ALUMINIUM
ANNUAL SURVEY FOR THE YEAR 1980*

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CONTENTS

1. INTRODUCTION REVIEWS

The volume of work published annually on organoaluminium chemistry remains almost constant. It is, however, increasingly scattered, particularly among journals dealing with organic chemistry. Like organoboron compounds, organoaluminium compounds have found widespread applications for stereo- and regio-selective synthesis. As they have become standard commercially available reagents, their uses have become

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* Aluminium Annual Survey covering the year 1979, see J. Organometal. Chem., 207 (1981) 67-109. No reprints available.

increasingly subtle and elegant. New and unusual structures continue to be found, however, particularly among organoaluminium compounds involving other metals, and there is continued interest in the possible involvement of such compounds in catalytic cycles.

The chemistry of organoaluminium compounds published during 1979 has been summarised in a Royal Society of Chemistry specialist periodical report [1]. Other important reviews have been on Ziegler-Natta catalysis [2, 3], and on formation and reactivity of complexes of carbonyl compounds with organoaluminium compounds [4]: this last article contains many useful tabulated data. Organoaluminium compounds are also referred to extensively in reviews covering wider topics, for example, homogeneous catalysis [5], alkali metal-transition metal complexes [6], thermochemistry of organic derivatives of non-transition metals [7], organomagnesium compounds in polymerisation [8], organozirconium compounds in organic synthesis [9], selectivity in organometallic reactions through anchimeric coordination [10], nucleophilic displacement at silicon [11], and synthesis, structure and vibrational spectra of organomethyl-compounds [12]. There have also been reviews in Japanese [13, 14] and an account, in Russian, of research on the chemistry of high molecular weight compounds in petroleum chemistry [15], which contains several papers on organometallic compounds of aluminium.

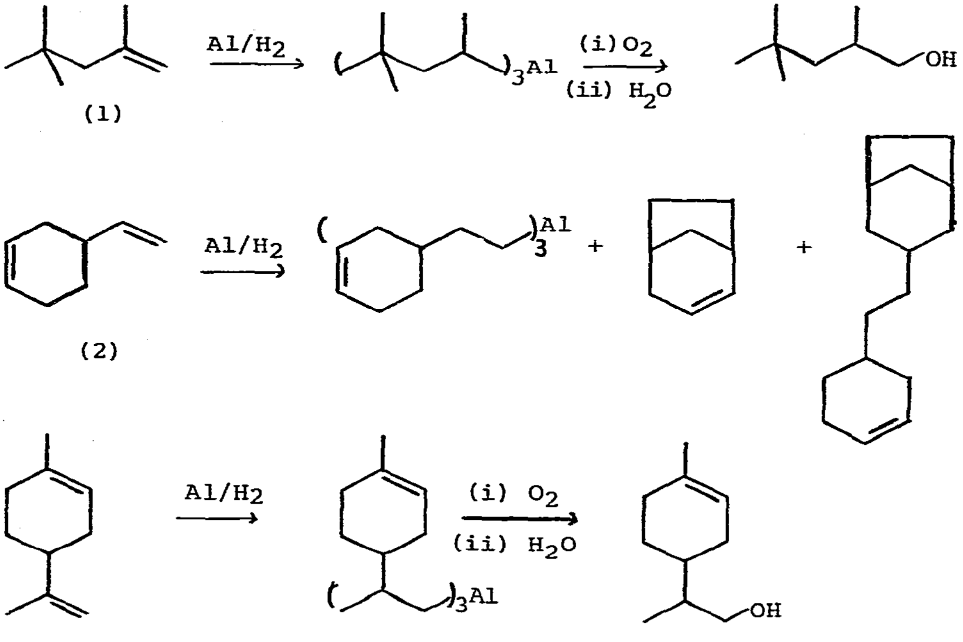
2. TRIALKYL- AND TRIARYLALUMINIUMS ATE COMPLEXES

A patent [16] describes the preparation of AlR_3 (C_5-C_{12} alkyl) from Al/Mg and RI at 80-110^o in inert hydrocarbons. The so-called 'direct synthesis' of organoaluminium compounds (Equation 1) from aluminium, hydrogen and the alkenes 2,4,4-trimethylpent-1-ene(1), 4-vinylcyclohexene(2) or the diene(3) has been investigated [7]. The products were identified by

$$2AlR_3 + Al + {}^3/_2H_2 \rightarrow 3AlR_2H \qquad \underline{1a}$$

$$AlR_2H + \text{alkene} \rightarrow AlR_3 \qquad \underline{1b}$$

oxidation or by reactions with sulphur dioxide. Syntheses from alkenes (1) and (3) were accomplished in an autoclave in a single step but for (2) there were concurrent rearrangements and oligomerisations. Trimethylvinylsilane, $Me_3SiCH{=}CH_2$, was converted in low yield to $Me_3SiCH_2CH_2Al(CHMeSiMe_3)_2$.

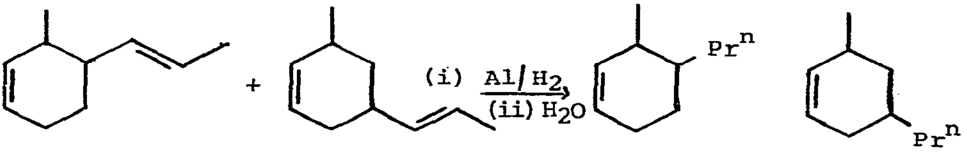


(1)

(2)

(3)

The dienes (4) and (5) obtained by thermal or catalytic dimerisation of pent-1,3-diene could also be converted to organoaluminium compounds; for this a two-stage process (Equations 1a and 1b) was most satisfactory.



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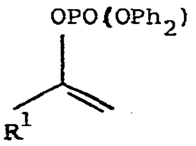
Because of their extreme sensitivity towards hydrolysis and oxidation, trialkylauminiums are not easily characterised by physical methods. The determination of the molecular weight distribution of trialkylauminiums and compounds $R_2Al(OAlR)_n$-$OAlR_2$ (R = Et or Bu^i) by gel permeation chromatography has been described [18], and details of the mass spectrometric fragmentation of the compounds $AlMe_3$, $AlEt_3$, $AlBu^i_3$, $AlEt_2H$, $AlBu^i_2H$ and $AlEt_2Cl$ have been given [19]. The trialkylaluminiums show no peaks in mass spectra from breakdown of dimers.

More than 75% of the ion current is carried by even-electron ions; in ions $[(Y_2C{=}CH_2)Al]^+$ (Y = H or Me) the aluminium may be bound through π-electrons. Mass spectra of the hydrides and $AlEt_2Cl$ show peaks from fragmentation of dimers (Compare also ref. 38 and 106).

Trialkyl- and triaryl-aluminiums have been used to activate magnesium metal for reaction with amines [20] and for a number of alkylation reactions. For example, reaction between triphenylaluminium and tellurium tetrachloride yields, after hydrolysis, triphenyltelluronium chloride Ph_3TeCl and aluminium hydroxide [24]. The phosphate esters (6), obtainable from enolisable ketones RCOMe (R = n-$C_{10}H_{21}$, Ph or 4-t-butylcyclohex-1-enyl) are alkylated with $AlMe_3$ or $AlEt_3$ in the presence of $Pd(PPh_3)_4$ as catalyst to give, after hydrolysis, good yields of the alkenes (7). With



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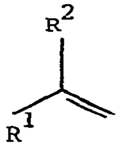

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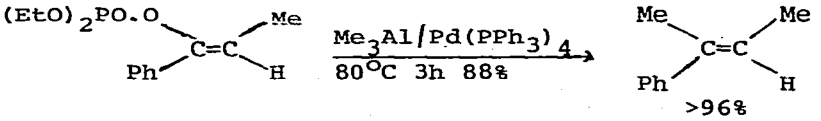
alkynylaluminium compounds $R^3C{\equiv}CAlEt_2$ (R^3 = Ph or n-C_5H_{11}), the phosphate functions are replaced exclusively by alkynyl groups to give (7) (R^2 = $C{\equiv}CR^3$) without trace of (7) (R^2= Et). The alkenylaluminium compound n-$C_5H_{11}CH{=}CHAlBu^i_2$ similarly gives $CH_2{=}C(R^1)CH{=}CHC_5H_{11}$. The high stereospecificity of the reaction is shown by the reactions of (*Z*) and (*E*)-1-phenyl-1-propenyl diethyl phosphates (Equations 2 and 3).



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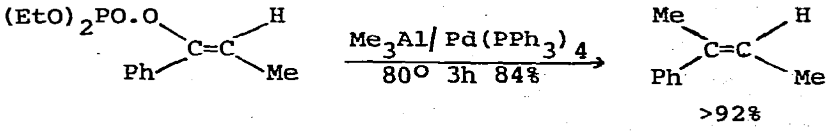

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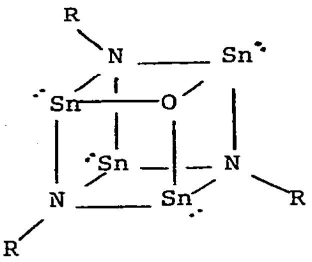
No reaction was observed in the absence of catalyst. Attempted alkylations with methyllithium or methylmagnesium iodide yielded only the original ketones on work-up. Alkylation of phosphate esters is discussed further in Section 8.

Trimethylaluminium forms a complex with the cage compound (8) which is related to the cubane derivative (9) by replacement of one NBu^t-group by oxygen [23]. The $AlMe_3$ is coordinated to



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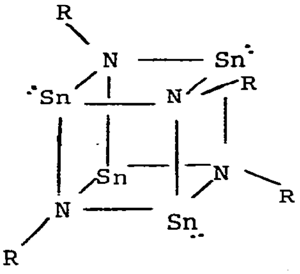
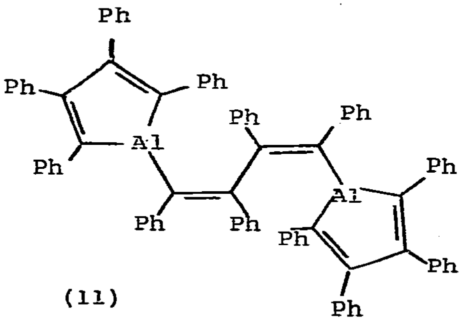


(9)

the oxygen atom of (8) and the resulting complex and (9) are isostructural. The Lewis basicity of the oxygen is surprisingly strong: the mass spectrum of the Me_3Al-complex shows an ion assigned to loss of methyl from the parent. On heating (8) is transformed into (9) but the other product of this reaction, presumably having stoichiometry $SnOAlMe_3$, has not been isolated. Chemical Abstracts refer to dielectric permittivity measurements on toluene solutions of the complexes formed by aromatic ethers Ph_2O, $4\text{-}PhOC_6H_4OPh$ and $(4\text{-}PhOC_6H_4)_2O$ with triisobutylaluminium [24] and to the preparation of the complexes $R_3POAlMe_3$ (R = Me or Ph) from the reaction between the phosphine oxide and the complex Et_2OAlMe_3 without solvent [25].

The compounds $MAlMe_2(C{\equiv}CMe)_2$ (M = Li or Na) and $LiAlMe_2(C{\equiv}CBu^t)_2$ have been obtained as 1:1 complexes with 1,4-dioxan from the reaction between $Me_2AlC{\equiv}CR$ and $MC{\equiv}CR$ ($R = Me$ or Bu^t) [26]. Solutions of the alkynylaluminates show significantly lower conductivities than those of $LiAlMe_4$, measured under the same conditions, suggesting that bridging between the two metal atoms may be stronger by alkynyl than by methyl groups. The low solubility of the complexes in hydrocarbons may indicate polymeric structures in the solid. The mixed alkynyl compounds $LiAlMe_2(C{\equiv}CMe)(C{\equiv}CBu^t)$ appear to rearrange in solution to $LiAlMe_2(C{\equiv}CMe)_2$ and $LiAlMe_2(C{\equiv}CBu^t)_2$.

The reaction between 1,2,3,4-tetraphenyl-1,4-dilithium butadiene (10) and $AlCl_3$ (mole ratio 3:2) yields a crystalline substance which is presumed to have the structure (11) together with solvent of crystallisation [27]. With (10) and $AlCl_3$ in mole ratio 2:1 in diethyl ether, the product is formulated as the lithium salt of the anion (12). Conductivity measurements show that the self-ionisation of (11) to (12) and the cation (13) is slight except in the presence of strong bases such as tetramethylethylenediamine which presumably stabilise (13). Both (11) and the lithium salt of (12) react with bis(cycloocta-1,5-diene)nickel to give compounds in which the cyclic, but not the acyclic, diene systems coordinate to nickel. With nickel(II) bromide the species (11) and (12) give the cyclooctatetraene (14) and with $[NiBr_2(diphos)]$ (diphos = $Ph_2PCH_2CH_2PPh_2$) in tetrahydrofuran (THF) they give the tetraphenyl-cyclobutadiene derivative (15). Since (15) may be converted to (14) by reaction with carbon monoxide it is likely that the aluminium species (11) and (12) are converted to (14) by cyclobutadiene intermediates.



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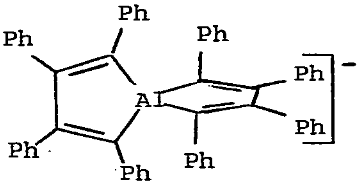

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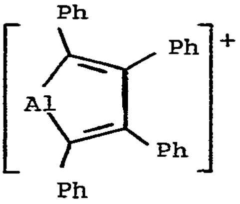

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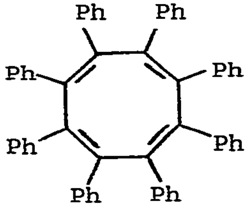

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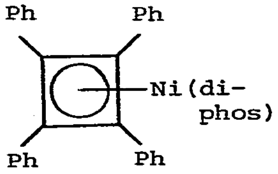

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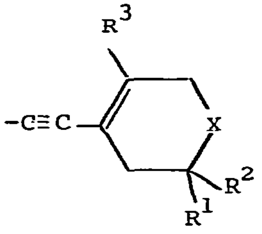
It has been known for some years that potassium tetraethylaluminate(III) may be obtained by the reaction between potassium metal and triethylaluminium at 110°C. In an attempt to detect radical intermediates, this reaction has been studied at 20°C [28]. ESR spectra of two paramagnetic species have been published, but one of these seems to be the biphenyl radical anion [29, 30] and the other is of unknown structure.

There have been several reports of the use of tetraorganoluminate anions in synthesis. For example, the compounds $\mathrm{LiAl(C{\equiv}CR)_4}$ (R = (16); X = O or S: $R^1 = R^2 = \mathrm{Me}$, $R^3 = \mathrm{H}$; X = NMe: $R^1 = R^3 = \mathrm{Me}$, $R^2 = \mathrm{H}$) react with diiodoacetylene to give $\mathrm{RC{\equiv}CI}$ or $\mathrm{RC{\equiv}CR}$ (R = (16)), depending on the mole ratio. The enediynes $\mathrm{RC{\equiv}CI}$ are more reactive, and are isolated in lower yield, than the dienetriynes $\mathrm{RC{\equiv}CR}$ (R = (16)) [31]. The use of aluminium ate complexes for control of stereochemistry has also been exploited [32, 33]. Thus the α-lithiosulphoxide (17), on treatment with triethylaluminium followed by D_2O, yields the product (18) with inversion of stereochemistry. This is the opposite of that observed in the absence of Lewis acid, perhaps indicating that the aluminium coordinates in an ate complex from the side opposite the lithium in (17). Methylation, by iodomethane, of (17) which normally proceeds with inversion at carbon, is not affected by the presence of triethylaluminium [32]. Aluminium ate complexes may also be used to control the regiochemistry of reactions of substituted allylic carbanions [33]. Thus the lithium compounds (19)



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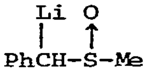
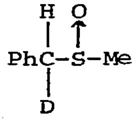


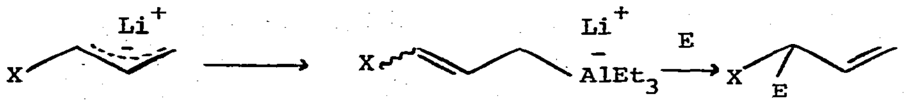
$\mathrm{Ph}\overset{\mathrm{Li}}{\mathrm{C}}\mathrm{H}-\overset{\mathrm{O}}{\overset{\uparrow}{\mathrm{S}}}-\mathrm{Me}$

(17)



$\mathrm{Ph}\underset{\mathrm{D}}{\overset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\uparrow}{\mathrm{S}}}-\mathrm{Me}$

(18)



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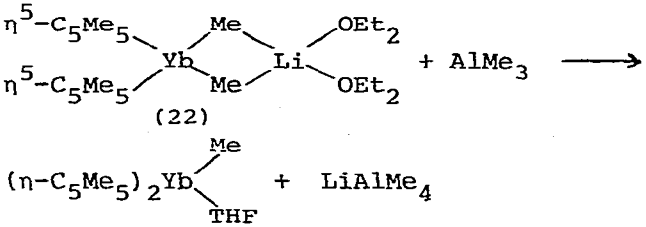
(19) (20) (21)

(X = OPr^i or SPr^i) react with triethylaluminium in ether/alkane solvent at -78^oC to give ate complexes (20) which react with electrophiles E ($MeCH{=}CHCH_2Cl$, $Me_2C{=}CHCH_2Cl$, aldehydes RCHO (R = Ph, MeCH=CH, Bu^n, Bu^i) or ketones cyclohexanone, octan-2-one or acetophenone) predominantly in the α position to give (21) (Equation 4). In contrast, without the triethylaluminium, the compounds (19) react at both α and γ positions; there is much poorer control over the regiochemistry.

The ready formation of lithium tetramethylauminate(III) assists in the conversion of the ytterbium compound (22) into (23) (Equation 5)



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(23)

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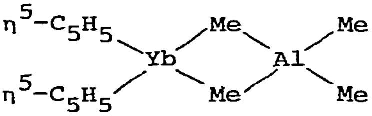
Even with an excess of trimethylaluminium, there is no evidence for formation of a compound analogous to the less sterically hinderered derivative (24) described in the 1979 Survey [34].



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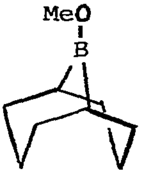


(25)

Two more papers [35, 36] on trimethylsilyl derivatives of aluminium have appeared. The direct mercury-catalysed reaction between lithium, aluminium and chlorotrimethylsilane in benzene-THF or (better) in diethyl ether yields the compounds $Al(SiMe_3)_3L$ (L = THF or Et_2O) as colourless, crystalline, spontaneous inflammable solids [35]. The sodium compound $[NaAl(SiMe_3)_4\ 2(MeOCH_2CH_2OMe)]$ was obtained similarly in only 10% yield after one week: a better preparation was from the mercury and aluminium derivatives according to Equation 6 (M = Na or K). Solvates with various ethers may be characterised, and the ether-free compounds may be isolated by sublimation in high vacuum [36]. Ether-free tris(trimethyl-

$$M + Hg(SiMe_3)_2 + Al(SiMe_3)_3 \xrightarrow[C_5H_{12}\ \ 12\ h]{Et_2O} MAl(SiMe_3)_4 \cdot xEt_2O \qquad \underline{6}$$

silyl)aluminium (25) may then be made from the sodium aluminate and aluminium(III) chloride in pentane (Equation 7).

$$3NaAl(SiMe_3)_4 + AlCl_3 \longrightarrow \underset{(25)}{4Al(SiMe_3)_3} + 3NaCl \qquad \underline{7}$$

It would be interesting to know the structure of (25) but attempts to obtain single crystals have met with difficulty and spectroscopic measurements have been hampered by the surprisingly low solubility in organic solvents [35].

3. ALKYL- and ARYL-ALUMINIUM HALIDES

Another patent (see last year's survey) refers to the preparation of dialkylaluminium halides R_2AlCl (C_4-C_{32}-alkyl) from ethylene and short chain dialkylaluminium chlorides in xylene using 0.3-2 mol.% $TiCl_n(OR')_{4-n}$ (R' = n-alkyl C_{1-10}, n = 0-3) [37].

The mass spectra of $AlBu^i_2Cl$, $AlEt_2Cl$ (compare ref. 19), $AlBu^iCl_2$, $AlEtCl_2$ and $AlCl_3$ have been described [38]. As expected, ions from dimeric species dominate increasingly along this series, indicating a decreasing tendency to dissociate to monomer. Complex fragmentations of pyridine and ether complexes of these compounds have also been documented.

An X-ray study [39] has shown that in $[Me_4N][AlMe_3I]$ the Al-I distance (266(1) pm) is significantly longer than that in $Me_3N:AlMe_2I$ (258 pm). Other parameters for the $[AlMe_3I]^-$ anion are: Al-C 196(4), 204(3), and 204(3) pm; I-Al-C 108(2) 103(2) and 98(1)°; C-Al-C 115(1), 118(2) and 112(2)°. The compound $Cs[AlMe_2I_2]C_6H_4Me_2$ is obtained as a p-xylene solvate. The anion is on a two-fold axis with Al-I 264.7(4) and Al-C 198 (2) pm. Bond angles are: I-Al-I 102.3(2); C-Al-C 115(1); I-Al-C 114(3) and 106(3)°. Cesium ions are separated by p-xylene molecules and linked by iodine atoms with which there may be some bonding (Cs...I 392.5(1) pm) [40]. In $Cs[AlMe_3NCS]$ [41], the aluminium is bound to nitrogen with Al-N 194 (1) pm. The SCN group is linear and the C-N-Al angle is 175(1)°.

In chemical syntheses, organoaluminium halides have been used to replace halogens or alkoxy groups by organic groups. For example, the reaction, first described in 1977, between aluminium compounds derived from allyl bromides $RCH{=}CHCH_2Br$

and MeO-9-BBN (25) to yield allyl-9-BBN derivatives has been used as part of a new procedure for stereoselective syntheses of β-substituted alcohol units of macrolide antibiotics [42]. Similarly, alkynylaluminium sesquibromides react with t-butoxy compounds, e.g., as in Equation 8, to give propargyl products without allenic impurities. In contrast, the ether (26)

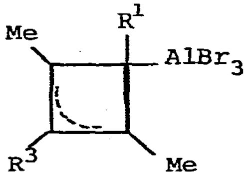
$$\underset{(26)}{\mathrm{Bu^tOCH_2NEt_2}} + (\mathrm{HC{\equiv}CCH_2})_3\mathrm{Al_2Br_3} \rightarrow \mathrm{HC{\equiv}CCH_2CH_2NEt_2} \qquad \underline{8}$$

and the sesquibromide from 1-bromo-but-2-yne give almost entirely the allenic amine $CH_2{=}C{=}CMeCH_2NEt_2$. With the sesquichloride from crotyl bromide $MeCH{=}CHCH_2Br$, a good yield of the rearranged product $CH_2{=}CHCHMeCH_2NEt_2$ is obtained. These examples are taken from many in a very detailed paper [43] describing the use of organometallic reagents for conversions of gem-amino ethers into unsaturated tertiary amines. A further instance of the use of organoaluminium halides for alkylation is in the conversion of the acid chlorides (27) to the bis(trimethylsilylpropyl) compounds (28) [44] (Equation 9).

$$\underset{(27)}{\mathrm{ClCO(CH_2)_nCOCl}} + \mathrm{Me_3Si(CH_2)_3AlCl_2} \rightarrow \qquad \underline{9}$$

$$\underset{(28)}{\mathrm{Me_3Si(CH_2)_3CO(CH_2)_nCO(CH_2)_3SiMe_3}} \qquad n = 4 \text{ or } 8$$

Previous surveys have described zwitterionic cyclobutadiene-aluminium bromide complexes, e.g. (29), formed by reactions between alkynes and aluminium(III) bromide. NMR evidence has now been



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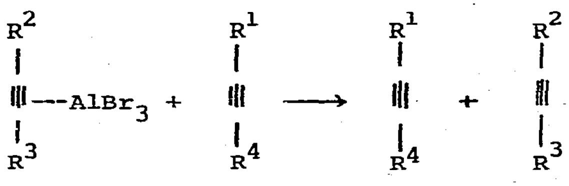

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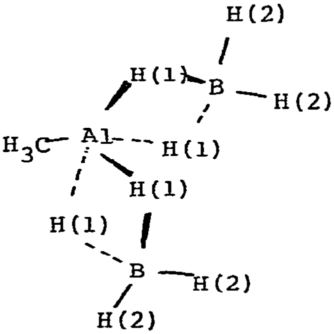
obtained for complexes such as (30) involving donation of alkyne π-electrons to aluminium. These react, rapidly on the NMR timescale, by a bimolecular reaction with an excess of alkyne (Equation 10). The reaction between aluminium(III) bromide and a 1:1 mixture of propyne and but-2-yne at $-85^{\circ}C$ in dichloromethane gave (29) (R^1 = H; R^3 = Me) in 76% yield, with < 5% of (29) (R^1 = R^3 = H) or (29) (R^1 = R^3 = Me), showing a marked preference for heterodimerisation [45]. Formation of an isobutene-aluminium halide complex has also been postulated during a detailed study of the polymerisation of isobutene by aluminium(III) chloride and bromide [46].

4. ALKYLALUMINIUM HYDRIDES

The structure of dimethylaluminium tetrahydroborate was described last year. An electron diffraction study [47] of methylaluminium bis(tetrahydroborate) shows that the compound (31) is monomeric with a planar $CAlB_2$ skeleton. The aluminium atom is five-coordinate and the BH_4-groups are bidentate with the Al $(\mu\text{-}H)_2B$ units not quite normal to the $CAlB_2$ plane.



(31)

The most important molecular parameters are: Al-C 194.1(9), Al-B 215.2(16), Al-H(1) 182.0(9), B-H(1) 124, B-H(2) 120 pm, B-Al-B 121.5(7), H(1)-Al-H(1) 70.3(4)°. As in Me_2AlBH_4, the similarity between the isoelectronic CH_3 and BH_4 groups is apparent. Mass spectra of some alkylaluminium hydrides are described in ref. 19 (See Section 2 above).

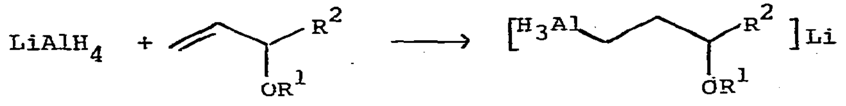
5. ADDITION TO CARBON-CARBON DOUBLE BONDS

Three closely related patents [48-50] describe reactions between organoaluminium compounds AlR^1_3 or $LiAlR^1_4$ and unsaturated substrates. The general reaction shown by Equation 11, in which R^{1-5} are organic groups or H and X is

$$R^2R^3C{=}CR^4CHR^5X + AlR^1_3 \rightarrow R^1R^2R^3C{-}CR^4{=}CHR^5 \qquad \underline{11}$$

halogen, is catalysed by various Cu(I) or Cu(II) compounds, e.g., CuCl, CuBr, CuCN, CuCl, $Cu(OCOMe)_2$ or $Cu(MeCOCHCOMe)_2$. Thus, for example, allyl chloride is converted by triethylaluminium to pent-1-ene [48], propargyl bromide with $LiAl(n\text{-}C_6H_{13})_4$ gives nona-1,2-diene [49] and $CH_2{=}C{=}CHBr$ with $LiAl(n\text{-}C_6H_{13})_4$ gives non-1-yne [50].

Alkenes react with diethylaluminium chloride under mild conditions in the presence of $Zr(OBu)_4$ as catalyst to give $REtC{=}CH_2$ in which the ethyl group has been placed at the β-position [51]. It is suggested that the reaction involves alkylzirconium intermediates. Bis(cyclopentadienyl)zirconium dichloride proved to be ineffective as a catalyst in this work. In another report [52], however, $[ZrCl_2(\eta^5\text{-}C_5H_5)_2]$ is said to catalyse the addition of triisobutylaluminium to alkenes to give high yields of saturated products. Substituents such as OH, SPh or Br, well removed from the double bond, are not affected by reaction with the aluminium compound. The complex $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ also appears to be the most effective catalyst for hydroalumination of allyl ethers using lithium aluminium hydride in THF at 30°C (Equation 12 $R^1 = n\text{-}C_6H_{13}$, EtMeCH–, $EtMe_2C$–, $PhCH_2$– or Ph; R^2 = H)



12

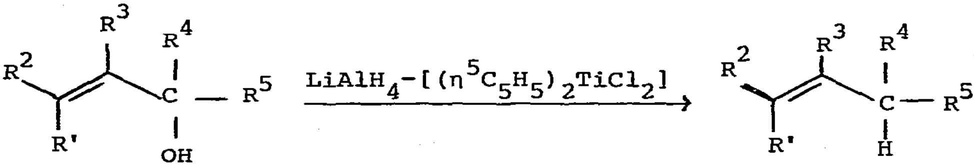
(32)

For hydroalumination of alkenols, zirconium(IV) chloride is the best catalyst (Equation 12, R^1 = H; R^2 = H, Me, Pr^n or Ph). Hydrolysis of (32) (R^1 = H, R^2 = Ph) with D_2O gives $PhCHOHCH_2CH_2D$, showing that the aluminium reacts only at the terminal position: the reaction is thus more cleanly regiospecific than hydroboration with BH_3 [53]. Zirconium(IV) and hafnium(IV) chlorides are also said to be good catalysts for hydroalumination of alkenes $RCH{=}CH_2$ (R = Bu, $n\text{-}C_5H_{11}$, $n\text{-}C_{10}H_{21}$, cyclohex-2-enyl)using $AlBu^i_2H$ [54].

Bis(cyclopentadienyl)dichlorotitanium has also been widely used as a hydroalumination catalyst. As part of an extensive study of hydrometallation, the effect of $[\mathrm{TiCl_2(\eta\text{-}C_5H_5)_2}]$ on the reactions of alkenes and alkynes with complex hydrides $\mathrm{LiAlH_4}$, $\mathrm{NaAlH_4}$, $\mathrm{LiAlMe_3H}$, $\mathrm{NaAlMe_3H}$, $\mathrm{LiAlH_2(NR_2)_2}$, $\mathrm{NaAlH_2(NR_2)_2}$ and $\mathrm{NaAlH_2(OCH_2CH_2OMe)_2}$ has been examined [55]. For terminal alkenes and internal alkynes, high yields of the corresponding alkyl- or alkenyl-aluminium compounds are obtained conveniently in THF at 20°C. Only low yields are obtained with internal alkenes and reactions with terminal alkynes are complicated by rearrangements. The hydrometallation step is thought to involve the titanium hydride $[\mathrm{TiHCl(\eta^5\text{-}C_5H_5)_2}]$ which is regenerated from the alkyltitanium product by transmetallation (Equation 13).

$$\begin{gathered}\mathrm{RCH_2CH_2TiCl(\eta\text{-}C_5H_5)_2 + LiAlH_4 \longrightarrow} \\ \mathrm{RCH_2CH_2AlH_3Li + (\eta\text{-}C_5H_5)_2TiClH}\end{gathered} \tag{13}$$

The catalysis by $[\mathrm{TiCl_2(\eta^5\text{-}C_5H_5)_2}]$ of hydroalumination of alkenes having oxygen substituents is complicated by deoxygenation reactions [56]. Contrast the catalysis by zirconium compounds described above [53]. Indeed, lithium aluminium hydride



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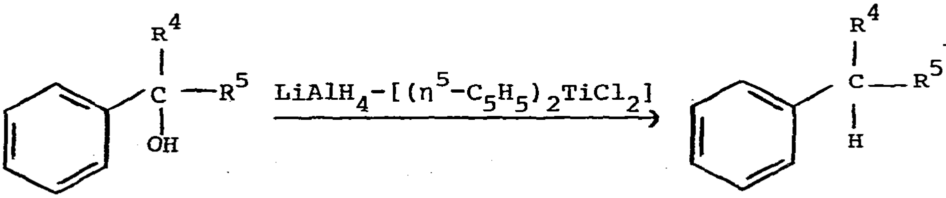
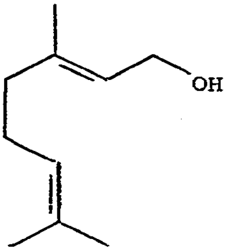


15

in the presence of $[\mathrm{TiCl_2(\eta^5\text{-}C_5H_5)_2}]$ is a convenient reagent for effecting the general reactions denoted by Equations 14 and 15. Thus geraniol (33) and nerol (34) are converted in good yield to the hydrocarbons (35) and (36); benzoyl alcohol,



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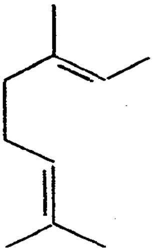

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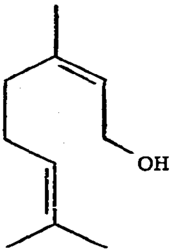

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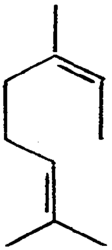
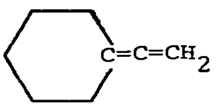


(36)

benzaldehyde and benzoic acid are all converted to toluene and phthalic anhydride is converted to o-xylene. Alkenes with terminal double bonds are simultaneously reduced. For example hex-3-en-1-ol is converted to n-hexane.

Diisobutylaluminium hydride has been used, without catalyst, to reduce selectively the more substituted double bond in allenes. Thus n-$C_6H_{13}CH=C=CH_2$ is converted in 96% yield to n-$C_7H_{13}CH=CH_2$. The allene (37) is converted to (38) [57].



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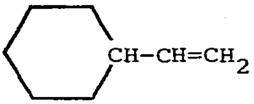
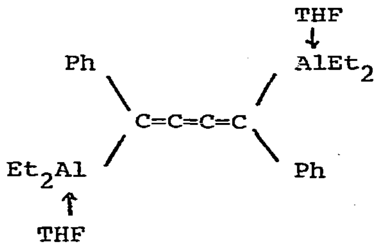


(38)

The cumulene (39) was described in 1978. It now appears that in UV light this is transformed (yield 42% in 6 days) to a colourless crystalline compound which is said from its hydrolysis products to have the structure (40). The same compound (40) is obtained in 30% yield when (39) is heated in toluene for 24 h at 90° [58].



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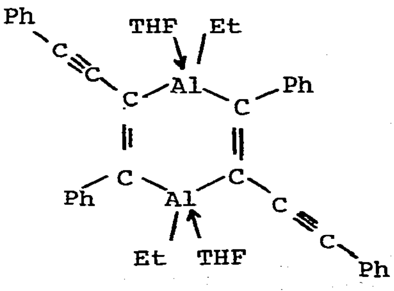


(40)

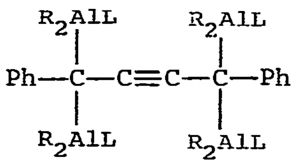
6. ADDITION TO CARBON-CARBON TRIPLE BONDS

An attempt has been made [59] to characterise the viscous liquids obtained from the reaction between hexyne (1 mol) and diethyl- or diisobutyl-aluminium hydride (2 mol) (Equation 16). From hydrolyses and deuteriolyses, these appear

$$BuC{\equiv}CH + 2AlR_2H \rightarrow (R_2Al)_2CHCH_2Bu \qquad 16$$

to be geminal organodialuminium compounds but it has not been possible to purify them by distillation or recrystallisation. The compounds form 1:1 complexes with triethylamine, 1:2 complexes with pyridine and seem not to react with the hindered N,N-diethyl(trimethylsilyl)amine. There are intriguing unsolved problems in this area of organoaluminium chemistry.

Another series of geminal dialuminium compounds (41) (R = Me or Et, L = Et_2O or THF) is obtained, surprisingly, from reactions between dialkylaluminium chlorides and 1,4-diphenylbutadiyne [60]. The structure of (41) has been



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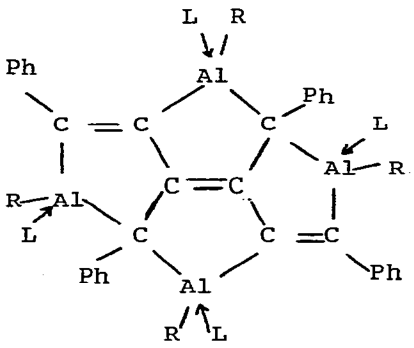
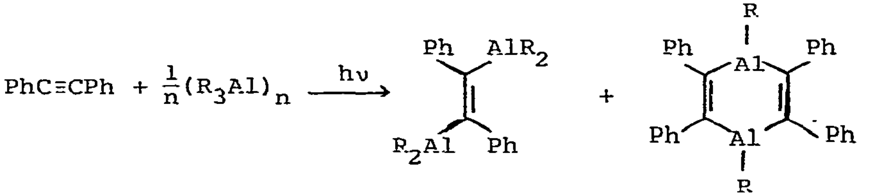


(42)

confirmed by spectroscopic measurements and by an X-ray study (details unpublished). On reaction with alcohol the product is 1,4-diphenylbutadiene; on heating, the compounds (41) are transformed to the red crystalline compounds (42). In the intramolecular rearrangement the complexes $R_3Al.L$ are eliminated. The reaction between dialkylaluminium chlorides, lithium metal and diphenylacetylene to give the heterocycles (43) and the dialuminium compound (44) was described in 1977. The photochemical reaction between diphenylacetylene and R_3Al (R = Et, Pr^i or Bu^i) has now been described (Equation 17). At 25°C the product when R = Et is the compound (43) assumed to form by dimerisation of the cis-dialuminium adduct. At 60°C, when the alkyl is more dissociated to monomeric Et$_3$Al the trans-adduct (44) predominates. The proportions of compounds (43) and (44) have been deduced from the amounts of stilbenes produced on hydrolysis; as reported earlier, both (43) and (44) may be isolated as crystalline THF adducts [61].

Terminal alkynes may be converted with high stereoselectivity into vinylsilanes (Equation 18) which are themselves useful synthetic intermediates [62].



(44) (43)

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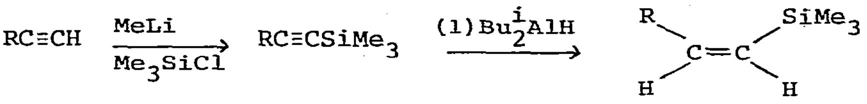
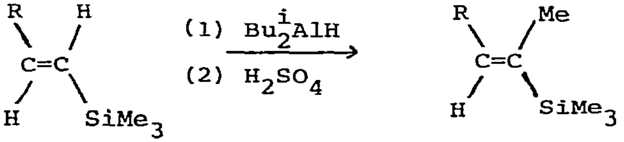


(45)

18

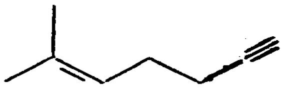
The (Z)-products (45) may be isolated photochemically with N-bromo-succinamide and pyridine to (E)-isomers (46) [63].



(46) (47)

Yields (%)/isomeric purity (%) are: R = Bu^n 77/96; R = Pr^i 76/98; R = cyclo-C$_6$H$_{11}$ 88/98; R = Bu^t 82/99; R = Cl(CH$_2$)$_3$ 88/97. Similarly,(Z)-2-trimethylsilylhept-2-ene is almost completely isomerised to the (E)-isomer, but from vinylsilanes having large substituents at the 1- and 2-positions, mixtures of (E) and (Z)-isomers are obtained. Good yields of the (E)-vinylsilanes (46) (R = CH$_2$OH,CH$_2$OTHP, Ph or C$_6$H$_4$OMe-p; THP = tetrahydropyranyl) may also be obtained from addition of tristrimethylsilylaluminium to the appropriate alkyne HC≡CR. For internal alkynes, e.g., MeC≡CR, higher concentrations of Al(SiMe$_3$)$_3$.OEt$_2$ and aluminium(III) chloride catalyst are necessary. Then (47) (R = CH$_2$OH) may be made in 78% yield and (47) (R = Ph) in 81% yield [64].

A rare example of chloroalumination [119] is described in Section 8 below. Trimethylaluminium has been used in a well-established procedure for conversion of (48) to (49) [65]. Organoaluminium intermediates have been implicated in the reduction of propargylic derivatives with various hydrides [66].



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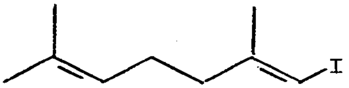
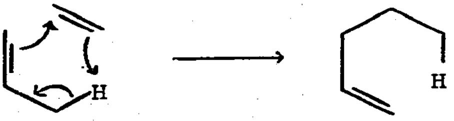


(49)

7. REACTIONS WITH CARBONYL COMPOUNDS

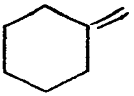
The ^1H NMR spectra of samples obtained by adding crotonaldehyde to diethylaluminium chloride, ethylaluminium sesquichloride or ethylaluminium dichloride in dichloromethane have been examined [67]. At $-60^{\circ}C$ many reactions involving transfer of organic groups between sites are slow on the NMR time-scale, so distinct signals for various complex species in solution are observed. A detailed examination of the chemical shifts provides evidence for complexes $(Et_2AlCl)_2L$ and $(Et_2AlCl.L)_2$ $(L = CH_3CH{=}CHCHO)$. With ethylaluminium sesquichloride, crotonaldehyde adds first to $EtAlCl_2$ and then to the weaker Lewis acid Et_2AlCl; finally a second mole of crotonaldehyde adds to the $EtAlCl_2$. With ethylaluminium dichloride, crotonaldehyde gives first diethylaluminium chloride and $AlCl_3L$, but with more crotonaldehyde these products recombine to give $(EtAlCl_2.L)_2$. As the L/Al ratio is increased further, another disproportionation - reproportionation squence gives first $(Et_2AlCl.L)_2$ and then $EtAlCl_2.2L$.

Studies of this kind in which specific complex species are identified are of interest in view of the increasing use of alkylaluminium halides as Lewis acids for catalysis of reactions in organic synthesis. This has been developed particularly by Snider [68] for reactions of the general type shown in Equation 19. The advantage of alkylaluminium chlorides

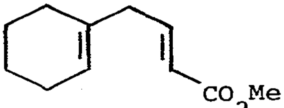


19

compared with say aluminium(III) chloride is that they are proton scavengers so that acid-catalysed rearrangements are largely prevented. Most of the reactions are assumed to involve complexing of alkylaluminium compounds at carbonyl functions; in many cases 50-200 mol % of aluminium compounds are used. For example, methylenecyclohexane (50) reacts with methyl propynoate $HC{\equiv}CCO_2Me$ to give a 92% yield of (51) without rearranged products, e.g., (52) [69]. Many examples of



(50)



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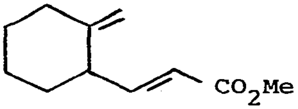
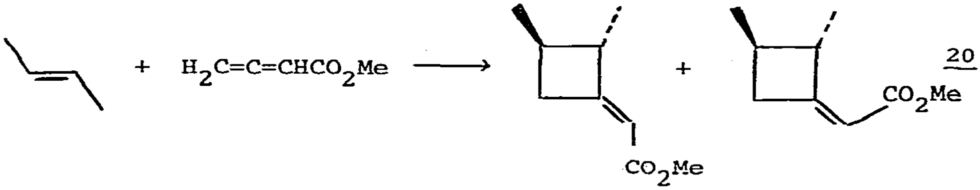


(52)

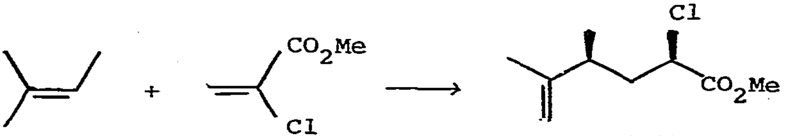
the reactions of methyl chloropropynoate or dimethyl acetylene dicarboxylate promoted by ethylaluminium dichloride have also been described [70]. With trisubstituted alkenes the reaction is regiospecific. The [2 + 2] cycloadditions of methyl buta-2,3-dienoate to alkenes as, for example, in Equation 20 are also promoted by ethylaluminium dichloride [71], as are the



(45%) (35%)

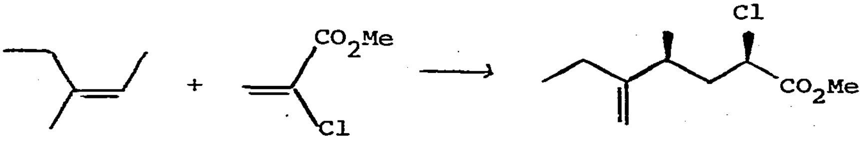
20

reactions of alkenes with methyl α-chloroacrylate [72]. The stereospecificity, producing 1,3-asymmetric centres is shown by Equation 21; the product (53) is contaminated with only 5% of the diastereomer. The regiospecificity is



(53)

21

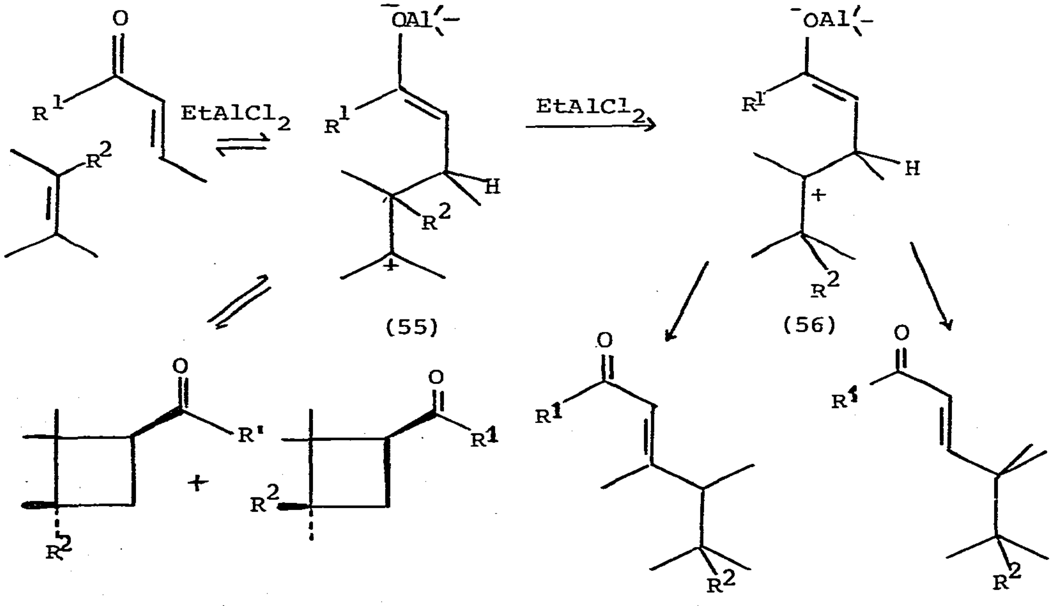


(54)

22

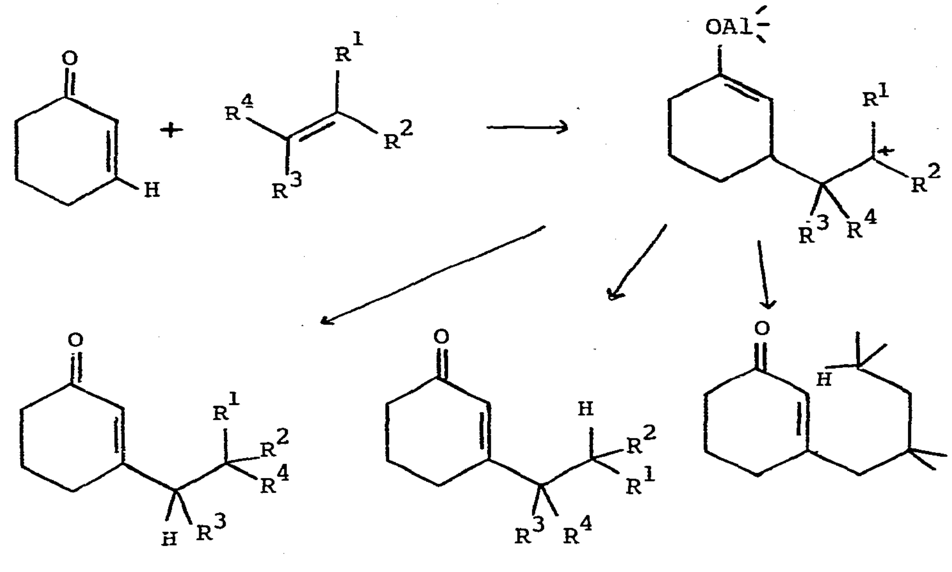
shown by equation 22. The compound (54) is obtained in 86% yield contaminated with 5% of the diastereomer and 10% of a diastereomer of $MeCH{=}CMeCHMeCH_2CHClCO_2Me$. The hydrogen is transferred from an alkyl group syn to the alkenyl hydrogen: in reactions with propynoates [70] the hydrogen is transferred from the alkyl group anti to the alkenyl hydrogen.

In another study [73], it has been found that α,β-unsaturated aldehydes or ketones in the presence of two mol of $EtAlCl_2$ react with alkenes either inter- or intramolecularly to generate α,β-unsaturated carbonyl compounds. This reaction appears to be of wide applicability and an extremely thorough study of the products and stereochemical consequences has been made. If the results of ref. 67 are correct, the presumed active species denoted by $L(EtAlCl_2)_2$ ($L = CH_3CH{=}CHCHO$, say) in [73] is predominantly $\frac{1}{2}(Et_2AlCl)_2 + LAlCl_3$. Yet $AlCl_3$ alone does not seem to be a good catalyst. The addition of alkenes to aldehydes or ketones seems to involve zwitterionic intermediates e.g. (55) or (56) (R^1, R^2 = Me or H), which collapse reversibly at low temperatures (−80°) to cyclobutane derivatives (57) or (58), and rearrange at high temperatures by hydride or alkyl shifts to products (59) and (60). Cyclohexanone reacts with $MeCH{=}CMe_2$, cis-$MeCH{=}CHMe$ or $Me_2C{=}CMe_2$ under similar conditions to give (61)-(62), or with $CH_2{=}CMe_2$ (2 mol)



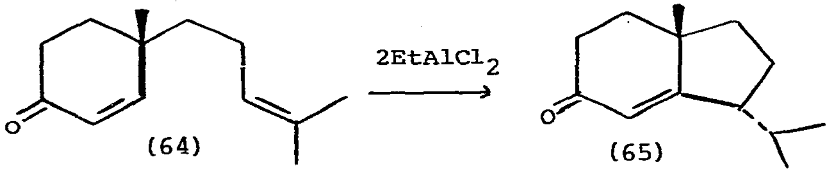
(55) (56)

(57) (58) (59) (60)



(61) (62) (63)

to give (63). The conversion of enone (64) to (65) (Equation 23) almost quantitatively is an example of a highly stereo- and regio-specific intramolecular addition. With less than 1 equivalent of $EtAlCl_2$ the

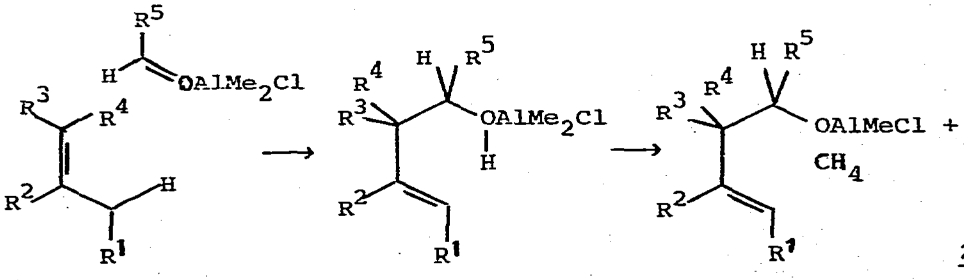


(64) (65)

23

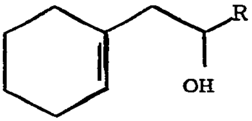
enones and alkenes react to a complex mixture of products. Full details are given in ref [73].

For reactions of aldehydes according to Equation 19, the less acidic dimethylaluminium chloride is an effective catalyst



24

(Equation 24). 1,1-Disubstituted alkenes are most reactive. Good yields of (66) R = Me, Bu^i, Ph, H or Bu^t are obtained from methylenecyclohexane and aldehydes RCHO. The effectiveness of dimethylaluminium chloride as a proton scavenger is shown by the lack of products from 1-methylcyclohexene. The compound (67), obtained in 16% yield from isoprene and Bu^iCHO is a sex attractant of the bark beetle Ips confusus: in this case the major product (60% yield) is the Diels-Alder adduct (68) [74]. Dimethylaluminium chloride also catalyses the reaction of alkynes $RCH_2C{\equiv}CH$ with formaldehyde to give the allenic alcohols $RCH{=}C{=}CHCH_2OH$ (69) and the (Z)-3-chloroallylic alcohols (70) without formation of the (E)-isomers [75].



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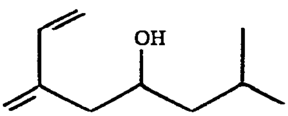

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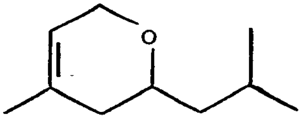

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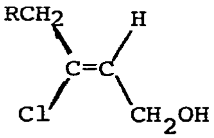

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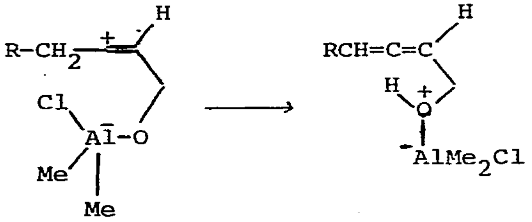
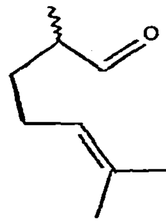


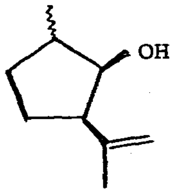
(71) (72)

The alcohols (69) are thought to result from elimination of methane from the vinyl cation (71) via (72). The compound (69) R = C_8H_{17} is an intermediate in the synthesis of the sex pheromone of the dried been beetle and (69) R = $(CH_2)_3CO_2Me$ made using methylaluminium sesquichloride as catalyst is a natural anti-fungal agent.

By varying the alkylaluminium halide catalyst it is sometimes possible to effect considerable changes in products isolated from reactions of carbonyl compounds with alkenes. For example, the cyclisation of 2,6-dimethylhept-5-enal (73) gives mainly (74) ($AlMe_2Cl$ 1 eq./$-80^{\circ}C$), (75) ($AlMe_2Cl$ 2 eq./ $-80^{\circ}C$), (76) and (77) ($AlMe_2Cl$ 2 eq./$0^{\circ}C$), (78) ($AlMeCl_2$ 2 eq./ $-80^{\circ}C$), or (78) and (79) ($EtAlCl_2$ 2 eq./$0^{\circ}C$). Several



(73)



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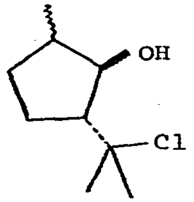

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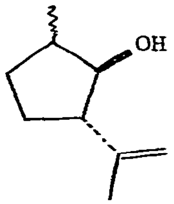

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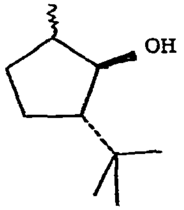

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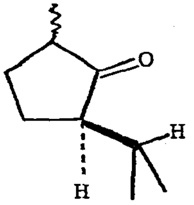

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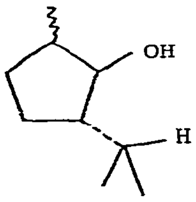

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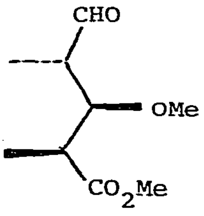

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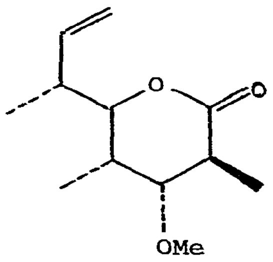
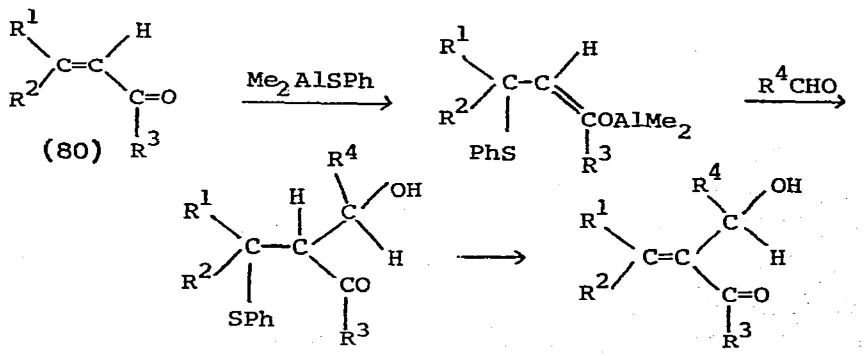


(82)

compounds other than (73) have been studied [76].

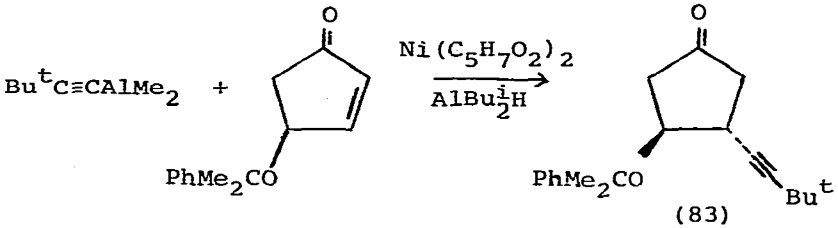
The compounds Me_2AlSPh or $Me_2AlSeMe$ react with α,β-unsaturated carbonyl compounds to give enolates which undergo aldol condensations with aldehydes (Equation <u>25</u>).



<u>25</u>

Good yields of α,β-unsaturated carbonyl compounds may be obtained by subsequent elimination of PhSH, e.g., by sodium iodate oxidation. The reaction seems to have wide applicability [77]. In some cases, e.g., where the starting material (80) is an ester, the ate complex $LiAlMe_3SPh$, made from Me_3Al and LiSPh, is a better reagent than Me_2AlSPh. Triethylaluminium is, however, less effective than triethylborane in enhancing the yield of the threo-compound in the reaction between but-2-enyl-lithium and aldehydes [78].

The reaction between the aldehyde (81) and cis-but-2-enyl-diethylaluminium giving (82) has been used in the synthesis of the polyether antibiotic monensin [79]. The nickel-catalysed conjugate addition of alkynyl groups to α,β-unsaturated ketones was described in a preliminary communication in 1978. The full paper [80] has now appeared. The reaction, exemplified by Equation 26, is highly stereospecific and often

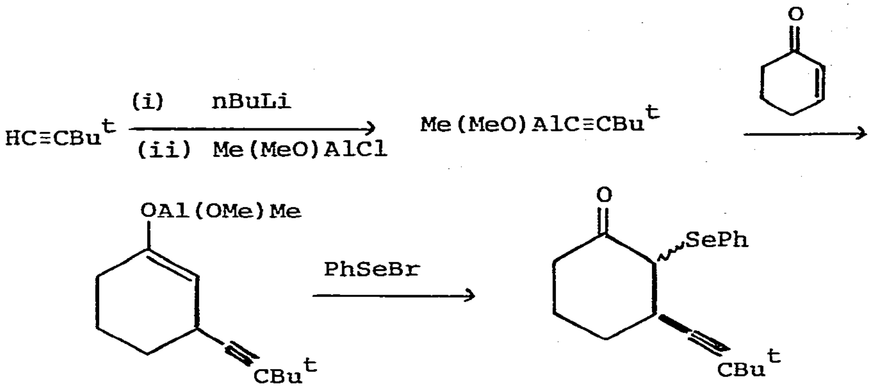


(83)

26

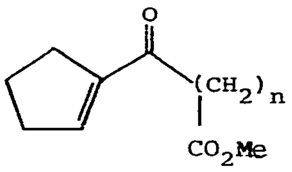
proceeds in high yield, e.g., 85% for (83). Only 1,4-addition is observed and only the alkynyl group is transferred from aluminium. The conjugate addition of alkenylzirconium compounds to α,β-unsaturated ketones has also been extensively documented [81]. Here a mixture of bis(pent-2,4-dionato)nickel and diisobutylaluminium hydride is used as catalyst. Zirconium or aluminium enolates produced in these reactions with α,β-enones have been treated with phenylselenium bromide to give good yields of α-(phenylselenyl)ketones. An example is shown in Equation 27. The Me(MeO)AlCl used as reagent was made from dimethylaluminium chloride and methanol in heptane [82].

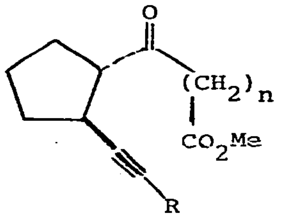
As in previous years, organoaluminium compounds have been widely studied as possible reagents in the synthesis of prostaglandins or prostaglandin analogues. For example, the alkenylaluminium reagents $RC{\equiv}CAlEt_2$ (R = Ph, n-C_6H_{13} or

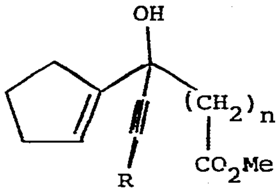


27

n-$C_5H_{11}CH(OSiBu^tMe_2)$) react with acyl cyclopent-1-enes (84) to give both (85) by 1,4-addition and (86) by 1,2-addition. The reaction between $PhC{\equiv}CAlEt_2$ and the tricyclic

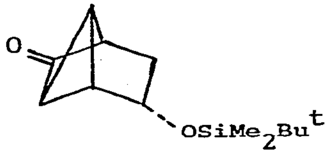


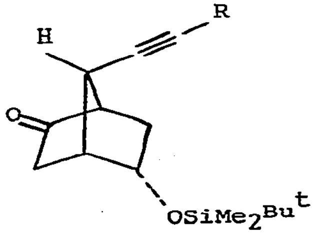




n = 4 or 5

(84) (85) (86)





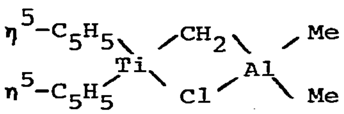
(87) (88)

ketone (87) gave a 70% yield of (88) (R = Ph), showing that homoconjugate addition had occurred on the side remote from the carbonyl group. In a similar reaction with R = $C_5H_{11}CH(OSiBu^tMe_2)$-, as required for prostaglandin synthesis, the yield was only 15%. A better yield of (88) (R =

$C_5H_{11}CH(OSiBu^tMe_2)$)was obtained with the organolithium compound RC≡CLi in hexamethyl phosphoric triamide (HMPT) [83]. Other cases where organoaluminium compounds have been used for the introduction of side chains are described in references [84] and [85].

Organoaluminium compounds have also been used as reducing agents, especially for conversion of lactones to semiacetals [86-91].

Another paper [92] on the reduction of esters describes the use of the reagent (89), first reported in 1978, to convert esters to vinyl ethers. Thus the esters PhCOOR (R = Me or Ph) are converted in excellent yields to $PhC(=CH_2)OR$, $PhCH_2COOEt$ to $PhCH_2C(=CH_2)OEt$ and the esters (90)-(94) to the corresponding compounds in which carbonyl is replaced by methylene. It is clear that both alkene and ketal functionality is tolerated and that no isomerisation of alkenes is induced.



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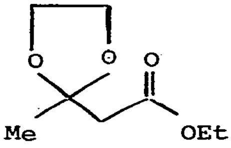

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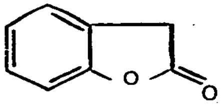

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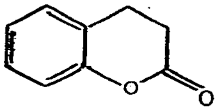

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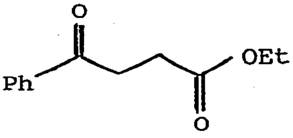

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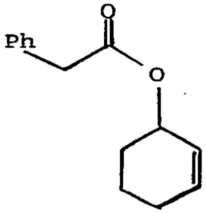
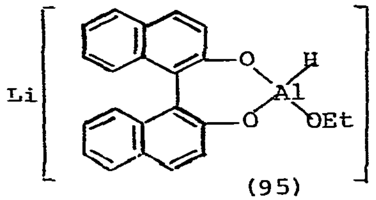


(94)

The chiral reducing agent (95) was mentioned in last year's survey. The (S)-enantiometer, made from (S)-(-)-2,2'dihydroxy-1,1'binaphthyl, $LiAlH_4$ and ethanol in THF, has been used for the synthesis of (S)-(+)-geraniol-1-d from geranial-1-d. Several other isotopically labelled chiral terpenic alcohols, for use in mechanistic studies, have been made in the same way [93 [94]. The reduction of 2-ethoxy-5-alkyl-3,4-



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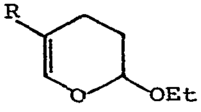

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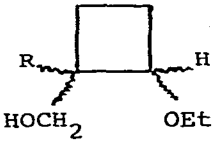


(97)

dihydro-pyrans (96) (R = Me or Pr^i) by trialkylaluminiums gives cyclobutyl derivatives (97). With triisobutylaluminium, the compounds (97) are formed exclusively, but with triethylaluminium, $RCH(CHO)(CH_2)_2CH(OEt)Et$ and $RCH(CH_2OH)(CH_2)_2$-$CH(OEt)Et$ are obtained as biproducts [95].

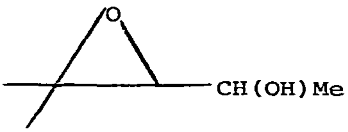
The reactions of ate complexes $NaAlEt_4$ and $LiAlBu^n_4$ with epoxides, first reported in 1975 in a preliminary communication, have been described in a full paper [96]. Aliphatic epoxides are alkylated at the less substituted carbon atoms and styrene oxide at the carbon adjacent to the ring. The alkylations are strongly catalysed by transition metal (especially nickel) salts and always involve inversion of configuration at the alkylated carbon. The complex $NaAlEt_4$ is also a good reagent for alkylation of ketones in hydrocarbons or other solvents of low basicity [97]. The stereochemistry of reactions of acetophenone, 1-phenylpropan-2-one and 4-t-butylcyclohexanone have been studied in detail.

The interaction of diethylaluminium chloride with methyl acrylate, methyl methacrylate and methacrylic acid has been studied by IR and NMR spectroscopy. Equilibrium and rate constants have been given for complex formation, and various additions and reductions are observed [98]. The reaction between tris(trimethylsilylmethyl)aluminium and 2-isopropyl-5-methylcyclohexanone has been mentioned in ref. 99 and the stereochemistry of an organoaluminium intermediate discussed in ref. 100 .

8. COMPOUNDS WITH ALUMINIUM-OXYGEN AND ALUMINIUM-SUPHUR BONDS

There has been a brief report [101] of chemiluminescence in the oxidation of trialkylaluminiums R_3Al (R = Et, Bu^i, n-C_6H_{13} or $PhCH_2$) with dioxygen. The mechanism of this process is of interest since the oxidation is an important step in the manufacture of long-chain alcohols.

Organoaluminium peroxides, made from trimethylaluminium or Al(OBu^t)$_3$ and t-butylperoxide are useful reagents for epoxidation of allylic alcohols or oxidation of secondary alcohols [102]. For example, oxidation of Me$_2$C=CHCH(OH)Me gives *thereo*-(98) in 80% yield with only 0.5% of the *erythro*-isomer. Cyclohex-2-enol and cyclohex-3-enol give almost entirely the *erythro* isomers. 1-Phenylethanol gives a



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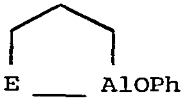

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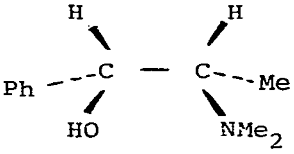


(101)

90% yield of acetophenone.

A patent [103] describes the manufacture of dialkylaluminium hydroxides R$_2$AlOH in dilute solutions of donor solvents (e.g. THF) and low temperatures, by mixing solutions of R$_3$Al and wet solvent. The hydrolysis of ethylaluminium dichloride has been described in a paper [104] on polymerisation of ethylene. At H$_2$O/AlEtCl$_2$ mole ratios of < 0.2, the products are soluble in benzene; however, volatile material is lost on heating in vacuum and the molecular weight of the residue increases. The controlled hydrolysis of the ate complexes NaAlR$_4$ and NaAlR$_3$H (R = Me, Et or Bu^i), mentioned in a preliminary publication in 1978, has been described in a full paper [105]. The products Na$_2$(R$_3$R1OAlR$_3$) are obtained as viscous etherates which give solvent-free crystals on heating in vacuum. They react with R^{2}X (R^2 = Me, Et or CH$_2$=CHCH$_2$–; X = Br or I) according to Equation 28

$$\mathrm{Na_2[R^1_3OAlOR^1_3]} \xrightarrow{\mathrm{R^2X}} \mathrm{Na[R^1_3AlOAlR^1_3]} + \mathrm{R^1R^2} + \mathrm{NaX} \qquad \underline{28}$$

The reaction between Na$_2$[Et$_3$AlOAlEt$_3$] and allyl bromide in benzene gives unsolvated Et$_2$AlOAlEt$_2$ (99). Alkali hydrides form adducts with alumoxides such as (99) but the reactions are complicated and depend on solvent and reaction conditions. Some ^{27}Al NMR spectra have been given. A third paper [106] in the series on mass spectra of organoaluminium compounds (See ref.19 and 38) deals with alkoxides. Fragmentations for (Me$_2$AlOMe)$_n$, (Et$_2$AlOEt)$_n$, (Bu$^i_2$AlOBu^i)$_n$ and Bu$^i_2$AlOPr^i)$_n$ have been documented: after initial loss of alkyl the major breakdown is by elimination of alkene and alkane. As expected the trimer/dimer mole ratio decreases as the alkyl group becomes bigger: for all except $(Me_2AlOMe)_3$ peaks from trimer are detected only when the samples are heated to 80–120°C. Peaks from mixtures of $(Et_2AlOEt)_n$ and $(Bu^i_2AlOBu^i)_n$ provide evidence for exchange of alkyl groups between species.

Several new cyclic alkoxides have been referred to briefly [107]. The compounds formulated as (100) (E = O or S) appear to catalyse the alkylation of phenol by $CH_2{=}CMe_2$, $CH_2{=}CMeCH_2Bu^t$, or $CH_2{=}CHSiMe_3$ without attack at the Al–C bond. Alkylation is predominantly at the ortho position, e.g., with isobutene and (100) (E = O), o-t-butylphenol is formed in 96% yield [108].

Reactions of lithium or sodium alkoxytrialkylaluminates with carbonyl compounds have been investigated in some detail [109] [110]. By treatment of tetraalkylaluminates with a chiral alcohol such as (101), chiral reagents $MAlR^1_3OR^*$ (M = Li or Na; R^1 = Me, Et, or Bu^n; R*OH = (101)) are obtained. These react with ketones to give chiral alcohols (Equation 29) but the yields and optical purity of the products depend critically on the solvent and reaction conditions. The reactions are catalysed by nickel salts but many details of the mechanism are obscure. A preliminary report [111] has appeared of the asymmetric alkylation of $PhCOCO_2Me$ with the chiral reagents made either from $LiAlBu^n_4$ and R*OH (101) or, better, [(4)-(2S, 3R)-4-dimethylamino-3-methyl-1,2-diphenyl-butan-2-ol], or from R*OLi and Bu^n_3Al (Equation 29 $R^2 = CO_2Me$)

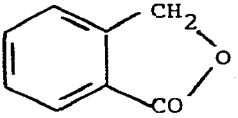
$$MAlR^1_3OR^* + PhCOR^2 \xrightarrow{H_3O^+} \underset{(102)}{PhR^1R^2COH} \qquad \underline{29}$$

The reactions of siloxyaluminium compounds $R_3SiOAlEt_2$ (R = Et or Ph) with carboxylic anhydrides have also been described [112]. With acetic anhydride the products arise from reaction at the Al–C bond (Equation 30) as well as from reaction at the Al–O

$$R_3SiOAlEt_2 + (MeCO)_2O \longrightarrow R_3SiOCOMe + Et_2AlOCOMe \qquad \underline{30}$$

$$R_3SiOAlEt_2 + (MeCO)_2O \longrightarrow C_2H_6 + CH_2{=}C{=}O + R_3SiOAl(Et)OCOMe \qquad \underline{31}$$

bond (Equation 31). A range of alkylated species are obtained from the reaction between $R_3SiOAlEt_2$ and phthalic anhydride, but the lactone (102) with triethylaluminium gives after hydrolysis a 86% yield of the diol (103).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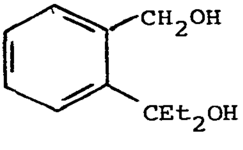
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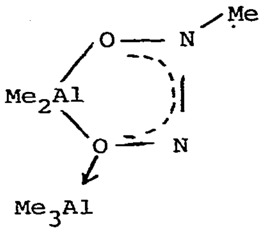
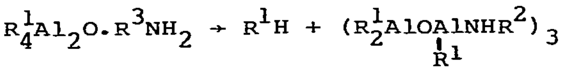

(105)

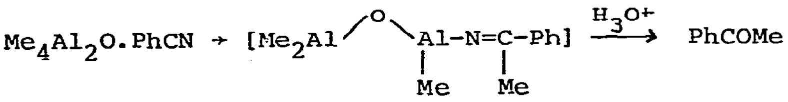
Another series of papers describes reactions of aluminoxanes $(R^1_2Al)_2O$ (R^1 = Me, Et or Bu^i). With primary amines R^2NH_2 complexes $R^1_4Al_2O.R^2NH_2$ of uncertain molecular complexity are obtained. On heating (Equation 32) these give alkanes quantitatively and trimeric compounds (104) which do not



$$R^1_4Al_2O.R^3NH_2 \rightarrow R^1H + (R^1_2AlO\underset{R^1}{Al}NHR^2)_3 \qquad \underline{32}$$

(104)

form complexes with strong electron donors such as benzonitrile. This suggests that the aluminium atoms are four-coordinate and that (104) may have a structure based on a framework of Al-O and Al-N bonds. The presence of various geometric isomers may explain the rather complicated ^1H and ^{13}C NMR spectra [113]. Tetraethylaluminoxane $(Et_2Al)_2O$ reacts with benzonitrile by a series of alkylations, C_2H_4 eliminations and multiple insertions into Al-N bonds. The compound obtained in highest yield (40% after hydrolysis) is Et-N=C(Ph)-N=C(Ph)NH_2. Tetramethylaluminoxane gives a much cleaner reaction (Equation 33);

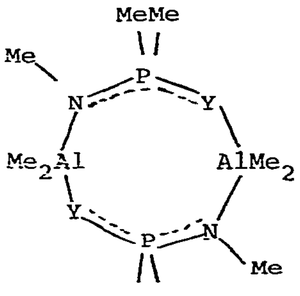


$$Me_4Al_2O.PhCN \rightarrow [Me_2Al\overset{O}{\frown}\underset{Me}{Al}-N=\underset{Me}{C}-Ph] \xrightarrow{H_3O^+} PhCOMe \qquad \underline{33}$$

the aluminoxane, like trimethylaluminium, adds across the C≡N bond [114]. The principal products of the reaction between the compounds R_4Al_2O in donor solvents and acetylacetone are methane, the complex $Al(C_5H_7O_2)_3$ ($C_5H_7O_2$ = pentane-2,4-dionato) and aluminoxane oligomers. By following the reaction in an NMR tube at low temperatures and at various $Al/C_5H_7O_2H$ ratios, evidence has been obtained for intermediates $R_3(C_5H_7O_2)Al_2O$

$R_2(C_5H_7O_2)_2Al_2O$ and $(C_5H_7O_2)_4Al_2O$. These become less stable with respect to $Al(C_5H_7O_2)_3$ and aluminoxane oligomers, as the number of $C_5H_7O_2$-groups increases, and more stable as the size of the alkyl group attached to aluminium increases [115].

The formation of the compound (105) by the reaction between nitric oxide and triethylaluminium was reported in 1978. Its structure has now been found by an X-ray study [116]. The principal mean bond lengths are Al–C 195.3(1), Al–O 189.5(6), N–O 132.2(8) N–N 125.3(9) pm, and the position of maximum basicity in the chelate ring has been confirmed by ab initio calculations. The compound (105) reacts with trimethylamine to form the adduct Me_3NAlMe_3; the other products seem to be complexes $[AlMe(ONNMeO)_2]$ and $[Al(ONNMeO)_3]$ but pure compounds have not been isolated [116]. The dimeric compounds (106) have been made from trimethylaluminium and the acid amides $HMeN(P{=}Y)Me_2$ (Y = O or S) and their vibrational spectra assigned [117]. NMR spectra show the presence of cis- and trans-isomers (106b) and (106a).



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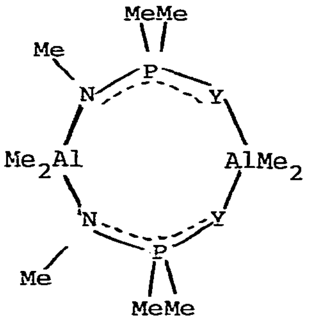
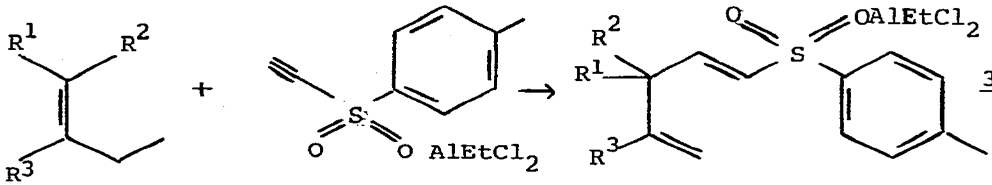


(106b)

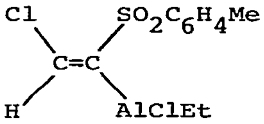
The compounds $[RMe_2Si(CH_2)_n]_3Al$ (R = Me, Bu^n or $n\text{-}C_8H_{17}$; n = 1 or 3) react with sulphur trioxide with insertion of SO_3 into Al–C bonds without cleavage of Si–C bonds. After hydrolysis the silylalkane-sulphonates $RMe_2Si(CH_2)_nSO_3Na$ are isolated in 65–90% yield [118]. The catalysis by organoaluminium compounds of the addition of carboxylic esters to alkenes is referred to in Section 7 above (Ref. 68–72). Similarly, ethynyl p-tolyl sulphone (107) reacts, under mild conditions in the presence of about 1 equiv. ethylaluminium dichloride, with a range of alkenes to give 1,4-dienyl p-tolyl sulphones (108) (Equation 32). Best yields are obtained with highly substituted,



(107) (108)

32

electron-rich alkenes, e.g. $Me_2C{=}CMe_2$ or $MeCH{=}C(CH_2)_4$ [119]. With 2 equiv. of $EtAlCl_2$, the sulphone (107) gives, after hydrolysis, a 58% yield of (109) which appears to result from a chloroalumination reaction giving (110) as intermediate.



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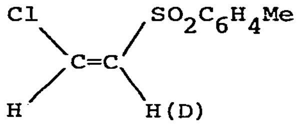

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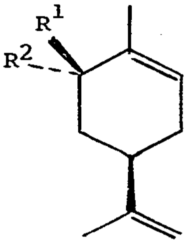
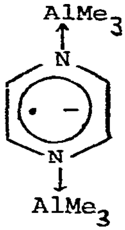


(111)

The reactions of the dimethylaluminium compounds Me_2AlX (X = OPh, SPh or NHPh) with allylic phosphates (111) ($R^1 = (EtO)_2P(:O)O, R^2 = H$ or $R^1 = H, R^2 = (EtO)_2P(:O)O$) was described in a preliminary communication last year. More details of this reaction, which proceeds with inversion of configuration, are given in the full paper [120]. In contrast to the reactions with Me_2AlX, trialkylaluminiums attack the compounds (111) from the side opposite the isoprenyl group, probably via carbocationic intermediates, to give (111) ($R^1 = H$; $R^2 =$ Me, Et, or Bu^i).

9. COMPOUNDS WITH ALUMINIUM-NITROGEN BONDS

The radical (112) has been generated by the reaction of pyrazine and trimethylaluminium with potassium in benzene and its ESR spectrum [30] has been compared with those of isoelectronic species. The radical formed in THF is different. It has been characterised as the radical cation (113). Corresponding radicals with triethylaluminium have also been



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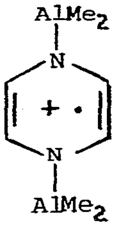
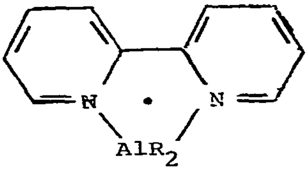


(113)

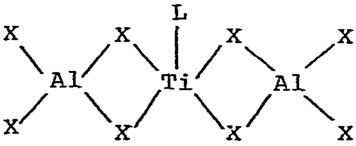


(114)

described. The reactions of 2,2'-bipyridyl with alkali metals and AlR_3 or AlR_2Cl yield the radicals (114) (R = Me or Et) [121].

10. ORGANOALUMINIUM COMPOUNDS INVOLVING OTHER METALS

In an NMR study of the alkylation of titanium(IV) chloride by triisobutylaluminium the compound $TiBu^iCl_3$ has been identified as a primary product [122]. A second paper [123] describes the reactions between the compounds (115) and (116) (L = η^5-C_5H_5 or η^6-C_6H_6; X = Cl or Et) and ethylaluminium chlorides. The species $[(\eta^5\text{-}C_5H_5)TiAl_2Cl_{8-x}Et_x]$



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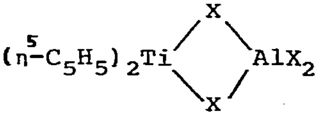
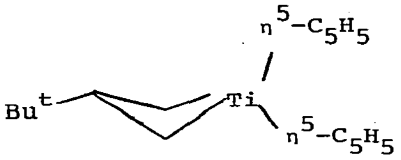


(116)

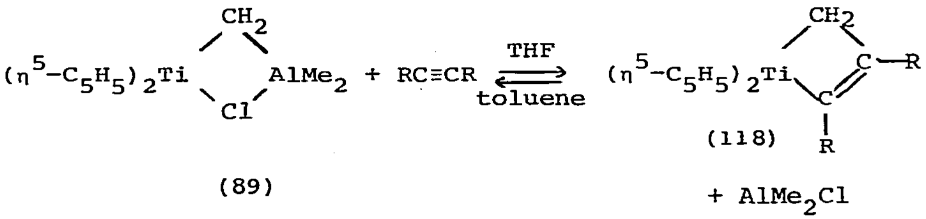
(115) (L = C_5H_5; X = Cl or Et, x = 1-4), $[(\eta^6\text{-}C_6H_6)TiAl_2Cl_7Et]$, $[(\eta^6\text{-}C_6H_6)TiAl_2Cl_6Et_2]$ (115) (L = C_6H_6) and $(\eta^5\text{-}C_5H_5)_2TiAlCl_{4-x}Et_x$ (116) (X = Cl or Et, X = 0, 1 or 2) have been characterised by ESR and UV spectroscopy.

When the alkene metathesis catalyst (89) is treated with isobutene having a ^{13}C-labelled methylene group, the label is transferred to the titanium compound [124]. Experiments with deuterium labelling confirm that the methylene group as a whole is transferred between $CH_2=CMe_2$, methylenecyclohexane and (89): this is explained most simply by a mechanism involving labile titanacyclobutane intermediates. One such species (117) has been isolated from (89) and $Bu^tCH=CH_2$ in pyridine or, better, in toluene in the presence of 4-vinylpyridine-styrene copolymer [125]. When (117) is



(117)

treated with dimethylaluminium chloride, (89) is regenerated; (117)-d_1, made from *trans*-$Bu^tCH{=}CHD$ and (89), is converted to a mixture of (89) and (89)-d_1. These experiments clarify the role of the aluminium-containing fragment in the metathesis reactions and provide powerful evidence for involvement of metalacyclobutane intermediates. Lewis bases remove Me_2AlCl from (89) so that the reactive $(\eta\text{-}C_5H_5)_2TiCH_2$ fragment is trapped by alkene. In the absence of base Me_2AlCl, displaces alkene from (117). However, it is not at present clear whether all metatheses proceed by the mechanism proposed. The compound (89) reacts with alkynes in THF to give titanacyclobutene derivatives (118) (R = Ph or $SiMe_3$); the structure of the diphenyl compound (118) has been confirmed by an X-ray



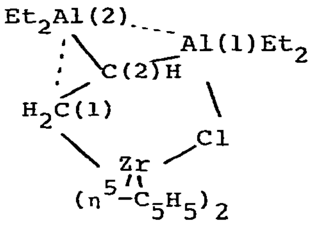
(89)

(118)

33

study. In toluene, however, the reaction is reversed (Equation 33). Again there appears to be competition between $AlMe_2Cl$ and alkyne for the $(\eta\text{-}C_5H_5)_2TiCH_2$ fragment. THF forms a sufficiently strong complex with $AlMe_2Cl$ to move the equilibrium in Equation 33 to the right [126].

Several further compounds obtained from the reactions between ethylaluminium- and cyclopentadienylzirconium-compounds have been characterised by X-ray crystallography. One compound (119) was described in a preliminary communication in 1974. The final data [127] for the bond system linking



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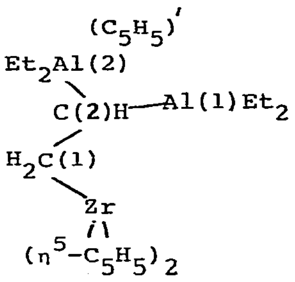

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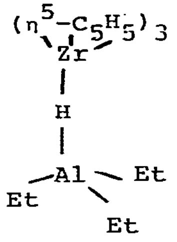


(121)

aluminium and zirconium are as follows: Zr-C(1) 225.2, C(1)-C(2) 151.8, C(2)-Al(1) 192.9, Al(2)-C(2) 195.6, Zr-C(2) 237.5, Al(2)-C(1) 226.0, Zr-Cl 268.6, Al-Cl 231.1, Al(2)-Al(2) 314.5 p.m. (E.s.d. for bonds between non-carbon atoms 0.9, otherwise 1.5). The Zr-C(1)-C(2) angle is 75.3°. The dark red compound (120), isolated from the reaction between $Zr(C_5H_5)_4$ or $(\eta^5-C_5H_5)_3ZrEt$ and $AlEt_3$ has one cyclopentadienyl ring which gives a signal at unusually low field in the NMR spectrum. The X-ray study [128] shows that this ring is symmetrically arranged between the zirconium centres so the compound may be described as $[(\eta-C_5H_5)_2ZrCH_2CH(AlEt_2)_2]^+[C_5H_5]^-$. The main molecular parameters are Zr-C(1) 225.9(6), C(1)-C(2) 152.5(7), C(2)-Al(1) 199.8(5), C(2)-Al(2) 199.7(5) pm. Again the angle at C(1) (76°) is small. The $Al-C(C_5H_5)'$ distances range from 219 to 301 pm. A third compound, isolated as a biproduct in reactions leading to (120) appears to be a μ-hydrido compound (121): it can also be made directly from $[ZrH(\eta^5-C_5H_5)_3]$ and triethylaluminium (Equation <u>34</u>)

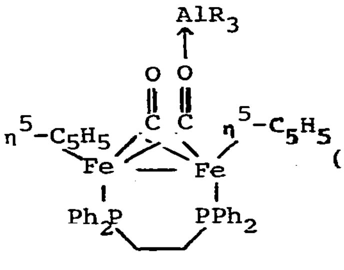
$$ZrH(C_5H_5)_3 + \tfrac{1}{2}Al_2Et_6 \rightleftharpoons \underset{(121)}{(C_5H_5)_3Zr{-}H{-}AlEt_3} \qquad \underline{34}$$

The equilibrium <u>34</u> is displaced to the left in THF. The Al-H and Zr-H distances have been given as 177 and 188 pm [129]. The C-C bond in one ethyl group is particular short (144.3 pm) and the C-C-Al angle is large (134°) but the implications of these data are not clear. The compound (121) is a long lived catalyst for polymerisation of ethylene. The activity is considerably enhanced by combination with oligomeric aluminoxanes e.g. $(MeAlO)_n$ (n = 5-16). With $[Zr(\eta^5-C_5H_5)_2Me_2]$ and $(MeAlO)_5$

productivities (g polythene per g Zr) of $>10^8$ are observed, and the changeover time between two insertions is as small as 0.3 ms. Molecular weights can be easily varied by choice of temperature [130].

Further studies of the interaction of alkylaluminium compounds with nickel derivatives have appeared. Diethylaluminium chloride reacts with bis(pentane-2,4-dionato)nickel in the presence of triphenylphosphine to give $[NiCl(Ph_3P)_3]_2$ and gaseous products C_2H_6, C_2H_4 and H_2. It is presumed that an ethylnickel intermediate is involved. The compound $[Ni(C_5H_7O_2)Et(PPh_3)]$ with $AlEt_2Cl$ and PPh_3 gives $[NiClEt(PPh_3)_2]$ [131]. A study of the $Ni(C_5H_7O_2)_2/AlBu^i_2H$ catalyst system by cyclic voltametry [133] suggests that the conjugate addition of alkenylzirconium compounds to enones involves initial electron transfer from Ni(I) species to the unsaturated ketone (See Section 7 and ref. 81). Polarographic and ESR measurements have also been made on the catalyst systems $AlBu^i_3/VOCl_3$ and $AlBu^i_3/VCl_4$ [133]. See also ref.27.

The remaining references in this section are to donor-acceptor complexes between trialkyl- or triarylaluminiums and transition metal carbonyl compounds. Thus the ^{18}O NMR spectrum of the adduct $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2.2AlPr^i_3$ has been recorded [134], and infrared spectra of the acyl complex $[Fe(\eta^5\text{-}C_5H_5)\text{-}(CO)_2(COMe).AlMe_3]$ [135] and the 1:1 complex (122) (R = Me or Et) [136]. The trialkylaluminiums may be removed



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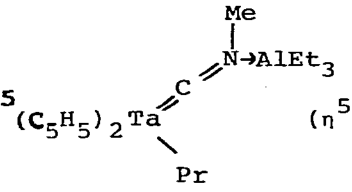

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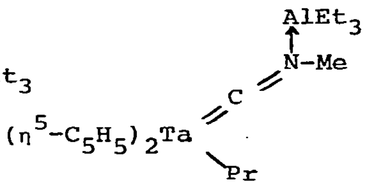


(124)

by reaction with tertiary amines. Triphenylaluminium causes a large increase in the rate of uptake of carbon monoxide by $[NEt_4][WPh(CO)_5]$ leading to the benzoyl complex , which may be freed from triphenylaluminium by treatment with dimethylamine [137]. The isocyanide complexes $[(Ta(\eta(C_5H_5)_2\text{-}$

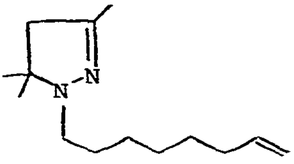
(R)CNMe] also give 1:1 complexes with triethylaluminium. NMR spectra of the compound when R = C_3H_7 suggest the presence of isomers (123) and (124). Rotation about the Ta-C-N axis appears to be hindered by addition of $AlEt_3$ [138].

11. CATALYSIS

As in previous years, aluminium compounds have been widely used in catalyst systems. The present review includes examples of their use for isomerisation, oligomerisation, polymerisation, metathesis, and hydrosilylation of alkenes.

A thorough search of the polymer chemistry literature has not been attempted.

The dimerisation of propene in the presence of chlorobenzene and ethylaluminium dichloride is catalysed by the π-allyl compound $[NiBr(\eta^3-C_3H_5)P(C_6H_{11})_3]$. The turnover number at the nickel centre at -55°C is estimated as 230 which may be extrapolated to ca 6000 at 25°C. The activity of the catalyst is thus similar to those of some enzymes [138]. The kinetics of the oligomerisation of butadiene to cyclododecatrienes with $AlEt_2OEt-[Ni(C_5H_7O_2)_2]$ as catalyst have been studied [140]. Related papers deal with the cyclo-homo- and co-oligomerisation of 2-cyclopropylbutadiene with 1,3-dienes [141], with reactions of conjugated dienes and trienes with pyrazolines, giving compounds such as (125) [142], with similar reactions of pyroles [143], and with the influence of the basicity of aniline derivatives on the direction and selecselectivity of their reactions with butadiene [144]. In ref. 142 - 144 the catalyst is derived from a $AlEt_3-PPh_3-Pd(C_5H_7O_2)_2$ mixture. Catalysts from triethyl- or triisobutylaluminium and CoX_2 or NiX_2 (X = pentane-2,4-dionato, 2-ethylhexanoate or stearate) are effective in inducing disproportionation of cyclohexa-1,3-diene to benzene and cyclohexene [145],



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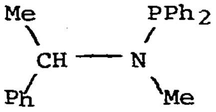

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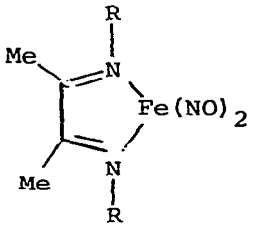

(127)

and the catalyst system Ni(cycloocta-1,5-diene)$_2$-AlEt$_2$Cl - L where L is a chiral phosphine such as (126) is suitable for the reaction between cyclohexa-1,3-diene and ethylene. At -70°C, and with L = (-)-(R)-(126) (+)-(S)-3-vinylcyclohexene may be obtained in 87% yield and with 73% optical purity [146]. Oligomerisation of ethylene to higher 1-alkenes under flow conditions in the presence of ethylaluminium chloride-titanium chloride catalysts has also been described [147]. The diazadiene complexes (127) in the presence of triethylaluminium catalyse not only the dimerisation of isoprene to 1,4- and 2,4-dimethyl-4-vinyl-1-cylohexenes but also polymerisation to 3,4-polyisoprene. When R = Pr^i only polymer is obtained at 25°C [148].

Initiation of the polymerisation of isobutene by aluminium halides is thought to involve cationic intermediates AlX$_2^+$ rather than donor-acceptor complexes between alkene and Lewis acid [46]. Polymerisation of other vinyl monomers is more complicated; with AlEt$_2$Cl- p-chloranil both free radical anc cationic processes are probable [149]. The activity of the catalysts (η^5-C$_5$H$_5$)$_2$TiClEt-AlEtCl$_2$ for polymerisation of ethylene is enhanced by preliminary controlled hydrolysis of the ethylaluminium dichloride, which probably produces aluminoxane species [104]. The effect of hydrogen, on the polymerisation of propene catalysed by V(C$_5$H$_7$O$_2$)$_3$-AlEt$_2$Cl [150], and on the polymerisation and isomerisation of various chiral and prochiral alkenes by chiral titanium alkoxide-AlBu$^i_3$ systems [151], has been described. The polymerisation, copolymerisation and oligomerisation of dienes using various catalytic systems have been reviewed [152], as well as polymerization of cis- and trans-hexa-1,4-diene and 5-methyl-hexa-1,4-diene [153]. Isotactic poly (trans-hexa-1,4-diene) made using the AlEt$_3$-αTiCl$_3$-HMPT system consists mainly of 1,2-polymerisation units in a regular head-to-tail sequence, and is an example of an ozone-resistant rubber with high unsaturation in side chains.

Stereospecific grafting of butadiene (i.e. with >90% cis-1,4-units in the grafted chains) to chlorinated polycyclobutadiene has been achieved with Et$_2$AlCl-[Co(C$_5$H$_7$O$_2$)$_2$] as catalyst [154]. Several other papers describe alkylation of polyvinyl chloride by triethylaluminium during or after polymerisation [155-7]. This process, which involves removal of labile chlorine atoms in the polymer, results in a significant improvement in thermal stability. The polymerisation of propadiene in the presence of $[Ni(C_5H_7O_2]_2$ and a range of organoaluminium compounds AlR_nX_{3-n} (R = Et or Bu^i; X = halogen or pentane-2,4-dionato) has also been studied [158]. Other papers on Ziegler-Natta type catalysts have dealt with supported systems [159] [160], with poisoning of active sites under a variety of reaction conditions [161] and with molecular orbital calculations of energy levels of π-alkene complexes of titanium in various oxidation states [162]. In both the homo- and co-polymerisations of 4-vinyl pyridine with various other alkenes [163] and the copolymerisation of vinyl acetate with acrylonitrile [164] it is necessary to postulate several polymerisation modes to explain the results.

As in previous years, there have been series of papers on alkene metathesis using organoaluminium catalysts [165-169] and on hydrosilylation [170-2].

Catalysts made from diisobutylaluminium hydride and triphenylphosphine, triphenylphosphite or tris(dimethylamino)-phosphine have been used for conversion of alcohols to carbonates. Equation 35 (ROH = pentane-1-ol, cyclohexanol, 3-methylcyclohexanol, or 2-ethylhexan-1-ol). Since the ammonia generated may be

$$2ROH + H_2NCONH_2 \rightarrow ROCOOR + 2NH_3 \qquad \underline{35}$$

reconverted to urea by reaction with carbon dioxide, the reaction makes possible the formation of carbonates directly from alcohols and CO_2. The process may also be used for production of polycarbonates [173].

12. STRUCTURAL STUDIES

X-ray and electron diffraction data are given in ref. 23, 39-41 , 47 , 116 , 127-9 .

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