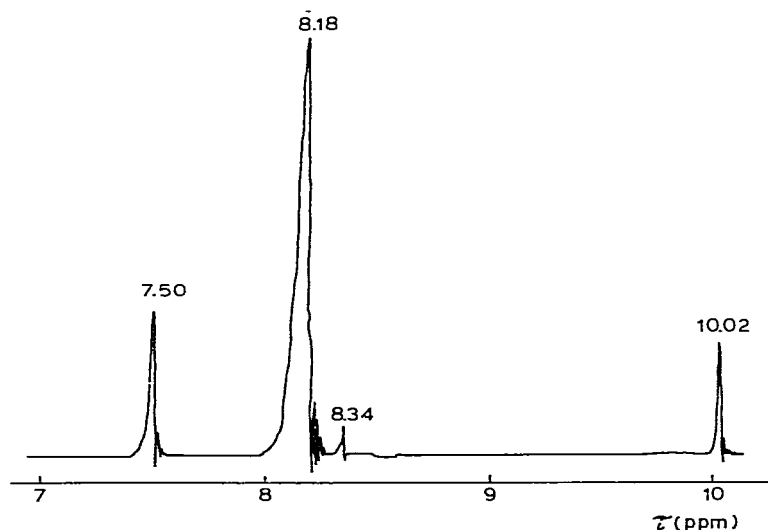


Fig. 1. ^1H NMR spectrum of the reaction product of molar ratio $\text{Me}_2\text{AlC}\equiv\text{CMe}/(\text{DBMP})\text{H}$ 1/2 (benzene solution).

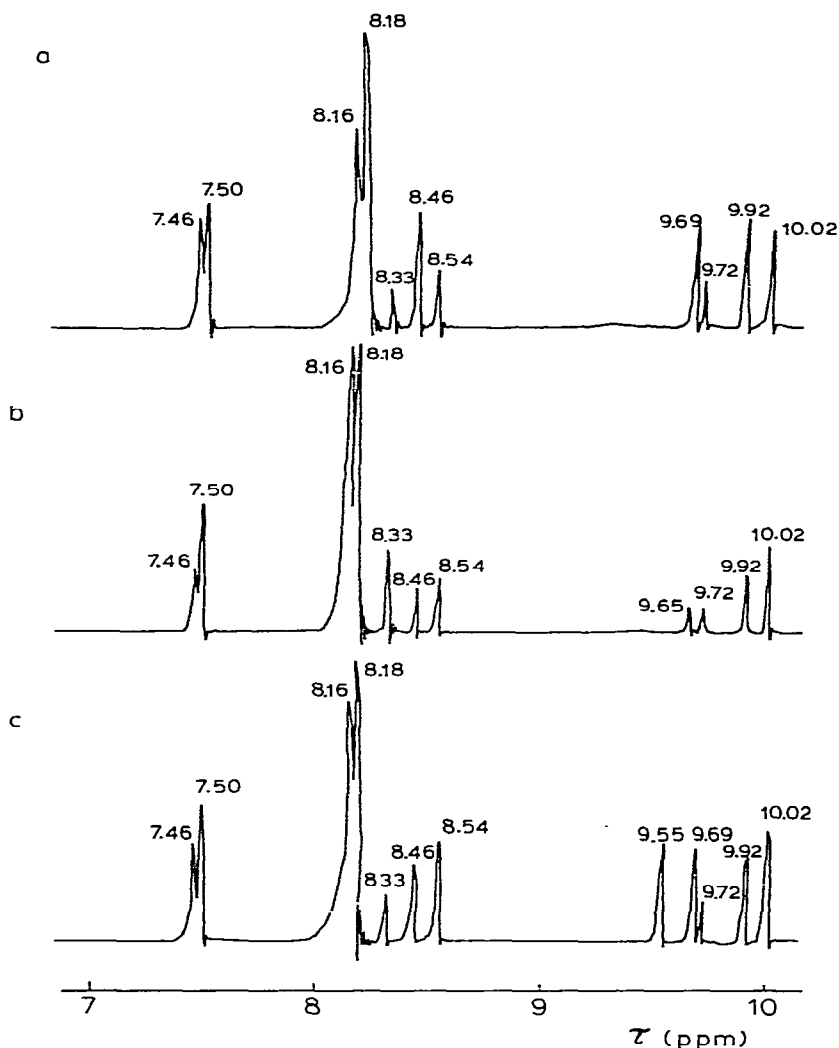


Fig. 2. ^1H NMR spectra of reaction products (benzene solutions) (a) $\text{Me}_2\text{AlC}\equiv\text{CMe}$ (DBMP)H (molar ratio 1/1), (b) $\text{MeAl}(\text{DBMP})_2\text{Me}_2\text{AlC}\equiv\text{CMe}$ (molar ratio 1/2), (c) $\text{Me}(\text{DBMP})\text{AlCl}$ with $\text{MeC}\equiv\text{CNa}$ after filtration of NaCl and an excess of unreacted $\text{MeC}\equiv\text{CNa}$.

9.73 (until it disappears) and 7.44 ppm, together with an increase in intensity of the signals at τ 10.02 and 7.50 ppm are observed. This latter observation indicates an increase in the amount of $\text{MeAl}(\text{DBMP})_2$ in the system upon distillation of $\text{Me}_2\text{AlC}\equiv\text{CMe}$. The above results prove that $\text{Me}_2\text{AlC}\equiv\text{CMe}$ exists in the reaction mixture perhaps as a mixed dimer with other aluminium compounds e.g. $\text{Me}_2\text{AlC}\equiv\text{CMe} \cdot \text{Me}(\text{DBMP})\text{AlC}\equiv\text{CMe}$.

(3). The addition of $\text{Me}_2\text{AlC}\equiv\text{CMe}$ to pure $\text{MeAl}(\text{DBMP})_2$, or to the mixture obtained from the 1 : 1 reaction of the former with (DBMP)H, causes an exchange of the groups bound to aluminium. From Fig. 2b one can see the appearance of new signals in the region of $\text{CH}_3\text{-Al}$ protons similar to the products of the reac-

tion $\text{Me}_2\text{AlC}\equiv\text{CMe}/(\text{DBMP})\text{H}$ 1/1. Moreover, the peak at τ 7.50 ppm of pure $\text{MeAl}(\text{DBMP})_2$ decreases in intensity as the new one at τ 7.46 ppm appears. The latter peak is always observed in the spectrum for the 1/1 molar ratio of $\text{Me}_2\text{AlC}\equiv\text{CMe} : (\text{DBMP})\text{H}$ and it must be due to a compound where the ratio of phenoxy groups to aluminium is less than 2.

(4). We did not succeed in obtaining the expected $\text{Me}(\text{MeC}\equiv\text{C})\text{Al}(\text{DBMP})$ from the reaction of $\text{Me}_2\text{Al}(\text{C}\equiv\text{CMe})$ with $(\text{DBMP})\text{H}$ and therefore attempted the reaction of $\text{Me}(\text{DBMP})\text{AlCl}$ with $\text{MeC}\equiv\text{CNa}$. After filtration of NaCl and an excess of $\text{NaC}\equiv\text{CMe}$, the PMR spectrum of the filtrate (which was chlorine free) gave nearly the same set of the signals (Fig. 2c) as those in the spectrum of 1 : 1 $\text{Me}_2\text{AlC}\equiv\text{CMe} : (\text{DBMP})\text{H}$ reaction products. This method is known for the preparation of alkynyl aluminium compounds. Thus, one can suggest that $\text{Me}(\text{MeC}\equiv\text{C})\text{Al}(\text{DBMP})$ when formed, equilibrates. The presence of $\text{MeAl}(\text{DBMP})_2$ was also confirmed in the reaction mixture.

Experimental

The reactions of Me_3Al , $i\text{-Bu}_3\text{Al}$ and Me_2AlCl with an equimolar amount of $(\text{DBMP})\text{H}$ were carried out in benzene or cyclopentane at room temperature. After evaporation of solvent the solid residue was crystallized from cyclohexane. Liquid $i\text{-Bu}_2\text{Al}(\text{DBMP})$ was not purified.

The analytical data for aluminium and chlorine of the compounds are given in the Table 3.

The reactions of $\text{Me}_2\text{AlC}\equiv\text{CMe}$ with $(\text{DBMP})\text{H}$ were carried out in toluene, benzene or cyclopentane. The reaction begins at -40°C . Gaseous samples were collected immediately from above the reaction mixture and their composition during the course of the reaction was established chromatographically (Table 4). The reactor was separated from the gas burette by an oil seal and it can be reasonably assumed that the thus collected samples did not give the average gas composition of the whole reaction. $\text{Me}_2\text{AlC}\equiv\text{CMe}$ was prepared according to Wilke and Müller [4]. NMR spectra were measured on a JEOL 100 MHz spectrometer using approximately 10% solutions in benzene, toluene or cyclopentane. Molecular weights were determined cryoscopically in benzene using a standard freezing point depression apparatus modified so as to enable the measurements to be made in an nitrogen atmosphere.

Acknowledgement

The authors wish to thank the Institute of Organic Chemistry (Polish Academy of Sciences, Warsaw) for financial support of part of this work and Marek Źaliński, MSc. for experimental assistance.

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