

Preparation and Characterization of Some Volatile Double Isopropoxides of Aluminium with Alkaline Earth Metals

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Reactions of the alkaline earth metals (Mg, Ca, Sr, Ba) with aluminium isopropoxide in boiling isopropanol in the presence of a mercuric chloride catalyst give the corresponding double alkoxides $[M[Al(OR^i)_4]_2]_n$ ($n = 1$, $M = Mg$; $n = 2$, $M = Ca, Sr, \text{ and } Ba$) which can be isolated by vacuum distillation or sublimation. Treatment of these double alkoxides with excess of the tertiary alcohols tert-butyl alcohol or tert-amyl alcohol in boiling benzene results in

partial alcoholysis of the isopropoxy groups to give $M[Al(OR^i)(OR)_3]_2$ ($M = Mg, Ca, \text{ and } Sr$) or $Ba[Al(OR^i)_2(OR)_2]_2$ ($R = \text{tert-butyl and tert-amyl}$) which are volatile and monomeric. Proton and carbon-13 n.m.r. spectra of some of these double isopropoxides suggest rapid interchange of bridging and terminal isopropoxy groups.

Introduction

In 1929 the first double metal alkoxides were reported by Meerwein and Bersin [1]. However,

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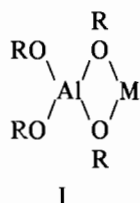
TABLE I. Double Alkoxides Prepared in This Work.

Compound	Liquid (L) or Solid (S)	Boiling or Sublimation Point, °C	Analyses			Molecular Weight	
			M	Al	OPr ⁱ		
Mg[Al(OPr ⁱ) ₄] ₂	L	114°/0.2 mm	Calcd.	4.2 (Mg)	9.8	86.0	550
			Found	4.2 (Mg)	9.8	85.9	562
Ca[Al(OPr ⁱ) ₄] ₂	S	220–230°/0.1 mm	Calcd.	7.1 (Ca)	9.5	83.4	567
			Found	7.1 (Ca)	9.5	82.7	1143
Sr[Al(OPr ⁱ) ₄] ₂	S	190–200°/0.1 mm	Calcd.	14.3 (Sr)	8.8	76.9	614
			Found	14.2 (Sr)	8.8	77.1	1204
Ba[Al(OPr ⁱ) ₄] ₂	S	145°/0.05 mm	Calcd.	20.6 (Ba)	8.1	71.3	663
			Found	20.7 (Ba)	7.9	70.9	1162
Mg[Al(OPr ⁱ)(OAm ^t) ₃] ₂	L	142°/0.1 mm	Calcd.	3.2 (Mg)	7.4	–	725
			Found	3.1 (Mg)	7.4	–	749
Ca[Al(OPr ⁱ)(OAm ^t) ₃] ₂	L	175°/0.05 mm	Calcd.	5.4 (Ca)	7.4	–	741
			Found	5.4 (Ca)	7.3	–	806
Sr[Al(OPr ⁱ)(OAm ^t) ₃] ₂	L	184°/0.1 mm	Calcd.	12.5 (Sr)	7.7	–	789
			Found	12.5 (Sr)	7.8	–	815
Ba[Al(OPr ⁱ) ₂ (OAm ^t) ₂] ₂	S	190–195°/0.1 mm	Calcd.	17.7 (Ba)	6.9	–	776
			Found	17.9 (Ba)	7.0	–	809
Mg[Al(OPr ⁱ)(OBu ^t) ₃] ₂	L	132°/0.1 mm	Calcd.	3.8 (Mg)	8.5	18.6	635
			Found	3.8 (Mg)	8.5	18.8	650
Ca[Al(OPr ⁱ)(OBu ^t) ₃] ₂	L	143°/0.05 mm	Calcd.	6.2 (Ca)	8.3	18.2	651
			Found	6.2 (Ca)	8.3	18.3	700
Sr[Al(OPr ⁱ)(OBu ^t) ₃] ₂	S	160–170°/0.2 mm	Calcd.	12.5 (Sr)	7.7	16.9	699
			Found	12.6 (Sr)	7.8	17.0	706
Ba[Al(OPr ⁱ) ₂ (OBu ^t) ₂] ₂	S	190–200°/0.1 mm	Calcd.	19.0 (Ba)	7.5	32.8	720
			Found	19.2 (Ba)	7.7	32.8	738

TABLE II. Characteristic Infrared Absorption Bands of $M[Al(OPr^i)_4]_2$.

$Mg[Al(OPr^i)_4]_2$	$Ca[Al(OPr^i)_4]_2$	$Sr[Al(OPr^i)_4]_2$	$Ba[Al(OPr^i)_4]_2$	Tentative Assignment
1375vs	1373vs	1374vs	1370vs	gem-Dimethyl
1190sh	1190s	1189s	1190s	Terminal $\nu(C-O)$
1170vs	1170vs	1171vs	1169vs	
1135vs	1133vs	1134vs	1132vs	Bridged $\nu(C-O)$
1035s	1030s	1032s	1029s	Terminal $\nu(C-O)$
1000sh				
975vs	969vs	968vs	968vs	Bridged $\nu(C-O)$
950s				
840s	835s	836s	839s	$\nu(Al-O)$
690vs	691vs	690vs	692vs	
680s	675s	672s	676s	
620sh	620w	618w	618w	
580ms	565m	568m	569m	$\nu(M-O)$
540m	525w	529w	527w	
470m	470sh	479m	468sh	$\nu(M-O)$
440m	458sh	441m	455sh	
438sh	440m		443m	

only in 1958 were the first concerted efforts [2] made to study in detail the physical and chemical properties of double metal alkoxides. Subsequently, a large number of double metal alkoxides of aluminum with various metals were prepared [3, 4] in which the unit $(RO)_2Al(OR)_2$ functions as a bidentate ligand as indicated in I.



In 1965 the first double alkoxides of aluminum with the alkaline earth metals were reported by Scholder and Protzer [6]. Their use of the methoxide group as the alkoxide led to insoluble and non-volatile derivatives which could not be characterized in detail. We decided to study the synthesis and properties of double alkoxides of aluminum with the alkaline earth metals derived from alcohols containing larger and more highly branched alkyl groups hoping to get soluble and volatile derivatives of lower molecular complexity than these previously studies methoxides [5]. The feasibility of such an approach is suggested by recent successes [6-8] in the syntheses of apparently covalent double alkoxides of the alkaline earth metals with various other metals which led to derivatives which were both volatile and soluble in organic solvents. Details of the preparations and properties of the new double alkoxides

of aluminum with the alkaline earth metals are presented in this paper.

Experimental

Isopropoxy groups were estimated by oxidation with potassium dichromate [9]. Aluminum, magnesium, calcium, strontium, and barium were estimated gravimetrically as aluminum oxinate, $NH_4MgPO_4 \cdot 6H_2O$, $CaC_2O_4 \cdot H_2O$, $SrSO_4$ and $BaSO_4$, respectively. A semimicro Gallenkamp ebulliometer with thermistor sensing was used for molecular weight determinations. Analytical and molecular weight data are presented in Table I.

Infrared spectra (Table II) were recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Proton n.m.r. spectra (Table III) were recorded at 100 MHz on a Varian HA-100 spectrometer in $CDCl_3$ or CCl_4 solutions using tetramethylsilane as an internal standard. Carbon-13 n.m.r. spectra (Table IV) were recorded in $CDCl_3$ solutions on a pulsed Fourier transform Jeolco PFT-100 spectrometer operating at 25.0336 MHz with proton noise decoupling and deuterium lock using a 3 to 4 second repetition rate.

All preparative reactions were conducted in all glass apparatus with standard quickfit joints taking stringent precautions to exclude moisture. Benzene, isopropanol (Pr^iOH), tert-butanol (Bu^tOH), and tert-pentanol (tert-amyl alcohol) (Am^tOH) were dried by the usual methods. Aluminum isopropoxide was obtained from the National Chemical Laboratory in

TABLE III. Proton N.M.R. Data on Double Alkoxides of Aluminum with Alkaline Earth Metals.

Compound	Proton N.M.R. Spectrum, τ				
	Isopropyl		Ratio	t-Butyl	Ratio of Gem-dimethyl to t-butyl
	Gem-dimethyl (doublet)	CH (multiplet)			
Mg[Al(OPr ⁱ) ₄] ₂	8.80	5.83	6:1	—	—
Ca[Al(OPr ⁱ) ₄] ₂	8.79 } ratio	5.89	6:1	—	—
	8.61 } 5:3				
Sr[Al(OPr ⁱ) ₄] ₂	8.83 } ratio	5.85	6:1	—	—
	8.75 } 5:2				
Ba[Al(OPr ⁱ) ₄] ₂	8.77 (very broad)	5.82	6:1	—	—
Mg[Al(OPr ⁱ)(OBu ^t) ₃] ₂	8.80	5.84	6:1	8.72	2:9
Ca[Al(OPr ⁱ)(OBu ^t) ₃] ₂	8.57	5.86	6:1	8.70	2:9
				8.74 } ratio	
				8.77 } 1:1:1	
Sr[Al(OPr ⁱ)(OBu ^t) ₃] ₂	8.78	5.87	6:1	8.66	2:9
				8.69 } ratio	
				8.73 } 1:2:1	
Ba[Al(OPr ⁱ) ₂ (OBu ^t) ₂] ₂	8.61 } 1:1	5.84	6:1	8.70	2:3
	8.75 }				

TABLE IV. Carbon-13 N.M.R. Data on the Double Alkoxides Prepared in This Work.

Compound	Carbon-13 N.M.R. Spectrum, δ^a		
	Isopropyl Group		tert-Butyl Group
	CH	CH ₃	CH ₃
Mg[Al(OPr ⁱ) ₄] ₂	63.9 (46)	27.1 (59)	—
	63.7 (14)	26.5 (13)	—
Ca[Al(OPr ⁱ) ₄] ₂	64.0 (35)	27.5 (61)	—
	65.7 (23)	27.1 (35)	—
Sr[Al(OPr ⁱ) ₄] ₂	63.5 (51)	27.5 (64)	—
	64.8 (12)	25.4 (17)	—
Ba[Al(OPr ⁱ) ₄] ₂	63.5 (16)	27.9 (68)	—
Mg[Al(OPr ⁱ)(OBu ^t) ₃] ₂	65.1 (8)	27.3 (21)	33.3 (58)
Ba[Al(OPr ⁱ) ₂ (OBu ^t) ₂] ₂	63.2 (11)	27.8 (22)	33.6 (77)
	64.2 (9)	—	34.4 (40)

^aThe relative heights of the resonances are given in parentheses.

Poona, India, and distilled at 81 °C/0.3 mm before use. Alkaline earth metals (from Koch-Light Laboratories) and cleaned magnesium wire were used as received.

Reactions of Aluminum Isopropoxide with Magnesium in a 1:2 Molar Ratio in Isopropanol Solution

A solution of 4.76 g (23.3 mmol) of aluminum isopropoxide in 50 ml of isopropanol containing 0.01 g of mercuric chloride catalyst was boiled under reflux up to 40 hours with 0.28 g (11.7 g -atom) of magnesium metal. The magnesium metal dissolved

to form a colorless clear solution. Excess isopropanol and other volatile materials were removed under reduced pressure. Distillation of the resulting colorless viscous liquid gave an 85% yield of Mg[Al(OPrⁱ)₄]₂, b.p. 114 °C/0.2 mm.

Details of similar reactions are summarized in Table V.

Reaction of Ca[Al(OPrⁱ)₄]₂ with Excess tert-Amyl Alcohol in Benzene

Approximately 10 ml of tert-amyl alcohol were added to a solution of 1.75 g (3.1 mmol as monomer)

TABLE V. Reactions of Alkaline Earth Metals with Aluminum Isopropoxide in Isopropanol Solution.

Metal (g, mg atom)	Al(OPr ⁱ) ₃ g (mmol)	Reaction Time (hr)	Product	Yield % ^a
Mg (0.28, 11.7)	4.87 (23.9)	40	Mg[Al(OPr ⁱ) ₄] ₂	89
Mg (0.30, 12.5)	2.55 (12.5)	40	Mg[Al(OPr ⁱ) ₄] ₂	50
Ca (0.66, 16.5)	6.90 (33.8)	120	Ca[Al(OPr ⁱ) ₄] ₂	86
Ca (0.53, 13.2)	2.69 (13.2)	80	Ca[Al(OPr ⁱ) ₄] ₂	45
Sr (0.91, 10.4)	4.34 (21.3)	12	Sr[Al(OPr ⁱ) ₄] ₂	66
Sr (0.63, 7.2)	1.47 (7.2)	20	Sr[Al(OPr ⁱ) ₄] ₂	45
Ba (0.74, 5.4)	3.04 (14.9)	8	Ba[Al(OPr ⁱ) ₄] ₂	25
Ba (1.33, 9.7)	1.96 (9.6)	17	Ba[Al(OPr ⁱ) ₄] ₂	20

^aThese yields were determined after distillation or sublimation.

TABLE VI. Alcoholysis Reactions of M[Al(OPrⁱ)₄]₂^a.

M[Al(OPr ⁱ) ₄] ₂ (g, mmol)	Alcohol (g, mmol)	Reaction Time (hr)	Isopropanol in Azeotrope, g			Yield %
			Calcd	Found	Product	
Mg (1.02, 1.85)	t-BuOH (10, 35)	35	0.67	0.66	Mg[Al(OPr ⁱ)(OBu ^t) ₃] ₂	70
Mg (1.80, 3.27)	t-AmOH (15, 170)	25	1.61	1.58	Mg[Al(OPr ⁱ)(OAm ^t) ₃] ₂	80
Ca (0.76, 1.34)	t-BuOH (10, 135)	35	0.48	0.47	Ca[Al(OPr ⁱ)(OBu ^t) ₃] ₂	68
Ca (1.75, 3.09)	t-AmOH (15, 170)	30	1.01	1.05	Ca[Al(OPr ⁱ)(OAm ^t) ₃] ₂	72
Sr (1.25, 2.04)	t-BuOH (15, 203)	35	0.75	0.73	Sr[Al(OPr ⁱ)(OBu ^t) ₃] ₂	60
Sr (0.86, 1.40)	t-AmOH (10, 114)	30	0.51	0.50	Sr[Al(OPr ⁱ)(OAm ^t) ₃] ₂	65
Ba (1.20, 1.81)	t-BuOH (20, 270)	45	0.45	0.44	Ba[Al(OPr ⁱ) ₂ (OBu ^t) ₂] ₂	57
Ba (1.50, 2.26)	t-AmOH (25, 284)	40	0.56	0.55	Ba[Al(OPr ⁱ) ₂ (OAm ^t) ₂] ₂	60

^aAll of these alcoholysis reactions were conducted in boiling benzene solution.

of Ca[Al(OPrⁱ)₄]₂ in 50 ml of benzene. The solution was boiled under reflux for about 25 hr. The liberated isopropanol was continuously fractionated out azeotropically with benzene. Excess solvent was removed in vacuum. Distillation of the resulting viscous mass gave a 72% yield of Ca[Al(OPrⁱ)(OAm^t)₃]₂, b.p. 175 °C/0.05 mm as a viscous paste which solidified on keeping.

Reactions of Ca[Al(OPrⁱ)₄]₂ with Excess tert-Butyl Alcohol in Benzene

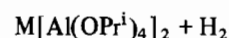
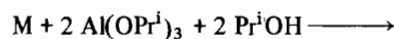
Approximately 15 ml of tert-butyl alcohol was added to a solution of 0.76 g (1.34 mmol as monomer) of Ca[Al(OPrⁱ)₄]₂ in 45 ml of benzene. The solution was boiled under reflux for approximately 30 hr. The liberated isopropanol was continuously removed azeotropically with benzene. Excess solvents were removed in vacuum. Vacuum sublimation of the white solid residue gave a 68% yield of Ca[Al(OPrⁱ)(OBu^t)₃]₂.

Details of similar alcoholysis reactions are summarized in Table VI.

Results and Discussion

Preparation of M[Al(OPrⁱ)₄]₂ (M = alkaline earth metal)

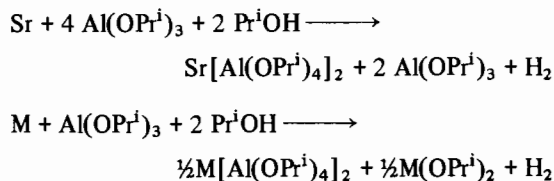
The alkaline earth metals react much more slowly than the alkali metals with alcohols to give alkoxides which are insoluble and non-volatile apparently because of a high degree of association to give polymeric species. In the presence of aluminum isopropoxide the rate of dissolution of the alkaline earth metals in isopropanol appears to increase significantly, particularly in the presence of a catalytic amount of mercuric chloride. From the resulting solutions double isopropoxides of aluminum with the alkaline earth metals can be isolated of the general formula M[Al(OPrⁱ)₄]₂ (M = Mg, Ca, Sr, and Ba). The overall reactions appears to be represented by the following equation:



In accord with this equation the optimum molar ratio of the alkaline earth metal to the aluminum isopropoxide is 1:2.

The double isopropoxides $M[Al(OPr^i)_4]_2$ ($M = Mg, Ca, Sr,$ and Ba) are more soluble in isopropanol and in other common organic solvents than the corresponding "simple" isopropoxides $[M(OPr^i)_2]_n$. The solubilities of the double isopropoxides decrease with increasing atomic number of the alkaline earth metal. The magnesium derivative $Mg[Al(OPr^i)_4]_2$ is a colorless viscous liquid at room temperature which can be distilled at $114^\circ C/0.1$ mm in $\sim 85\%$ yield. The products $Ca[Al(OPr^i)_4]_2$ and $Sr[Al(OPr^i)_4]_2$ are white crystalline solids which can be sublimed at $220^\circ-230^\circ C/0.1$ mm and $200^\circ C/0.2$ mm, respectively, in about 75–80% yields. The barium derivative $Ba[Al(OPr^i)_4]_2$ is also a solid which distills in poor yields ($\sim 25\%$) at $145^\circ C/0.05$ mm. Ebullioscopic determinations of the molecular weights of the double alkoxides $M[Al(OPr^i)_4]_2$ in benzene solution show that the molecular association increases with increasing atomic weight of the alkaline earth metal in the sequence $Mg(\text{monomeric}) \ll Ca(\text{dimeric}) < Sr(\text{dimeric}) < Ba(\text{dimeric in isopropanol})$ (Table I).

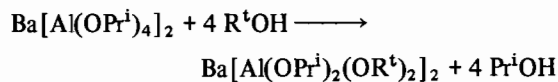
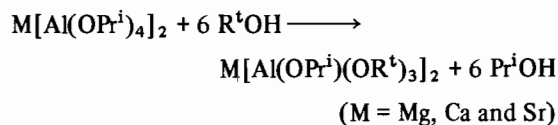
When the alkaline earth metals and aluminum isopropoxide are allowed to react in stoichiometries other than 1:2, the only double alkoxides obtained are the products $M[Al(OPr^i)_4]_2$ in every case. For example, the reaction between strontium metal and aluminum isopropoxide in isopropanol in a 1:4 molar ratio gives a colorless viscous liquid after removal of the solvent. Vacuum distillation of this liquid gives the following two fractions: a colorless viscous liquid, b.p. $90-95^\circ C/0.1$ mm identified as aluminum isopropoxide and a white crystalline solid subliming at $200^\circ C/0.1$ mm identified by analysis as $Sr[Al(OPr^i)_4]_2$. When the alkaline earth metals and aluminum isopropoxide are mixed in isopropanol in a 1:1 molar ratio and the reaction allowed to proceed to completion, the supernatant liquid gives the double alkoxides $M[Al(OPr^i)_4]_2$ leaving the alkaline earth isopropoxide $M(OPr^i)_2$ as an insoluble solid. These reactions thus can be represented by the following equations:



Alcoholysis of $M[Al(OPr^i)_4]_2$

Alcoholysis of metal alkoxides with higher alcohols not only provide an excellent route for the synthesis of higher alkoxides in some cases but sometimes provides valuable information on the structural features of the alkoxides [10]. Alcoholysis of the

double alkoxides $M[Al(OPr^i)_4]_2$ with the tertiary alcohols Bu^tOH and Am^tOH proceeds slowly in boiling benzene. The rates of the reactions slow down even further as the isopropoxy groups are replaced by the more highly branched tertiary alkoxy groups. In the reactions of $M[Al(OPr^i)_4]_2$ ($M = Mg, Ca,$ and Sr but not Ba) with the tertiary alcohols, six out of eight isopropoxy groups per mole of the double isopropoxide could be replaced. However, in the case of the barium derivative $Ba[Al(OPr^i)_4]_2$ even when attempts were made to push the reaction as far as possible by removing the liberated isopropanol by azeotropic distillation with benzene, only four out of eight isopropoxy groups per mol of the double isopropoxide could be replaced. These results can be represented by the following equations ($R^t =$ tert-butyl or tert-amyl):



The residual products were found by analysis to correspond to $M[Al(OPr^i)(OR^t)_3]_2$ ($M = Mg, Ca,$ and Sr) and $Ba[Al(OPr^i)_2(OR^t)_2]_2$ and are monomeric in boiling benzene in all cases. The tert-butoxy derivatives are white solids sublimable in vacuum whereas the tert-amoxy derivatives are colorless liquids distillable in vacuum. All of these products are soluble in common organic solvents.

Preparation of derivatives of the type $M[Al(OBu^t)_4]_2$ was also attempted by boiling the alkaline earth metals ($Mg, Ca, Sr,$ and Ba) with aluminum tert-butoxide in tert-butyl alcohol under reflux. In all of these reactions the rate of dissolution of the alkaline earth metal was so small that even after boiling for 15 days only trace amounts of the alkaline earth metals could be dissolved.

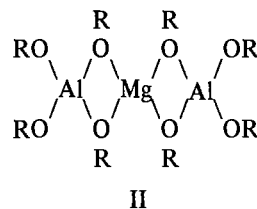
Spectroscopic Observations

Some information about the presence of two types of isopropoxy groups, *i.e.* terminal and bridging, in the products $M[Al(OPr^i)_4]_2$ can be obtained from the infrared spectra of these double alkoxides (Table II). As in the case of bridging isopropoxy groups the coordination occurring from oxygen to metal tends to drain electrons away from the carbon-oxygen bond and weaken it with a resulting lowering of the carbon-oxygen stretching frequency. In the products $M[Al(OPr^i)_4]_2$ the $\nu(C-O)$ frequencies of the terminal and bridging isopropoxy groups have been observed in the regions 1030 ± 5 cm^{-1} and 970 ± 5 cm^{-1} as strong bands with some splitting [11, 12]. Medium to strong bands at 690 and 672 cm^{-1} observ-

ed in all of the products can be assigned to $\nu(\text{Al-O})$ [14] and the bands at $\sim 440 \text{ cm}^{-1}$ are probably due to $\nu(\text{M-O})$ (Table II).

The proton and carbon-13 n.m.r. spectra of the double alkoxides have also been determined (Tables V and VI) but so far have proven to be of rather little value in helping to elucidate definitive structures for these compounds. The difficulty appears to arise from rapid interchange of bridging and terminal alkoxy groups relative to the n.m.r. time scale. For example, all of the double alkoxides must necessarily have some bridging and some terminal alkoxy groups for any conceivable structure; therefore the n.m.r. spectra should exhibit more than one type of alkoxy resonance in all of the double alkoxides. However, this is by no means the case. The most dramatic example occurs in the proton n.m.r. spectrum of the magnesium derivative $\text{Mg}[\text{Al}(\text{OPr}^i)_4]_2$ which exhibits a single type of isopropyl group even upon cooling to -70°C . This is inconsistent with any possible static structure for this compound including the obvious II ($\text{R} = \text{CH}(\text{CH}_3)_2$) containing tetrahedral magnesium and aluminum atoms. The carbon-13 n.m.r. spectrum of the barium derivative $\text{Ba}[\text{Al}(\text{OPr}^i)_4]_2$ also exhibits only one type of isopropyl group indicating that this type of apparent rapid interchange of alkoxy groups can also be observed in the carbon-13. n.m.r. spectrum and in dimeric rather than monomeric derivatives. At the present time we have no basis for interpreting the more complex patterns observed in the proton and carbon-13 n.m.r. spectra of some of the other double alkoxides (Tables III and IV). However, the generally non-simple ratios between the different types of alkoxy groups in these more complex n.m.r. spectra suggests mixtures of different species in solutions of these double alkoxides. The carbon-13 n.m.r. spectra, however, are useful for

confirming the presence of the two different types of alkoxy groups in the correct ratios in the mixed alkoxides such as $\text{Mg}[\text{Al}(\text{OPr}^i)(\text{O}i\text{Bu}^t)_3]_2$ and $\text{Ba}[\text{Al}(\text{OPr}^i)_2(\text{O}i\text{Bu}^t)_2]_2$ obtained in the alcoholysis reactions.



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