

INSERTION REACTIONS OF DIALKYLALUMINIUM DERIVATIVES

VII. PREPARATIVE APPLICATION OF THE REACTIONS OF (DIMETHYLALUMINO)(TRIMETHYLSILYL)METHYLAMINE WITH CARBONYL COMPOUNDS

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SUMMARY

Five types of reactions between (dimethylalumino)(trimethylsilyl)methylamine $\text{Me}_2\text{Al-NMe-SiMe}_3$ and carbonyl compounds (ketones, esters and amides) were found to occur, depending on the structure of the carbonyl compounds. Among others two new interesting compounds, 4-(dimethylamino)-4-(methylamino)-3-buten-2-one $\text{CH}_3\text{-CO-CH=C(NHMe)NMe}_2$ from acetamide and *N,O*-dimethylacylimidatetetramethyldialumoxane $\text{R-C(OMe)=NMe}_2 \cdot (\text{Me}_2\text{Al})_2\text{O}$ from esters could be prepared.

INTRODUCTION

In previous papers¹⁻⁶, various insertion reactions and addition/elimination reactions of Et_2AlX ($\text{X}=\text{NR}_2$, OR or SR) and $(\text{Et}_2\text{Al})_2\text{S}$ with heterocumulenes or unsaturated compounds have been reported. From these studies, several preparative methods novel in organic synthesis were disclosed. As an extension of these studies, we have attempted to prepare Al-X-Si compounds and examine the reactivity of these new Al-X-Si compounds toward organic compounds.

Only few compounds of the type Al-X-Si have been reported so far: $\text{R}_2\text{Al-NH-SiR}_3$ ⁷, $(\text{R}_2\text{N})_2\text{Al-N(SiMe}_3)_2$ ^{8a,b}, $\text{Et}_n\text{Al(S-SiEt}_3)_{3-n}$ ($n=1, 2$)⁹ and $\text{Cl}_2\text{Al-S-SiMe}_3$ ¹⁰. Schmidbauer and his co-workers have studied in detail compounds $\text{R}_2\text{Al-O-SiMe}_3$ as representatives of a series of isosteric compounds^{11a-f}.

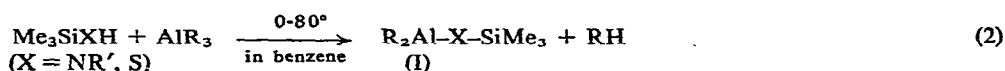
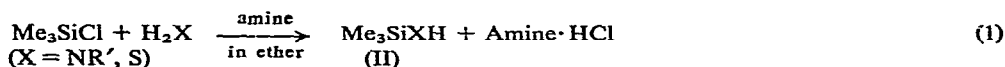
In this paper, the following new five compounds have been prepared: $\text{Me}_2\text{Al-NMe-SiMe}_3$ (Ia), $\text{Me}_2\text{Al-NPh-SiMe}_3$ (Ib), $\text{Et}_2\text{Al-NPh-SiMe}_3$ (Ic), $\text{Me}_2\text{Al-S-SiMe}_3$ (Id) and $\text{Et}_2\text{Al-S-SiMe}_3$ (Ie). The reactivity of these Al-X-Si compounds might be expected to be different from those of $\text{R}_2\text{Al-X}$ compounds. As expected, the reactions of Al-X-Si compounds with carbonyl compounds were found to open a new area in synthetic chemistry. Among five new Al-X-Si compounds, in particular (Ia) gave interesting results in the reactions with ketones, esters and amides.

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RESULTS AND DISCUSSION

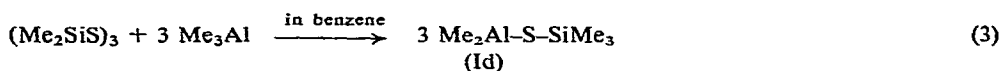
1. Preparations of $R_2Al-X-SiMe_3$ (I) compounds

(Trimethylsilyl)(dimethylalumino)methylamine (Ia), (trimethylsilyl)(dimethylalumino)aniline (Ib) and (trimethylsilyl)(diethylalumino)aniline (Ic) were prepared according to eqns. (1) and (2). (Trimethylsilyl)methylamine (IIa) ($X=NMe$) and



N-(trimethylsilyl)aniline (IIb) ($X=NPh$) were obtained in a yield of 61% and 24%, respectively. (Ia) could be prepared quantitatively in the reaction of (IIa) with Me_3Al and was found to be a dimer in benzene solution. (Ib) and (Ic) were obtained analogously, but with lower yields (21–23%). (Ia)–(Ic) were white crystalline solids. Their b.p., m.p. and yields are shown in Table 1, and their IR and NMR spectral data in Table 2.

Trimethylsilanethiol (IIc) ($X=S$) was prepared in the reaction of Me_3SiCl with H_2S by the method of Champetier *et al.*¹² (yield 11%). Trimethylsilyl diethylaluminium sulphide (Ie) was obtained in a yield of 60% from the reaction between Et_3Al and (IIc). However, trimethylsilyl dimethylaluminium sulphide (Id) could not be prepared



analogously, and an alternative method was adopted, eqn. (3). Both (Id) and (Ie) are white crystalline solids. Their IR and NMR spectral data are shown in Table 2.

2. Reactions of $Me_2Al-NMe-SiMe_3$ (Ia) with ketones

Four different ketones were used in the reactions with (Ia): diisopropyl ketone, pinacolone, acetophenone and benzophenone. An equimolar mixture of the ketone and (Ia) in benzene solution was kept at room temperature for 12–24 h. The colour of the solution changed from colourless to yellow. This was accompanied by the appearance of a new IR absorption band $\nu(C=N)$ together with the decrease of $\nu(C=O)$ of the ketone. In the cases of pinacolone and acetophenone, the reactions were completed

TABLE 1

B.P., M.P. AND YIELDS OF $R_2Al-X-SiMe_3$ (I)

(I)	R	X	B.p. ($^\circ C/mm$)	M.p. ($^\circ C$)	Yield (%)
(Ia)	Me	NMe	82-84/0.24	58-61	96
(Ib)	Me	NPh	103-108/1.0	77-80	23
(Ic)	Et	NPh		81-84	21
(Id)	Me	S			20
(Ie)	Et	S			60

after 15 h at room temperature, while heating at 80° for more 24 h was necessary in the reaction with diisopropyl ketone or benzophenone. The products obtained are tabulated in Table 3. IR and NMR spectral data are presented in Table 4.

TABLE 2

 IR AND NMR SPECTRAL DATA OF $R_2Al-X-SiMe_3$ (I)

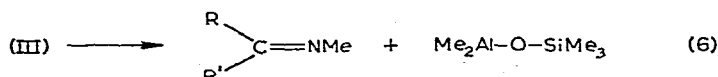
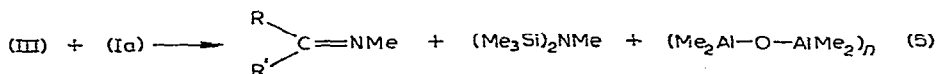
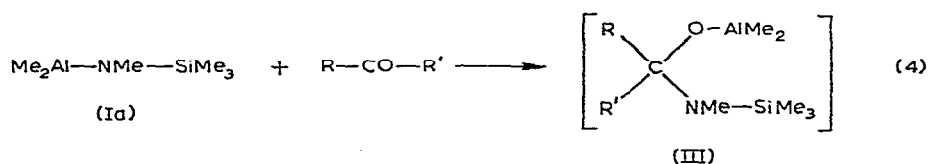
(I)	IR (cm^{-1} in benzene)			NMR (τ in benzene)	
	$\nu(Si-C)$	$\nu(Al-X-Si)$	Others	$\tau(AIR_2)$	$\tau(SiMe_3)$
(Ia)	1253	838	1195, 956, 757	10.44(s)	9.85(s)
(Ib)	1250	837	1600, 1480, 1295, 898, 755	10.22(s)	10.11(s)
(Ic)	1252	841	1600, 1480, 1295, 899, 760	8.77(t)	9.83(s)
				9.68(q)	
(Id)	1192	845	775	10.32(s)	10.13(s)
(Ie)	1252	835	757, 615	8.76(t)	9.79(s)
				9.71(q)	

TABLE 3

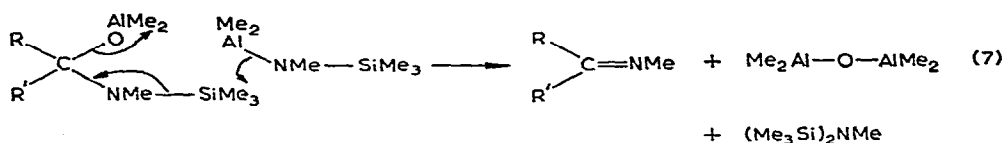
REACTION PRODUCTS OF (Ia) WITH KETONES

Ketone	Products (%)
i-Pr ₂ CO	i-Pr ₂ C=NMe (65), i-PrCO-CMe ₂ -AlMe ₂ (30), (Me ₃ Si) ₂ NMe (73)
t-BuMeCO	t-BuMeC=NMe (38), t-BuCOCH=CMe-t-Bu (11), (Me ₃ Si) ₂ NMe (55)
MePhCO	MePhC=NMe (14), PhMeC(OAlMe ₂) (NMeSiMe ₃) (50), Me ₂ Al-O-SiMe ₃ (11), (Me ₃ Si) ₂ NMe (48)
Ph ₂ CO	Ph ₂ C=NMe + Me ₂ Al-O-SiMe ₃ (42), Ph ₂ CH-O-AlMe ₂ (43), (Me ₃ Si) ₂ NMe (25)

The product composition suggests that the reactions between (Ia) and ketones take place through the intermediate (III), followed by path (5) or (6). In the cases of aliphatic ketones, diisopropyl ketone and pinacolone, the reaction paths would be



(4) + (5). Reaction (6) involves an intramolecular β -elimination of (III), which occurred in the reactions of acetophenone and benzophenone with (Ia). Reaction (5) may be explained by scheme (7). The adduct (III) could be isolated in 50% yield in the reaction



of acetophenone. On the other hand, the reaction of (Ia) with benzophenone gave benzhydroxydimethylaluminium (IV) Ph₂CH-O-AlMe₂ (43% yield), which would be an addition (reduction) product of the ketone with Me₂AlH. Me₂AlH could not be isolated, but the formation of Me₂AlH might be interpreted in terms of thermal disproportionation of (Me₂Al)₂O, a product of reaction (5).

3. Reactions of Me₂Al-NMe-SiMe₃ (Ia) with esters

Both the equimolar and 2/1 reactions of (Ia) with methyl acetate in benzene solution occurred at room temperature, affording three products: *N,O*-dimethyl acetimidate tetramethyldialumoxane (Va) (b.p. 32-35°/0.20 mm) 54, 65%, *N*-methyl-

TABLE 4

NMR AND IR SPECTRAL DATA OF THE PRODUCTS FORMED IN THE REACTIONS OF (Ia) WITH KETONES

Products	NMR (τ in CCl ₄)	IR (cm ⁻¹ in C ₆ H ₆)
(Me ₃ Si) ₂ NMe	9.95(s), 7.65(s)	ν (Si-C) 1250
i-Pr ₂ C=NMe	9.07(d), 7.33(h), 7.00(s)	ν (C=N) 1653
i-PrCO-CMe ₂ -AlMe ₂ (II')	10.40(s), 8.95(d), 8.59(s), 8.29(s), 7.53(d) (6/6/3/3/1)	ν (C=O) 1710
t-BuMeC=NMe	8.95(s), 8.60(s), 7.05(s)	ν (C=N) 1650
t-BuCO-CH=CMe-t-Bu	9.01(s), 8.89(s), 8.00(s), 3.72(br, s) (9/9/3/1)	ν (C=O) 1675
PhMeC=NMe	8.26(s), 6.88(s)	ν (C=N) 1633
Me ₂ Al-O-SiMe ₃	10.44(s), 9.88(s)	ν (Si-C) 1255
PhMeC(OAlMe ₂)(NMeSiMe ₃) (III)	10.44(s), 9.88(s), 8.55(s), 7.63(s) (2/3/1/1)	
Ph ₂ C=NMe	6.82(s)	ν (C=N) 1625
Ph ₂ CH-O-AlMe ₂ (IV)	11.18(s), 4.18(s), 2.82(s) (6/1/10)	ν (Al-O-C) 1191

disilazane 44, 39% and trimethylmethoxysilane 32, 18%. When methyl benzoate was reacted with (Ia), the reaction could be completed after heating the mixture at 80° for 44. The yields of the products are shown in Table 5. The main product, *N,O*-dimethylbenzimidatetetramethyldialumoxane (Vb) (b.p. 82-83°/0.3 mm) was obtained in excellent yield. IR and NMR spectral data, analysis and mol.wt. determination identified the structure of (Va) and (Vb).

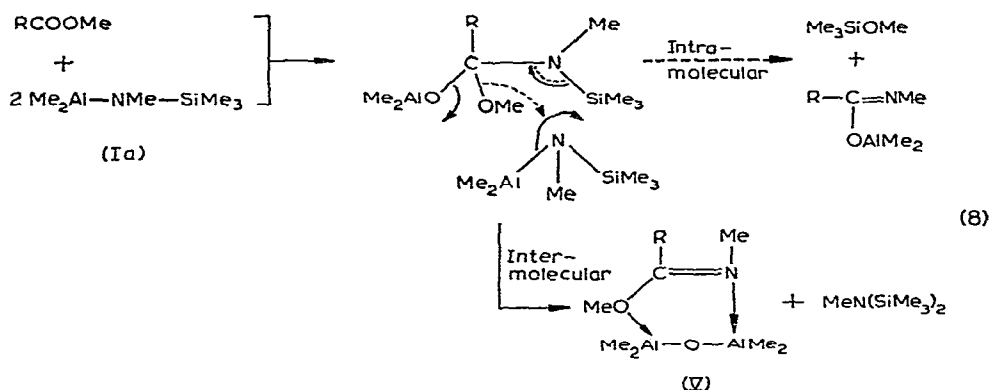
(Va) and (Vb) seem to be interesting compounds, in which monomeric tetraalkyldialumoxane is fixed by coordinating with an acylimidate molecule. (R₂Al)₂O

TABLE 5

YIELDS OF THE PRODUCTS FORMED IN THE REACTIONS OF (Ia) WITH ESTERS

Ester	Molar ratio (Ia)/ester	Products (%)			Recovered reactants (%)	
		(V)	(Me ₃ Si) ₂ NMe	Me ₃ SiOMe	Ester	(Ia)
MeCOOMe	1/1	54	44	32	5	0
	2/1	65	39	18	0	0
PhCOOMe	1/1	74	54	12	33	0
	2/1	78	51	8	0	0
t-BuCOOMe	1/1	0	0	3	15	48
	2/1	0	0	5	7	63

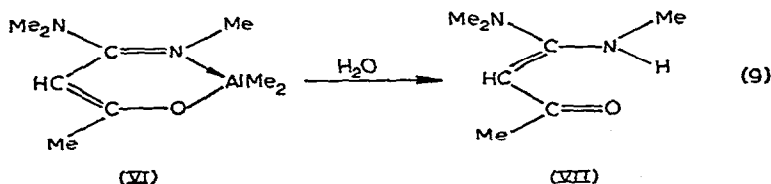
has been known to exist in polymeric form and is a useful catalyst for the stereospecific polymerization of alkylene oxide and acetaldehyde^{13,14}. The reaction between (Ia) and esters might be explained in terms of the following scheme:



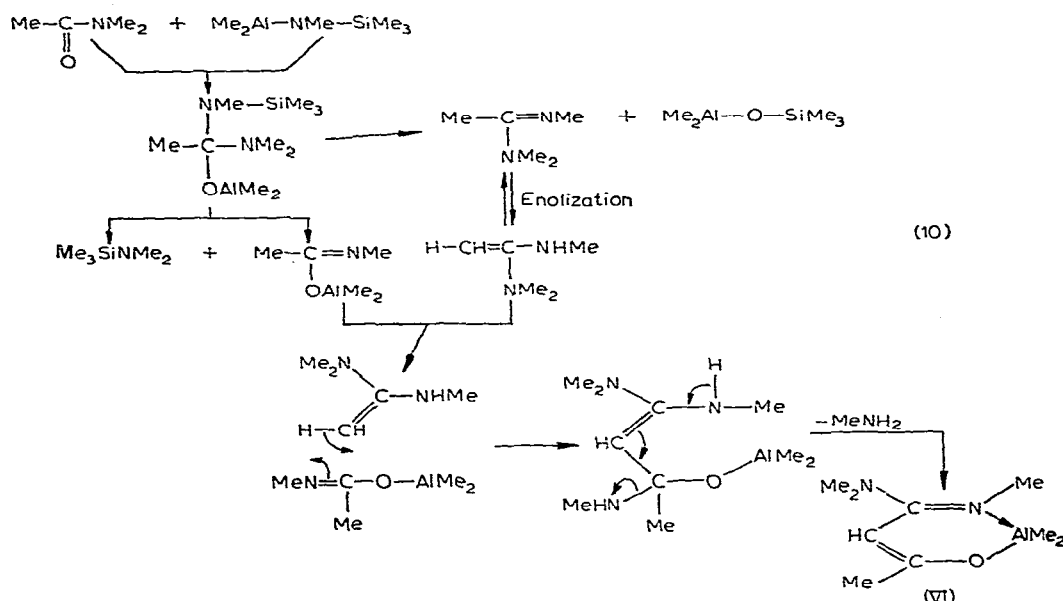
In the case of methyl pivalate, the steric hindrance prevented the reaction with (Ia) (cf. Table 5).

4. Reaction of Me₂Al-NMe-SiMe₃ (Ia) with *N,N*-dimethylacetamide

The reaction between (Ia) and *N,N*-dimethylacetamide MeCONMe₂ takes place at room temperature, giving Me₃SiNMe₂ 33%, MeN=CMe(NMe₂) 10% and 4-(dimethylamino)-4-(methylimino)-2-(dimethylalumoxy)-2-butene (VI) (m.p.95–98°) in 30% yield. Compound (VI) (white crystals) was identified by NMR, IR spectra, mol.wt. and analysis, together with the formation of (VII) on hydrolysis.



The formation of $\text{MeN}=\text{CMe}(\text{NMe}_2)$ and (VI) may be understood by assuming an enolization of $\text{Me}_2\text{N}=\text{CMe}(\text{NMe}_2)$ followed by a condensation reaction as shown in eqn. (10).



5. Reactions of $\text{R}_2\text{Al}-\text{X}-\text{SiMe}_3$ (I) with isocyanates

As isocyanates may be considered as a kind of carbonyl compound, the reactions of $\text{Me}_2\text{Al}-\text{NMe}-\text{SiMe}_3$ (Ia) and $\text{Et}_2\text{Al}-\text{NPh}-\text{SiMe}_3$ (Ic) with phenyl or methyl isocyanate were also investigated. As shown in Table 6, three sets of reactions were performed by heating the reactants in benzene at 80° for two days. The products obtained were carbodiimide, $\text{Me}_2\text{Al}-\text{O}-\text{SiMe}_3$ and $(\text{Me}_3\text{Si})_2\text{NR}$. Yields are shown in Table 6. NMR and IR data of these products are shown in Table 7.

The reaction between $\text{Et}_2\text{Al}-\text{S}-\text{SiMe}_3$ (Ie) and phenyl isocyanate gave 49% yield of phenyl isothiocyanate and 39% of $\text{Et}_2\text{Al}-\text{O}-\text{SiMe}_3$.

TABLE 6

YIELDS OF THE PRODUCTS FORMED IN REACTIONS OF $\text{Al}-\text{N}-\text{Si}$ COMPOUNDS WITH ISOCYANATES

(I)	Isocyanate	Products	Yield (%)
(Ia)	MeNCO	$\text{Me}-\text{N}=\text{C}=\text{N}-\text{Me}$	7
		$\text{Me}_2\text{Al}-\text{O}-\text{SiMe}_3$	14
		$(\text{Me}_3\text{Si})_2\text{NMe}$	30
(Ia)	PhNCO	$\text{Ph}-\text{N}=\text{C}=\text{N}-\text{Me}$	3
		$\text{Me}_2\text{Al}-\text{O}-\text{SiMe}_3$	19
		$(\text{Me}_3\text{Si})_2\text{NMe}$	36
(Ic)	PhNCO	$\text{Ph}-\text{N}=\text{C}=\text{N}-\text{Ph}$	5
		$\text{Et}_2\text{Al}-\text{O}-\text{SiMe}_3$	31
		$(\text{Me}_3\text{Si})_2\text{NPh}$	15

6. Reaction of $\text{Me}_2\text{Al-S-SiMe}_3$ (Id) with xanthone

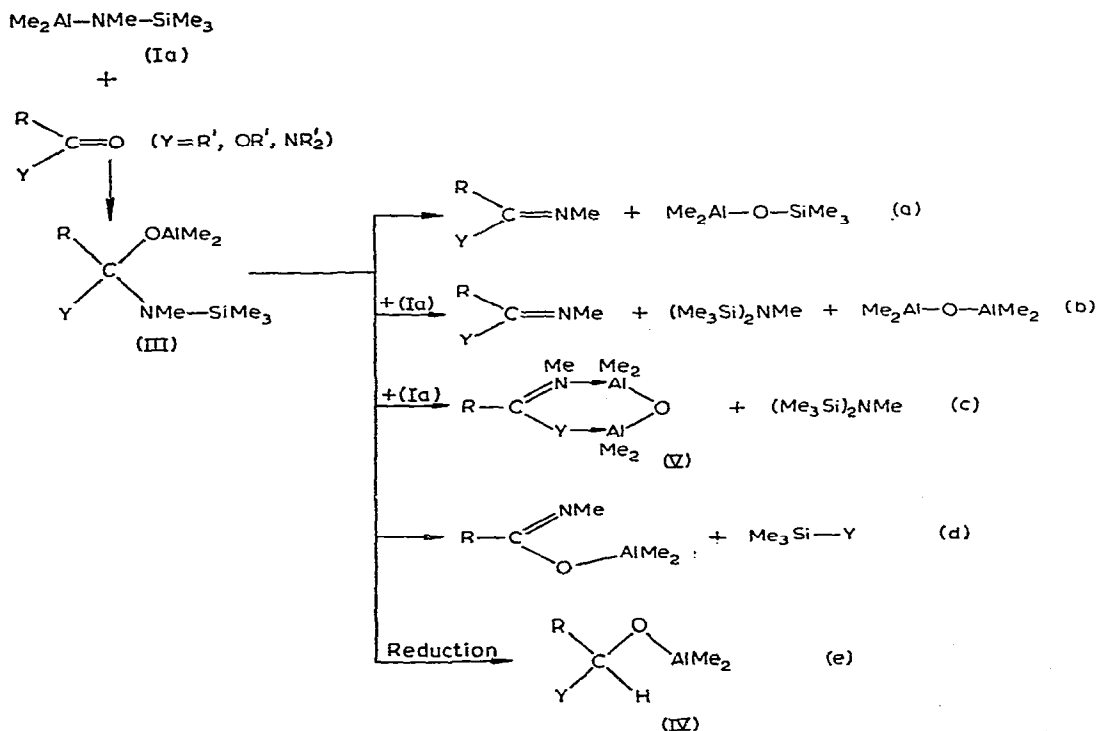
The reaction of xanthone with (Id) occurred at room temperature to give 65% yield of thioxanthone, quite similar to the reaction with $(\text{Et}_2\text{Al})_2\text{S}$, which was reported previously⁴.

TABLE 7

NMR AND IR SPECTRAL DATA OF THE PRODUCTS MENTIONED IN TABLE 6

Product	NMR (τ in benzene)	IR (cm^{-1} in benzene)
Me-N=C=N-Me	7.05(s)	$\nu(\text{N=C=N})$ 2140
Me-N=C=N-Ph	7.55(s)	$\nu(\text{N=C=N})$ 2140, 1594, 1500
Ph-N=C=N-Ph	2.9(m) (in C_6D_6)	$\nu(\text{N=C=N})$ 2135
$\text{Et}_2\text{Al-O-SiMe}_3$	8.80(t), 9.72(q), 9.84(s)	1260, 1197, 840, 760
$(\text{Me}_3\text{Si})_2\text{NPh}$	9.92(s), 2.87(s) (in CCl_4)	1252, 1050, 900, 840.

In conclusion, among five new $\text{R}_2\text{Al-X-SiMe}_3$ (Ia-Ie) compounds, the reactions of $\text{Me}_2\text{Al-NMe-SiMe}_3$ (Ia) with ketones, esters, amides and isocyanates may be classified according to five reaction types, as shown in the following scheme:



For reactions of (Ia) with aliphatic ketones, the reaction path would be (b). Acetophenone afforded the adduct (III) and the products of path (a). The formation of (IV) occurred only in the case of benzophenone (path c). The reactions of methyl acetate

and methyl benzoate took place through paths (b), (c) and (d), giving an interesting Al-O-Al complex.

The reaction with *N,N*-dimethylacetamide was found to be more complicated, but it probably involves paths (a) and (d), and then the coupling product (VI) would be obtained. In the case of isocyanates, path (b) would be preponderant.

EXPERIMENTAL

All reactions and spectroscopic measurements were carried out under dry nitrogen. The solvents used were carefully dried with metallic sodium and calcium hydride. IR and NMR spectra were recorded with JASCO IR-S and DS-403G, and on JEOL C-60HL spectrometers, respectively.

Preparation of (dimethylalumino)(trimethylsilyl)methylamine (Ia)

Trimethylchlorosilane (31.6 g, 0.21 mole) was added dropwise to anhydrous methylamine (31 g, 1.0 mole) cooled in dry ice/acetone bath. The mixture was kept at 35° for 5 h, during which excess of methylamine evaporated. After centrifuging methylaminehydrochloride salt, distillation of the ether extract gave (trimethylsilyl)-methylamine, Me₃SiNHMe, b.p. 69–71° in 61% yield.

The solution of Me₃SiNHMe (8.11 g, 0.079 mole) in 10 ml benzene was added dropwise for ½ h to trimethylaluminium Me₃Al (5.66 g, 0.079 mole) in 20 ml benzene cooled in ice bath with stirring. Then the mixture was gradually heated to 60° and kept at 60° for 5 h, giving quantitative amounts of methane (1880 ml, calcd. 1870 ml). After removal of the solvent, (dimethylalumino)(trimethylsilyl)methylamine (Ia) was obtained (b.p. 82–84°/0.25 mm; 11.8 g, yield 96%), white crystals (benzene), m.p. 58–61°. (Found: C, 44.98; H, 11.19; Al, 19.34. C₆H₁₈AlNSi calcd.: C, 45.24; H, 11.39; Al, 16.94%). Molecular weight determination in benzene showed the dimeric structure of (Ia) (*n* = 2.08). IR and NMR data are shown in Table 2.

Preparation of N-(dimethylalumino)-N-(trimethylsilyl)aniline (Ib) and N-(diethylalumino)-N-(trimethylsilyl)aniline (Ic)

The preparations of (Ib) and (Ic) were performed in the same manner as in the case of (Ia). These compounds were isolated as white crystals. Their yield, m.p., b.p., IR and NMR data are shown in Tables 1 and 2.

Preparation of dimethylaluminium trimethylsilyl sulphide (Id)

Hexamethylcyclotrisilthiane (Me₂SiS)₃, b.p. 136–138°/0.20 mm was prepared by the reaction between dimethyldichlorosilane and hydrogen sulphide (yield, 31%)¹⁵. (Me₂SiS)₃ (1.31 g, 14.5 mmole) in 5 ml benzene was added dropwise to Me₃Al (1.05 g, 14.5 mmole) in 15 ml benzene cooled in ice bath with stirring. The mixture was kept at 80° for 45 h with stirring. After removal of the solvent, a white solid was obtained, which was purified by washing several times with *n*-hexane, affording brilliant white crystals (0.91 g) of (Id). (Id) was identified by IR and NMR spectra.

Preparation of diethylaluminium trimethylsilyl sulphide (Ie)

Initially, trimethylsilanethiol, b.p. 76–78.5° was obtained in 11% yield by Champetier's method^{16,12}. τ (benzene): 9.87 (s, 9H; Me₃Si) and 4.17 (br, s, 1H; SH). $\nu_{\max}$ (benzene) 2572 ν (SH) and 1253 cm^{-1} ν (Si–C).

Into an ice-cooled solution of Et₃Al (2.14 g, 18.7 mmole) in 15 ml benzene, trimethylsilanethiol (1.87 g, 17.6 mmole) in 5 ml benzene was added dropwise with stirring for 3 h. The extent of the reaction could be estimated by the amount of ethane gas evolution. Then, the mixture was kept at 80° for 2 h. After distilling off Et₃Al (b.p. 51–53°/0.20 mm), the vacuum distillation of the product gave a white viscous residue. White crystals (1.63 g) of (Ie) were obtained by purification of the residue by washing with n-hexane.

Reactions of Me₂Al–NMe–SiMe₃ (Ia) with ketones

1. *With diisopropyl ketone.* When the mixture of diisopropyl ketone (0.932 g, 8.2 mmole) and (Ia) (1.33 g, 8.3 mmole) in benzene solution was kept at room temperature for 24 h and then heated at 80° for 50 h, the ν (C=O) (1708 cm^{-1}) of the starting ketone decreased whereas the intensity of the 1653 cm^{-1} ν (C=N) absorption increased. The products were (Me₃Si)₂NMe (0.531 g, 73%), i-Pr₂C=NMe (0.456 g, 43%) white needle-like crystals (II') (0.281 g, 20%) and recovered i-Pr₂CO (0.320 g, 34%). From IR and NMR spectral data of (II') shown in Table 4, the compound (II') was identified as (Me₂Al)Me₂C–CO–i-Pr. In Table 4, IR and NMR data of the products obtained are tabulated.

2. *With pinacolone.* In the case of the reaction of (Ia) with pinacolone, the colour of the mixture turned orange after 20 h reaction at room temperature, and ν (C=O) (1705 cm^{-1}) disappeared completely, while new IR absorption bands at 1675, 1650 and 1605 cm^{-1} emerged. Major products were t-BuMeC=NMe and (Me₃Si)₂NMe, for which IR and NMR data are shown in Table 3.

3. *With acetophenone.* In this case, the reaction was completed after 12 h at room temperature, as evidenced by the disappearance of ν (C=O) (1686 cm^{-1}). The products identified were PhMeC=NMe (14%), Me₂Al–O–SiMe₃ (11%), (Me₃Si)₂NMe (48%) and an orange-coloured liquid, PhMeC(OAlMe₂) (NMeSiMe₃) (III), b.p. 90–100° at 0.50 mm in 50% yield.

4. *With benzophenone.* The reaction was completed after heating at 80° for 24 h. After leaving the mixture for one night, white needle-like crystals of Ph₂CH–O–AlMe₂ (IV), m.p. 133–136° had crystallized out in a yield of 43%. (Found: C, 74.81; H, 7.13; Al, 10.68. Calcd.: C, 74.98; H, 7.04; Al, 11.23%.) Active methyl group: found 1.94, calcd. 2.00 per mole. Hydrolysis of (IV) gave quantitatively benzhydrol Ph₂CHOH, m.p. 68°. Upon distillation of the filtrate, (Me₃Si)₂NMe (25%) and a fraction (42%) with a b.p. range of 65–85°/0.20 mm were obtained. The NMR spectrum of this fraction (Table 4) showed the formation of two products, Ph₂C=NMe and Me₂Al–O–SiMe₃ with a combined yield of 42%.

Reactions of $\text{Me}_2\text{Al-NMe-SiMe}_3$ (Ia) with esters

1. *With methyl acetate.* When an equimolar mixture of (Ia) and methyl acetate in benzene was kept at room temperature for 20 h and heated at 60° for 20 h, a new IR absorption band at 1590 cm^{-1} appeared, but the $\nu(\text{C=O})$ (1745 cm^{-1}) of ester group had remained. The reaction products were *N,O*-dimethylacetimidate tetramethyldialumoxane adduct (Va) 54%, $(\text{Me}_3\text{Si})_2\text{NMe}$ 44% and Me_3SiOMe 32%.

(Va) was a colourless liquid with b.p. $32\text{--}35^\circ/0.20\text{ mm}$. $\tau(\text{benzene})$: 10.63 (s, 6H; $\text{N}\rightarrow\text{AlMe}_2$), 10.58 (s, 6H; $\text{O}\rightarrow\text{AlMe}_2$), 8.66 (s, 3H; CMe), 7.80 (s, 3H; NMe) and 6.80 (s, 3H; OMe). $\nu(\text{benzene})$: 1580(s) and 1682(w) cm^{-1} . Mol.wt. 213 (calcd. for monomer 217). (Found: C, 44.27; H, 9.70; Al, 25.25. $\text{C}_8\text{H}_{21}\text{Al}_2\text{NO}_2$ calcd.: C, 44.23; H, 9.75; Al, 24.84%). Active methyl groups found 4.07, calcd. 4.00/mole.

When the 1/2 molar reaction of methyl acetate with (Ia) was carried out at room temperature for two days, the $\nu(\text{C=O})$ of the ester disappeared completely. Distillation of the product afforded (Va) in 65%, $(\text{Me}_3\text{Si})_2\text{NMe}$ in 39% and Me_3SiOMe in 18% yield.

2. *With methyl benzoate.* The reaction of an equimolar mixture of (Ia) and methyl benzoate needed more severe reaction conditions than that of methyl acetate. Heating the mixture at 60° for 14 h and then at 80° for 27 h was necessary. The colour of the mixture turned orange, with the appearance of a new IR band at 1580 cm^{-1} , but without disappearance of $\nu(\text{C=O})$ (1725 cm^{-1}) of the ester. In the case of 1/2 molar ratio reaction, the $\nu(\text{C=O})$ absorption band disappeared completely after heating the mixture at 80° for 44 h. The products obtained in both reactions are shown in Table 5. The major product was *N,O*-dimethyl benzimidate tetramethyldialumoxane (Vb), a colourless liquid with b.p. $82\text{--}83^\circ/0.30\text{ mm}$. $\tau(\text{benzene})$: 10.47 (s, 6H; $\text{N}\rightarrow\text{AlMe}_2$), 10.45 (s, 6H; $\text{O}\rightarrow\text{AlMe}_2$), 7.59 (s, 3H; =NMe) and 6.83 (s, 3H; OMe). $\nu(\text{benzene})$: 1585 (s) and 1672(w) cm^{-1} . Mol.wt. 267 (calcd. 279). (Found: C, 55.47; H, 8.09; Al, 19.60. $\text{C}_{13}\text{H}_{22}\text{Al}_2\text{NO}_2$ calcd.: C, 55.91; H, 8.30; Al, 19.32%) Hydrolysis of (Vb) gave *N*-methylbenzamide, m.p. $179\text{--}181^\circ$, and methane.

3. *With methyl pivalate.* The 1/1 and 1/2 molar ratio reactions between methyl pivalate and (Ia) did not afford (Vc) and $(\text{Me}_3\text{Si})_2\text{NMe}$, but the starting reactants were recovered. The results were shown in Table 5.

Reaction of $\text{Me}_2\text{Al-NMe-SiMe}_3$ (Ia) with *N,N*-dimethylacetamide

An equimolar mixture of (Ia) and *N,N*-dimethylacetamide reacted at room temperature for 26 h, and new IR absorption bands at 1620 and 1580 cm^{-1} appeared, accompanied by the disappearance of $\nu(\text{C=O})$ (1655 cm^{-1}) of the amide. After distillation of $\text{Me}_3\text{SiNMe}_2$ (33%) and $\text{Me-C(NMe}_2\text{)=NMe}$ (10%), sublimation of the residue gave white crystals, m.p. $95\text{--}98^\circ$, in 30% yield. This compound was identified as 4-(dimethylamino)-4-(methylimino)-2-(dimethylalumoxy)-2-butene (VI). $\tau(\text{benzene})$: 10.22 (s, 6H; AlMe_2), 8.54 (s, 3H; =CMe), 7.74 (s, 6H; NMe_2), 7.46 (s, 3H; =NMe) and 5.97 (s, 1H; =CH). $\nu(\text{benzene})$: 1610 (m) and 1545 (s) cm^{-1} . (Found: C, 53.83; H, 9.18. $\text{C}_5\text{H}_{19}\text{AlN}_2\text{O}$ calcd.: C, 54.53; H, 9.66%.) Hydrolysis of (VI) gave white needle-like crystals of 4-dimethylamino-4-methylamino-3-buten-2-one

(VII), m.p. 64–65°. $\tau(\text{CCl}_4)$: 8.15 (s, 3H; =CMe), 7.18 (s, 7H; NMe₂ and NH), 7.09 (s, 3H; =NMe) and 5.62 (s, 1H; =CH). $\nu(\text{KBr})$: 3150 (br) and 1605 (s) cm^{-1} . (Found: C, 59.15; H, 9.56; N, 19.32. $\text{C}_7\text{H}_{14}\text{N}_2\text{O}$ calcd.: C, 59.13; H, 9.92; N, 19.70%.)

Reactions of $\text{R}_2\text{Al-X-SiMe}_3$ (Ia, Ic, Ie) with isocyanates

1. *Reaction of (Ia) with phenyl isocyanate.* An equimolar mixture of (Ia) and phenyl isocyanate in benzene was allowed to react at 80° for two days. $\nu(\text{N=C=O})$ (2265 cm^{-1}) had disappeared and new strong IR absorption bands at 1627 and 1590 cm^{-1} had emerged. The reaction products were methylphenylcarbodiimide 3%, $\text{Me}_2\text{Al-O-SiMe}_3$ 19% and $(\text{Me}_3\text{Si})_2\text{NMe}$ 36%.

2. *Reaction of (Ia) with methyl isocyanate.* The reaction was carried out analogously. The products obtained are shown in Table 6.

3. *Reaction of (Ic) with phenyl isocyanate.* This reaction was carried out in the same way as the previous two reactions. The products obtained are shown in Table 6. IR and NMR data are shown in Table 7, including those for the above two reaction products.

4. *Reaction of (Ie) with phenyl isocyanate.* The reaction between $\text{Et}_2\text{Al-S-SiMe}_3$ (Ie) and phenyl isocyanate occurred similarly. The products were phenyl isothiocyanate 49% and $\text{Et}_2\text{Al-O-SiMe}_3$ 39%.

Reaction of $\text{Me}_2\text{Al-S-SiMe}_3$ (Id) with xanthone

Immediately after mixing the equimolar amounts of (Id) and xanthone in benzene, the colour of the solution changed into light green. The colour turned to dark green after keeping the mixture at room temperature for 18 h, after which $\nu(\text{C=O})$ (1657 and 1607 cm^{-1}) of xanthone had disappeared completely. Hydrolysis of the mixture gave dark green-coloured crystals of thioxanthone in 65% yield, m.p. 154–156°, $\nu(\text{C=S})$ 1320 cm^{-1} .

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