ALUMINIUM

ANNUAL SURVEY COVERING THE YEAR 1975*

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CONTENTS

1. INTRODUCTION, REVIEWS

The survey of the 1975 literature follows the same pattern as last year. About the same number of papers on organoaluminium chemistry have appeared in 1975 as in 1974, but there seems to be rather less emphasis on structure and more on chemistry and reactions.

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* Aluminium, Annual Survey covering the year 1974, see J. Organometal. Chem., 103 (1975) 39-90.

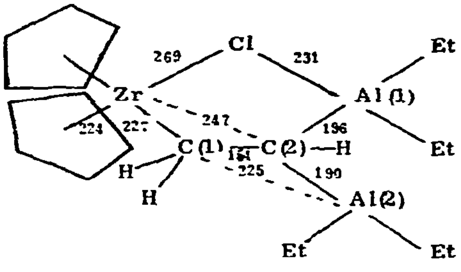
The organometallic chemistry of aluminium, gallium, indium and thallium has been summarised in two Chemical Society Specialist Periodical Reports [1,2] covering the 1973 and 1974 literature. Further information and discussion has been given in the same volumes in chapters on organometallic compounds containing metal-metal bonds [3], homogeneous catalysis [4], and diffraction studies [5]. Another survey has been published in the M.T.P. Series [6] and an authoritative review on unsaturated organoaluminium compounds [7] has appeared.

The March and April (1975) issues of *Annalen*, dedicated as a memorial to Professor Karl Ziegler, contain several important papers describing recent work on organoaluminium compounds; the April issue concludes with an assessment [8] of Ziegler as a scientist and a person.

2. MOLECULAR STRUCTURE AND BONDING

The structure of a further anion in the series $[AlXY_3]^-$ has been described [9]. In caesium azidotrimethylaluminate(III), made by slow decomposition of the liquid benzene adduct, the anion has *m*-symmetry with molecular parameters: Al-N, 197(1); N-N, 113(2), 121(2); Al-C, 196(2), 199(1) pm; $<$ Al-N-N 123.2(9)°.

Full details of the crystal structures of two compounds with both aluminium and a transition metal have also been published. In μ-chloro-1-[bis(η^5-cyclopentadienyl)zirconium(IV)]-2,2-bis(diethylalumino)ethane (1), isolated from the reaction between bis(cyclopentadienyl)zirconium dichloride and triethylaluminium, zirconium and aluminium atoms are bridged both by chlorine and by a two-carbon fragment [10]. The second aluminium, Al(2), is in an unusual pendant position; however, the ZrC(1)C(2)Al(1)Cl-ring is in a chair form with a small ZrC(1)C(2) angle. This brings C(1) within 225 pm of the pendant Al(2) [*cf.* Al-C(bridge) in Al_2Me_6, 212 pm] and C(2) within 247 pm of Zr [*cf.* Zr-C(C_5H_5), 254 pm]. The Al-Cl distance is normal [*cf.* Al-Cl(bridge) in Al_2Cl_6, 225 pm] but the Zr-Cl distance is long [*cf.* Zr-Cl in $(C_5H_5)_2ZrCl_2$, 230 pm].

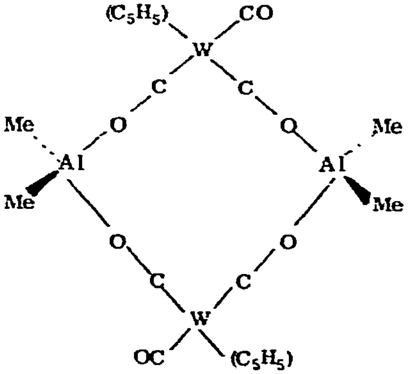


ZrC(1)C(2)	76°
C(1)C(2)Al(1)	145°
C(2)Al(1)Cl	100°
Al(1)ClZr	81°
ClZrC(1)	118°
Al(1)C(2)Al(2)	109°
C(1)C(2)Al	78°

(1)

Distances in pm

In di-μ-(tricarbonyl-η^5-cyclopentadienyltungsten-$\underline{OO}'$)bis-dimethylaluminium, (2), the molecules have slightly puckered twelve-membered rings, in which carbonyl groups [C–O, 122(2) pm] are linked through carbon to tungsten and



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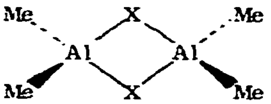


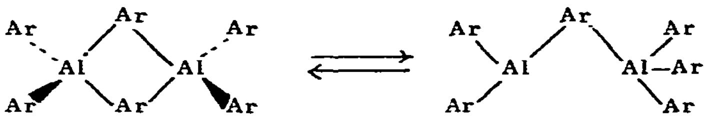
(3)

through oxygen to aluminium [Al–O, 181(1) pm, Al–C, 194(2) pm; C–Al–C, 123(1)°]. The structure may be viewed as of the general type $(Me_2AlX)_2$ (3) with X = $(C_5H_5)W(CO)_3$. The ring is easily broken by protonic species HX [X = Cl, OH, MeCOCHCOMe(acac)] giving the hydride $(C_5H_5)W(CO)_3H$ and the compounds $(Me_2AlX)_n$, and by donors D (D = NMe_3, OEt_2), giving complexes $[(C_5H_5)W(CO)_3AlMe_2].D$. One of the carbonyl groups may be replaced by a phosphine, e.g., PMe_2Ph, PEt_2Ph. It is interesting that the corresponding gallium compound $[(C_5H_5)W(CO)_3(GaMe_2)]$ appears to be monomeric with a direct Ga–W bond [12].

Bonding in organoaluminium compounds has been discussed in a conference report [13]. Detailed information about energy levels has been obtained from photoelectron spectra. Most of the compounds Me_nAlX_{3-n} ($n = 0$–2; X = halogen) may be observed as both monomers [14] and dimers [15]; Me_3Al could be studied only as a monomer. The highest occupied orbital in trimethylaluminium (IP 9.76 eV) is primarily Al-C bonding ($\underline{e}'$); in Me_2AlCl, Me_2AlBr and Me_2AlI the corresponding $\underline{b}_1$ orbitals interact with lone pairs of the halogens and in the chloride (IP 10.25 eV) and bromide (IP 9.90 eV) they are stabilised by inductive effects. For the dimeric species (3), the predominantly halogen bridging orbitals ionise at higher IP than the Al-halogen bonding orbitals in the monomers, in accord with decreased electron density at bridging halogen atoms. Spectra of both monomeric and dimeric species have been discussed in detail, but complex arguments, backed up by some *ab initio* SCFMO calculations, are involved in assignments.

3. NMR STUDIES ON EXCHANGE REACTIONS

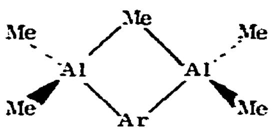
Rates of exchange between bridge and terminal methyl groups of hexamethyldialuminium have been remeasured [16]; the results agree with those of previous workers. Lifetimes of tolyl groups in bridge and terminal positions of hexa-*p*-tolyl- and hexa-*m*-tolyl-dialuminium (4), Ar = C_6H_4Me, are independent of concentration, showing that the rate-determining step in exchange is unimolecular activation of the dimer. The activation energies are, however, much smaller than required for complete dissociation, in spite of extensive evidence that, in mixed alkyl-aryl compounds, aryl groups preferentially occupy bridge positions. This suggests that only one bridge bond is broken in the exchange process.



(4)

The species $(Me_2AlAr)_2$ (3) X = Ar, and Me_5Al_2Ar (5), are identified in solutions containing both trimethylaluminium and tri-*p*-tolylaluminium.

The rates of exchange of p-tolyl groups between $(Me_2AlC_6H_4Me)_2$ and $Me_5Al_2C_6H_4Me$ (5) are also consistent with a mechanism involving partial dissociation pf p-tolyl bridges in $(Me_2AlC_6H_4Me)_2$ and reactions of the partially dissociated species with trimethylaluminium.



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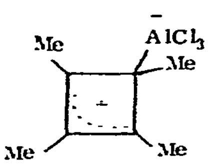

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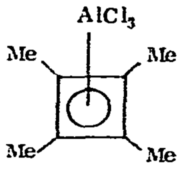
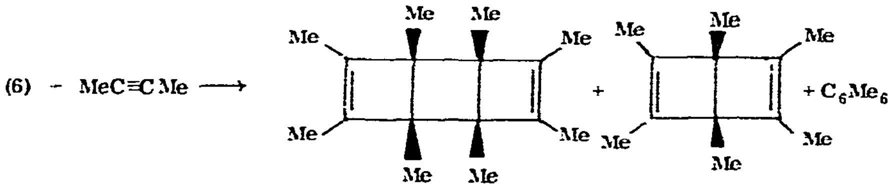


(7)

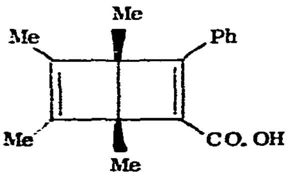
NMR spectra of the aluminium trichloride-tetramethylcyclobutadiene complex (6), at various temperatures [17], show that the $AlCl_3$ group migrates round the ring, probably via the intermediate (7). In dimethylsulphoxide, the complex (6) undergoes Diels-Alder reactions either with tetramethylcyclobutane, to give (8), or with dienophiles to give Dewarbenzene derivatives, e.g., (9).



(8)

(9)

With the ester Ph.C≡C.CO.OR (R = menthyl), the complex (6) gave, after hydrolysis, the acid (10) with 21% optical purity [18].



(10)

Exchange processes are also referred to in references [103] and [105].

4. PREPARATIONS

Few papers deal with the preparation of new organoaluminium compounds There is a useful summary of electrochemical methods in a more general review [19], and patents [20-24] describe variations of well-established preparative procedures. The reaction between aluminium, chloromethane and ethylene in the presence of $Me_3Al_2Cl_3$, gives a mixture of $RXAlCH_2CH_2AlXR$ and $R_2AlCH_2CH_2AlX_2$ (R = Me, X = Cl), said to be polymerisation catalysts. Corresponding bromides (R = Me, X = Br) and ethyl derivatives (R = Et, X = Cl) have also been made, but no structural data are given [23].

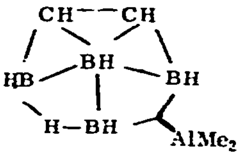
Cyclopentadienyl derivatives $Me_2Al(C_5H_5)$ and $Et_2Al(C_5H_5)$ (11), have been made from the chlorides and alkali metal derivatives $M'C_5H_5$ [24].

$$R_2MCl + M'C_5H_5 \longrightarrow R_2MC_5H_5 + M'Cl$$

(R = Me or Et; M = Al, Ga, or In; M' = Na or K)

For the ethyl compound (11), much better yields are obtained with potassium than with sodium cyclopentadienide. These compounds, and $MeAl(C_5H_5)_2$, have been described previously, but have not hitherto been well characterised. The compound $Me_2Al(C_5H_5)$ is of interest because a previous electron diffraction study showed that the molecules in the vapour were monomeric with very unsymmetrical η^2-co-ordination of the cyclopentadienyl ring. An attempt to throw more light on this result by ab initio MO calculations [25] on the unsubstituted compound $H_2Al(C_5H_5)$ has suggested that the equilibrium conformation is with the AlH_2 group in the symmetry plane. The barrier to rotation of the C_5H_5-ring is 9.9 kJ mol^{-1} and that to exchange of H atoms 49.5 kJ mol^{-1}. Another interesting organoaluminium compound is formed by reaction of dimethylaluminium chloride with the lithium salt of the ion 2,3-$C_2B_4H_7^-$ [26]. The product is too unstable for thorough study (in solution, or in the liquid phase, dimethylaluminium hydride and the parent carborane $C_2H_4H_8$ are formed) but the mass spectrum is consistent with the formulation $Me_2AlC_2B_4H_7$. The structure (12) is probably similar to those of derivatives with other metals, with a B-Al-B three-centre two-electron bond.

Pyrolysis at 100° C gives a compound which may be closo-$CH_3AlC_2B_4H_6$ (13), analogous to the known gallium compound.



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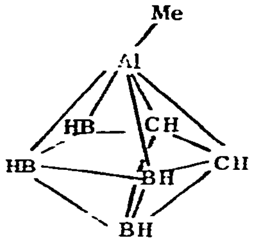

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5. ALKYLATIONS, REACTIONS WITH HALIDES

The preparation of triethylgallium and triethylindium of high purity for the semiconductor industry has been achieved from triethylaluminium with low silicon content [27]. Very pure trimethylgallium has also been obtained from gallium trichloride and trimethylaluminium [28]. Phosphorus trichloride has been alkylated with the halides Me_2AlCl, $MeAlCl_2$ or $Me_3Al_2Cl_3$ in benzyl cyanide, to give dichloro(methyl)phosphine $MePCl_2$ [29]. Transition metal halides also react smoothly with organoaluminium compounds to give good yields of alkyl or aryl derivatives. This is illustrated by the preparation of cyclopentadienyldinitrosyl derivatives of chromium, molybdenum and tungsten [30].

$$(C_5H_5)M(NO)_2Cl + R\text{-}Al\!< \xrightarrow{\text{benzene}} (C_5H_5)M(NO)_2R + Cl\text{-}Al\!<$$

($M = Cr$, Mo; $R\text{-}Al\!< = Ph_3Al$, Me_3Al, Et_3Al, Bu^i_2AlH; $M = W$, $R\text{-}Al\!< = Me_3Al$, Ph_3Al)

With di-isobutylaluminium hydride, the isobutyl group rather than the hydrogen is transferred to the transition metal. These preparations fail with more reactive alkylating agents, such as RLi or RMgX, which presumably attack functional groups other than the chloro-ligand. Trimethylaluminium has also been used to make the highly explosive compounds WMe_6, $ReMe_6$ and ReO_2Me_3 from the corresponding halides [31].

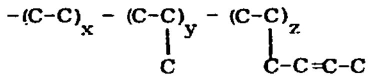
Trialkynylaluminium compounds participate in a simple and convenient tertiary alkyl-alkynyl coupling, unaccompanied by the eliminations and other side reactions initiated by alkynyl-lithium or -magnesium compounds. Dialkylalkynylaluminiums are unsatisfactory alkynylating reagents. Some yields are given in Table 1 [32]. The coupling is thought to involve carbocation intermediates, formed under weakly basic conditions where they are reasonably stable with respect to elimination.

Table 1. Yields for $RX + (R'C{\equiv}C)_3Al \xrightarrow{0^0 C} RC{\equiv}CR'$

R	X	R'	Solvent	Yield (%)
Bu^t	Cl	Bu^n	CH_2Cl_2	98
Bu^t	Cl	cyclo-C_6H_{11}	$(CH_2Cl)_2$	90
Bu^t	Cl	$CH_2Cl.CH_2CH_2$	$(CH_2Cl)_2$	86
$MeCH_2CMe_2-$	Cl	Bu^n	(CH_2Cl)	95
1-adamantyl	Br	Bu^n	CH_2Cl_2	96
1-methylcyclohexyl	Cl	Bu^n	$(CH_2Cl)_2$	71
Pr^i	OSO_2Me	Bu^n	CH_2Cl_2	99
cyclopentyl	OSO_2Me	Bu^n	CH_2Cl_2	60

Selective alkylation by trialkylaluminiums of chlorobromoalkanes has been examined [33]. With t-butyl chloride-bromide mixtures and trimethylaluminium, in chloromethane at -70 to -50⁰ C, the chloride is methylated first, but the bromide is also quickly attacked by the product, dimethylaluminium chloride. With $Me.CMeBr.CH_2.CMeCl.Me$, no monomethylated product was isolated, possibly because ionisation of the bromine in the intermediate $Me.CMeBr.CH_2.Bu^t$ is facilitated by strain relief. Selective methylation is, however, achieved with $Me.CMeBr.CH_2.CH_2.CMeCl.Me$ and 50% of the chlorine is substituted before loss of bromine is detected.

Triethylaluminium is more selective than trimethylaluminium, perhaps because diethylaluminium chloride is a less good Lewis acid than the dimethyl compound. These results have been exploited [34,35] for the preparation of block and graft copolymers based on the Du Pont polymer Nordel which has the structure (14) with x ca. 47.5%, y 49.5% and z 3.0%.



$-(C-C)_x - (C-C(C))_y - (C-C(C-C{=}C-C))_z$

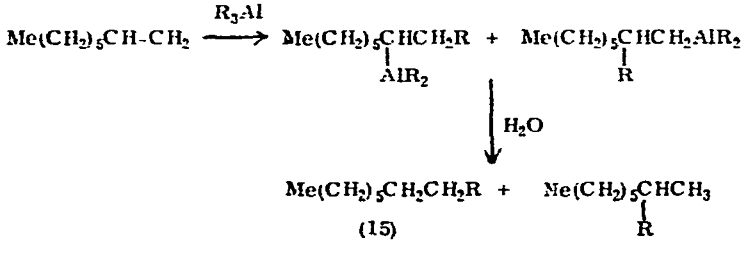
(14)

This material may be chlorinated and brominated with t-butyl hypochlorite and hypobromite, which react preferentially at the allyl positions. Then polystyrene may be grafted at chloro-substituted atoms, using diethylaluminium chloride as initiator, and subsequently poly-α-methylstyrene or polyisobutene may be grafted at the bromo-substituted positions.

Reactions between acid chlorides and alkylaluminium dichlorides $RAlCl_2$ have also been studied. Besides the expected alkylations, reductions are observed when R = Et [36] and Friedel-Crafts reactions when R = $PhCH_2CH_2$ or CH_3CHPh [37].

6. REACTIONS WITH CARBON-CARBON DOUBLE AND TRIPLE BONDS

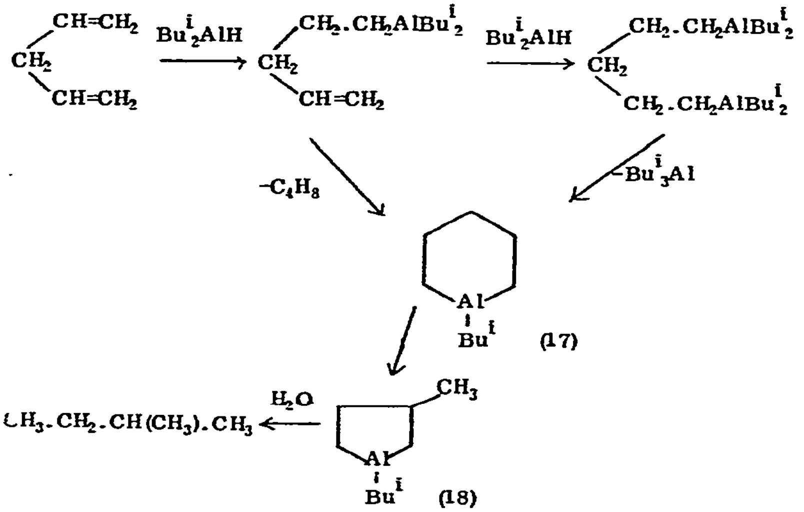
A detailed study [38] of the direction of addition of organometallic compounds to oct-1-ene shows that, although Bu^tLi and Pr^iLi react regioselectively with addition of the metal to the C-1 atom, Bu^tMgBr and Bu^t_3Al react with addition of the metal mainly to the C-2 atom, giving, after hydrolysis, the product (15). With tri-isopropylaluminium, the ratio of products (15)/(16) (R = Pr^i) is about 62/38.



(16)

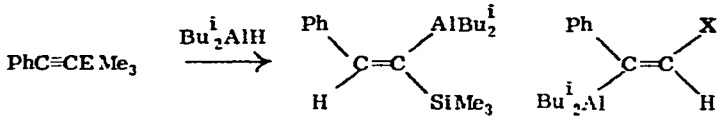
All the additions are complicated by side reactions involving elimination of R_2AlH or, for reactions with tri-isopropylaluminium, isomerisation to n-propyl derivatives.

The products from addition of di-isobutylaluminium hydride to penta-1,4-diene isomerise above 140° C to yield, after hydrolysis, 2-methylbutane [39].



The reaction is thought to involve rearrangement of six-membered (17) to five-membered (18) aluminium heterocycles. Similar isomerisations are observed with substituted pentadienes e.g., $H_2C{=}C(CH_3).CH_2.CH{=}CH_2 \longrightarrow CH_3.CH(CH_3).CH(CH_3).CH_3$; $H_2C{=}C(CH_3).CH_2.C(CH_3){=}CH_2 \longrightarrow CH_3CH(CH_3)C(CH_3)_2.CH_3$; $H_2C{=}CH.C(CH_3)_2.CH{=}CH_2 \rightarrow CH_3.CH_2.\underset{CH(CH_3)_2}{\underset{|}{C}H}.CH_3$

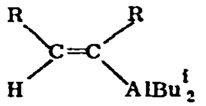
The role of π-complexes in the carbometallation of alkynes by boron and aluminium alkyls has been reviewed [40]. For a series of alkynes $PhC{\equiv}CX$ the relative rate constants for hydroalumination are (X=) Ph, 1; Me, 1.16; H, 11.8; SEt, 24.6; Bu^t, 27.8; $AlPh_2$, 185; $SiMe_3$, 431; NMe_2, 19000. Consideration of data for a wide range of reactions, together with the nature of the products and regiospecificity, leads to the conclusion that the rate-determining step is electrophilic attack of the aluminium hydride to give a transition state approximating to a π-complex. This collapses rapidly to the *cis*- adduct [41]. Addition of di-isobutylaluminium hydride to trimethyl(phenylethynyl)silane, (19) E = Si, yields the *trans*-adduct (20), in contrast to addition to the alkyne (19) E = C, which gives the *cis*- adduct (21, X = CMe_3).



(19) (20) (21)

The kinetic order is one in alkynylsilane and one third in hydride [42], and activation parameters and kinetic deuterium isotope effects can be explained by assuming that the rate-determining step is *cis*-hydroalumination followed by rapid *cis* → *trans* isomerisation. It is not necessary to assume any p_π-d_π electronic effects in the hydroalumination step, but these may well be important in lowering the C-C bond order during the subsequent rapid isomerisation.

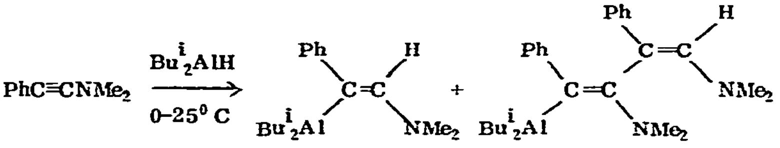
In kinetic studies of this kind it is found that the reaction is slowed by formation of complexes between the alkenylaluminium products such as (20) or (21) and unreacted di-isobutylaluminium hydride. Further insight into these complexes has been obtained from kinetic studies of the reactions between dec-5-yne and 1:1 mixtures of alkenyl(dialkyl) compounds (22) and di-isobutylaluminium hydride.



(22)

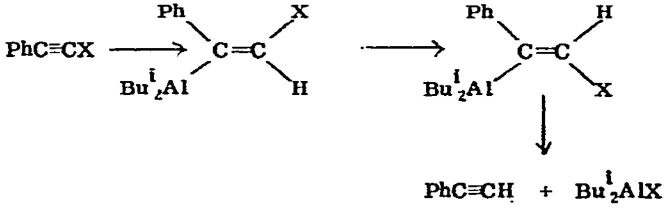
When R = n-C_3H_7, the reaction is first-order in decyne and half-order in aluminium hydride. Variable temperature NMR measurements show that the compound (22), R = Bu^t, forms several structurally distinct dimers, and that these interact with di-isobutylaluminium hydride to give a series of dimeric or trimeric complexes. The situation is further complicated, since, at the temperatures used for hydroaluminations, these complexes are in equilibrium with tri-isobutylaluminium formed by alkyl group exchange. Alkenyl(dialkyl)aluminium species must be intermediates in the second stage of hydroalumination of alkynes and so much detailed knowledge is required before the reaction is understood.

Di-isobutylaluminium hydride reacts with dimethyl(phenylethynyl)-amine (23) to give the trans- product (24) and the compound (25) by reductive dimerisation [44].



(23) (24) (25)

In the presence of N-methylpyrrolidine, hydroalumination is slowed, production of (25) is suppressed, and the formation of an initial cis-adduct (21, X = NMe_2) may be detected by NMR. Hydroalumination of ethyl(phenylethynyl)sulphide gives cis- products in which the Bu^i_2Al is attached to the Ph-substituted and the S-substituted vinyl carbon atoms in the ratio 17:83. Hydroalumination of 1-ethoxyhex-1-yne $C_4H_9C\equiv COEt$ gives mainly the cis- adduct with Bu^i_2Al α to the butyl group, but di-isobutylaluminium hydride reacts with $PhC\equiv CLi$ and $PhC\equiv CAlPh_2$ to give products with R_2Al β to the phenyl group. Hydroalumination of alkynes $PhC\equiv CX$ (X = Br, Cl, SEt, OEt) yields also the alkyne $PhC\equiv CH$, probably by elimination of compounds Bu^i_2AlX from trans- adducts.



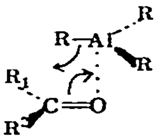
Evidence for π-interaction between ethylene and aluminium atoms has been obtained from ESR measurements on matrix-isolated species [45].

In reactions between dialkylaluminium hydrides R'_2AlH and terminal alkynes $RC\equiv CH$, metallation, giving products $RC\equiv CAlR'_2$, may compete with addition. It has been stated in a conference report [46] that the rate of metallation of alkynes $RC\equiv CH$ by hydrides $MAlH_4$ ($M = Li, Na, K$) in ether increases for the series Li → K. The addition of $LiAlBu^i_3H$ to $PhC\equiv CH$ in the presence of $Ni(acac)_2$ gives a 70% yield of $PhC(:CH_2)AlBu^i_2$. Reactions between styrene derivatives and organoaluminium compounds are complicated by side reactions [47].

7. REACTIONS WITH CARBONYL COMPOUNDS

Sections on aluminium compounds are included in reviews on the reactions of organometallic compounds with carbon dioxide [48] and on the stereochemistry of addition of organometallic compounds to ketones [49].

There is continued interest in the mechanism of addition of organoaluminium compounds to carbonyl functions. It has commonly been assumed that this involves intermediates such as (23) or (24). However, if the formation of the new C-C bond and the breaking of the Al-C bond are synchronous, the configuration of a chiral group R should be retained in the addition.



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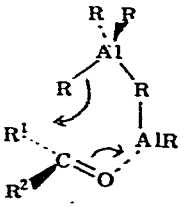
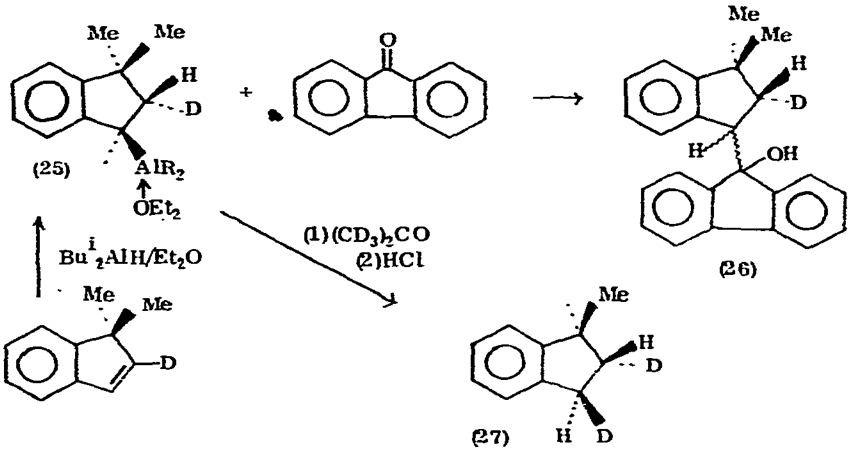


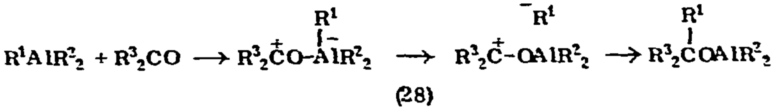
(24)

Optically active organoaluminium compounds, of known configuration, may be made by hydroalumination of indene derivatives, as described last year, and the reaction of the derivative (25) with 9-fluorenone leads, after hydrolysis, to the adduct (26) with complete loss of configuration [50].



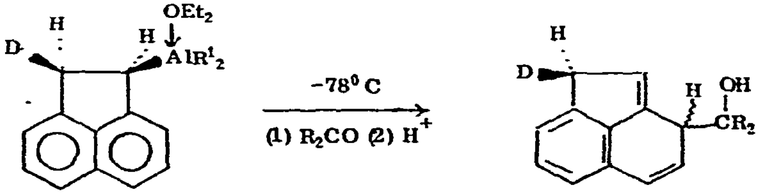
(25) (26) (27)

With deuteroacetone, addition is insignificant, and in the predominant enolisation, the aluminium substituent in the ring is replaced by deuterium with complete retention of configuration giving only the *trans*-2,3-dideuterio-derivative (27). Thus, neither co-ordination of aluminium by the carbonyl oxygen, nor enolisation leads to loss of configuration. It is suggested that addition of organoaluminium compounds to carbonyl groups involves carbenium intermediates (28), which decompose stereospecifically with hydrogen transfer, or non-stereospecifically to insertion products. Acenaphthylene derivatives, *e.g.* (29), at low temperatures, may give allyl rearrangement products [(30), R_2CO = 9-fluorenone].



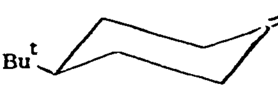
$$R^1AlR^2_2 + R^3_2CO \longrightarrow R^3_2\overset{+}{C}O\text{-}\overset{R^1}{\overset{|-}{Al}}R^2_2 \longrightarrow R^3_2\overset{+}{C}\text{-}OAlR^2_2\ \ {}^{-}R^1 \longrightarrow R^3_2\overset{R^1}{\overset{|}{C}}OAlR^2_2$$

(28)



(29) (30)

Work on additions of organoaluminium compounds to cyclic ketones has continued with experiments involving addition of one aluminium alkyl, AlR^1_3, to the ketone complex $R_2COAlR^2_3$ of another (R^2 = Me, Ph, Cl) [51]. With triethylaluminium and the trimethylaluminium complex (30), the products show ethylation, methylation, and reduction processes, suggesting that alkyl group exchange reactions are faster than addition across the >C=O bond. As in the work described in the last two surveys, at Al: ketone ratios less than 1:1, predominant attack is from the equatorial side to give the axial alcohol (31) and with excess aluminium the preferred attack is from the more hindered side to give the equatorial alcohol (32). Ethyl groups are transferred faster than methyl with Al:ketone ratios < 1 and methyl groups faster than ethyl when Al:ketone is > 1. The ratios of axial to equatorial alcohols are not very different for the various aluminium compounds studied. Reduction is more important for reaction with triethylaluminium than for reaction with Me_3Al/Et_3Al mixtures, and is also enhanced by election-withdrawing groups, e.g., Cl,on aluminium.

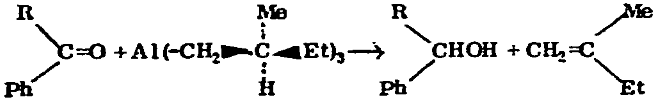


(30)

(31)

(32)

As described last year, asymmetric reductions of carbonyl compounds may be achieved by chiral organoaluminium compounds with α-hydrogen atoms. Between 0 and -60° C, over 90% conversion of alkyl phenyl ketones to the reduced products (33) may be achieved, without addition or enolisation, by reaction with tris[(S)2-methylbutyl]aluminium and tris[(S)2-methylbutyl]aluminium diethyl etherate [52].



$$\mathrm{R(Ph)C{=}O + Al(\text{–}CH_2\text{–}C(Me)(H)\text{–}Et)_3 \longrightarrow R(Ph)CHOH + CH_2{=}C(Me)Et}$$

(33)

The temperature dependence of the stereoselectivity may be explained in terms of enthalpy and entropy effects in the diastereomeric transition state.

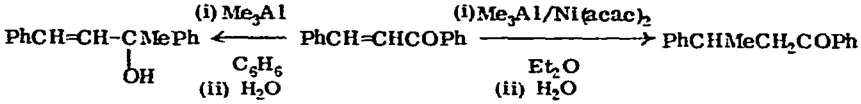
The 1,4- addition of an organoaluminium compound to an α,β-unsaturated ketone has been described as part of a 'one pot' synthesis of alkyne derivatives [53].

$$\mathrm{MeC{\equiv}CH} \xrightarrow[\text{TMEDA}]{\text{BuLi}} \mathrm{LiCH_2C{\equiv}CLi} \xrightarrow[\text{hexane}]{\text{BuBr}} \mathrm{BuCH_2C{\equiv}CLi} \xrightarrow{\mathrm{Et_2AlCl}} \mathrm{BuCH_2C{\equiv}CAlEt_2}$$

$$\xrightarrow{\mathrm{PhCOCH{:}CHPh}} \mathrm{Bu.CH_2.C{\equiv}C.CHPh.CH{:}CPh.OAlEt_2}$$

$$\xrightarrow{\mathrm{H_2O}} \mathrm{BrCH_2C{\equiv}C.CHPh.CH_2COPh}$$

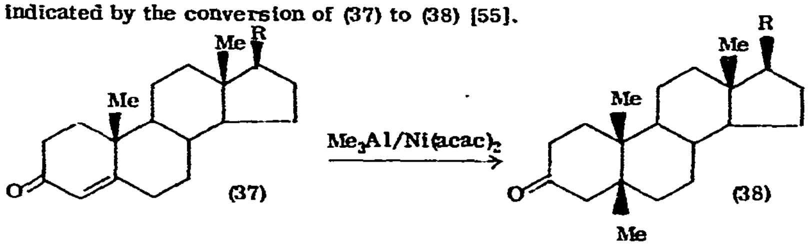
Further examples of nickel-catalysed addition of trimethylaluminium to carbonyl compounds have been described [54]. Whereas 1,3-diphenyl-prop-2-en-1-one (34) is converted by trimethylaluminium in benzene to the 1,2- adduct which may be hydrolysed to the alcohol (35), reaction with $Me_3Al/Ni(acac)_2$ in ether gives the product of 1,4- addition (36).



$$\underset{\textbf{(35)}}{\mathrm{PhCH{=}CH{-}\underset{\displaystyle OH}{C}MePh}} \xleftarrow[\text{(ii) }\mathrm{H_2O}]{\text{(i) }\mathrm{Me_3Al}\ \ \mathrm{C_6H_6}} \underset{\textbf{(34)}}{\mathrm{PhCH{=}CHCOPh}} \xrightarrow[\mathrm{Et_2O}\ \ \text{(ii) }\mathrm{H_2O}]{\text{(i)}\mathrm{Me_3Al/Ni(acac)_2}} \underset{\textbf{(36)}}{\mathrm{PhCHMeCH_2COPh}}$$

(35) (34) (36)

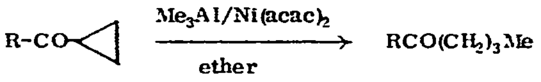
Products formed from a variety of cyclic α,β-unsaturated ketones have been documented and the results have been interpreted in terms of π-allyl(methyl)-nickel intermediates. The application of the reaction in steroid chemistry is indicated by the conversion of (37) to (38) [55].



(37) (38)

[R = C_8H_{17}, COOEt, COOMe]

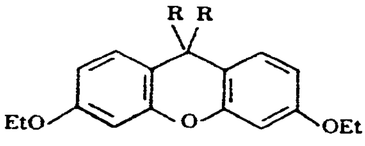
Nickel-catalysed conjugate addition of trimethylaluminium to cyclopropyl ketones gives the open-chain compounds (39), R = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 3,4-$Me_2C_6H_3$, in 50% yield. Lower yields are reported when R = 4-BrC_6H_4 (10%) or cyclopropyl (30%) [55].



(39)

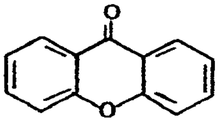
The possible biological activity of 2,6-diethoxyxanthen derivatives has prompted an investigation of the reaction between the ketone (40) and trimethylaluminium. Only a small amount of the gem-dimethyl derivative (41), R = Me is obtained. The major product is the olefin (42); the reaction is autocatalytic and care must be taken to keep it under control [56]. The gem-diethyl derivative, (41) R = Et, is obtained in 29% yield from the xanthone (40) and triethylaluminium; and the unsubstituted compound, (41)

(40) (42)



(41)

R = H, may be made in 75% yield by reduction, first with di-isobutylaluminium hydride, and then with excess tri-isobutylaluminium. Xanth-9-one itself (43), with trimethylaluminium, gives the gem-dimethyl derivative (44), so that the



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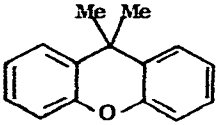
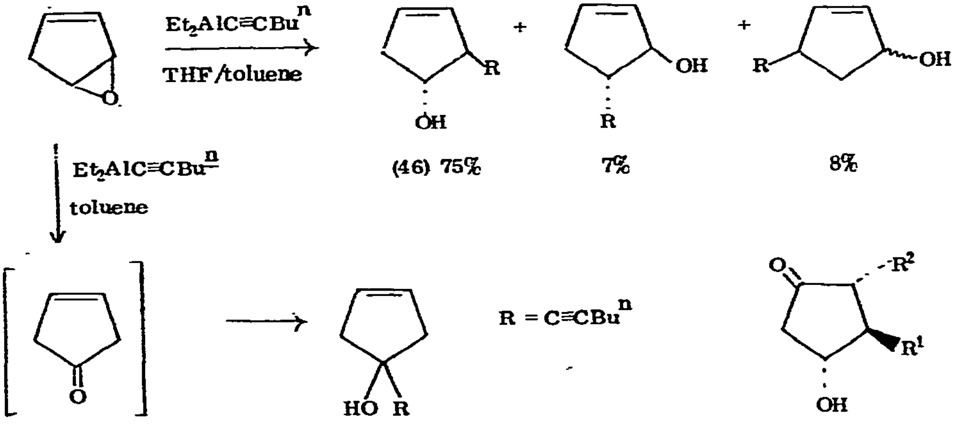


(44)

formation of the olefin (42) must result from the two ethoxy-substituents in the ketone (40).

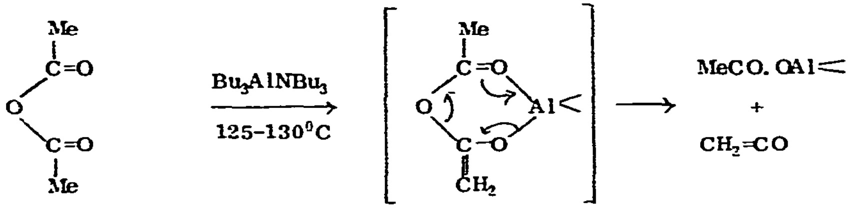
There is a good deal of current interest in development of synthetic methods, with carefully controlled stereochemistry, for prostaglandins (45). As part of a study of possible uses of organoaluminium compounds, it has been found that the epoxide ring opening of 3,4-epoxycyclopentene with diethylhex-1-ynylaluminium, generated in situ from butyl-lithium, hex-1-yne and diethylaluminium chloride, depends on the solvent [57]. In THF-toluene, the main product is the desired alcohol (46). In toluene, however, the main product is the tertiary alcohol (47); in the absence of ether the organoaluminium compound causes rearrangement to the ketone (48), which is attacked further.



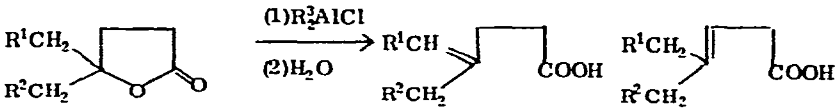
(46) 75%   7%   8%

(48)   (47)   (45)

The reaction between organoaluminium compounds and carboxylic acid anhydrides is a convenient route to ketenes. Yields may be increased from 9-43% to 70-80%, by addition of tertiary amines so that the aluminium compound is present as a donor acceptor complex [58].



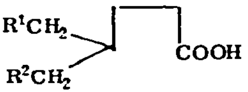
With lactones, organoaluminium compounds give adducts which may be hydrolysed to unsaturated carboxylic acids. Products from reactions of butanolides with dimethyl- and diethyl-aluminium chlorides have been estimated by ozonolysis [59], (Table 2).



(48)

(49)

(50)



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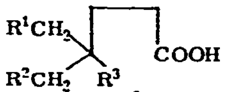
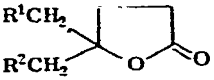


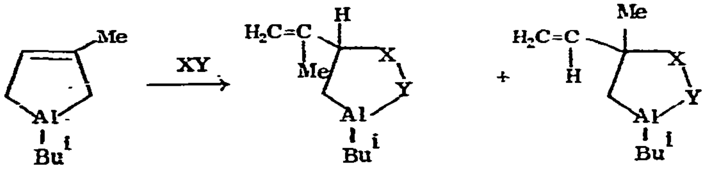
(52)

Table 2 Yields (%) from Reaction between Et$_2$AlCl and



R^1	R^2	(48)	(49)	(50)	(51)	(52) R^3 = Et
H	Me	1	20	64	5	10
Me	Me	80	10	0	5	5
H	C_5H_{11}	13	17	55	5	10
Me	C_5H_{11}	58	18	14	5	5

Several patents have described insertion reactions of 1-isobutyl-3-methylaluminiacyclopent-3-ene (53); the products (54) and (55) may be hydrolysed to give alkenols (XY = Et_2CO) [60], alkenones (XY = PhCN) [61] [product (54) only], or alkenoic acids (XY = CO_2) [62].

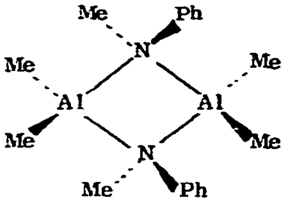


(53) (54) (55)

Reactions of allylaluminium compounds with various carbonyl derivatives have been investigated as part of a wider survey of organometallic compounds of electropositive elements [63-64]. The products often involve rearrangements. Thus ethyl chloroacetate with $(EtCH=CHCH_2)_3Al_2Br_3$ gives, after hydrolysis, a 87% yield of the chlorohydrin $ClCH_2C(OH)[CHEt-CH=CH_2]_2$ and the arylaldoxime *O*-ester Ph-CH=NOEt with $(CH_2=CHCH_2)_3Al_2Br_3$ gives $PhNH-CH(CH_2-CH=CH_2)_2$ by a Beckmann rearrangement.

8. REACTIONS WITH ORGANIC NITROGEN DERIVATIVES

Interconversion of *cis*- and *trans*-isomers (56) (57) of the dimer $(Me_2AlNMePh)_2$ has been observed by NMR. At room temperature the equilibrium ratio of *cis*-:*trans*- is about 5.0 in dichloromethane and a plot of the ratio against $^1/T$ gives $\Delta H = 4.47 \pm 0.09$ kJ mol^{-1}, $\Delta S = 1.74 \pm 0.48$ J K^{-1} mol^{-1}. The rate of interconversion is accelerated by bases such as 4-methyl-pyridine or THF, which cause the ^1H NMR signal due to the



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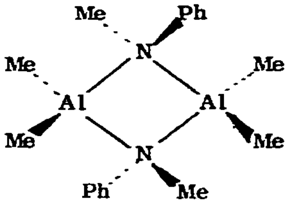
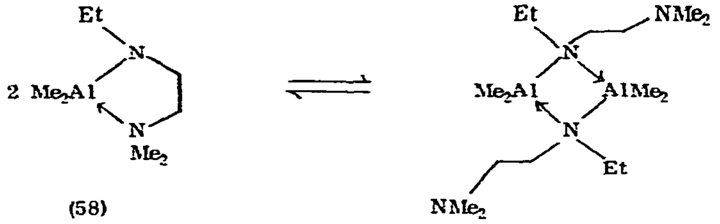


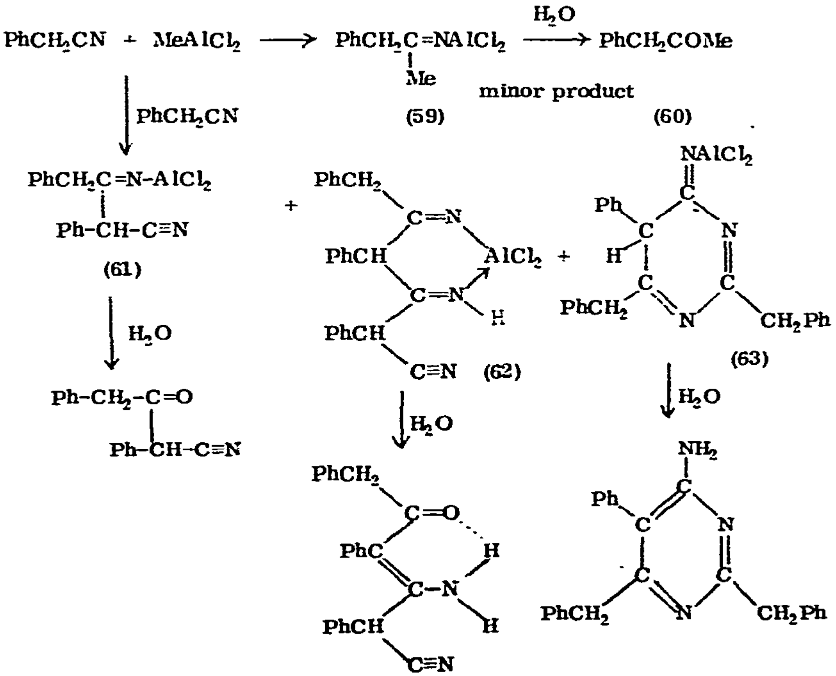
(57)

separate isomers to collapse [65]. The interconversion probably involves ring-opening, followed by rotation about Al-N bonds. The compound $Me_2AlNEtCH_2CH_2NMe_2$ made from trimethylaluminium and N-dimethyl-N'-ethylethylenediamine, is monomeric (58) in benzene and toluene, and, at room temperature, in cyclopentane. As the cyclopentane solution is cooled or concentrated, however, new bands, ascribed to the dimer, appear in the NMR spectrum [66]. The diamine is displaced by dimethylamine with formation of the compound $(Me_2AlNMe_2)_2$.



(58)

Reactions between organoaluminium compounds and cyanides are described in several papers. Methylaluminium dichloride and benzyl cyanide in molecular proportions 1:1 at 135° C give only small amounts

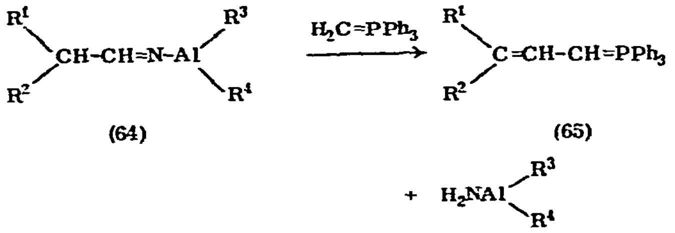


(59) (60) (61) (62) (63)

of the adduct (59) which may be hydrolysed to the ketone (60); the major reaction involves elimination of methane [67]. With an excess of the cyanide it is possible to isolate the dimer (61) or trimers (62) and (63).

In the presence of bis(N-methylsalicylaldimine)nickel, tri-isobutylaluminium reduces t-butyl cyanide to the aldehyde Bu^tCHO; only poor conversions are obtained at 67° C in the absence of catalyst. With phenyl cyanide the uncatalysed reaction gives exclusively reduction to aldehyde, but the nickel-catalysed reaction gives about equal amounts of the aldehyde PhCHO and the ketone addition product $PhCOCH_2CHMe_2$ [68].

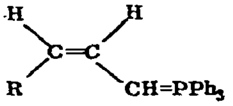
Dialkylaluminium hydrides react with cyanides to give dialkylaluminium-alkylidenamides (64).



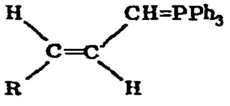
(64)

(65)

These react with methylene(triphenyl)phosphorane in ether to give ylides (65) which may be crystallised at -78° C and thus separated from the dialkylaluminium amides [69]. A wide range of ylides $RCH{=}CH{-}CH{=}PPh_3$ has been prepared and characterised. Where R = Me, Et, Pr^n, Bu^n, $i{-}C_5H_{11}$, $n{-}C_6H_{13}$, $n{-}C_7H_{15}$, $n{-}C_8H_{17}$, $n{-}C_9H_{19}$, the products are predominantly in the cis-form (65a) and where R = Bu^t, Ph, the main products are trans- (65b).

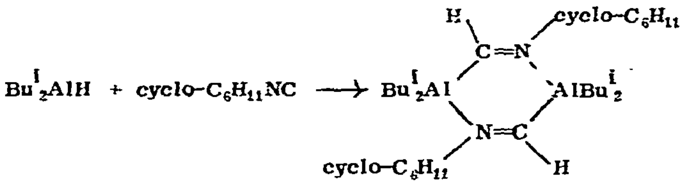


(65a)



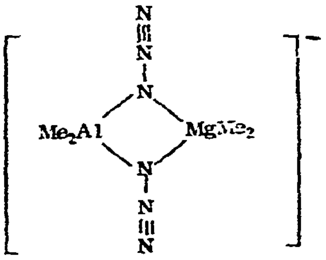
(65b)

Reactions between di-isobutylaluminium hydride and isocyanides have also been studied [70]. The products are shown to be associated to dimers both in the vapour (by mass spectra) and in solution (by cryoscopic measurements), and an unpublished X-ray study of cyclohexyliminomethyl(di-isobutyl)-aluminium (66) shows that the molecules contain six-membered rings.



(66)

Peaks in the IR and Raman spectra of the compound $[(Me_2AlCN)_4]$ have been assigned by comparison with analogous gallium and indium compounds and with the isoelectronic anion $[(Me_2MgCN)_4]^{4-}$ [71]. Mass spectra have also been reported. The reaction between the compounds $[(Me_2AlN_3)_3]$ and tetramethylammonium azide yields salts $[Me_4N][Me_2Al(N_3)_2]$ (67), which form complexes $[Me_4N][Me_2Al(N_3)_2(AlMe_3)_n]$ [(68), n = 1,2] [72]. With dimethylmagnesium, the salt (67) gives a compound $[Me_4N][Me_2Al(N_3)_2MgMe_2]$ with an anion (69) isoelectronic with $[(Me_2AlN_3)_2]$. Compounds $[(Me_2EN_2C_4H_5)_4]$[$N_2C_4H_5$ = 2-methylimidazolyl, E = B, Al, Ga, In] have been described, but the aluminium derivative, the only one of the series to react with air, has been incompletely characterised [73, 74].



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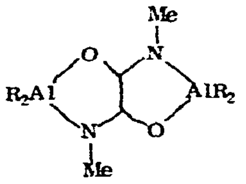
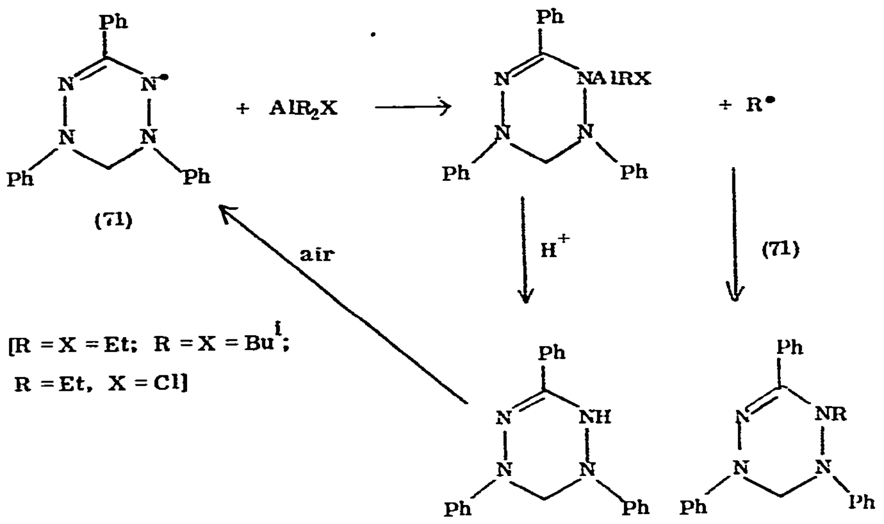


(70)

The oxamide derivatives [(70) R = Me, Et] are obtained from alkyls AlR_3 and *N,N'*-dimethyloxamide [75]. The vibrational spectra indicate an almost planar $Al_2O_2C_2N_2$ skeleton with S_2 symmetry.

Solutions of the stable free radical (71) are decolourised by alkylaluminium compounds and the products detected after hydrolysis suggest that alkyl radicals are expelled by homolytic substitution. The radical (71) may be regenerated by atmospheric oxidation [76].



[R = X = Et; R = X = Bu^i; R = Et, X = Cl]

9. ORGANOALUMINIUM ALKOXIDES AND RELATED COMPOUNDS

Organometallic peroxides have been reviewed [77]. Oxidation of dialkylaluminium chlorides at 12–125° C in decane has been studied in a circulating system in which the partial pressure of oxygen is kept constant [78]. The rate law,

$$\text{Rate} = p(O_2)\left\{k_1[R_2AlCl] + k_4[R(RO)AlCl]\right\},$$

is consistent with a mechanism involving peroxide and alkoxide intermediates.

$$R_2AlCl + O_2 \xrightarrow{k_1} R(ROO)AlCl \xrightarrow{k_2} (RO)_2AlCl$$

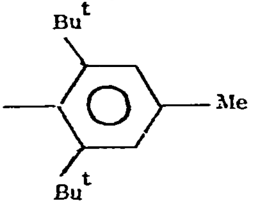
$$R(ROO)AlCl + R_2AlCl \xrightarrow{k_3} 2R(RO)AlCl$$

$$R(RO)AlCl + O_2 \xrightarrow{k_4} (ROO)(RO)AlCl$$

The rates of oxidation of compounds R(RO)AlCl, made independently, agree with those derived from oxidation of R_2AlCl. Dialkylaluminium bromides are oxidised faster than chlorides. Rates of oxidation are also accelerated by addition of titanium(IV) chloride, which, of course, reacts with alkylaluminium compounds to give Ti^{III} species. In another investigation, isomeric di-isobutylaluminium n-hexanolates $R_2AlO(CH_2)_{3-n}CH{=}CH(CH_2)_nCH_3$

were treated with oxygen and acetic anhydride. Besides the expected hexenol acetates, hexanetriol acetates were isolated. These are considered to be formed from epoxides derived from organoaluminium peroxides [79].

Di-2,6-t-butyl-4-methylphenoxyaluminium compounds $R^1_2Al(OR^2)$, $R^1Al(OR^2)_2$ [R^1 = Me, Bu^i; $R^2 = C_6H_2Bu^t_2Me$ (72)] obtained from the trialkyls and the phenols are monomeric in benzene, unlike associated alkoxides with smaller alkoxy- groups, and very sensitive towards oxygen [80].



(72)

Dimethylaluminium chloride reacts with lead(II) oxide to give (besides tetramethyl-lead, lead(II) chloride and metallic lead) a substance with composition $Me_3ClAl_2O.OEt_2$ [81]. This is monomeric in benzene when freshly prepared, but becomes associated on standing; various oxygen-bridged structures have been proposed.

The preparation of aluminoxanes by hydrolysis of organoaluminium compounds is made difficult by the strongly exothermic reaction. Copper(II) sulphate pentahydrate, suspended in benzene, has been used as a controlled source of water for hydrolysis [82]. Alkyls R_3Al (R = Et, Bu^i) give compounds $R_2AlOAlR_2$ and chlorides R_2AlCl (R = Et, Bu^i) give RClAlOAlRCl. Ethylaluminium dichloride gives a 60:40 mixture of $Cl_2AlOAlCl_2$ and EtClAlOAlClEt. Rates of hydrolysis decrease in the series $RAlCl_2 > R_2AlCl > R_3Al$.

Alkoxides Et_2AlOR^1 (R^1 = $CMePh_2$, CMe_2Ph, CMePhH, CH_2Ph, CPh_2H) decompose in sealed ampoules at 150-210° C [83]. Where there is at least one methyl group in the substituent R^1, the main product is the olefin formed by loss of hydrogen. It is assumed that the other product is Et_2AlOH which reacts with more alkoxide. The compound Et_2AlOCH_2Ph, decomposes preferentially at the Al-ethyl groups, leaving the OCH_2Ph group intact. $Et_2AlOCHPh_2$ gives mainly aromatic hydrocarbons, *e.g.*, Ph_2CHEt and Ph_2CH_2.

Several miscellaneous studies involving organoaluminium compounds and alcohols are mentioned briefly. The reactions between R_3Al (R = Bu^i, Ph) and diphenylglyoxime have been studied [84]. Trimethyl aluminium reacts with the dimethylarsinous acid derivative $Me_2AsO(CH_2)_2OH$ to give an insoluble polymer [85]. Reactions between organoaluminium compounds and anthranilic acid give materials said to be useful as anti-inflammatants [86]. Aluminium chloride alcoholates react with sodium cyclopentadienide in THF, to give brown moisture-sensitive complexes $C_5H_5AlCl_2,3ROH$ [87].

10. SULPHUR AND PHOSPHORUS DERIVATIVES

In the reaction between hydrogen sulphide and an excess of triethylaluminium, the initial product seems to be EtAlS (73) which then reacts with more triethylaluminium to give the product $(Et_2Al)_2S$ [88]. The sulphide (73) is insoluble in hydrocarbons, but gives soluble adducts EtAlS,2D with donors D such as pyridine. The sulphur may be displaced from the aluminium compound by treatment with amides.

$$\underset{(73)}{(EtAlS)_n} + RCONMe_2 \longrightarrow (EtAlO)_n + RCSNMe_2$$

$$[R = H,\ Me,\ Ph]$$

The driving force for this reaction presumably comes from the strong affinity between aluminium and oxygen. The compounds $(Me_2AlPR_2)_n$ have been made from dialkyl(trimethylsilyl)phosphines and dimethylaluminium hydride [89]. The values of the molecular complexities n, from cryoscopic data, ($n = 4$ for R = Me; $n = 2$ for R = Et), differ from those obtained previously ($n = 3$ for both compounds) [90]; the source of these discrepancies is not clear.

11. DONOR-ACCEPTOR COMPLEXES

Diethyl ether and trimethylamine complexes of tris(pentafluorophenyl)-aluminium have been described [91]. The dissociation of complexes Et_3Al,D has been studied by plotting NMR chemical shifts against concentrations in chlorobenzene [92]. Not surprisingly, the stability of the complexes falls in the series (D=) $NEt_3 > THF > OEt_2 > SEt_2$.

Disproportionation of ethylaluminium dichloride is induced by diphenylether.

$$2EtAlCl_2 + Ph_2O \longrightarrow Et_2AlCl + Ph_2O,AlCl_3$$

This reaction proceeds best in paraffin hydrocarbons, from which the aluminium trichloride adduct is precipitated. The adduct $Ph_2O,AlEtCl_2$ may be made in benzene or by mixing together the components without solvent [93]. Similar disproportionations may be effected by dimethylsulphoxide (DMSO) [94]. Thus a 1:1 mixture of diethylaluminium chloride and DMSO gives an adduct $DMSO,AlEt_2Cl$. With an excess of DMSO, however, the products are complexes of triethylaluminium and aluminium trichloride.

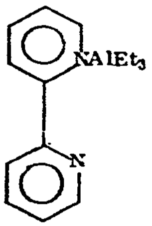
$$3DMSO,AlEt_2Cl + 5DMSO \longrightarrow AlCl_3(DMSO)_6 + 2DMSOAlEt_3$$

Ethylaluminium dichloride with a deficiency of DMSO gives the sesquichloride and the complex $DMSO,AlCl_3$.

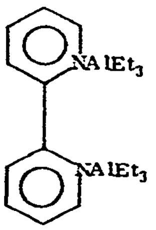
$$2EtAlCl_2 + DMSO \longrightarrow AlCl_3DMSO + Et_3Al_2Cl_3$$

With an excess of DMSO reactions are more complex; only $[AlCl_3(DMSO)_6]$ is identified with certainty among the products.

Enthalpy changes associated with reactions between triethylaluminium and a series of donors (bipyridyl, pyridine, Et_2O, Bu_2O, PhOMe, Ph_2O) in hydrocarbon solvents, have been measured [95]. The similarity between the pyridine complex and 1:1 pyridyl complex (74), suggests that the aluminium is four-co-ordinate in both.



(74)



(75)

The enthalpy change for formation of the 1:2 complex (75) from the 1:1 complex (74) is consistent with the experimental observation that the 1:2 complex cannot be made in diethyl ether or benzene. The shift in equilibrium when (75) is precipitated from paraffin hydrocarbons is, however, sufficient to permit its formation in the presence of bases such as anisole or even dibutyl ether.

The coupling constants $^2\underline{J}$(Pt–H) in complexes $[4\text{Pt}(\text{PEt}_3)_2\text{CN}]\rightarrow\text{L}$ has been suggested [96] as a measure of the acceptor strength of the Lewis acid L. On this basis, trimethylaluminium is a weak acceptor, comparable with triphenyl borate $B(OPh)_3$.

12. BIMETALLIC COMPOUNDS

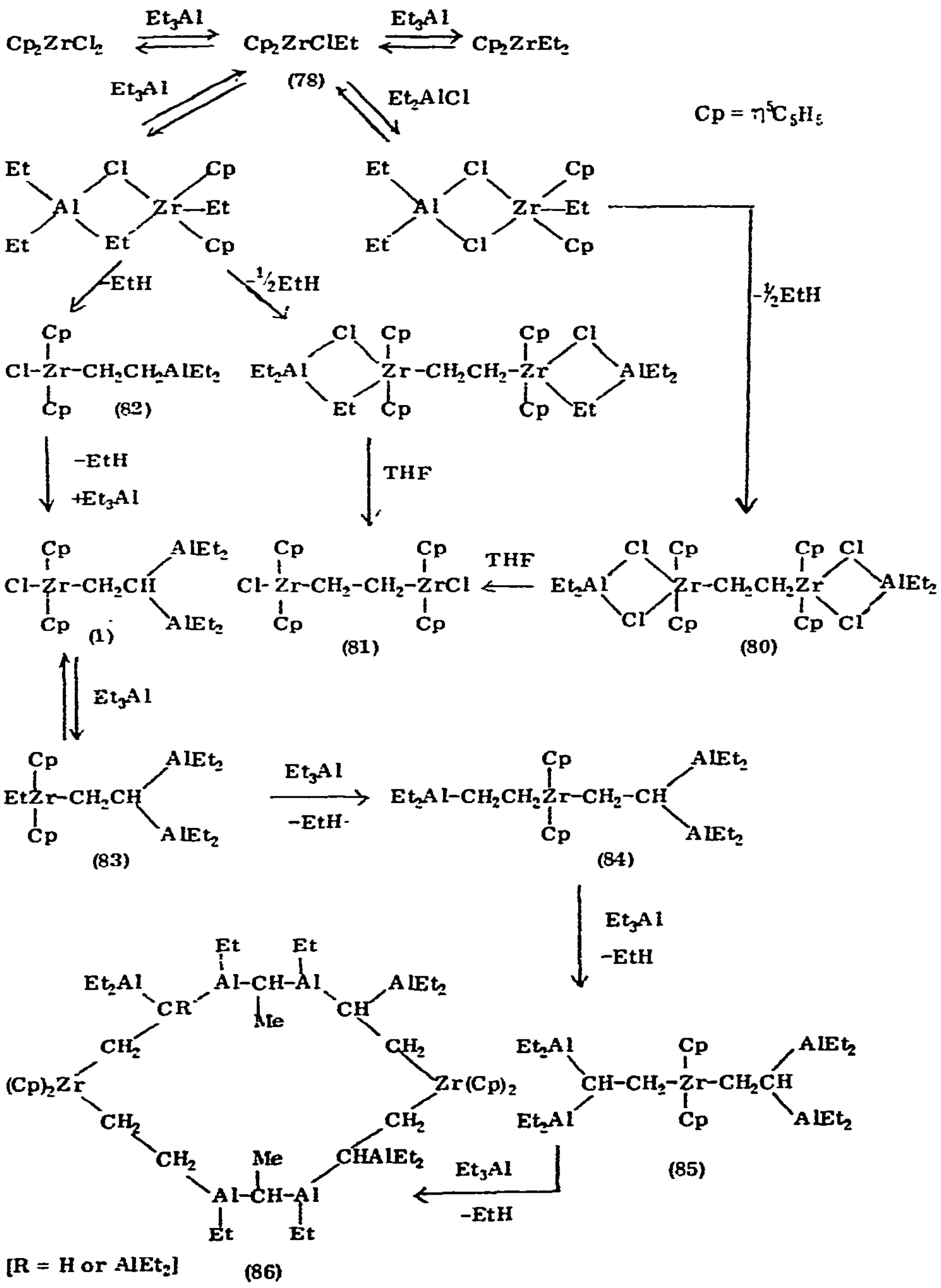
The reaction of alkaline earth metals with organomercury compounds in the presence of organoaluminium compounds constitutes a general route to compounds $M(AlR^1_3R^2)_2$ (M = Ca, Sr, Ba; R^1, R^2 = alkyl or aryl).

$$M + HgR^2_2 + 2AlR^1_3 \longrightarrow M(AlR^1_3R^2)_2 + Hg$$

The best solvent is xylene or heptane; if amines or ethers are used, donor molecules are incorporated in the products [97]. More details of the reactions of alkaline earth tetraethylaluminates with halogens ($\rightarrow$EtX + $AlEt_3$ + MX_2) and with aluminium halides ($\rightarrow AlEt_3$ + MX_2) have been published [98]. Calcium bis(tetraethylaluminate) reacts with indene at 50-150° C with liberation of ethane, giving the complex $Ca[C_9H_7AlEt_3][AlEt_4]$ which loses triethylaluminium during distillation in vacuum [99]. Aluminium alkyls react with Grignard reagents to give soluble products with Mg/Al 1-20 [100]. These are thought to have the structures $R_2Al(R_2Mg)_n$-R_2AlR_2 with electron deficient bridges such as those in trimethylaluminium and dimethylmagnesium. Alkyl group exchange between aluminium and magnesium is shown by NMR.

Organometallic compounds containing both aluminium and transition metals have, of course, been studied extensively as catalytic systems, but surprisingly little is known about the bonding between the two metals. Tribenzylaluminium and tetrabenzyltitanium in benzene react with elimination of toluene to give a mixture which is a catalyst for α-olefin polymerisation [101]. Formation of species (76) and (77) in which titanium and aluminium are linked by carbon atoms may be detected, after hydrolysis with deuteromethanol, by mass spectroscopy.

$$R_3TiCH_2Ph \xrightarrow[-PhMe]{R_2AlCH_2Ph} \underset{(76)}{R_3TiCHPhAlR_2} \xrightarrow[-PhMe]{R_2AlCH_2Ph} \underset{(77)}{[R_3TiC(Ph)(AlR_2)_2]}$$



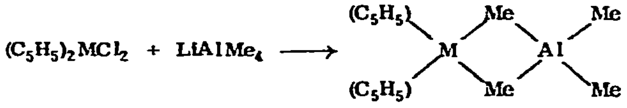
$Cp = \eta^5C_5H_5$

[R = H or $AlEt_2$]

Reduction to Ti^{III} species may be estimated from the bibenzyl generated and information about the extent of formation of low-molecular-weight bimetallic species deduced from cryoscopic measurements. The extent of toluene formation is maximum at Al/Ti ratios of 4-5.

Bis(cyclopentadienyl)zirconium dichloride and triethylaluminium interact to give a series of compounds [(1), (78)-(86)] having Zr-C-C-Al sequences. One of these substances (1) has been characterised by X-ray methods [10]; structures of the others have been inferred from cryoscopic and NMR measurements and by identification of products from hydrolysis with deuterated solvents [102-104]. Kinetic studies, following concentrations by NMR, have established a qualitative order for many of the rate constants, and data for compound (1) at various temperatures have been interpreted as showing changes in ring conformations.

Several further compounds with electron deficient bridges between aluminium and transition metals (87) have been described [105]. Exchange between bridge and terminal methyl groups is slow on the NMR time scale at -45° C, but rapid at 40° C. The Ti compound (87) decomposes slowly at room temperature, but the yttrium compound may be sublimed at 120° C without decomposition. The reaction between $LiAlMe_4$ and $[\{Ti(\pi\text{-}C_5H_5)_2Cl\}_2]$ gave the known compound $[Ti(\pi\text{-}C_5H_5)_2Me_2]$ and Al_2Me_6.

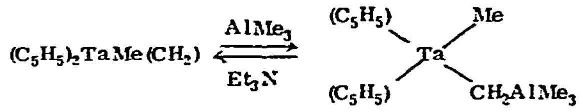


(87)

[M = Y, Ti]

Reaction of the compounds $[(C_5H_5)_2M(CH_2Ph)_2]$ (M = Ti, Zr, Hf) with carbon monoxide in the presence of triethylaluminium gives good yields of the carbonyl derivatives $[(C_5H_5)_2Ti(CO)_2]$ [106]. It is suggested that the function of the triethylaluminium catalyst is to co-ordinate the insertion product $[(C_5H_5)_2Ti(CH_2Ph)(COCH_2Ph)]$, but the reaction may well be more complicated. $[(C_5H_5)_2Ti(CO)_2]$ may be made in 30% yield from $[(C_5H_5)_2TiCl_2)]$ by the same method.

The adduct (88) formed from the carbene complex and trimethylaluminium is another example of a molecule with an Al-CH_2-transition metal sequence [107].

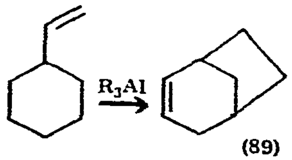


(88)

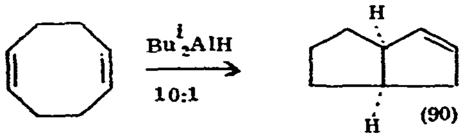
Uncharacterised intermediates from alkylaluminium dichlorides may be involved in the formation of cyclopentadienylmolybdenum compounds [108], and the redistribution of alkyl groups in organolead compounds [109]. Complexes of $CuAlRCl_3$ with various solvents have also been described [110].

13. CATALYSIS

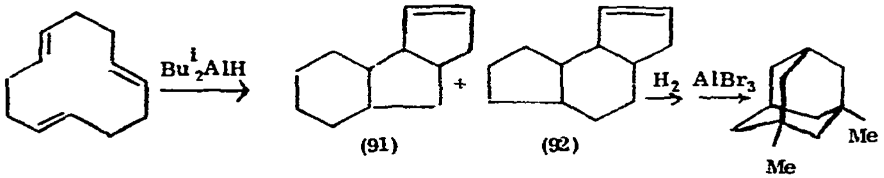
Organoaluminium compounds are widely used as catalysts for isomerisation of olefins. For reactions at 200° C, triethylaluminium, tri-isobutylaluminium and di-isobutylaluminium hydride are usually more effective than alkylaluminium chlorides or triphenylaluminium, probably because they more easily initiate hydroalumination reactions. Vinylcyclohexane is converted to the tricyclic olefin (89), cyclo-octadiene to (90) and trans-,trans-,trans-cyclododecatriene to (91) and (92) [111]



(89)

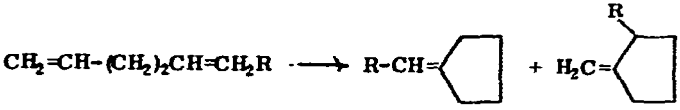


(90)



(91) (92)

Isomerisation of 1,4- and 1,5-dienes, catalysed by trialkylaluminiums, has been studied at 150-200° C in teflon-coated reaction vessels [112].



The gas-phase reaction is homogeneous and unimolecular and probably involves multiple insertions and β-eliminations.

Organoaluminium compounds are often components, together with transition metal compounds, of catalysts used in the olefin metathesis reaction under mild conditions.

$$2R^1R^2C{=}CR^3R^4 \rightleftharpoons R^1R^2C{=}CR^1R^2 + R^3R^4C{=}CR^3R^4$$

Two important reviews [113] [114] and many papers have appeared, e.g., [115-124] including one [117] which describes catalysts on a polystyrene support. The reaction is now generally considered to involve metal-carbene intermediates at the transition metal centre, but since the role of the aluminium compound is probably in the initial formation of these, rather than in the subsequent metathesis process, details are not given here.

Tri-isobutylaluminium enhances the rate of hydrogenation of ethylene by the catalyst $RhCl(PPh_3)_3$ [125], but why is not clear. Hydrosilylation of 1,3-butadiene with trimethylsilane, $Ni(acac)_2$ and triethylaluminium gives 90% cis-1-trimethylsilylbut-2-ene. Similar reactions with isoprene, 3-methylhepta-1,4,6-triene and piperylene with a variety of silanes $R^1R^2R^3SiH$ have also been described [126].

Production of catalysts for oligomerisation of butadiene, from arenes and metal vapours, has been described with much detail [127]. These catalysts usually, but not always, require alkylaluminium chlorides R_nAlCl_{3-n} (n = 1-3) as cocatalysts. A catalyst for dimerisation of propene to linear hexenes has been made from $Pd(acac)_2$, PR_3 [R = Bu, Ph] or $(PhO)_3P$ and ethylaluminium dichloride [128]. The nature of the product requires that insertion of propene into the Pd-H bond gives the normal rather than the iso-propyl derivative. In the presence of moisture, the catalyst causes polymerisation rather than dimerisation. Another oligomerisation described during 1975 is the cyclotrimerisation of phenyl acetylene to 1,3,5- and 1,2,4-triphenylbenzenes, using titanium, vanadium or niobium catalysts and organoaluminium compounds R_3Al (R = Et, Bu^i) or Et_2AlCl. The proportions of the products may be controlled by choice of catalytic systems [129].

Catalysts for polymerisation have been described in a published lecture [130], and in a rather general paper [131]. As in previous years, the literature on Ziegler-Natta polymerisation is very extensive and only an extremely brief summary is given here. The use of ^{14}C tracers to estimate active sites in the polymerisation of styrene has been critically reviewed [142], and there has been a theoretical discussion [133] of microtacticities (obtained from ^{13}C NMR spectra) in propene polymerisation. A brief ESR study has also been reported [134]. A kinetic investigation [135] of the polymerisation of 3-methylbut-1-ene with $TiCl_3$ or $TiCl_4$ - AlR_3 catalysts shows that the reactions are second-order in catalyst. The catalyst activity decreases in the order $AlBu^i_3/TiCl_4 > AlEt_3/TiCl_4 \sim AlBu^i_3/TiCl_3 > AlEt_2Cl/TiCl_4$ but the polymer stereoregularity does not depend very markedly on the aluminium compound. The low yields are attributed to adsorption of polymer on catalytic sites and to competing isomerisation reactions. Stereospecificty of alkylaluminium-titanium chloride catalysts has been enhanced by replacement of some of the surface chlorine atoms by bromine or iodine [136] or by treatment with carbon disulphide, which seems to complex preferentially at sites leading to oligomerisation rather than polymerisation [137]. Internal olefins such as 4-methyl-pent-2-ene [137] isomerise before polymerising to poly-4-methyl-pent-1-ene. Cyclohexa-1,4-diene similarly polymerises to polycyclohexa-1,3-diene [138].

The activity of catalysts such as $(C_5H_5)_2TiCl_2/Me_2AlCl$ [140] or $VOCl_3/Et_nAlCl_{3-n}$ [141] is enhanced by addition of small amounts of water, and the effect has been attributed to the increased Lewis acidity of the aluminium. A $TiCl_3/AlEt_3$ catalyst is said to induce simultaneous ionic and radical polymerisation of ethylene [142].

Experiments with vanadium chloride/alkylaluminium catalysts have yielded data on molecular weight distributions and stereoregularity of polypropylenes [143], on polymerisation of chiral alk-1-enes [144], and on the isomerisation copolymerisation of but-2-ene and pent-2-ene with hex-2-ene [145]. The ethene-propene copolymerisation in the presence of the homogeneous catalyst $Ti(OPr^i)_4/Et_2AlF$ appears to be similar to syndiotactic polymerisation with $VCl_4/AlEt_3$ [146]. ^{13}C NMR has proved a powerful tool for obtaining information about $(CH_2)_n$ sequences. A detailed study has been made of copolymerisation of conjugated dienes such as buta-1,4-diene, isoprene or chloroprene with monomers such as acrylonitrile or methyl methacrylate with a variety of catalysts, particularly ethylaluminium sesquichloride and $Et_3Al_2Cl_3/VOCl_3$ [147].

A very detailed account of the polymerisation and copolymerisation of alkenes by mixtures of alkylaluminium halides and halogens or interhalogens has appeared [148-152]. The results have been interpreted as showing that the aluminium compound acts as a Lewis acid and that the attacking species are halonium ions. This suggestion is supported by experiments with 2,4,4-trimethyl pent-1-ene, which cannot polymerise for steric reasons; chlorinated products from reaction with Cl_2/Et_2AlCl may be isolated and identified and thus throw light on intermediates in polymerisation of isobutene and other alkenes.

Mixtures of triethylaluminium and boron trifluoride induce copolymerisation of cyclic ethers and chlorohydrins. The high resistance of the polymers to alkali suggests that there is a random distribution of chlorohydrin units. In this case, the active initiator is thought to be $[AlEt_2^+][BF_3Et^-]$ [153]. A further example of initiation of the polymerisation of aldehydes by triethylaluminium has been described [154]. At −10 to −20° C, allyloxyacetaldehyde $CH_2{=}CH_2CH_2OCH_2CHO$ polymerises to highly crystalline poly(allyloxymethyl)oxymethylene $[-CH(CH_2OCH_2CH{=}CH_2)O-]_n$. At higher temperatures, the ester $CH_2{=}CH.CH_2O.CH_2(CO)OCH_2CH_2O.CH_2CH{=}CH_2$ is formed in a side reaction.

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