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Organic Derivatives of Aluminium.
Part I. Reactions of Alkanolamines with Aluminium Isopropoxide

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Abstract

Reactions of alkanolamines [R_1R_2NXOH; R_1 = H, CH_3, C_2H_5; R_2 = H, CH_3, C_2H_5 and X = $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CHCH_3$, $-C_6H_4CH_2CH_2-$] with aluminium isopropoxide in different molar ratios (1 to 3) yield compounds of the type $Al(OPr^i)_{3-n}(OXNR_1R_2)_n$, where 'n' can be 1, 2 and 3. Most of the derivatives are distillable liquids, soluble in common organic solvents and susceptible to hydrolysis even by atmospheric moisture. The new derivatives are characterized by elemental analysis, IR and ^1H NMR spectra. Molecular weight measurements of $Al(OPr^i)_{3-n}(OXNR_1R_2)_n$ reveal them to be tetrameric in nature.

Introduction

A survey of the literature reveals that in spite of fascinating chemistry [1–3] of aluminium alkoxides (particularly isopropoxide), alkoxyaminate derivatives of aluminium have received very little attention [4, 5]. It would be interesting to study the effect of amino (NH_2, NHR, NR_2) groups on the degree of association of the alkoxyaminate derivatives. A preliminary study of simple unsubstituted ethanolamine ($HOCH_2CH_2NH_2$) derivatives showed [5] that the products $Al(OPr^i)_{3-n}(OCH_2CH_2NH_2)_n$ are all non-volatile and insoluble in organic solvents. It was therefore considered of interest to see the effect of substituents on the NH_2 group in the above derivatives.

Results and Discussion

This paper deals with the reactions of aluminium isopropoxide with alkanolamines, *viz.*, 2-methylaminoethanol, 2-ethylaminoethanol, 3-dimethylamino-1-propanol, 1-diethylamino-2-propanol and p-aminophenethyl alcohol.

The reactions may be summarised as follows:

$$Al(OPr^i)_3 + nHOXNR_1R_2 \xrightarrow{\text{benzene}} Al(OPr^i)_{3-n}(OXNR_1R_2)_n + nPr^iOH\uparrow$$

(where 'n' varies from 1 to 3, R_1 = H, CH_3, C_2H_5; R_2 = H, CH_3, C_2H_5 and X = $-CH_2CH_2-$, $-CH_2CH_2CH_2-$; $-CH_2CHCH_3$, $-C_6H_4CH_2CH_2-$).

Aluminium isopropoxide was refluxed with alkanolamines in different stoichiometric ratios using benzene as solvent. The progress of the reaction was followed by the estimation of the azeotrope collected with the help of a fractionating column. It was observed that the liberation of first two moles of isopropanol was fast when aluminium isopropoxide and alkanolamines were reacted in 1:3 molar ratios. However, the liberation of the third mole was rather slow, but it could be achieved by prolonging the refluxing time, except in the case of the reaction with *p*-aminophenethyl alcohol. In fact, 1:3 molar ratio reaction between aluminium isopropoxide and *p*-aminophenethyl alcohol resulted in the formation of $Al(OPr^i)(OCH_2CH_2C_6H_4NH_2\text{-}p)_2$, an insoluble compound in benzene, even after 18 h of refluxing. Non-formation of $Al(OCH_2CH_2C_6H_4NH_2\text{-}p)_3$ could probably be explained on the basis of insoluble nature of $Al(OPr^i)(OCH_2CH_2C_6H_4NH_2\text{-}p)_2$, steric hindrance and hydrogen bonding.

The non-reactivity of the aminohydrogen in the reactions of aminoalkanols is confirmed by the fact that only one mole of isopropanol is liberated in 1:1 molar ratio reactions of the type:

$$Al(OPr^i)_3 + HOXNHR \longrightarrow Al(OPr^i)_2(OXNHR) + Pr^iOH\uparrow$$

(where X = $-CH_2CH_2-$ and R = CH_3, C_2H_5)

This shows that in this regard aluminium resembles boron [6], titanium and silicon but differs from alkyltins [7]. It may be noted that $Al(OPr^i)_{3-n}(OXNHR)_n$ products are stable to heat and can be volatilised unchanged, whereas the corresponding

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TABLE I. Physical Properties Comparison.

S. No.	Compound	Physical Nature	(B.P. (°C/mm)	Solubility in benzene	Molecular Complexity
1	$Al(OPr^i)_2(OCH_2CH_2NH_2)$	White solid	–	Slightly soluble	
2	$Al(OPr^i)(OCH_2CH_2NH_2)_2$	White solid		Slightly soluble	
3	$Al(OCH_2CH_2NH_2)_3$	White solid		Insoluble	
4	$Al(OPr^i)_2(OCH_2CH_2NHMe)$	Yellow solid	132/4.0	Soluble	3.94
5	$Al(OPr^i)(OCH_2CH_2NHMe)_2$	Yellow viscous liquid	168/2.0	Soluble	4.03
6	$Al(OCH_2CH_2NHMe)_3$	Yellow viscous liquid	190/2.0	Soluble	3.98

TABLE II. ^1H NMR Data (δ values).[a]

S. No.	Compound	Me	NCH_2	OCH_2	OPr^i	
					CH	CH_3
1	$HOCH_2CH_2NHMe$	2.40s	2.67t	3.64t		
2	$Al(OPr^i)_2(OCH_2CH_2NHMe)$	2.40s	2.70t	3.72t	3.74–4.10m	1.05d
3	$Al(OPr^i)(OCH_2CH_2NHMe)_2$	2.44s	2.70m	3.74t	3.80–4.10m	1.20d
4	$Al(OCH_2CH_2NHMe)_3$	2.44s	2.70t	3.76t		

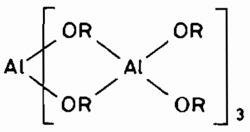
[a] Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet.

boron derivatives, even if formed in solution disproportionate on distillation to give the component tris-ester.

The volatility and solubility of $Al(OPr^i)_{3-n}(OXNR_1R_2)_n$ compared to those of $Al(OPr^i)_{3-n}(OXNH_2)_n$ derivatives can be understood on the basis of lesser hydrogen bonding in the former derivatives. It also appears that volatility and solubility improves with substituted alkanolamines, as shown by the data given in Table I.

Most of the new derivatives reported in Table III are liquids, soluble in common organic solvents and hygroscopic in nature.

In view of the observed tetrameric nature, it is plausible to suggest that these derivatives have the structure of the tetrameric aluminium isopropoxide type:



IR Spectra

The IR spectra of these compounds were recorded in the region 4000–400 cm^{-1}. A comparison of the IR spectra of the new derivatives with those of aluminium isopropoxide and aminoalcohols exhibits the following changes:

(i) The disappearance of the νO–H band present in the region 3650–3590 cm^{-1} in aminoalcohols;

(ii) The presence of the νN–H band in the region 3250–3150 cm^{-1}, which is lower by 30 to 120 cm^{-1} in comparison to its position in the corresponding N-alkylaminoalcohols;

(iii) The appearance of νAl–O bands in the region 680–540 cm^{-1} in the products being reported.

The lowering of the N–H stretching frequency appears to indicate molecular association in these derivatives. The appearance of νN–H band in the spectra also emphasizes the non-reactivity of the hydrogen present on nitrogen. The important characteristic bands of the aminoalcohol moiety in these derivatives are in good agreement with the assignments for this part in such complexes of boron [6] and gallium [8]. Earlier literature [9] suggests the presence of a set of five bands in the region 699–539 cm^{-1} for νAl–O stretching and these bands in turn were ascribed to the presence of terminal and bridging groups in polymeric alkoxides [10]. Absence of any significant bands in the region for aminoalcohols and appearance of bands in the region 680–540 cm^{-1} indicates similarity with aluminium isopropoxide.

^1H NMR Spectra

The ^1H NMR spectra of 2-methylaminoethanol and the derived derivatives do not differ much and the various signals are summarised in Table II.

TABLE III. Reactions of Aluminium Isopropoxide with Aminoalcohols. Analytical Data.

S. No.	Reactants (g)		Molar ratio	Product and Nature	Yield (%)	B.P. (°C/mm)	Analyses			Mol. Wt.
							Pr^iOH in azeotrope (g) Found (Calcd)	Al % Found (Calcd)	N % Found (Calcd)	Found (Calcd)
1	$Al(OPr^i)_3$	6.74	1:1	$Al(OPr^i)_2(OCH_2CH_2NHMe)$	60	132/4.0	1.90	12.31	6.33	862
	$MeNHCH_2CH_2OH$	2.55		Yellow solid			(1.98)	(12.30)	(6.38)	(219)
2	$Al(OPr^i)_3$	2.42	1:2	$Al(OPr^i)(OCH_2CH_2NHMe)_2$	81	168/2.0	1.40	11.33	11.76	943
	$MeNHCH_2CH_2OH$	1.81		Yellow viscous solid			(1.42)	(11.51)	(11.95)	(234)
3	$Al(OPr^i)_3$	2.05	1:3	$Al(OCH_2CH_2NHMe)_3$	63	190/2.0	1.78	10.65	16.73	994
	$MeNHCH_2CH_2OH$	2.28		Yellow viscous liquid			(1.82)	(10.81)	(16.83)	(250)
4	$Al(OPr^i)_3$	3.45	1:1	$Al(OPr^i)_2(OCH_2CH_2NHEt)$	67	126/0.6	1.00	11.48	5.90	917
	$EtNHCH_2CH_2OH$	1.52		Yellow solid			(1.02)	(11.56)	(6.00)	(233)
5	$Al(OPr^i)_3$	4.23	1:2	$Al(OPr^i)(OCH_2CH_2NHEt)_2$	72	146–147/0.6	2.42	10.20	10.53	1070
	$EtNHCH_2CH_2OH$	3.76		Colourless viscous liquid			(2.49)	(10.28)	(10.68)	(263)
6	$Al(OPr^i)_3$	3.24	1:3	$Al(OCH_2CH_2NHEt)_3$	75	150/0.5	2.80	9.17	14.28	1150
	$EtNHCH_2CH_2OH$	4.23		colourless viscous liquid			(2.86)	(9.25)	(14.40)	(292)
7	$Al(OPr^i)_3$	3.86	1:1	$Al(OPr^i)_2(OCH_2CH_2CH_2NMe_2)$	53	134/0.6	1.14	10.87	5.53	1000
	$Me_2NCH_2CH_2CH_2OH$	1.95		Colourless viscous liquid			(1.14)	(10.91)	(5.66)	(247)
8	$Al(OPr^i)_3$	3.12	1:2	$Al(OPr^i)(OCH_2CH_2CH_2NMe_2)_2$	51	164/0.6	1.81	9.21	9.52	1147
	$Me_2NCH_2CH_2CH_2OH$	3.16		Colourless viscous liquid			(1.84)	(9.29)	(9.64)	(290)
9	$Al(OPr^i)_3$	3.25	1:3	$Al(OCH_2CH_2CH_2NMe_2)_3$	100[b]	[a]	2.82	8.04	12.41	1301
	$Me_2NCH_2CH_2CH_2OH$	4.93		White solid			(2.87)	(8.09)	(12.59)	(334)
10	$Al(OPr^i)_3$	2.37	1:1	$Al(OPr^i)_2(O\underset{CH_3}{\underset{\vert}{C}}HCH_2NEt_2)$	90	129–30/0.6	0.68	9.80	5.00	
	$Et_2NCH_2CH(OH)CH_3$	1.57		Colourless viscous liquid			(0.70)	(9.80)	(5.08)	
11	$Al(OPr^i)_3$	2.48	1:2	$Al(OPr^i)(O\underset{CH_3}{\underset{\vert}{C}}HCH_2NEt_2)_2$	89	135–36/0.6	1.33	7.78	8.01	
	$Et_2NCH_2CH(OH)CH_3$	3.06		Colourless viscous liquid			(1.40)	(7.78)	(8.08)	
12	$Al(OPr^i)_3$	2.12	1:3	$Al(O\underset{CH_3}{\underset{\vert}{C}}HCH_2NEt_2)_3$	62	137–38/0.5	2.07	6.46	9.98	
	$Et_2NCH_2CH(OH)CH_3$	4.58		Colourless viscous liquid			(2.09)	(6.46)	(10.06)	
13	$Al(OPr^i)_3$	2.79	1:1	$Al(OPr^i)_2(OCH_2CH_2C_6H_4NH_2\text{-}p)$	97[b]	[a]	0.80	9.51	4.95	
	$p\text{-}NH_2C_6H_4CH_2CH_2OH$	1.88		Gum like sticky solid (insoluble in benzene)			(0.82)	(9.59)	(4.98)	
14	$Al(OPr^i)_3$	2.11	1:2	$Al(OPr^i)(OCH_2CH_2C_6H_4NH_2\text{-}p)_2$	100[b]	[a]	1.22	7.46	7.76	
	$p\text{-}NH_2C_6H_4CH_2CH_2OH$	2.84		Amorphous buff coloured solid (insoluble in benzene)			(1.24)	(7.50)	(7.81)	

[a] Could not be distilled uptil 240 °C/0.6 mm pr. [b] Yield of undistilled product.

Experimental

Stringent precautions were taken to exclude moisture throughout the experiments. Benzene and alcohols were dried by following literature procedures [11] and aluminium isopropoxide was prepared by literature methods. Isopropanol in the azeotrope was estimated by an oxidation method [12].

Aluminium was estimated gravimetrically as oxinate and nitrogen by the Kjeldahl method.

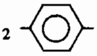
Molecular weights were determined in a semimicro ebulliometer (Gallenkamp) in boiling benzene. IR spectra were recorded on a Perkin-Elmer 735B spectrophotometer (4000–400 cm^{-1}) as neat liquid films or as solutions in CCl_4 and ^1H NMR spectra on a Perkin-Elmer R 32 spectrometer (MHz 90) in $CDCl_3$ using TMS as internal standard.

Reaction between Aluminium Isopropoxide and 2-Methylaminoethanol in 1:1 Molar Ratio

To 6.74 g of aluminium isopropoxide was added 2.55 g of 2-methylaminoethanol, followed by ~50 ml of benzene. The contents were shaken and refluxed for 6 h. The benzene-isopropanol azeotrope was removed till the boiling point of the distillate rose to and remained constant at 80 °C. Excess solvent was removed under reduced pressure (4 mm) at room temperature yielding a yellow solid, which was purified by distillation at 132 °C/4.0 mm pressure (60% yield).

Similarly, the reactions of aluminium isopropoxide with 2-methylaminoethanol in 1:2 and 1:3 molar ratios and other aminoalcohols in different molar ratios resulted in the formation of the desired products and are summarised in Table III.

Attempted 1:3 Molar Ratio Reaction between Aluminium Isopropoxide and p-*Aminophenethyl Alcohol*

To 2.26 g of aluminium isopropoxide was added 4.57 g of *p*-aminophenethyl alcohol, followed by ~60 ml benzene. The contents were shaken and refluxed for 18 h; when no more isopropanol was detected in the azeotrope the excess of benzene was removed by a pump (4 mm) at room temperature, a buff coloured solid was obtained. On distillation, ~1.4 g of *p*-aminophenethyl alcohol was removed (b.p. 145 °C/ 3mm) and amorphous buff-coloured solid was obtained in the residue (3.98 g), which corresponded in composition to $Al(OPr^i)(OCH_2CH_2$  $NH_2)_2$. [Al 7.42% (Found), 7.50% (Calcd.); N 7.71% (Found), 7.81 (Calcd.)] The residue does not distil until 240 °C/0.6 mm pr. and remains unaffected by heat.

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