ALUMINIUM

ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

1.   INTRODUCTION, REVIEWS

    This survey covers most of the papers published in the primary
journals during 1974, including English translations of Russian articles

published earlier. Some patents have been mentioned, but no attempt
has been made to cover the patent literature comprehensively.

Three full surveys of the recent literature on organoaluminium
compounds have appeared - one [1] in the present series, and the other
two [2] in the series of Chemical Society Specialist Periodic Reports.
Structural studies on organoaluminium chemistry for the period 1972-3
have been well summarised in another Chemical Society publication [3].
There have also been two short general accounts [4,5], and the chapter
on aluminium, gallium, indium and thallium [6] in 'Annual Reports in
Inorganic and General Synthesis 1973' deals mainly with organometallic
compounds. There are sections on organoaluminium compounds in
reviews on metallocarboranes [7], allylic compounds [8], vibrational
spectra of aromatic derivatives [9], gas chromatography of organo-
metallic compounds [10], and homolytic substitution at metal atoms [11].

2.   MOLECULAR STRUCTURES AND DIMENSIONS

Details of bond lengths and angles in three anions of the type $[AlXY_3]^-$
have been published (Table 1). In all cases, the ions have m-

Table 1.   Bond Lengths and Angles in Anions $[AlXY_3]^-$

	Al-C $Å$	Al-X $Å$	C-Al-C $\circ$	C-Al-X $\circ$	Ref.
K[MeAlCl$_3$]		2.16 (X = Cl)			12
		2.17			
[Me$_2$Tl][Me$_3$AlNCS][a]	2.02(4)	2.08(4)	108(2)	100(2)	13
	1.95(4)	(X = N)	120(2)	104(2)	
K[Me$_3$AlH][b]	1.998(6)	1.73(6)	109.2(3)	104(2)	14
	1.991(5)	(X = H)	117.6(2)	112(2)	

[a] From TlSCN and Me$_6$Al$_2$

[b] From decomposition K[Me$_3$AlSiH$_3$] in ether

symmetry, and the bond lengths are similar to those in related compounds. The ion [Me$_3$AlNCS]$^-$ is of interest because the isomeric [Me$_3$AlSCN]$^-$ has been postulated in the tetramethylammonium salt. It is suggested [13] that the co-ordination requirements of the thallium atoms [with two bonded methyl groups at 2.15(2) Å, two sulphur atoms at 3.13(1) Å and two non-bonded methyl groups at 3.15 Å] are responsible for the stabilisation of the Al-N bonded compound relative to the Al-S bonded isomer.

The reaction between hexamethyldialuminium and potassium thiocyanate or potassium azide yields compounds K[Al$_2$Me$_6$SCN] (1) or K[Al$_2$Me$_6$N$_3$] (2) which form remarkable liquid complexes K[Al$_2$Me$_6$X], 2.5-5ArH with aromatic solvents. The crystal structure of the azide complex (2) [15] shows that in the asymmetric unit there are two different anions (3), (4), each with a single bridging nitrogen atom.


$\underline{C}_{2v}$ (3) $\underline{C}_s$ (4)
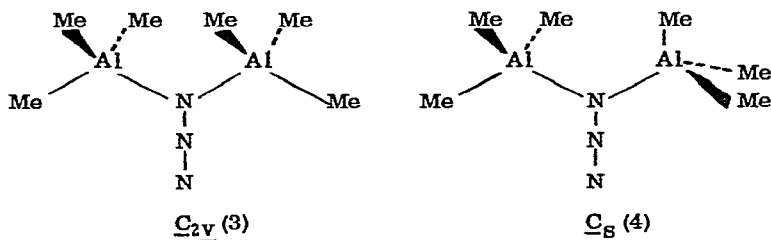
The Al-N and Al-C distances are normal and the Al-N-Al angle is about 128^0. The two potassium ions also have different environments: one is associated with four methyl groups and two terminal nitrogen atoms of azide groups and the other is associated only with four methyl groups. To see why the related compound K[Al$_2$Me$_6$F] does not form a liquid adduct with benzene, the structure of the solvate K[Al$_2$Me$_6$F], C$_6$H$_6$ was examined [16]. The anion, with linear Al-F-Al, has a mean Al-C distance 1.951(4) Å and mean Al-F 1.782(2) Å; these dimensions are similar to those found previously in K[Al$_2$Et$_6$F]. The shortest K-C(C$_6$H$_6$) distance is 3.947(7) Å and there is no strong arene-ion interaction which is assumed to be important in the liquid adducts. The thermal decomposition of K[Al$_2$Me$_6$SCN] (1) at 120^0 results in the breaking of C-S bonds and formation of the compound (Me$_2$AlNCMe$_2$)$_2$ (5). The centrosymmetrical molecules of this substance have dimensions [17]: Al-N, 1.927(2); Al-C, 1.973(3); C-C, 1.514(5); N-C, 1.273(3) Å; < N-Al-N, 83.7(1); <Al-N-Al, 96.3(1)^0.

The molecular structure of dimethylaluminium chloride dimer (6), first determined more than thirty years ago, has been studied again by gas phase electron diffraction [18]. The molecular dimensions are: Al-C, 1.935(4);


(5)

(6)
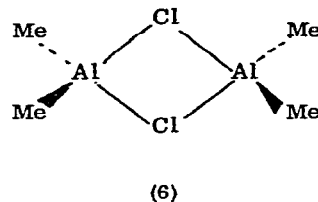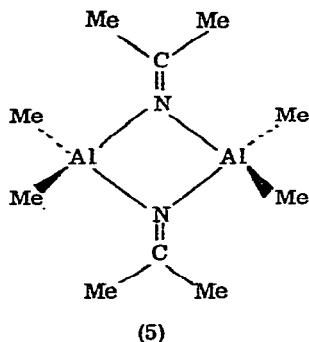
Al-Cl, 2.303(3) $\mathring{A}$; $<$C-Al-C, 126.9(8); $<$Cl-Al-Cl, 89.4(5)^0. The Al-C bond is thus significantly shorter than the Al-C (terminal) bond in Me_6Al_2 [1.957(3) $\mathring{A}$] and the Al-Cl bond significantly longer than the Al-Cl (bridge) bond [2.252(4) $\mathring{A}$] in Al_2Cl_6. The aluminium atomic orbitals used for bonding to the terminal carbon atoms have more $\underline{s}$-character in $[Me_2AlCl]_2$ than in $[Me_3Al]_2$.

Two other crystallographic studies have thrown light on possible reaction intermediates. First, the structure of the compound $Me_4C_4AlCl_3$ (7), formed as an intermediate in the trimerisation of but-2-yne, shows non-planar C_4 rings joined to Al by Al-C σ-bonds [19]. The molecules have $\underline{m}$-symmetry with mean Al-Cl 2.134(2) $\mathring{A}$ and Al-C 1.979(5) $\mathring{A}$ and the bond angles within the ring [$<$C4-Cl-C2, 72.0(3); $<$Cl-C2-C3, 98.9(2); $<$C2-C3-C4, 79.6(3)] suggest severe strain, with positive charge spaced over the atoms C2-4. Secondly, the crystal structure of diphenyl(phenyl-ethynyl)aluminium dimer (8) shows [20] that the bridging phenylethynyl groups,

(7)

(8)
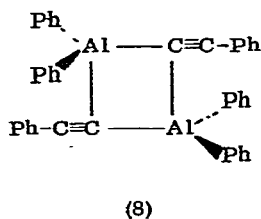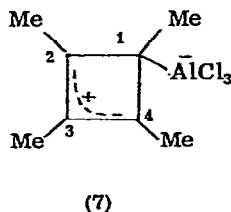
already identified by NMR spectroscopy, are unsymmetrical. The Al–C≡C group is almost linear and the C≡C bond length is 1.207(2) Å, as in other ethynyl compounds. The Al–C (bridging) distances (2.184 and 1.992 Å) and the Al–C–Al angle of 91.7° suggest bonding by one Al–C σ-bond and overlap between one carbon $2p$ π-orbital and the aluminium $3p_z$ orbital; the ethynyl group is thus a three-electron donor.

Full details have been published of the crystal structures of two compounds, [MoH(C$_5$H$_5$)C$_5$H$_4$)$_2$Al$_3$Me$_5$ (9) (solved independently by two groups of workers [21,22]) and [Mo(C$_5$H$_4$)$_2$Al$_2$Me$_3$]$_2$ (10) [22].

(9)   (10)
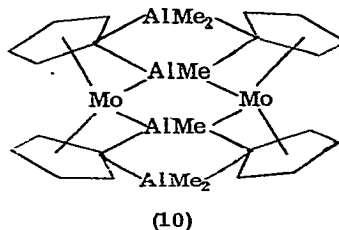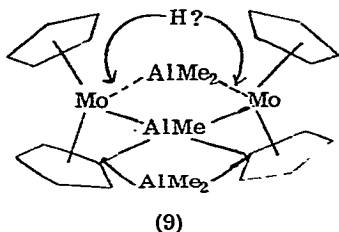
3. NUCLEAR MAGNETIC RESONANCE STUDIES OF EXCHANGE REACTIONS

After the extensive ^{1}H NMR studies in previous years of the bridge-terminal exchange in alkylaluminium dimers, a ^{13}C study [23] has provided further evidence that the reaction is faster in toluene than in cyclohexane. It is suggested that the exchange may be intramolecular, involving the recombination of two monomers derived from the same dimer, or intermolecular, involving recombination of two monomers derived from different dimers. The intramolecular mechanism is likely to predominate for hexamethyldialuminium in cyclohexane (where the heat of dissociation of dimer is high) and the intermolecular mechanism is likely to become important in aromatic solvents or with higher trialkylaluminium dimers, since monomers are stabilised (relative to dimers) by solvation and the dissociation energy of dimer is less.

The kinetics of [7]Li exchange between the alkyls LiR and LiAlR$_4$ (R = Me,. Et, CH$_2$SiMe$_3$) in diethyl ether solution have been studied by NMR line-shape

analysis [24]. The rates are determined by the dissociation of the alkyl-lithium tetramers and the activation energies $\underline{E}_a$ and pre-exponential factors $\underline{A}$ are given in Table 2.

Table 2   Exchange between LiR and LiAlR$_4$

R	Me	Et	Me$_3$SiCH$_2$
$\underline{E}_a$/kcal·mol^{-1}	12.4 ± 1.5	11.3 ± 1.7	Too fast for
$\underline{A}$/s^{-1}	1.43 x 10^{13}	2.12 x 10^{12}	study by NMR

The dissociation of the alkyl-lithium tetramers is promoted by electron-release and/or increased steric requirements. Alkyl group exchange between Me$_3$SiCH$_2$Li and LiAl(CH$_2$SiMe$_3$)$_4$ is slow on the ^{1}H NMR time-scale at room temperature. Exchange of methyl groups between trimethyl-aluminium and tetramethyltitanium, in hexane containing some diethyl ether, has been studied by ^{2}H NMR [25]. At Ti/Et$_2$O ratios greater than 1, rapid exchange occurs between unsolvated metal alkyls. At higher ether concentrations, there is rapid transfer of one methyl group from Me$_4$Ti to aluminium and subsequent slow exchange of the remaining groups, but when trimethylaluminium-diethyl ether is added to tetramethyltitanium in excess ether, a new downfield signal (τ, 5.6), ascribed to Me$_3$Ti$^+$AlMe$_4^-$, is observed. These results are said to show that hexamethyldialuminium reacts more quickly with tetramethyltitanium than with excess ether, but it is not easy to see why this should be.

A ^{1}H NMR study [26] of the exchange between the complex Me$_3$Al, PMe$_3$ and an excess of hexamethyldialuminium has suggested a bimolecular reaction between complex and monomeric trimethylaluminium.

4.   THERMODYNAMIC STUDIES

Two further papers describing the detailed and careful thermodynamic measurements of M.B. Smith have appeared. The first [27] gives data for monomer-dimer equilibria in Pr$^n_3$Al, Bu$^n_3$Al and (n-C$_8$H$_{17}$)$_3$Al. By plotting

the values for the heat and entropy of dissociation against chain length it is possible to interpolate values for other aluminium alkyls and, in combination with data obtained earlier, to derive self-consistent data for monomer–dimer equilibria in benzene and mesitylene, and for the heat of complexation of monomeric alkyls with triethylamine. The second paper [28] gives a critical survey of available heats of formation of organoaluminium compounds and attempts to sort out the many inconsistencies. New experimental values for the heats of formation of liquid ethylaluminium halides have

Table 3 Heats of Formation $-\Delta \underline{H}^0_f$ (l)/kcal mol^{-1} for Organoaluminium Compounds

R	Me	Et	Pr	Bu
R_3Al [a]	36.0 $\pm$ 1.6	45.9	63.1	80.8
R_2AlH [b]	27.3 $\pm$ 3.6	35.0	47.2	59.4
R_2AlCl [c]	84.7 $\pm$ 2.1	92.1 $\pm$ 1.5	104.1	116.1
R_2AlBr [c]	71.2 $\pm$ 2.1	78.6 $\pm$ 1.5	90.6	102.6
R_2AlI [c]	53.7 $\pm$ 12.2	61.1 $\pm$ 1.6	73.1	85.1
$RAlCl_2$ [c]	125.2 $\pm$ 1.7	128.9 $\pm$ 0.8	134.9	140.9
$RAlBr_2$ [c]	98.1 $\pm$ 1.7	101.8 $\pm$ 0.8	107.8	113.8
$RAlI_2$ [c]	63.9 $\pm$ 2.0	67.6 $\pm$ 1.3	73.6	79.6
$R_3Al_2Cl_3$	210.5 $\pm$ 2.7	221.6 $\pm$ 1.7	239.0	257.6
$R_3Al_2Br_3$	169.9 $\pm$ 2.7	181.1 $\pm$ 1.7	199.0	217.0
$R_3Al_2I_3$	118.1 $\pm$ 3.0	129.2 $\pm$ 2.1	147.2	165.2

[a] Me and Et derivatives dimeric, higher alkyls mixture of monomer and dimer. Uncertainties for higher alkyls similar or slightly greater than for Me derivative.

[b] Trimers. Uncertainties for higher alkyls similar.

[c] Dimers. Et compounds experimental, others calculated; uncertainties as for Me derivatives.

been found from measurement of the heats of redistribution. The range
of thermodynamic data is illustrated in Table 3. Values for $R = n\text{-}C_5H_{11}$,
$n\text{-}C_6H_{13}$, $n\text{-}C_7H_{15}$, $n\text{-}C_8H_{17}$, Bu^i, $i\text{-}C_5H_{11}$, $i\text{-}C_6H_{13}$, $i\text{-}C_7H_{15}$, $i\text{-}C_8H_{17}$ are
listed in the original publication [28]. The heats of formation of some
alkoxides have been found from experimental heats of combustion [29]:
$-\Delta \underline{H}_f^0$ /kcal mol^{-1}: $Et_4Al_2(OEt)_2$, 125.0 ± 1.3; $Et_4Al_2(OPr)_2$ -156.3 ± 3.4;
$Et_4Al_2(OBu^t)_2$, -184.9 ± 4.1.

5. PREPARATION OF ORGANOALUMINIUM COMPOUNDS

The reduction of aluminium chloride by potassium or sodium in tetra-
hydrofuran or xylene gives highly reactive aluminium powder, suitable for
for the preparation of halides Ph_nAlX_{3-n} ($X = Cl$, Br, I) [30]. The chloride
may be used in an improved synthesis of triphenylaluminium [31].

$$Ph_nAlCl_{3-n} + 2(3-n)/3R_3Al \longrightarrow (3-n)R_2AlCl + n/3Ph_3Al$$

$$[R = Me, Et]$$
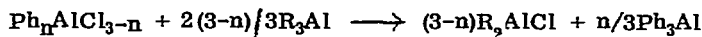
The dialkylaluminium chloride is easily separated by distillation from the
product triphenylaluminium and reconverted to trialkylaluminium by
reaction with sodium in decalin. The troublesome formation of ate-
complexes $Na[AlR_nCl_{4-n}]$ is avoided.

Tris(trimethylsilylmethyl)aluminium has been made from aluminium
metal and bis(trimethylsilylmethyl)mercury [24,32], and the etherate
$(Me_3SiCH_2)_3Al, OEt_2$ from the Grignard reagent Me_3SiCH_2MgCl and
aluminium chloride in ether [33]. The compounds $(n\text{-}C_6H_{13})_3Al$, $(n\text{-}C_9H_{19})_3Al$,
$(n\text{-}C_{10}H_{21})_3Al$ have been prepared in 98% yield from alkenes and tri-
isobutylaluminium [34,35]. The reactions are zero-order in olefin
and first-order in tri-isobutylaluminium, suggesting that the rate-determining
step is the dissociation of the tri-isobutyl-compound to hydride and olefin.

$$Bu^i_3Al \longrightarrow Bu^i_2AlH + i\text{-}C_4H_8$$
$$\downarrow C_nH_{2n}$$
$$Bu^i_2AlC_nH_{2n+1} \longrightarrow \underline{etc.}$$
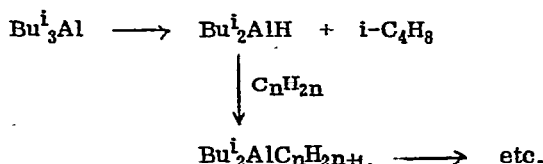
The alkyls may be mixed with titanium tetrachloride to give Ziegler-Natta catalysts which are said to be less reactive towards oxygen than those from lower alkylaluminium derivatives. Several patents refer to improved syntheses of organoaluminium compounds [36-39].
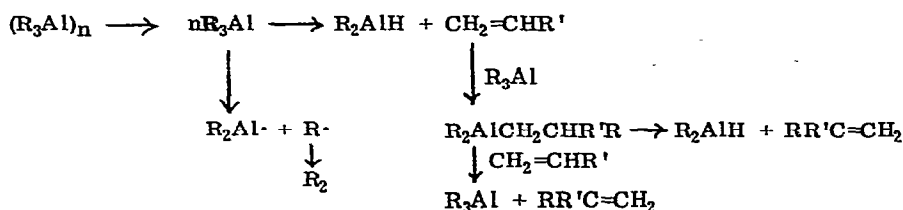
6. THERMAL DECOMPOSITION

Comparative data [40] on the thermal decomposition of organo-aluminium compounds is shown in Table 4.

Table 4   Thermal Decomposition[a]

Compound		Compound	
Et_3Al	$120-5^0/63.7\%$	Et_2AlF	$187-8^0/0\%$
Pr^n_3Al	$110^0/79.9\%$	Et_2AlCl	$124^0/2.2\%$
Bu^n_3Al	$98-100^0/86.6\%$	Bu^i_2AlCl	$165^0/7.5\%$
Bu^i_3Al	$\sim 50^0/91.7\%$	Et_2AlBr	$170^0/2.4\%$
$(n-C_8H_{17})_3Al$	$60^0/89.6\%$		

[a]The table gives the temperature at which decomposition begins and the percentage conversion at 180^0 in 180 min at 760 mm pressure.

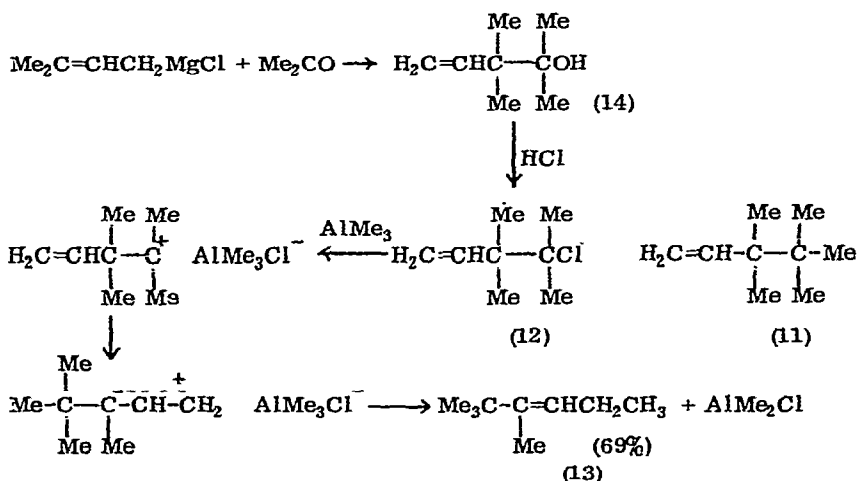The results are interpreted in terms of the following reactions:

$$(R_3Al)_n \longrightarrow nR_3Al \longrightarrow R_2AlH + CH_2{=}CHR'$$

$$\downarrow \qquad\qquad \downarrow R_3Al$$

$$R_2Al\cdot + R\cdot \qquad R_2AlCH_2CHR'R \longrightarrow R_2AlH + RR'C{=}CH_2$$

$$\downarrow \qquad\qquad\qquad \downarrow CH_2{=}CHR'$$

$$R_2 \qquad\qquad R_3Al + RR'C{=}CH_2$$

The formation of aluminium coatings by decomposition of tri-isobutyl-aluminium at 250^0 [41] and of aluminium-chromium coatings by decomposition of a mixture of tri-isobutylaluminium and di(ethylbenzene)chromium at $450-500^0$ C [42] have also been described.

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7. ALKYLATIONS, REACTIONS WITH HALIDES

Reliable, checked, synthetic procedures have been given for the preparation of trimethyl- and triethyl-borane [43] and of trimethyl-gallium [44] using alkylaluminium compounds. The yield and purity of R_3M (M = Ga, In) from MCl_3 and R_3Al is said to be improved by the addition of a hydrocarbon with boiling point between that of R_3M and R_3Al. Normal hexane or heptane are recommended for the preparation of trimethyl- or triethyl-gallium [45]. Only very small yields of the trialkylgallium compound are obtained when the Al/Ga mole ratio in the reaction mixture is less than 2 [46].

Although allylaluminium compounds are not easily isolated because they easily undergo a self-addition reaction(so that 4-methylpent-1-ene is obtained after hydrolysis), further evidence for unstable allylaluminium species has been obtained in mixtures of trialkylaluminiums and triallyl-borane [47]. An attempt [48] to make 3,3,4,4-tetramethyl-pent-1-ene (11) by methylation of 4-chloro-3,3,4-trimethyl-pent-1-ene (12) with trimethyl-aluminium has yielded mainly 2,2,3-trimethyl-hex-3-ene (13) probably by rearrangement of the initially formed carbonium ion to the more stable tertiary allylic ion.

$$Me_2C=CHCH_2MgCl + Me_2CO \rightarrow H_2C=CHC(Me)(Me)-C(Me)(Me)OH \quad (14)$$

$$\downarrow HCl$$

$$H_2C=CHC(Me)(Me)-C(Me)(Me) \; AlMe_3Cl^- \xleftarrow{AlMe_3} H_2C=CHC(Me)(Me)-C(Me)(Me)Cl \quad (12) \qquad H_2C=CH-C(Me)(Me)-C(Me)(Me)-Me \quad (11)$$

$$\downarrow$$

$$Me-C(Me)(Me)-C(Me)-CH-CH_2 \; AlMe_3Cl^- \longrightarrow Me_3C-C(Me)=CHCH_2CH_3 + AlMe_2Cl \quad (69\%) \quad (13)$$

A second product, $C_{17}H_{32}$, is formed in 31% yield. The preparation of the tertiary alcohol (14) is of interest; the internal carbon atom of the allylic system, rather than the carbon adjacent to magnesium, reacts with the carbonyl group.

8 REACTIONS WITH CARBON-CARBON DOUBLE AND TRIPLE BONDS

A series of careful cryoscopic measurements has shown [49] that whereas tri-n-alkylaluminiums $(R_3Al)_m$ show degrees of association $\underline{m}$ of 2, trialkenylaluminiums $Al[(CH_2)_nCH=CH_2]_3$ ($n=2,3$) are monomeric. The NMR parameters, which show perturbations (compared with related saturated compounds) in the chemical shifts of the vinyl protons and the protons attached to the α-carbon atoms, also suggest a strong interaction between the metal and the π-electrons of the alkenyl group (15).
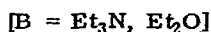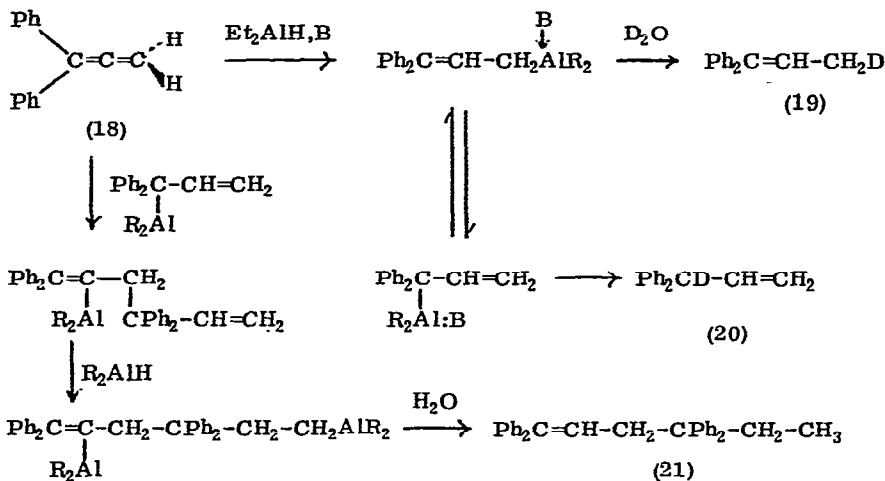

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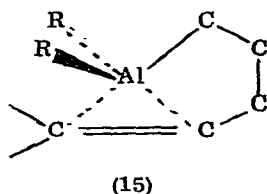
A similar intermediate has been proposed [50] to account for the isolation of tris(cyclopentylmethyl)aluminium $Al[CH_2cycloC_5H_9]_3$, rather than the open-chain derivative, from the reaction between aluminium and di(hex-5-enyl)mercury. Cyclisations are also observed with hept-6-enyl but not with oct-7-enyl or undec-10-enyl derivatives.

The systematic study of the addition of di-isobutylaluminium hydride to double bonds has continued with experiments on hydroalumination of conjugated olefins. Thus 1,1-diphenylethylene (16) gives only the 2-alumino-adduct (17), which appears to be both kinetically favoured and thermodynamically more stable than the 1-alumino- adduct, as shown by experiments with colloidal nickel, which catalyses the alkyl-hydride/olefin interconversion [51].

Equation (17) scheme.
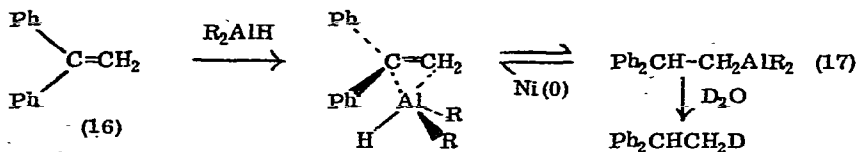
1,1-Diphenylallene (18) in the presence of triethylamine gives, after hydrolysis, a mixture of 1,1-diphenylpropene (19) (42%) and 3,3-diphenyl-propene (20) (58%). In diethyl ether the proportions are $Ph_2C=CH-CH_3$ 13% and $Ph_2CH-CH=CH_2$ 87%.

$$Ph_2C=CH-CH_2D \quad (19)$$

$$Ph_2CD-CH=CH_2 \quad (20)$$

$$Ph_2C=CH-CH_2-CPh_2-CH_2-CH_3 \quad (21)$$

[B = Et_3N, Et_2O]

In the absence of donors, the only well defined product is 1,1,4,4-tetraphenylhex-1-ene (21). Hydroalumination of 1,1-diphenylbuta-1,3-diene (22) gives a mixture of trans-1,1-diphenylbut-2-ene (23) and 1,1-diphenylbut-1-ene (24).

$$Ph_2C=CH-CH=CH_2 \xrightarrow{Et_2AlH} \xrightarrow{H_2O} Ph_2C=CHCH_2CH_3 +$$

(22) (24) (23)
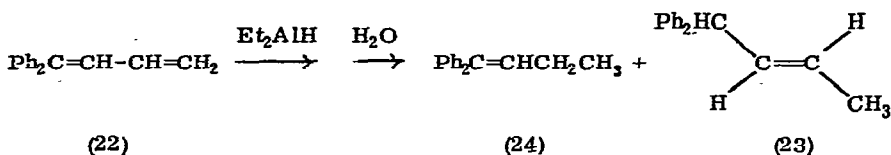
The proportions of these isomers vary with reaction temperature, suggesting that the ratio is kinetically controlled at lower temperatures. Hydroalumination

of triphenyl(vinyl)silane and triethyl(vinyl)silane gives a mixture of the compounds $R''_3SiCH_2CH_2AlR_2$ and $R''_3SiCH(R_2Al)-CH_3$, with the sterically less favoured adduct the major product. Thus in the alkenes $R'HC=CH_2$, attachment of Al at the internal carbon atom is easier when $R' = R''_3Si$ than when R is phenyl or alkyl. The stereospecific cis-hydroalumination of the strained olefin 1,1-dimethylindene (25) in the presence of diethyl ether, has been demonstrated [52].
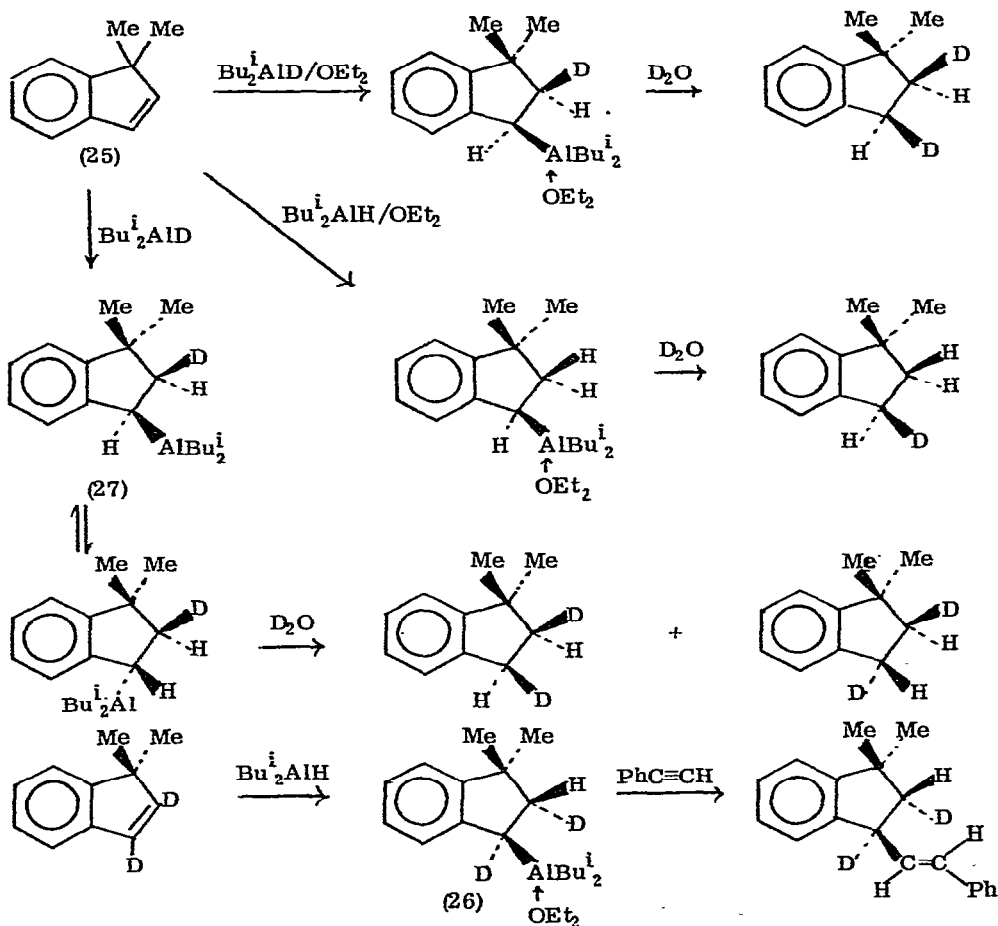
The insertion of the aluminium adduct (26) into phenylacetylene occurs with retention of configuration. The intermediate dialkylaluminium adduct (27) is not stereochemically stable in the absence of diethyl ether. Although ethers or amines normally retard the hydroalumination of olefins, the

hydroalumination of 1,1-dimethylindene (25) may be effected without loss of cis-stereospecificity, if nickel salts are added as catalysts.

A very short note [53] describes the isomerisation of cis,trans-cyclodeca-1,5-diene (28) in the presence of tri-isobutylaluminium. Two
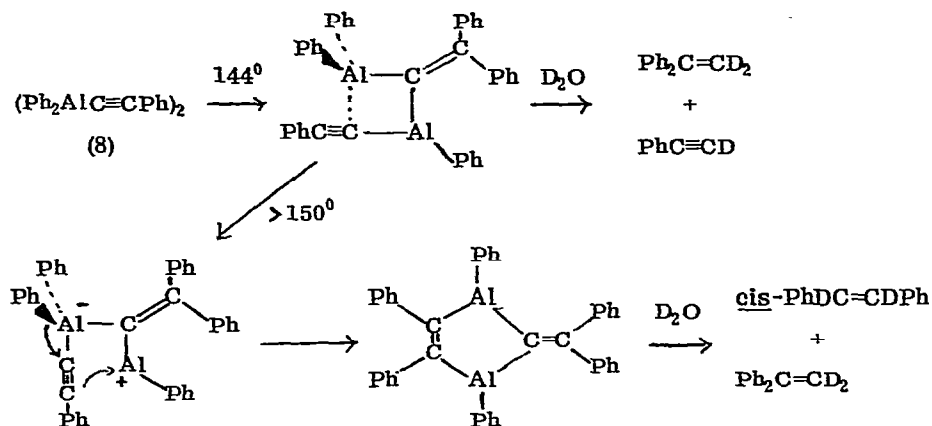

(28)
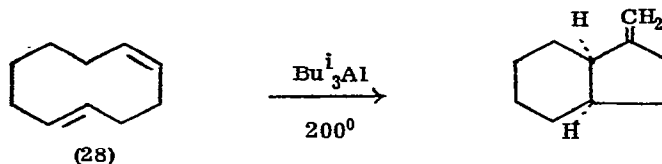
similar papers [54] describe the catalytic addition of diethylaluminium chloride to ethylene under a variety of reaction conditions and give details of the distribution of products obtained after oxidation and hydrolysis. Improvements in procedures for oxidation of aluminium alkyls have also been claimed [55].

In an account [56] of the reaction between tri-isobutylaluminium and alkynes, relative amounts of various products isolated after hydrolysis have been documented.
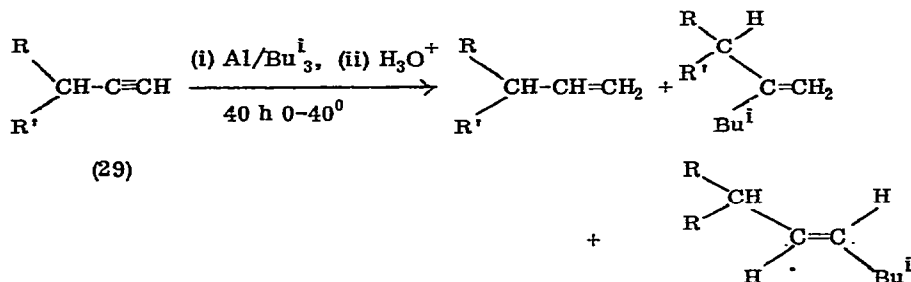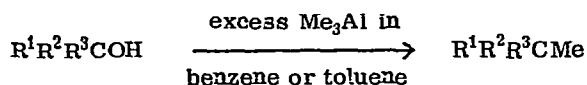

The reaction of (+)(S)-3,4-dimethylpent-1-yne [(29) R = Pr^i, R' = Me] occurs without racemisation. Diphenyl(phenylethynyl)aluminium (8) melts at 144° to a red liquid which, on hydrolysis with D_2O gives $Ph_2C=CD_2$ and $PhC≡CD$ [20]. After prolonged heating of the red melt above 150°, the products from hydrolysis include cis-PhDC=CDPh and $Ph_2C=CD_2$. These results are explained by succesive additions across the carbon-carbon triple bond, with the regiospecificity controlled by π-complex formation.

$$(Ph_2AlC{\equiv}CPh)_2 \xrightarrow{144^0} \quad \xrightarrow{D_2O} \quad \begin{array}{c} Ph_2C{=}CD_2 \\ + \\ PhC{\equiv}CD \end{array}$$

(8)

$$\xrightarrow{>150^0}$$

$$\xrightarrow{} \quad \xrightarrow{D_2O} \quad \begin{array}{c} \underline{cis}\text{-}PhDC{=}CDPh \\ + \\ Ph_2C{=}CD_2 \end{array}$$

The compound $(Ph_3Si)_2AlEt.2LiBr.2THF$ (30) was described in 1971: its composition has been further substantiated by its reactions with mercury and cadmium acetates to yield diethyl and bis(triphenylsilyl)-metal derivatives [57]. The product from the reaction with diphenylacetylene is hydrolysed to $Ph_3Si(Ph)C{=}CPhH$; there is no evidence for addition of the Al-Et bond to the alkyne [58].

9   REACTIONS WITH ORGANIC OXYGEN DERIVATIVES

Some of the most important and extensive work of the year has been concerned with reactions of organoaluminium compounds with ketones, ethers, alcohols and esters. Tertiary alcohols are C-methylated by an excess of trimethylaluminium at temperatures of 100–200⁰ (usually 120–130⁰) [59]. This reaction has been documented for $R^1 = R^2 = R^3 = Ph$,

$$R^1R^2R^3COH \xrightarrow[\text{benzene or toluene}]{\text{excess Me}_3\text{Al in}} R^1R^2R^3CMe$$

p-$EtOC_6H_4$, Me; $R^1 = Ph$, $R^2 = R^3 = Me$; $R^1 = R^2 = Ph$, $R^3 = Me$; and $R^1R^2R^3C = 1$-adamantyl, and the scope is thought to be limited mainly by the reactivity of trimethylaluminium towards functional groups such as esters, nitriles, amides, epoxides and nitro- compounds. Triaryl carbinols are particularly reactive and are methylated by an excess of trimethylaluminium at 80⁰ for several hours. Aryl alkyl carbinols are

less reactive and require 120-130^0 for several days.   Adamant-1-ol
requires 200^0.   The initial step is thought to be the formation of an
alkoxide, which may give the C-methyl product by pyrolysis or reaction
with an excess of trimethylaluminium.   Three alkoxides have been

$$ROH \longrightarrow ROAlMe_2 \xrightarrow{\text{pyrolysis}} RMe + \text{'MeAlO'}$$

$$\downarrow Me_3Al$$

$$RMe$$
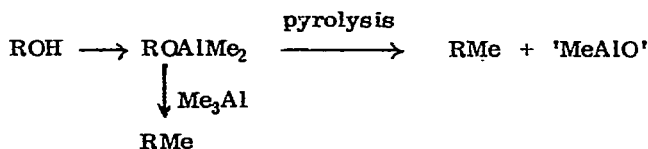
isolated and the temperatures required for pyrolysis are: R = CPh$_3$, 157^0;
R = CH$_2$Ph, 300^0; R = 1-adamantyl, 385^0.   Elimination of olefin is
sometimes a significant side reaction.

$$\underset{\underset{OAlMe_2}{|}}{>\!\!C}\!\!-\!\!Me \longrightarrow >\!\!C\!\!=\!\!CH_2 \quad \text{or} \quad >\!\!C\!\!-\!\!Me$$
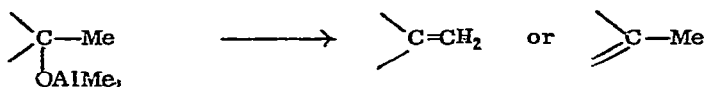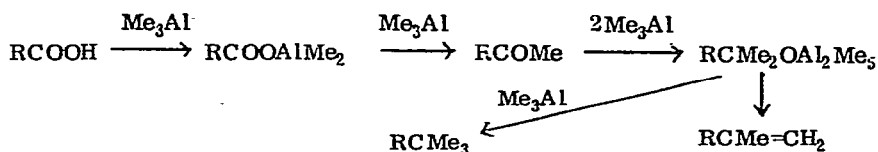
The methylation, which is autocatalytic, shows many features which in-
dicate a mechanism involving carbonium ions.

Ketones react similarly with an excess of trimethylaluminium to
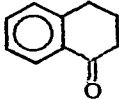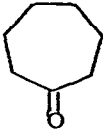give gem-dimethyl derivatives [60].

$$R^1R^2C\!\!=\!\!O \xrightarrow{Me_3Al} R^1R^2CMe_2$$
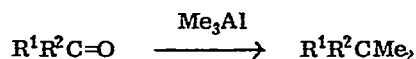
In some cases, olefins are formed from the intermediate alkoxide
$R^1R^2MeCOAlMe_2$.   The conversion of carboxylic acids to t-butyl
derivatives usually requires a 5:1 excess of trimethylaluminium, but
the final step in the reaction sequence is usually complete after about 20 h
at 120^0 [61].

$$RCOOH \xrightarrow{Me_3Al} RCOOAlMe_2 \xrightarrow{Me_3Al} RCOMe \xrightarrow{2Me_3Al} RCMe_2OAl_2Me_5$$
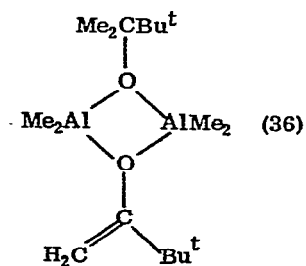
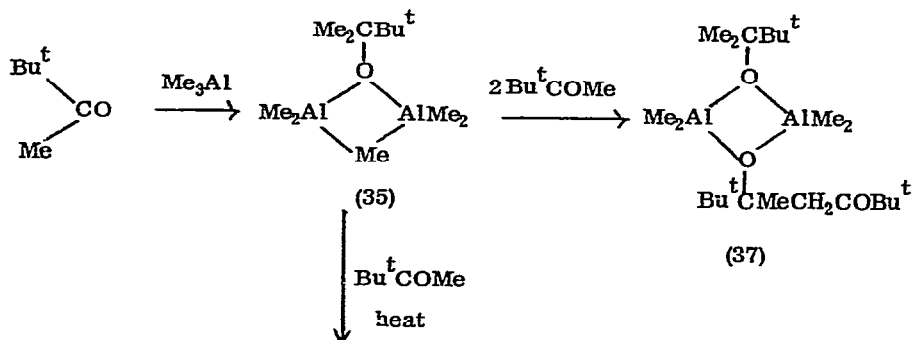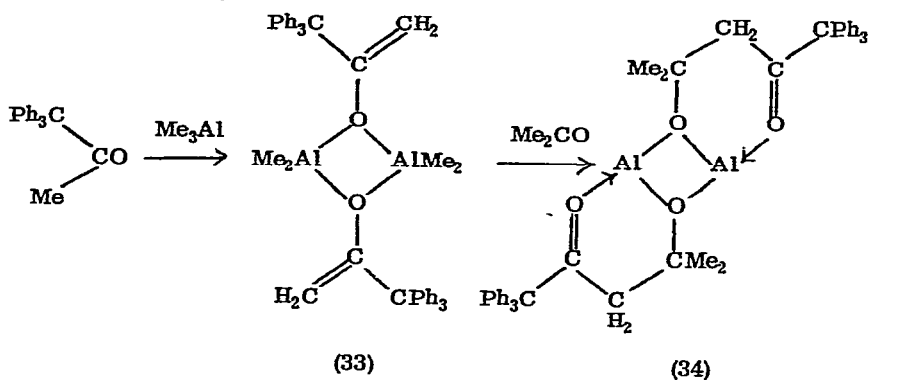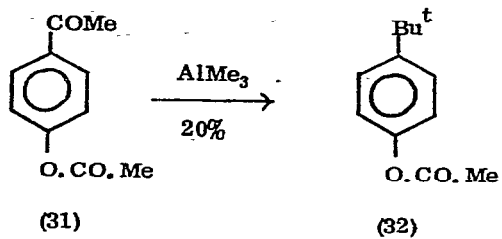$$RCMe_3 \xleftarrow{Me_3Al} \qquad RCMe\!\!=\!\!CH_2$$

Again formation of olefins becomes more important for highly branched groups R. The exhaustive methylation constitutes an important synthetic procedure which can be used for a wide range of compounds, and safe experimental techniques for the manipulation of the highly air-sensitive reagents have been described [59].

Later work [62] has shown that the methylation of ketones by trimethylaluminium is catalysed by nickel compounds of which bis(acetylacetonato)nickel(II) is the most easily made and handled. The catalyst allows the methylation to be effected in ether as well as hydrocarbon solvents, but leads to mixtures of products even at ketone:aluminium ratios of 1:1.1–1.2. Thus the reaction of RR^1CO with trimethylaluminium gives (in addition to $R^1R^2MeCOAlMe_2$) $R^1R^2CMe_2$, $R^1R^2C=CH_2$ and R^1R^2CHMe (Table 5).

Table 5   Nickel-catalysed methylation of ketones by trimethylaluminium in ether

Yields (%)	R^1R^2CO	R^1R^2MeCOH	$R^1R^2C=CH_2$	$R^1R^2CMe_2$	R^1R^2CHMe
PhCOMe	10	40–50	10	20–30	1
PhCOPh	4	58	29	–	9
(1-tetralone)	50	–	27	11	4
(cycloheptanone)	56	11	18	–	15

(31)   (32)

(33)   (34)

(35)   (37)

(36)

There has been further progress in elucidating the factors deter-
mining the stereochemistry of addition of trimethylaluminium to cyclic
ketones. In an important paper by Ashby et al., referred to last year [1],
it was shown that addition of trimethylaluminium to 4-t-butylcyclohexanone
(38) gave 75% axial alcohol (39) when the Al/ketone mole ratio was < 1 and
90% equatorial alcohol (40), indicating attack from the more sterically
hindered side, when it was > 2. The change in stereochemistry was con-
sidered to result from a change in transition state. At high aluminium/ketone
ratios, attack by a second molecule of AlMe$_3$ was perhaps assisted by com-
pression from the methyl groups (a, b) of the AlMe$_3$ initially complexed at the
carbonyl group, against substituents at the 2- and 6- positions (41). This
work has been extended by studies on 2- and 6- substituted methyl 4-t-butyl-
cyclohexanones and decalones [64]. In trans-2-methyl-4-t-butylcyclohexanone
(42) the axial 2-methyl substituent hinders equatorial attack even at low Al/ketone
ratios. (80% equatorial alcohol is formed when Al/ketone = 1.)

(42)   (43)

(44)
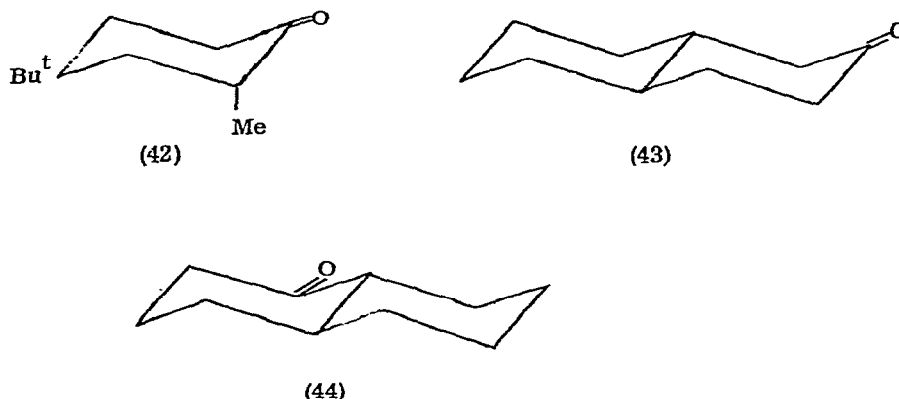
In trans-decal-2-one (43) the results are almost the same as in 4-t-butyl-
cyclohexanone (38). In cyclohexanones with an equatorial 2-methyl sub-
stituent [including trans-decal-1-one (44)] the stereoselectivity (giving
axial alcohols at low Al/ketone ratios and equatorial at high Al/ketone
ratios) is enhanced compared with 4-t-butylcyclohexanone, though the

extent of axial attack decreases with increasing introduction of the equatorial 2-methyl groups. Moreover, the stereoselectivity persists in 2,2,6-trimethylcyclohexanone (45), even though there is an axial 2-methyl substituent. It is suggested that the 2-equatorial substituents are bent upwards in the transition state (41) to hinder the incoming methyl group. cis-Decalones have also been studied [64].

Reactions between the ate complexes $LiAlMe_4$, $LiAlMeBu^i_3$ and $[(C_8H_{17})_3PrN][AlMe_3Br]$ and 4-t-butylcyclohexanone (38) give predominantly equatorial alcohol (40) as methylation product at all mole ratios in donor solvents [65]. (The major product with $LiAlMeBu^i_3$ is from reduction.) This contrasts with the reactions with ate complexes of boron, magnesium and zinc, where mainly axial alcohol (39) is formed. Mechanisms of these reactions have not been elucidated, but it has been suggested that the ketone may complex initially at the lithium atom, in a transition state similar to (41).

C-Methylation of a carbonyl group already complexed to aluminium is observed in the reaction between dimethylaluminium acetylacetonate and trimethylaluminium. This is said to give a derivative $Me_2AlOCMe_2CH=CMeOAlMe_2$ (partly associated in solution), but little structural data has been obtained. Reactions with methylaluminium chloride have also been studied [66].

The reaction between trimethylaluminium and α,β- unsaturated ketones in the presence of bis(acetylacetonato)nickel(II) yields products from 1,4- addition instead of those from normal 1,2- addition [67]. Thus mesityl oxide $Me_2C=CHCOMe$ and trimethylaluminium react to give the Z (46) and E (47) isomers of dimethylaluminium-4,4-dimethylpent-2-en-2-olate. The Z-isomer is dimeric in benzene. At 100-150° it is isomerised to the E-isomer which may be separated by distillation into a dimer and a trimer. The association is probably, from spectroscopic evidence, through Al-O-Al rather than Al-O-C-C-Al bridges. The enolates form 1:1 complexes with Lewis bases. The Z-isomer reacts with acetaldehyde or benz-aldehyde by an aldol condensation [68] with formation of a dimeric chelate compound with threo- configuration in which the aluminium is probably

Z (46)   E (47)   (48)
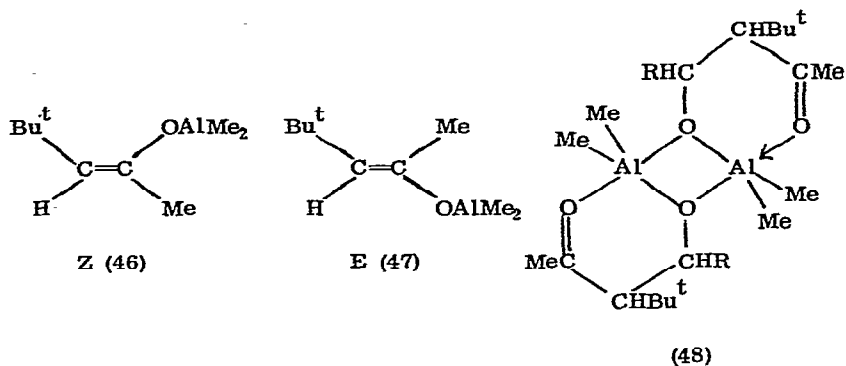
5-co-ordinate (48). In the molecules of these compounds each ligand is chiral and so there are two stereoisomers - one with enantiomorphous ligands (RS) and the other with identical ligands (RR or SS). Temperature-dependent ^{1}H NMR spectra have been interpreted in terms of rearrangement of the co-ordinated carbonyl groups with the Al_2O_2 ring remaining intact, and indicate that the predominant isomer is the RR/SS form. With tri-methylaluminium, the chelates (48) form 1:1 complexes (49) which are monomeric in benzene and show a low value (1640 cm^{-1}) for the carbonyl stretching frequency. The aluminium is probably complexed with the alkoxy rather than the carbonyl oxygen.

(49)   (50)
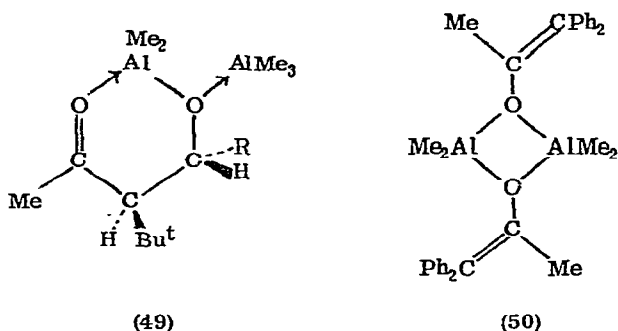
Spectra of the solution obtained from the reaction between the E-isomer (47) and acetaldehyde have been taken to show the initial formation of dimers with erythreo- configuration; these slowly change to threo-ketolates (48) formed directly from the Z-enolates. Reactions between the Z-enolate and diphenylketene or phenyl isocyanate have been briefly described.

The catalysed addition of trimethylaluminium to mesityl oxide may involve a nickel enolate. Since such compounds have been little studied, a substance MeNi(OCMe:CPh$_2$)(PMe$_2$Ph)$_2$ has been made from diphenyl-ketene and Me$_2$Ni(PMe$_2$Ph)$_3$ [69]. There are, however, no bands in the IR spectrum attributable to $\diagdown$C=C$\diagup$ or C=O stretching, and it has been suggested that the C=C=O system may be bound to nickel like a π-allyl group. The nickel compound reacts with trimethylaluminium to give the aluminium enolate (50) which is made cleanly from diphenylketene and tri-methylaluminium. It is dimeric in boiling benzene and sublimes at 180–200° in high vacuum with slight decomposition.

The transition metal-catalysed methylation of isophorone (51) or cyclohex-2-en-1-one by trimethylaluminium also gives 1:4 addition [70].
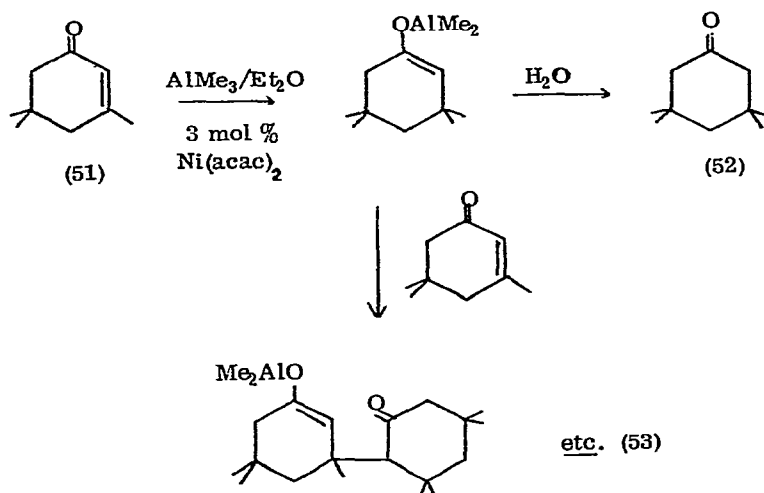
2,2,4,4-Tetramethylcyclohexanone (52) is isolated in 85% yield after less than 30 min; the only other product is polymer obtained from successive Michael addition (53) of the unsaturated ketone to the dimethylaluminium enolate. Freshly prepared lithium tetramethylaluminate is also an effective methylating agent in the presence of 3 mol % of bis(acetylacetonato)nickel(II).

Reactions between ketones and organoaluminium compounds with β-hydrogen atoms yield products from reduction besides those from addition.

Alkyl methyl ketones and (+)tris[(S)-2-methylbutyl]aluminium (54) yield
tertiary alcohols in which the S-isomer predominates [71].

$$\begin{array}{c}R\\ \diagdown\\ \diagup\\ Me\end{array}C{=}O \ + \ Al(CH_2{\blacktriangleright}\!\!\underset{\underset{H}{|}}{\overset{\overset{Me}{|}}{C}}\!\!{\longleftarrow}Et)_3 \quad \xrightarrow[\text{pentane } 0^0]{2 \text{ h}} \quad Me{\blacktriangleright}\!\!\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}\!\!{\longleftarrow}OH \ + \ CH_2{=}C\!\!\begin{array}{c}Me\\ \diagup\\ \diagdown\\ Et\end{array}$$

(54)
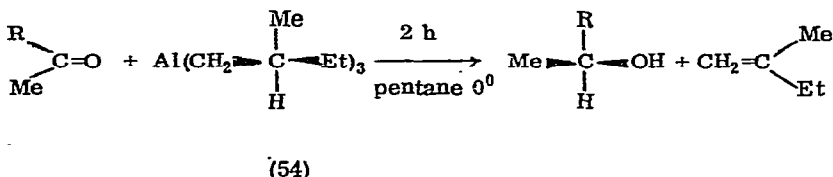
The optical purity of the product increases for the series (R =) Et, Pr^i,
Bu^t. Preferential formation of the S alcohol is also observed when
(+)tris[(S)-2-methylbutyl]aluminium diethyl etherate is used as reducing
agent. The importance of addition relative to reduction in the reactions
between benzaldehyde and triethyl- or tripropyl-aluminium is increased by
the addition of tetrabutylammonium halides or alkali fluorides MX [72]. The
effect of added salts is greater, the less easily dissociated the complexes
$MX.R_3Al$ or $MX.2R_3Al$. The addition/reduction ratio for reactions of ketones
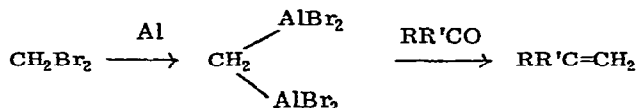with $CaAl_2Et_8$ is greater than that for reaction with RCaI [73].

A procedure has been described [74] for the conversion of carbonyl
compounds to olefins by reaction with methylenedialuminium tetrabromide,
made from bromomethane and aluminium foil.

$$CH_2Br_2 \ \xrightarrow{\ Al\ } \ CH_2\!\!\begin{array}{c}\diagup AlBr_2\\ \\ \diagdown AlBr_2\end{array} \ \xrightarrow{\ RR'CO\ } \ RR'C{=}CH_2$$

Olefins made in this way are various substituted styrenes $p\text{-}XC_6H_4CH{=}CH_2$
(Yields: X = H, 60%; X = Cl, 50%; X = NO$_2$, 60%; X = Me, 60%) and
vinylnaphthalene (yield 80%).

$$CH_2{=}CH{-}CH{=}CH{-}CH_2Cl \ \xrightarrow[\text{THF}]{Al} \ (CH_2{=}CH{-}CH{=}CH{-}CH_2)_3Al_2Cl_3$$

$$\downarrow RCOR'$$

$$\underset{\underset{RR'COH \quad (40\text{-}80\%)}{|}}{CH_2{=}CH{-}CH{-}CH{=}CH_2}$$

$$(RR' = Et_2, \ MePr^i, \ Pr^n_2, \ Pr^i_2, \ Bu^n_2, \ Bu^i_2)$$
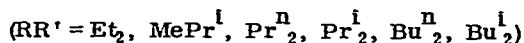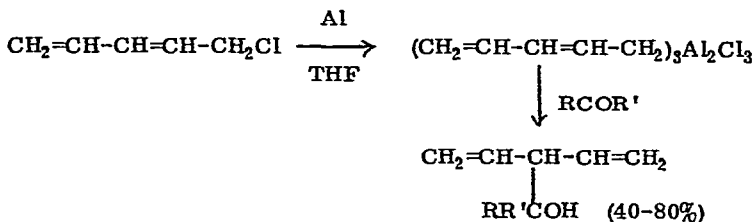
The reaction of organoaluminium halides with ketones may also be used for the preparation of branched chain alcohols [75]. (Compare p. 10 and [48]).

A study [76] by IR and ^{1}H NMR spectroscopy of the complexes between lactones and diethylaluminium chloride or ethylaluminium dichloride shows the formation of 1:1 (55) and 1:2 (56) complexes.

$$
\begin{array}{cc}
\text{CH}_2\text{---CH}_2 & \text{CH}_2\text{---CH}_2 \\
R_1\diagdown\ |\quad\quad | & \cdot R_1\ |\quad\quad | \\
\quad C\quad\quad C=\text{OAlEt}_n\text{Cl}_{3-n} & \quad C\quad\quad C=\text{OAlEt}_n\text{Cl}_{3-n} \\
R_2\diagup\quad O & R_2\diagup\quad O \\
\text{(55)} & \quad\quad\downarrow \\
& \text{AlEt}_n\text{Cl}_{3-n} \\
& \text{(56)}
\end{array}
$$
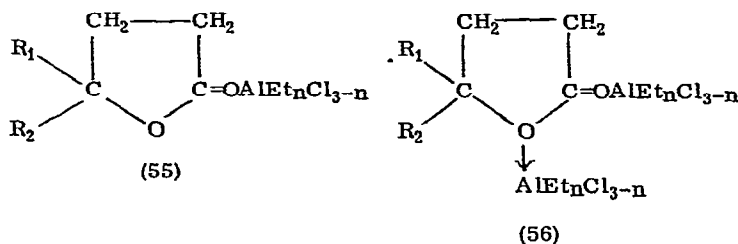
Only 1:1 complexes are formed with triethylaluminium. Under more vigorous conditions lactones are reduced. The transfer of the β-hydrogen of the ethyl group has been confirmed by deuterium substitution [76]. Lactones are methylated by methylaluminium dichloride.

$$
\begin{array}{l}
\xrightarrow{\text{EtAlCl}_2}\ \text{RR'HCCH}_2\text{CH}_2\text{COOH}\ (90\text{--}98\%) \\[1em]
\xrightarrow{\text{MeAlCl}_2}\ \text{RR'MeCCH}_2\text{CH}_2\text{COOH}\ (42\text{--}91\%)
\end{array}
$$

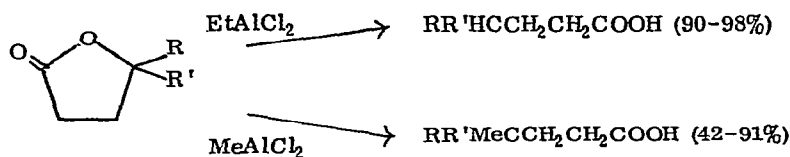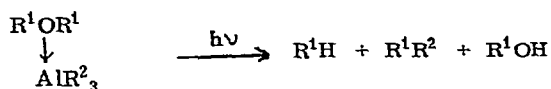Ethers form thermally stable 1:1 complexes with trialkylaluminiums, but is has now been shown [77] that irradiation of these complexes in benzene or cyclohexane may give cleavage of the ether linkage.

$$
\begin{array}{c}
R^1\text{OR}^1 \\
\downarrow \\
\text{AlR}^2{}_3
\end{array}
\xrightarrow{h\nu}\ R^1\text{H}\ +\ R^1R^2\ +\ R^1\text{OH}
$$

Di-p-tolyl ether reacts twice as fast as bis-2-phenylethyl ether. Benzyl phenyl ether is cleaved by triethylaluminium exclusively at the benzylic carbon-oxygen bond but anisoles are cleaved predominantly at the aryl-oxygen bond. Photochemical cleavage of dibenzyl ether yields some n-propylbenzene but no benzyl alcohol suggesting that any initially formed alcohol is alkylated

as in the thermal alkylations described above (p. 15). The photochemical alkylations do not require excess aluminium alkyl and the order of reactivity (Bu^i_3Al > Et_3Al > Me_3Al) is the reverse of that in the thermal reaction. It is suggested that the photochemical reaction may be by homolytic breaking of the C—O bonds.

The use of the sterically hindered diethyl(2,2,6,6-tetramethylpiperidido)-aluminium [57] as base for the isomerisation of epoxides to allylic alcohols has been described [78].


(58)　　　　　(57) 0^0 3 h　　　　　(59)
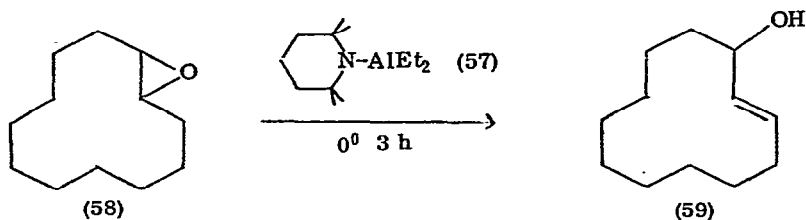
Thus (E)-cyclododecene oxide (58) is converted in 90% yield to (E)-2-cyclododecen-1-ol (59). The Z-isomer of (58) reacts much more slowly. Reactions of several other epoxides, including several important inter-mediates in hormone syntheses, have also been documented. The good stereochemical control is thought to result from non-bonding interactions in a cyclic transition state (60).

(60)
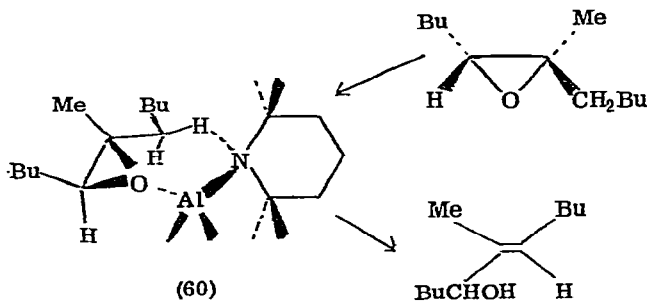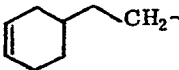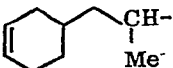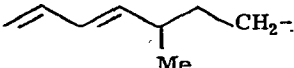
It was shown several years ago that the reaction between propylene oxide and triethylaluminium resulted in alkylation at the more substituted carbon atom. The similar reaction with trimethyaluminium has been described [79].

$$\text{Me-CH} \overset{\displaystyle |}{\underset{\displaystyle CH_2}{\diagdown}}\text{O}\!\rightarrow\!\text{AlMe}_3 \quad \xrightarrow[\text{(ii) } H_2O]{\text{(i) } 130^0} \quad \underset{\displaystyle Me}{MeCH\text{-}CH_2OH} \quad + \quad \underset{\displaystyle OH}{Me\text{-}CH\text{-}CH_2\text{-}Me}$$

$$(61) \quad 90\% \qquad\qquad\qquad 6\%$$
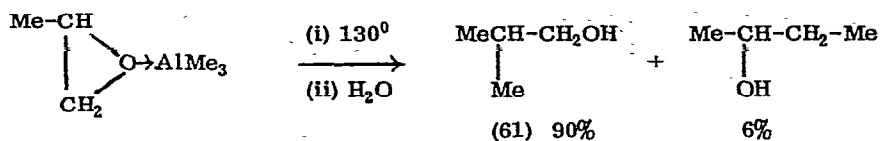
Reaction with the stronger Lewis acid dimethylaluminium chloride is less clean; besides 2-methyl propanol (61) the products include methane and the various butenes. Only methane and unsaturated hydrocarbons are obtained from the methylaluminium dichloride adduct.
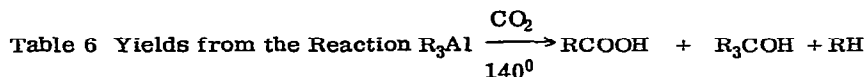
Carbonation of trialkylaluminiums yields (after hydrolysis) both carboxylic acids and tertiary alcohols. Relative yields of acid and alcohol from several unsaturated organoaluminium compounds (made by trans-alkylation from tri-isobutylaluminium and olefins) have been documented (Table 6) [80, 81], and the results are consistent with the following reaction scheme.

Table 6 Yields from the Reaction $R_3Al \xrightarrow[140^0]{CO_2} RCOOH + R_3COH + RH$

R	RCOOH/%	R₃COH/%	RH/%
(cyclohexenyl)–CH₂–	31	20	
(cyclohexenyl)–CH(Me)–	26	12	45
(dienyl)–CH(Me)–CH₂–	45	5.5	36
(trienyl)–CH(Me)–CH₂–	22		

$$R_3Al \xrightarrow{CO_2} R_2AlOCR \xrightarrow{R_3Al} RCR + R_2AlOAlR_2$$

(with the carbonyl structures R₂AlOĊR and RĊR showing =O)

$$R_3COAlROCOR \xleftarrow{CO_2} R_3COAlR_2$$

with arrow R_3Al pointing up to RCR region, and $2CO_2$ arrow down to $RCO.OAlR.OAlR.OCOR$

$$R_3COAlR_2 \text{ (via } R_3Al)$$

$$\downarrow H_2O$$

$$RCOOH + RH + R_3COH$$

$$RCO.OAlR.OAlR.OCOR$$

$$\downarrow H_2O$$

$$2RCOOH + 2RH$$
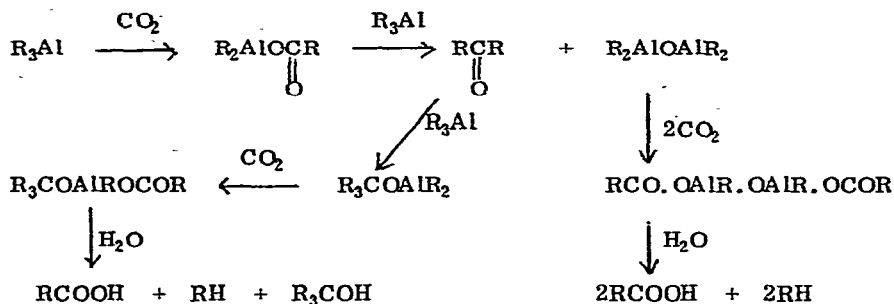
Thus the intermediates $R_2AlOAlR_2$ and R_3COAlR_2 have been isolated and shown to be rapidly carbonated giving the required products after hydrolysis.

10. REACTIONS WITH ORGANIC NITROGEN COMPOUNDS

Organoaluminium compounds react with amines to give donor-acceptor complexes, which on heating eliminate hydrocarbons to give derivatives $(R^1R^2AlNR^3R^4)_n$. When R^1-R^4 are all different a variety of stereoisomers may be obtained and these have been characterised for the first time in a study [72] of the compounds $(EtBrAlNHBu^t)_2$ (62). Of the five possible isomers two [(62a), (62b)] have been separated by fractional sublimation and a third (62c) identified in solution by 220 MHz NMR spectroscopy.

(62a)   (62b)   (62c)

(62d)   (62e)
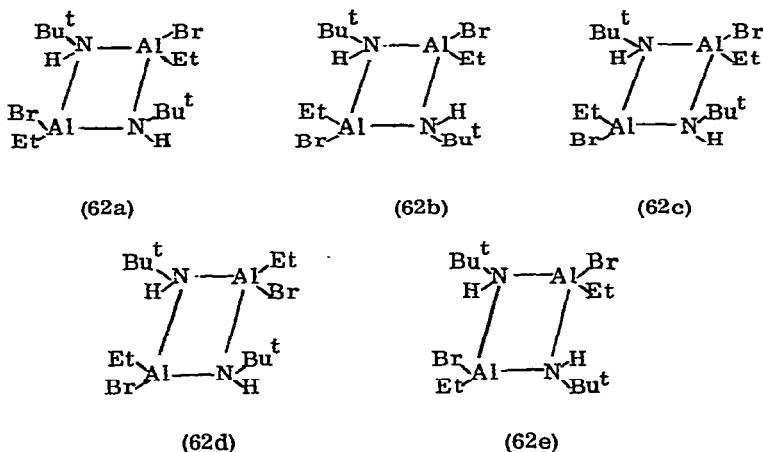
A preliminary X-ray investigation of the isomer (62a) suggests that the ring is not planar. This gives maximum separation of t-butyl groups without

creating close bromine-bromine interactions. Both cis- and trans-isomers of the compound $(Et_2AlNHBu^t)_2$ have been identified from 220 MHz NMR spectra. Various isomeric species interconvert in solution and exchange is observed between the halogeno- groups X when different compounds $(EtX^1AlNHBu^t)_2$ and $(EtX^2AlNHBu^t)_2$ are mixed. All these reactions are thought to involve ring-opening and monomeric species $R^1R^2AlNR^3R^4$. A second paper [83] on the dimethylamine and t-butylamine adducts of diethyl-aluminium halides Et_2AlX shows that the rate of thermal elimination of ethane decreases for the series (X =) Et > Cl > Br > I, and describes the inte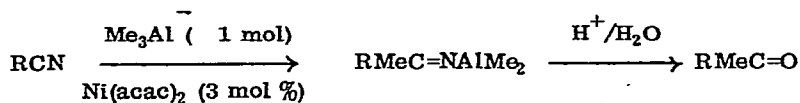r-esting observation that the decomposition of $Et_2ClAlNHMe_2$ follows zero-order kinetics and appears to be surface catalysed.

The reaction between pyrazole and the compounds R_3Al or R_2AlCl (R = Me, Et) gives a series of volatile derivatives (63); the molecules are apparently in the boat configuration, with rapid inversion on the NMR time scale in solution [84]. Two isomers [(64a), (64b)] are indicated for the compounds $(MeClAlN_2C_3H_3)_2$ (64). The preparation of dimethylaluminium azide, $(Me_2AlN_3)_3$ from $Me_3SiN_3, AlMe_3$ has been described [85].


(63)   (64a)   (64b)
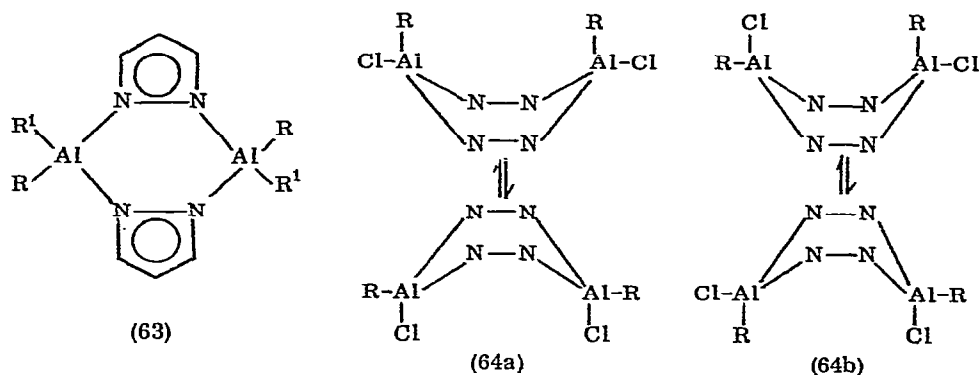
[The carbon atoms of the pyrazole rings are omitted from formulae (64).]

Several reports deal with reactions between organoaluminium compounds and unsaturated carbon-nitrogen functions. The addition of trimethylaluminium to nitriles, like the addition to carbonyl compounds described in Section 9, is catalysed by bis(acetylacetonato)nickel(II) [86].

$$\text{RCN} \xrightarrow[\text{Ni(acac)}_2 \ (3 \text{ mol } \%)]{\text{Me}_3\text{Al} \ (\overline{} 1 \text{ mol})} \text{RMeC=NAlMe}_2 \xrightarrow{\text{H}^+/\text{H}_2\text{O}} \text{RMeC=O}$$

The reaction occurs in hydrocarbon solvents at about 20^0, but not in ether, and the following yields have been obtained: PhCOMe, 80%; $C_{12}H_{25}$COMe, 80%; PhCH$_2$COMe, 70%; Ph$_2$CHCOMe, 80%; p-ClC$_6$H$_4$COMe, 66%; CH$_3$CO(CH$_2$)$_2$-COCH$_3$, 34%. Side reactions such as ketenimide formation (R^{1}R^{2}CHCN $\rightarrow$ R^{1}R^{2}C:C:NAlR$^3_2$) and subsequent condensation seem to be less troublesome than in the corresponding methylations with methyl-lithium or Grignard reagents.

The reaction between acetonitrile and trimethylaluminium to give a ketimine derivative is well established. The reactions with dimethyl-aluminium chloride and more especially methylaluminium dichloride under vigorous conditions 120–170^0 yield methane and products from trimerisation of the acetonitrile [87] formulated as follows:
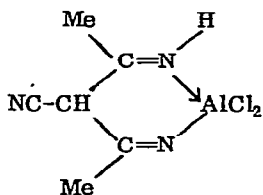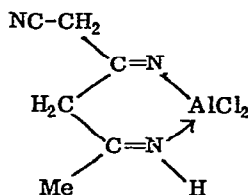
(65) (66)

The reaction of methylaluminium dichloride with diacetyldianil (67) yields a donor-acceptor complex. The corresponding compound with trimethyl-aluminium has not been isolated; the product (68) after hydrolysis yields 2-(N-phenylamino)2-methylbutan-3-one anil (69) [88]. Ethylaluminium chlorides react similarly.
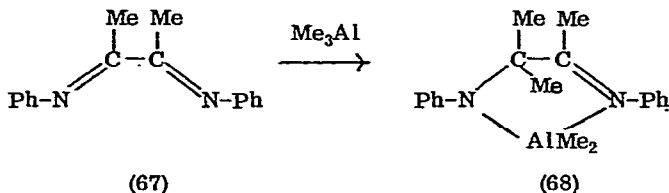
(67) (68)
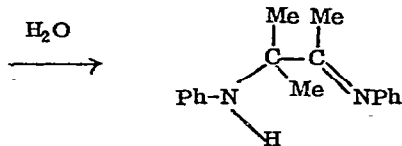
(69)

Diphenylamidodiethylaluminium reacts with aldimines with insertion of the C=N bond into a C-_ortho_-H bond to give aluminium heterocycles. A similar reaction has been observed with N-alkyl phenylamido derivatives [89].

$[R^1 = $ Me or Ar; $R^2 = $ H or Me; R^3, $R^4 = $ Ar: yields 36–78%]
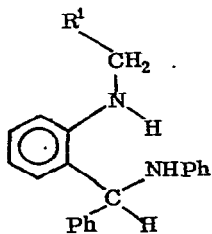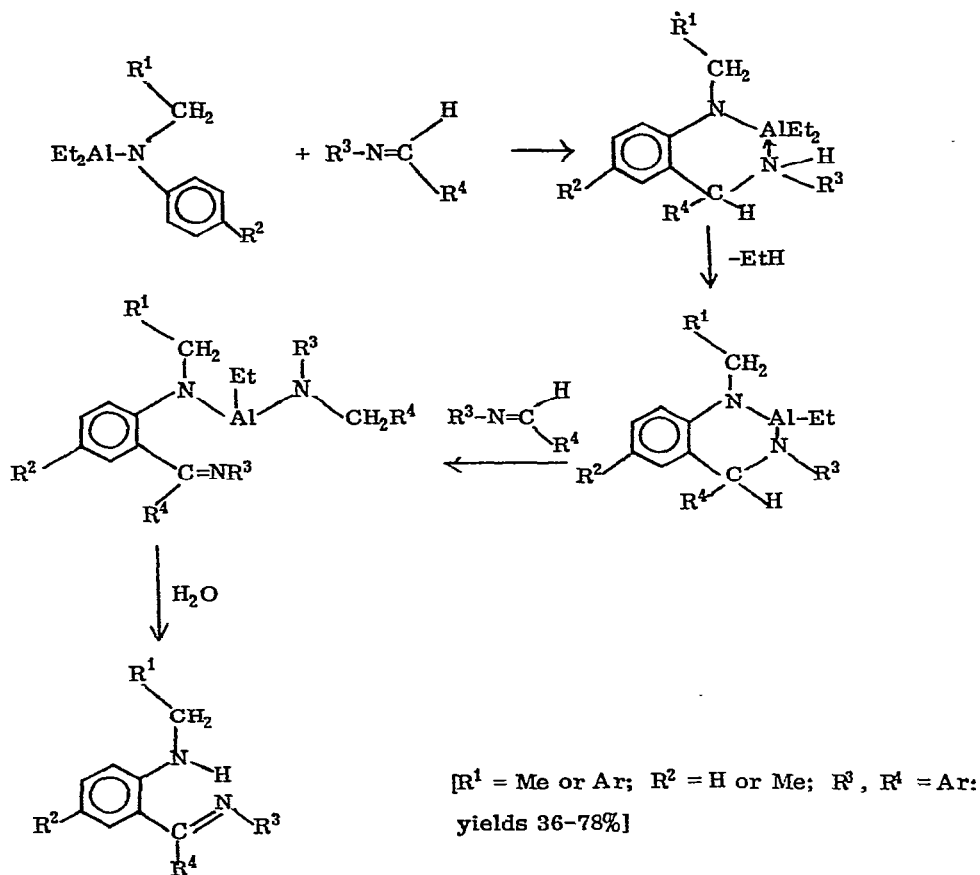
(70)

The reaction of $Cl_2AlN(Ph)CH_2R^1$ with PhN=CHPh also yields
a compound (70) from attack at the <u>ortho</u>-ring position. Similar cyclic
adducts result from the reaction between diethyl(dimethylamido)aluminium
and ketenimines [90].

$$Et_2AlNMe_2 + 2Me_2C=C=N-Ar \longrightarrow$$

(71)

$$[Ar = Ph, \underline{p}-CH_3C_6H_4]$$
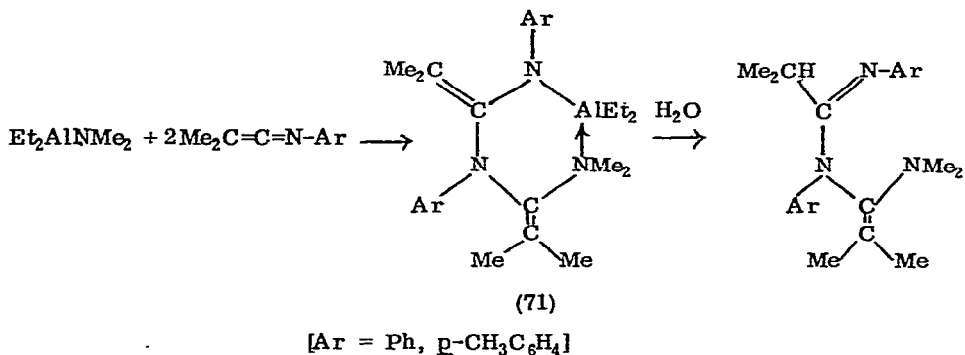
The corresponding reaction with Et_2AlSEt gives the 2:1 adduct $(ArNC=CMe_2)_2AlEt_2SEt$ analogous to (71) and a 1:1 adduct which is hydrolysed to
$Me_2CH-C(SEt)=NAr$.

11. REACTIONS WITH SULPHUR COMPOUNDS

Bis(dimethylaluminium)sulphide has been isolated from the reaction
between trimethylaluminium in heptane and liquid hydrogen sulphide at
-78^0 [91]. Like the ethyl compound $(Et_2Al)_2S$ reported in 1970, it easily
disproportionates. It is sparingly soluble in hydrocarbon solvents, but
forms complexes with donor solvents such as benzonitrile, pyridine or
dioxan. There is no structural information. Bis(dimethylaluminium)-
sulphide is also formed in the reaction between trimethylaluminium and lead
sulphide [92]. The other products are tetramethyl-lead and metallic lead,
and the best transfer of methyl groups from Me_3Al to Me_4Pb (about 22%)
is obtained with a Me_3Al/PbS mol ratio of 1 at 135^0 for $\frac{1}{2}$ h.

The amido compounds Me_2AlNPh_2, $Me_2AlNMePh$ but not Me_2AlNMe_2,
react with carbon disulphide to give $Me_2AlS_2CNPh_2$ (75% yield) or
$Me_2AlS_2CNMePh$ (50%). The CS_2 thus inserts into Al–N rather than the
Al–C bonds [93].

12. ORGANOALUMINIUM HYDRIDES

Complexes of pentafluorophenylalanes $(C_6F_5)_xAlH_{3-x}nL$ ($x = 1, 2$; $n = 1, 2$; $L = OEt_2$, NMe_3) have been made from chloroalane and pentafluorophenyl-lithium in ether [94] and a patent [95] has described the preparation of dioctylaluminium hydride $(C_8H_{17})_2AlH$ from powdered aluminium (activated by milling with titanium isopopoxide in benzene-triethylaluminium), n-octene and hydrogen.

The compound $NaAlH_2Et_2$ has been used for reduction of phosphates, phosphonates, or phosphinates to intermediates which react with alkyl halides to give tertiary phosphine oxides.

$$(RO)_nP(O)R'_{3-n} \xrightarrow{\ NaEt_2AlH_2\ } \xrightarrow{\ R''X\ } R''_nP(O)R'_{3-n}$$
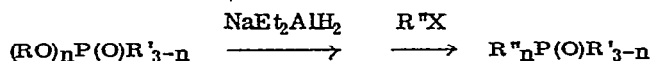
Yields are comparable with those from reactions using Grignard reagents and in some cases procedures are simpler and more convenient. Di(sec-butyl)aluminium hydride has been used for the stereospecific reduction of the ketosilane $Me_3SiCHPrCOPr$ [97].

13. MISCELLANEOUS OXYGEN DERIVATIVES

Several compounds R_2AlX, in which X is an oxyanion, have been characterised by vibrational spectroscopy. For example, freshly prepared bis(dimethylaluminium)sulphate (72), from dimethylaluminium chloride and sodium sulphate in cyclohexane, appears to monomeric (D_{2d}) in hydrocarbon solvents, but solutions slowly precipitate a polymeric material, presumably with Me_2Al- bridges between sulphate groups [98].
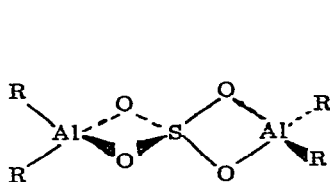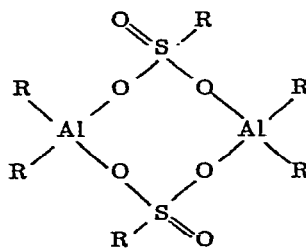
(72)   (73)

Dialkylaluminium sulphonates [99], made some years ago from tri-alkylaluminiums and sulphonic acids, may also be obtained from the reaction between trialkylaluminiums and sulphur trioxide. The sulphonates do not react with a second mole of sulphur trioxide. The compound Me_2AlO_3SMe is trimeric in benzene but Et_2AlO_3SMe and Et_2AlO_3SEt are dimers. The vibrational spectra – particularly in the region characteristic of S=O stretching – suggest that the bridging sulphate groups are bidentate (73). The aluminium compounds are isolated as easily sublimed solids which react with air and water. In contrast the indium and thallium compounds dissolve in water and apparently ionise to $R_2M^+RSO_3^-$.

Similar studies of the reactions of trialkylaluminiums with phosphorus oxyacids yield similar results, and compounds $(Me_2AlO_2PF_2)_3$, $(Me_2AlO_2PCl_2)_3$, $(Me_2AlO_2PH_2)_3$ and $(Me_2AlOSPMe_2)_2$ have been characterised [100]. Vibrational spectra [101, 102] have been interpreted in terms of puckered rings, twelve membered (D_3) for trimers and eight membered for   dimers, in which the phosphorus oxyanions are bidentate.

Dialkyl phosphoromethylamidates $(RO)_2P(O)NHMe$ react with tri-ethylaluminium in benzene to give compounds $[(RO)_2P(O)NMeAlEt_2]_2$ (74). Association to dimers is complete in freezing benzene when R = Me, Et, but not when R = Pr^i, Bu^i, Am^i. The derivatives $[(R_2N)_2P(O)NMeAlEt_2]_2$ (R = Me, Et) have also been isolated, and reactions with aldehydes and phenyl iso-cyanate to give imines have been described [103]. The elimination products (75), (76) are formed less readily from compounds with bulky substituents (R = Bu^i, Am^i) than from the methyl and ethyl derivatives. Sulphur compounds $R_2P(S)NMeAlEt_2$ and $R_2P(S)SAlEt_2$ are monomeric in benzene [104] and vibrational spectra confirm the structure (78) with intramolecular co-ordination of sulphur to aluminium.

$(RO)_2P(O)NMeAlEt_2$ (74) $\xrightarrow{ArCHO}$ [cyclic structure with RO, P=O, AlEt$_2$, N, O, Me, C, Ar, H] $\longrightarrow$ $(RO)_2P$ [cyclic O–O AlEt$_2$]

$+$ Ar$\backslash$C=N–Me with H (75)

PhNCO $\searrow$

$(RO)_2P(O)NMeCONHPh$ $\xleftarrow{H_2O}$ [cyclic structure: RO, P=O, AlEt$_2$, N, O, Me, C, N, Ph] (77) $\longrightarrow$ $(RO)_2P$ [cyclic RO, O–O AlEt$_2$]

$+$ Ph–N=C=N–Me (76)

$+$ PhNHCONHMe

$R_2P(S)NHMe$ $\xrightarrow{Et_3Al}$ R_2P [cyclic S, AlEt$_2$, NMe] (78) $(R = Me, Et, Pr^i, Bu^t)$

PhNCO(R=Me) $\swarrow$

[cyclic Me$_2$P, S, AlEt$_2$, N, O, Me, C, N, Ph] (79) $\xrightarrow{H_2O}$ Me_2P =S with NMeCONHPh

Et_2P [cyclic S, AlEt$_2$, S, O, C, N, Ph] (80)

The reaction of $Et_2P(S)SAlEt_2$ with phenyl isocyanate gave the cyclic product
(80) [cf., (77), (79)] but ca. 10% decomposed to PhNCS and $Et_2P(S)OAlEt_2$
by an elimination reaction. Eliminations were also observed in the reaction
between $Me_2PS(NMe)AlEt_2$ and benzaldehyde.

The reaction between squaric acid $H_2C_4O_4$ and trimethylaluminium
has been described, but the product $(Me_2Al)_2C_4O_4$ was not obtained pure [105].

Salicylaldoximato derivatives of nickel and palladium (but not copper) react with tri-isobutylaluminium to give compounds (81) analogous to the diphenylaluminium compounds described last year [106].
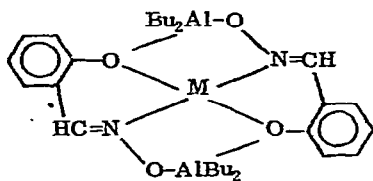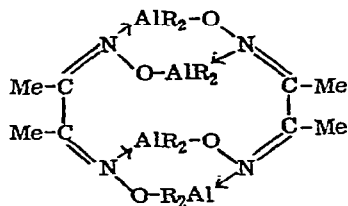
(81)   (82)

Organoaluminium compounds react with dimethylglyoxime or salicylaldoxime to give compounds which are formulated with cyclic molecules (82), (83) [107].
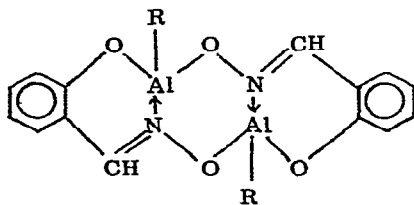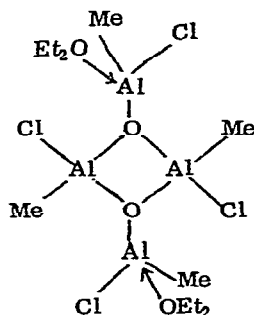
(83)   (84)

These react with pyridine to give adducts by co-ordination to aluminium.

Partial hydrolysis of the complex Me_2AlCl, OEt_2 yields a colourless viscous liquid formulated as $[(MeAlCl)_2O.OEt_2]_2$ (84). The ether may be displaced by benzonitrile [108]. No complex formation was however detected by IR spectroscopy between the alkoxides Me_2AlOPh, Et_2AlOPh, $Me_2Al(2,6-Me_2C_6H_3O)$ and benzonitrile [109].

Thermal decompositions of organoaluminium alkoxides and their silicon analogues have been compared [110].

$$2Me_2AlOSiPh_3 \xrightarrow{250^0/50\ h} MePhAlOSiPh_2Me + Ph_2AlOSiMe_2Ph$$

$$Ph_3COAlEt_2 \xrightarrow{150^0/2-6\ h} Ph_3CH + C_2H_4$$

$$Ph_3COAlMe_2 \xrightarrow{125-30^0/1\ h} Ph_3CMe$$

Although there is extensive scrambling of organic groups in molecules of the compounds with Si–O–Al links, there is no reaction corresponding to the reduction or methylation observed for compounds with the C–O–Al sequence.

Several papers on reactions of organoaluminium compounds with peroxides have appeared. The compound $EtAl(SiPh_3)_2, 2LiBr, 2THF$ (30) reacts at 20^0 with t-butylhydroperoxide with cleavage of both aluminium–carbon and aluminium–silicon bonds [57].

$(Ph_3Si)_2AlEt2LiBr2THF$ (30)

$\downarrow Bu^tOOH$

$EtH + (Ph_3Si)_2AlOOBu^t + Ph_3SiAlOOBu^t + Ph_3SiH$

                                              |
                                              Et

$\downarrow$

$Ph_3SiOAlSiPh_3$ $\searrow$ $Ph_3SiOAlOBu^t$
       | |
       OBu^t Et

$\downarrow$ $\xrightarrow{H_2O/OH^-}$

H_2O/H^+

$Ph_3SiOH + Bu^tOH + Ph_3SiH$ $2Ph_3SiOH + Bu^tOH + H_2$

The ethylbis(triphenylsilyl)aluminium complex (30) does not react with t-butyl peroxide below 70^0. Above 85^0, however, the products are $(Ph_3Si)_2$, $Ph_3SiEtAlOBu^t$, and Ph_3SiOBu^t, showing that there is predominant cleavage of the Al–Si bond. The compound $EtAl(OSiPh_3)_2$ reacts with benzoyl peroxide to give (benzoyldioxy)triphenylsilane (85) and (benzoyloxy)ethyl(triphenylsiloxy)aluminium (86) without attack at the Al–C bond [110].

$$EtAl(OSiPh_3)_2 + (PhCOO)_2 \longrightarrow Ph_3SiOOCOPh + Ph_3SiOAlEt$$
$$\underset{\displaystyle OCOPh}{|}$$

(35)   (86)

The reaction of the carbon analogue $EtAl(OCPh_3)_2$ with benzoyl peroxide gives a variety of products including ethane, ethylene, ethyl benzoate, biphenyl and carbon dioxide, with both homolytic and heterolytic cleavage of the Al–C bond.

14   DONOR-ACCEPTOR COMPLEXES

The donors D (D = Me_3N, Me_2O, Me_2S) react with the cyclic compound $(Me_2AlNPh_2)_2$ to form complexes $Me_2(NPh_2)Al,D$ [111]. Evidently the NPh_2 group (unlike NMe_2) is insufficiently basic to compete with the donors D for the acidic aluminium. The similarity between NPh_2 and Me as bridging groups between $AlMe_2$ fragments was shown some years ago by the isolation of μ-NPh_2-μ-$MeAl_2Me_4$. This compound, with a limited supply of donor D gives Me_3Al,D and $(Me_2AlNPh_2)_2$, showing that Me_3Al is a better Lewis acid than Me_2AlNPh_2. Triethyl-aluminium reacts with bis(diphenylphosphino)amines $(Ph_2P)_2NR$ (R = Pr, Bu) to give 1:1 adducts similar to those reported earlier. Presumably the aluminium is 5-co-ordinate and interacts with two neighbouring phosphorus atoms in the donor. When R = PhCHMe, $PhCH_2$, or with $(Ph_3P)_2NNMe_2$, no complex formation is detected, suggesting that bulky substituents at nitrogen prevent complex formation with the lone pairs on the phosphorus atoms [112]. No complex is detected between trimethylaluminium and carbon monoxide: trimethylaluminium and phosphorus trifluoride react to give a complex mixture which is thought to contain methylphosphines [113].

The complexes $Et_2AlCl,bipy$ and $EtAlCl_2,bipy$ (bipy = 2,2'-bipyridine) have been isolated [114]; $EtAlCl_2,bipy$ separates when bipyridine is added to the sesquichloride $Et_3Al_2Cl_3$. Bipyridine displaces dioxan from complexes with ethylaluminium chlorides. Another study of complex formation between triethylaluminium and the polydentate ligand polyethylene glycol is said to show that at low Al/glycol ratios the aluminium is 5-co-ordinate [115]. A complex $Me_3PbCl,MeAlCl_2$ has been proposed from IR, Raman and conductivity studies [116].

The photoelectron spectra of the complexes of triethylaluminium with diethyl ether, dimethyl sulphide and pyridine have been published [117]. The peaks at 8-10 eV which correspond to the removal of electrons from the lone pair of the free donors are shifted in the expected way on complex formation. It is confirmed that triethylaluminium is a harder acid than dimethylzinc.

Finally, the molecules Me_3NAlMe_3 have been chosen for a study by NMR techniques of molecular motion. It is possible to distinguish reorientation of the N-methyl groups and reorientation of the whole molecule about the Al–N bonds [118].

15. TETRA-ALKYLALUMINATES

The direct formation of the Group II tetraethylaluminates from metal and triethylaluminium – a reaction well known for Group I metals – has been described [119]. The rate depends on the state of division of the alkaline earth metal and grinding with glass balls has been found to be effective. Triethylaluminium is a convenient solvent, and yields have varied from 42% (for Ba) to 77% for Ca.

$$3M \ + \ 8AlEt_3 \ \longrightarrow \ 3M[AlEt_4]_2 \ + \ 2Al$$
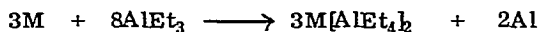
Lower yields are obtained in paraffins. The reaction is suppressed in diethyl ether or THF, but remarkably fast in diglyme: for example, a 95% conversion of calcium to $Ca[AlEt_4]_2$, $D_{2.3-2.5}$ (87) (D = $CH_3OCH_2CH_2OCH_2CH_2OCH_3$) is obtained after only 3 h [120]. The viscous oils, e.g., (87), contain a higher proportion of diglyme than the crystalline complexes $M[AlEt_4]2D$. The tetra-alkyl compounds $M[AlEt_4]_2$ react with bromine or iodine at -80^0 – -70^0 in toluene or -40^0 – -20^0 in ether to give MX_2, EtX, (X = Br, I) and Et_3Al, and with aluminium halides AlX_3 (X = Br, Cl) to give MX_2 and Et_3Al.

NMR spectra of the compound $Li[Me_3SnAlMe_3]$ have been recorded during an investigation of metal-metal bonding in trimethyltin organometallic compounds, and the value of the coupling constant $^3J(SnAlCH)$ (29.6 Hz), confirms the Sn–Al bond [122].

16. CATALYSIS

No attempt has been made in this survey to cover all the catalytic applications of organoaluminium compounds, but the examples quoted illustrate some of the areas where there is current research activity.

Reaction between a 3:2 mixture of butadiene (88) and methyl sorbate (89) in the presence of a catalyst of $Ni(acac)_2$, Et_3Al, Ph_3P yields products which show that the butadiene has reacted as a diene and the methyl sorbate as a dienophile. In the absence of the catalysis the roles of the starting materials are reversed, but the mechanism of the catalysis has not been elucidated [123].
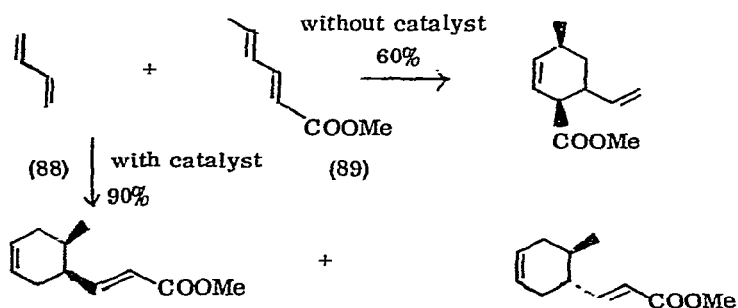

Similar results were obtained with 2,3-dimethylbutadiene in place of butadiene.

Similar catalyst systems $[M(acac)_n$-$AlEt_3$, $(M = Ni, Co, Fe)]$ catalyse hydrosilylation of 1,3-dienes or terminal acetylenes by compounds $HSiX_3$ [123]. With isoprene or penta-1,3-diene the 1,4-adducts $MeCH=CMeCH_2SiX_3$ or $MeCH_2CH=CHCH_2SiX_3$ are the major products. Terminal acetylenes $RC\equiv CH$ yield products in which hydro-silylation is accompanied by linear dimerisation e.g. to $H_2C=CRCR=CHSiX_3$. Much detailed information and a discussion of the mechanism have been given [124]; the role of the organoaluminium compound is thought to be to reduce the nickel compounds to reactive zerovalent intermediates. The reaction between trimethylaluminium and tris-(acetylacetonato)cobalt(III) gives a Co(II) acetylacetonate and finally metallic cobalt. The gaseous products are methane, ethane and ethylene [125].

Several other studies are concerned with systems related to Ziegler–Natta catalysis. Thus gas evolution from mixtures of tri-isobutylaluminium and tetrabutoxytitanium in hydrocarbon solvents and hydrolysis with D_2O are said to show formation of $Ti-CH_2-CMe_2-Ti$ and $Ti-CH_2-CH_2-Ti$ bridges. In $Me_3Al-Ti(OBu)_4$ mixtures, $TiCH_2CH_2Ti$ and $TiCH_2Ti$ bridges have been postulated. Hydrolysis products show that hydrogen atoms from the bridging chains are readily replaced by aluminium [126]. The preparation and physical properties of polyacetylene films on the quiescent surface of a concentrated solution of $Et_3Al-Ti(OBu^n)_4$ have been described [127].

A mixture of bis(cyclopentadienyl)vanadium dichloride and ethyl-aluminium dichloride in dichloromethane-heptane is a catalyst for polymerisation of ethylene. ESR spectra of the solution can be ascribed to three species, only one of which remains after three weeks [128]. This is not catalytically active and appears to be $(C_5H_5)_2VAlCl_5$ (90). The
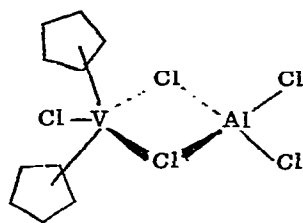
(90)

The structures of the other species have not been identified. ESR spectra of $Et_3Al-(C_5H_5)_2TiCl_2-PR_3$ mixtures have also been described but detailed conclusions about the structures of various species have not been possible [129]. A detailed study [130] of the soluble Ziegler-Natta catalyst $(C_5H_5)_2RTiCl-R'AlCl_2$ has shown that the kinetics depend in a complicated way on added olefin and on changes in solvent. The ligand R is expelled half as alkane and half as alkene. The results suggest that the rate equation is:

$$\text{Rate} = k[(C_5H_5)_2RTiClR'AlCl_2][\text{olefin}]$$

Simple kinetics are observed in the presence of a non-polymerisable olefin. In the absence of added olefin, the kinetics are more complicated because olefin derived from the group R during the reduction catalyses the reaction. This catalysis is affected by changes in solvent which give variations in the rates of competing olefin polymerisation reactions. IR and NMR spectra of Ziegler–Natta catalysts formed from diethylaluminium bromide and $TiCl_4$, VCl_4, $VOCl_3$ in carbon tetrachloride and from complexes with methyl methacrylate have been published, but no conclusions about the structures of these species have been reached [131].

Ethylaluminium dichloride is a constituent of many olefin metathesis catalysts, and several investigations concerned with this reaction have been described [132–134].

Organoaluminium compounds without transition metal derivatives have also found applications as catalysts in organic chemistry. Thus photolysis of N-benzylanilines in the presence of even a small excess of ethylaluminium dichloride (above that required for complex formation) gives m-, as well as o- and p-benzylaniline [135].
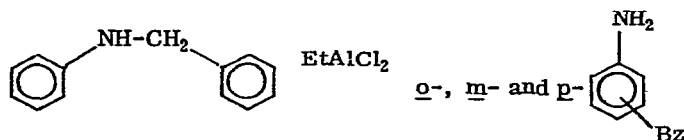
m–Migration of this kind is unusual. The m-benzylaniline has been shown not to result from isomerisation of initially formed o- and p- derivatives.

The dimerisation of methyl crotonate is catalysed by trialkylaluminium-t-amine complexes [136].

(92)

(91)   (93)
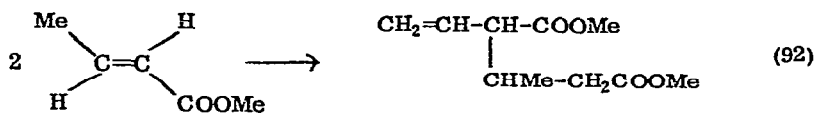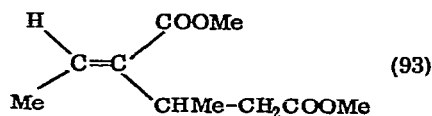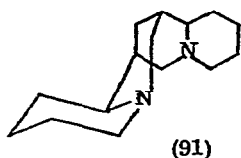
With the triethylaluminium complex of the bidentate ligand sparteine (91)
the product is dimethyl 2-methylpent-4-ene-1,3-dicarboxylate (92) and
with the complex Et_3Al, NEt_3 the product is dimethyl 2-methylpent-cis-
3-ene-1,3-dicarboxylate (93). Triethylaluminium-triethylamine also
induces the co-dimerisation of methyl 4-methyl-trans-2-hexenoate (94)
with methyl isopropylacrylate (95) and methyl crotonate (96).

$R^1 = H, R^2 = Pr^i;$ $R^1 = Me, R^2 = H;$ $R^1 = Bu^s, R^2 = H$

(95)   (96)   (94)
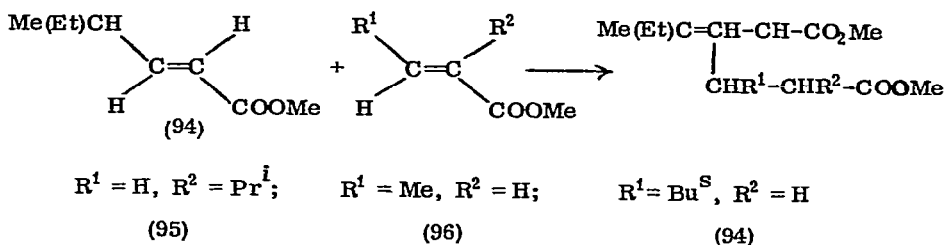
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