

ALUMINIUM

ANNUAL SURVEY COVERING THE YEAR 1978*

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1. INTRODUCTION REVIEWS

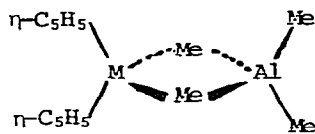
The number of papers on organoaluminium compounds published in 1978 was about the same as in previous years. The basic reactions in this field have been well established for some time but there is still a good deal of structural work and exploration of the use of organoaluminium compounds in organic synthesis and catalysis.

*Aluminium Annual Survey covering the year 1977, see J. Organometal. Chem. 163(1978) 97-140.

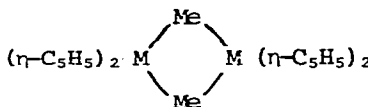
Progress in organoaluminium chemistry is summarised as usual [1] in the Chemical Society Specialist Periodical Report which covers the literature on organometallic compounds for 1977. A brief account [2] of the use of group III organometallic compounds in syntheses is given in the Report on general and synthetic methods. Important reviews stress the high selectivity of many reactions using organoaluminium reagents [3] and the application of organoaluminium compounds in the initiation of carbenium ion polymerisation [4]. An extended review (56 pp. 193 ref.) has been published in an encyclopedia [5]. Other reviews have appeared in Polish [6] (on reactions with lead compounds), Hungarian [7], Finnish [8] (on structures),^{and} Japanese [9], [10] (on hydrocyanation using organoaluminium compounds). As in previous years, there have been reviews on olefin metathesis [11] [12].

2. MOLECULAR STRUCTURES

Full details of the crystal structures of the methyl-bridged lanthanoid-aluminium complexes (1) ($R = \text{Me}$, $M = \text{Y}$ or Yb) have been published [13] [14]; some bond lengths and angles are given in Table 1. The compounds (1) ($R = \text{Me}$; $M = \text{Sc}$, Y , Gd , Dy , Ho , Er , Tm or Yb ; $R = \text{Et}$; $M = \text{Sc}$, Y or Yb),



(1)



(2)

made from the lanthanoid chloride and lithium tetraalkylaluminate (Equation 1), are air-sensitive solids, soluble in benzene or toluene but much less so in saturated hydrocarbons.



The solubility decreases from right to left across the lanthanoid series; this may indicate that the compounds of the earlier members of the series are the most ionic.

The compounds (1) are thermally quite stable and in many cases melt (100–150°C) without decomposition. The titanium compounds $[(\eta\text{-C}_5\text{H}_5)_2\text{TiAlMe}_4]$ and $[(\eta\text{-C}_5\text{H}_5)_2\text{TiAlMe}_3\text{Cl}]$ (from $[\{\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}\}_2]$ and Al_2Me_6) have also been obtained. However, as they are much more reactive than the corresponding

Table I. Molecular parameters[†] for $[(\eta\text{-C}_5\text{H}_5)_2\text{M}(\mu\text{-Me})_2\text{AlMe}_2]$ (1) M = Y or Yb

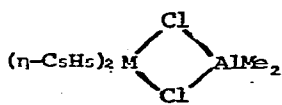
	M-C (bridge) pm	Al-C (bridge) pm	Al-C (terminal) pm	M-C-Al °
$(\eta\text{-C}_5\text{H}_5)_2\text{Y}(\mu\text{-Me})_2\text{AlMe}_2$ [13]	258 (2)	210 (2)	194 (3)	80.8 (7)
$(\eta\text{-C}_5\text{H}_5)_2\text{Yb}(\mu\text{-Me})_2\text{AlMe}_2$ [14]	259 (3)	212 (2)	200 (2)	78.8 (7)
$\text{Me}_2\text{Al}(\mu\text{-Me})_2\text{AlMe}_2$	—	212.4 (3)	195.2 (4)	75.7 (1)

†std for least significant figure in parentheses

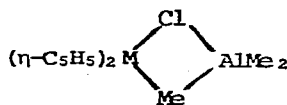
lanthanoid compounds, their structures have not been unequivocally determined. It is possible that these too contain di- μ -methyl or μ -chloro- μ -methyl bridges. A further species, identified by ESR spectroscopy, may be $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})_2\text{AlMe}_2]$. See also ref. [140] discussed in Section 12.

The scandium and yttrium compounds, unlike the other members of the series, are diamagnetic, so that structural studies by ^1H and ^{13}C NMR spectroscopy are feasible. The yttrium compounds (1) (M = Y, R = Me or Et) are fluxional at 40°C, but separate NMR signals, corresponding to bridging and terminal alkyl groups, are observed at -40°C. ΔG^\ddagger for bridge-terminal site exchange in $\text{C}_6\text{D}_5\text{OD}_3$ is 66.5 kJ mol⁻¹ at 392 K. The scandium compound $[(\eta\text{-C}_5\text{H}_5)_2\text{Sc}(\mu\text{-Me})_2\text{AlMe}_2]$ gives distinct signals corresponding to bridging and terminal methyl groups at 35°C but these collapse to a single resonance at >100°C. The compounds (1) (M = Y, Dy, Ho, Er, Tm or Yb) were earlier reported to react with pyridine (py) to give $\text{Me}_3\text{Al.py}$ and the methyl-bridged compounds (2).

Experiments in NMR tubes show that the yttrium compound (2) reacts with hexamethyldialuminium to regenerate the di- μ -alkyl-bridged compound (1) (M = Y). With $[\text{Al}_2\text{Me}_2\text{Cl}_4]$ the product is the di- μ -chloro compound (3). The mixed bridged compound (4) could not be isolated; it appears to disproportionate to $[(\eta\text{-C}_5\text{H}_5)_2\text{M}(\mu\text{-Cl})_2]$ and $[\text{Al}_2\text{Me}_6]$. The scandium compound (1) reacts with pyridine to give $[(\eta\text{-C}_5\text{H}_5)_2\text{ScMe.py}] + \frac{1}{2}\text{Al}_2\text{Me}_6$. Thus it appears that the Lewis acidity towards pyridine in these compounds increases in the order Y < Al < Sc [15].



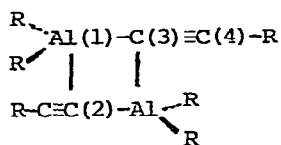
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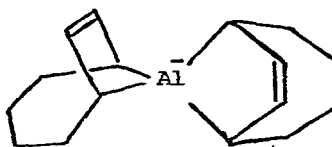
(4)

The complexes (1) and (2) are active homogeneous polymerisation catalysts for ethylene [16], but they are deactivated by hydrogen abstraction from the cyclopentadienyl ring. Catalytic activity persists longer in the aluminium compounds (1) than in the homometallic compounds (2).

After the discovery in 1974 that di(μ -phenylethynyl)bis(diphenylaluminium) had the unsymmetrical structure (5) (R = Ph) in the solid it was important to establish whether unsymmetrical bridging was characteristic of ethynyl groups or whether it merely reflected crystal packing forces.



(5)

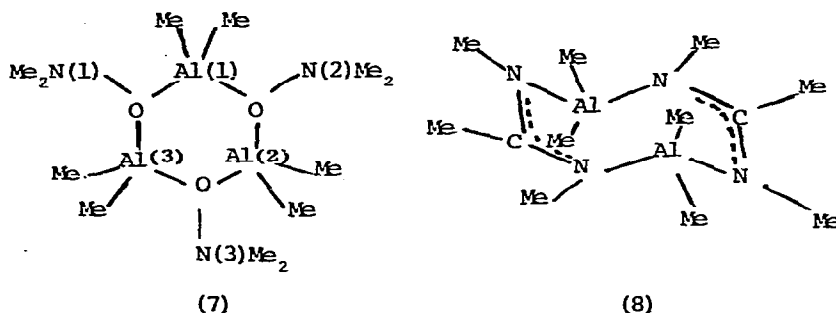


(6)

The analogous methyl derivative $[(Me_2AlC\equiv CMe)_2]$ has now been examined in the gas phase by electron diffraction [17] and the structure (5) (R = Me) has been confirmed. The main molecular parameters are Al-C(Me) 195.6(5), Al(1)-C(3) 205.0(15), Al(1)-C(2) 215(3), C(3)-C(4) 122.9(4) pm. The Al-Al distance [303(3) pm] is significantly longer than that in $[Me_6Al_2]$ or $[Me_4Ph_2Al_2]$. It appears that two monomer $Me_2AlC\equiv CMe$ units are linked by donation of π -electrons from the triple bond to empty orbitals on aluminium; in accord with this, the C=C bond is longer than that in $MeC\equiv CMe$. In the corresponding indium derivative $Me_2InC\equiv CMe$ the monomer units are linked to a polymeric structure [18]. Attempts to determine the structure of the aluminium compound (5) (R = Me) from vibrational spectra were inconclusive, but detailed assignments of IR and Raman data have been made both for the uncomplexed compound and its etherate. All these compounds $Me_2MC\equiv CMe$ (M = Al, Ga or In) may be made from propynylsodium and the halides Me_2MX (X = Cl or Br) [18].

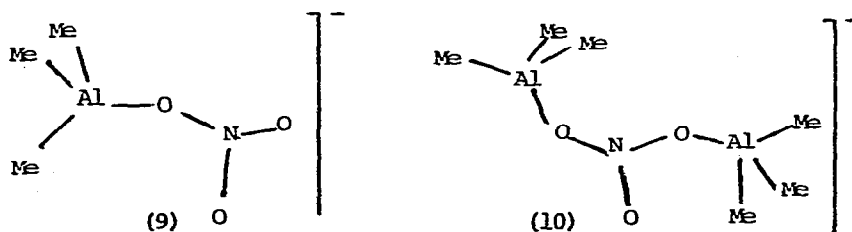
Structural data have also been obtained on a series of compounds having aluminium-containing heterocycles. The reaction between hexamethyldialuminium, potassium and cyclooctadiene in tetrahydrofuran (THF) at 0°C yields a compound $K^+[(C_8H_{12})_2Al]^-$ in which the anion has structure (6). The C-Al-C angles (88°) within the chelate rings are considerably reduced from the tetrahedral value. A similar compound is obtained from butadiene with sodium in THF. In general, the products of such reactions depend markedly on the solvents used. Another organo-

aluminium ring compound $[(\text{Me}_2\text{AlONMe}_2)_3]$ (7) is obtained from hexamethyldialuminium and N-dimethylhydroxylamine.



This has been shown [19] by X-ray diffraction to be trimeric with six-membered $(\text{Al}-\text{O})_3$ rings in the skew boat conformation. The mean Al-C (196.1 pm) and N-C (145.9 pm) bond distances and C-Al-C angles ($119-122^\circ$) are similar to those in related molecules, but the Al-O (186.7 pm) and N-O (147.7 pm) distances are long. The Al-N bond distances [Al(1)-N(2) 231.5 and Al(2)-N(3) 233.1 pm] suggest that two out of the three aluminium atoms have coordination numbers increased from four to five, thus locking the conformation of the ring [20]. The reaction between hexamethyldialuminium and NN'-dimethylacetamide gives the dimeric compound (8) which has an eight-membered puckered centrosymmetric ring. The main bond lengths are Al-N 192.5(1) Al-C 197.4(1) C-N 133.0(2) pm and the angles at all the atoms are roughly tetrahedral [21]. The gallium derivative is isostructural. See also ref. [135].

Structures of two further adducts between trimethylaluminium and alkali metal salts have been described. In $\text{Rb}[\text{AlMe}_3\text{N}_3]$ the coordination round aluminium is approximately tetrahedral and the Al-N bond distance is 194.4(8) pm [22]. The coordination round aluminium is similar in $\text{K}[\text{AlMe}_3\text{NO}_3]$, C_6H_6 , made by treatment of the liquid clathrate $\text{K}[\text{Al}_2\text{Me}_6\text{NO}_3]$, $7\text{C}_6\text{H}_6$ with dibenzo-18-crown-6.

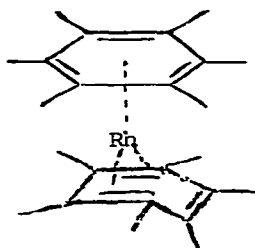


In the anion (9) the nitrate is bound to aluminium by only one oxygen with Al-O 193.0(6) pm [23,24]. Other complexes $M[Al_2Me_6NO_3]_n C_6H_6$ ($M = Rb$, $n = 9.4$; $M = Cs$, $n = 12.0$; $M = NMe_4$, $n = 7.8$; $M = NEt_4$, $n = 9.8$) have also been obtained. The benzene may be removed from the alkali metal compounds to give the complexes $M[Al_2Me_6NO_3]$, and the potassium compound has been shown to contain the anion (10) which has two different configurations in the solid. The mean Al-C bond length is 198 pm and the mean Al-O distance is 199 pm.

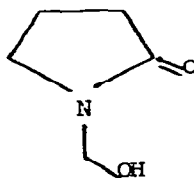
After reports on the adducts $Me_3Al.NMe_3$ and $Me_3Al.O(Me)_2$ described in previous surveys the structure of the complex $Me_3Al.PMe_3$ has now been found by gas phase electron diffraction. The main molecular dimensions are Al-C 197.3(3), Al-P 253(4), P-C 182.2(3) pm, P-Al-C 100.0(1.3) and Al-P-C 115.0(0.7)°. The Al-C distance is longer than that in monomeric trimethylaluminium and the P-C distance is shorter than that in free trimethylphosphine. As expected, the Al-P bond length is longer than that in aluminium phosphide [25]. Vibrational spectra of the adducts $(CH_3)_3Al.NH_3$, $(CD_3)_3AlNH_3$, $(CH_3)_3Al.ND_3$ and $(CD_3)_3Al.ND_3$ have been described [26]. Normal coordinate calculations give a value of 1.544 mdyn/Å for the force constant of the Al-N bond.

The determination of the rates of exchange between bridge and terminal positions in organoaluminium compounds from ^{13}C NMR spectra is complicated by scalar coupling between the ^{27}Al and ^{13}C nuclei, modulated by rapid quadrupole relaxation of the ^{27}Al nucleus. The line shapes obtained from spectra of samples at various temperatures have been analysed [27] in conjunction with earlier work [28] to separate the effects of chemical exchange and scalar coupling. The exchange rates in hexamethyldialuminium found in this way agree with those from 1H spectra. The temperature range over which the activation energy is derived is thus considerably extended.

Another process studied by variable-temperature NMR is the methyl-site interchange in bis(hexamethylbenzene)ruthenium(0) (11) which both in the solid and in solution has η^6 - and η^4 -rings.



(11)



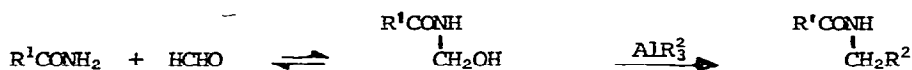
(12)

This is catalysed by trimethylaluminium, and site exchange in the η^4 -ligand is observed at lower temperatures than complete interchange between η^4 - and η^6 - ligands.

No complex formation between (11) and AlMe_3 or Al_2Me_6 is detected by NMR. These effects are not yet explained, but they seem to be important in understanding the function of (11) as a hydrogenation catalyst. Indeed, the presence of trimethylaluminium enhances the rate of arene hydrogenation by a factor of 4-5 [29].

3 PREPARATION AND PROPERTIES OF TRIALKYLALUMINIUMS

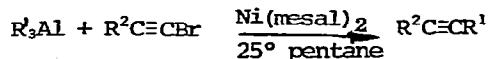
The reaction between aluminium powder and bis(trimethylgermyl)mercury in THF - pentane yields the THF adduct of tris(trimethylgermyl)aluminium. This is reasonably stable thermally; it melts without decomposition at 81°C but ignites spontaneously in air and is hydrolysed by water [30]. In attempts to make the corresponding tin compound, only decomposition products were obtained. Although tris(trimethylsilylmethyl)aluminium $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ may be obtained from the reaction between $(\text{Me}_3\text{SiCH}_2)_2\text{Hg}$ and aluminium foil, di[bis(trimethylsilyl)methyl]mercury does not react with aluminium under comparable conditions [31]. An improved synthesis of trivinylaluminium, from divinylmercury and aluminium powder, has been reported [32]. By working at -25°C in dichloromethane yields of $>95\%$ may be obtained. Trivinylaluminium decomposes slowly above -10°C . Its NMR spectrum shows only one ABC pattern above -60°C ; if it is dimeric in solution, there must be fast exchange of vinyl groups between bridge and terminal positions. Trialkylaluminiums have been used mainly as alkylating agents. For example, methylols, easily made from amides and formaldehyde, may be converted into N-alkyl amides in good yield [33] (Equation 2). Best results are obtained with four equivalents of AlR_3 in refluxing benzene.



$\text{R}^1 = \text{C}_5\text{H}_{11}, \text{Ph}, 4\text{-O}_2\text{NC}_6\text{H}_4, \text{C}_5\text{H}_4\text{N}(3\text{-pyridyl}), \text{PhCH}_2, \text{Et}_2\text{N}, \text{EtO}$; $\text{R}^2 = \text{Me}, \text{Et}$ or Bu^i .

It is interesting that under these conditions there appears to be no attack by the trialkylaluminium on either the $>\text{NH}$ or the $>\text{CO}$ group. Poor yields of the N-alkyl derivatives are obtained from the pyrrolidone methylol (12).

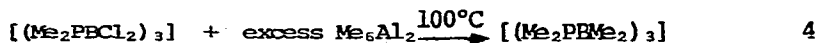
Alkynyl bromides have been converted to alkynes [34] (Equation 3).



$\text{R}^1 = \text{Et}$ or Bu^i ; $\text{R}^2 = \text{Bu}^n, \text{Bu}^s, \text{Bu}^t, \text{CHMe}$ or Ph ; mesal = N-methylsalicylaldiminato

Good yields based on $R^2C=CB_r$ may be obtained conveniently and under mild conditions but only one group of the trialkylaluminium is used: the others appear as alkane R_2 . A catalytic process involving alkylnickel intermediates $L_nNiR(C=CR)$ has been proposed. The vinylation of alkyl halides at $-50^\circ C$ in CH_2Cl_2 has been explored [32]. *t*-Butyl chloride gives $Bu^tHC=CH_2$, but $H_2C=CHCHMeCl$ and $H_2C=CHMe_2Cl$ give a variety of products. Allyl and benzyl chlorides do not react under these conditions.

Alkylation of B-hexahalocyclotriboraphosphanes has also been investigated [35]. In general, Me_6Al_2 is more effective than Me_3B , Me_2Zn or Me_4Sn . For example, $[(Me_2PBrMe_2)_3]$ may be made in 95% yield (Equation 4) when $X = Cl$ or Br ; when $X = F$, Me_3B is a more effective alkylating agent than is Me_6Al_2 .



Reactions using Et_6Al_2 or Ph_6Al_2 result in partial substitution or degradation by reduction. From partially halogenated cyclotriboraphosphanes, mixtures of B-alkylated derivatives may be obtained but reactions are non-specific; e.g., $[2,4-Br_2H_4B_3P_3Me_6]$ gives as products $[H_6B_3P_3Me_6]$ 0.9%, $[MeH_5B_3P_3Me_6]$ 7.2%, $[Me_2H_4B_3P_3Me_6]$ 80.2%, $[Me_3H_3B_3P_3Me_6]$ 10.0%, $[Me_4H_2B_3P_3Me_6]$ 1.7%. Hexamethyldialuminium does not react with halogen-free $[H_6B_3P_3Me_6]$ during 8h at $100^\circ C$.

A method has been described [36] for quantitative determination of Al-C or Al-H bonds in hydrocarbon solutions by addition of an excess of a low molecular weight alcohol such as methanol and back titration with a reagent such as sodium anthracene.

4. ALKYLALUMINIUM HALIDES

As in previous years, several patents describe improvements in production of alkylaluminium halides. For example [37], methylaluminium sesquichloride may be made by the reaction between aluminium and gaseous chloromethane without a liquid phase.

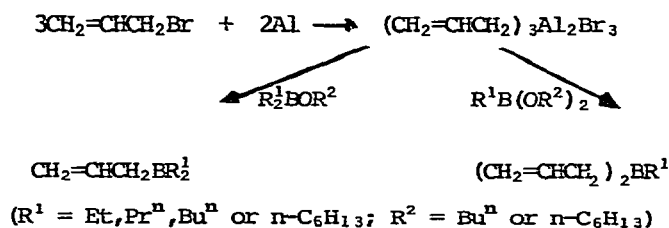
Trimethylaluminium and halides RA_2X_2 ($X = Cl, Br$ or I) may be made [38] in high yield by reaction 5. With $Me_3Al_2Cl_3$ and Et_3Al in 1:1 mole ratio, Me_2AlCl and Et_2AlCl may be separated [34]. Dialkylaluminium chlorides



or alkylaluminium dichlorides (alkyl = C_{1-6}) may be recovered from reaction mixtures containing trialkylaluminium by treatment with aluminium (III) chloride [40]. The halide $\{(Me_3Si)_2CH\}_2AlCl$ has been made from

the reaction between bis(trimethylsilyl)methyl-lithium and aluminium(III) chloride in ether; $\{(\text{Me}_3\text{Si})_2\text{CH}\}_3\text{Al}$ is not formed, even with an excess of the lithium compound under forcing conditions in toluene under reflux for 14h. It is interesting that diethylether may be easily pumped away from $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{AlCl}$ whereas it is held tenaciously by diethylaluminium chloride with smaller alkyl groups [31]. Bis(trimethylsilylmethyl)-aluminium chloride is easily made from $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ and AlCl_3 .

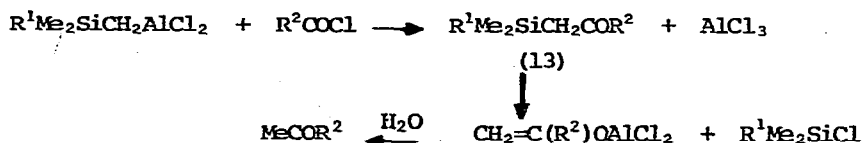
Alkylaluminium halides, like trialkylaluminiums, have been used mainly for alkylations. In one interesting application, the formation of tetramethyltin or dimethylmercury at sacrificial anodes in a melt of $\text{Na}[\text{MeAlCl}_2]$ has been studied, but several problems must be overcome before the process becomes efficient. $\text{Na}[\text{MeAlCl}_2]$ has a high specific conductivity ($19\Omega^{-1}\text{m}^{-1}$) at 180°C [41]. It is sometimes possible to use organoaluminium halides directly in one-pot syntheses. For example, good yields of allyl(alkyl)boranes may be obtained by running allyl bromide and an ester of a dialkylborinic or alkylboronic acid simultaneously on to aluminium shavings in ether [42] [43] (Equation 6).



6

The crotonyl derivatives $\text{MeCH}=\text{CHCH}_2\text{BR}_2$ ($\text{R} = \text{Et}, \text{Pr}^n$ or Bu^n) may be made similarly. Allylic groups are removed from boron by reaction with alcohols.

Attempts to use alkylaluminium chlorides $\text{R}^1\text{Me}_2\text{SiCH}_2\text{AlCl}_2$ ($\text{R}^1 = \text{Me}, \text{Bu}$ or C_8H_{17}) to make ketones $\text{R}^1\text{Me}_2\text{SiCH}_2\text{COR}^2$ (13) ($\text{R}^1 = \text{Pr}, \text{C}_5\text{H}_{11}, \text{C}_7\text{H}_{15}$ or $\text{C}_{11}\text{H}_{23}$) from acid chlorides R^2COCl have not been successful [44]. The products, after hydrolysis, are ketones MeCOR^2 . It is possible that the ketones (13) are unstable in the presence of aluminium(III) chloride (Eq. 7).



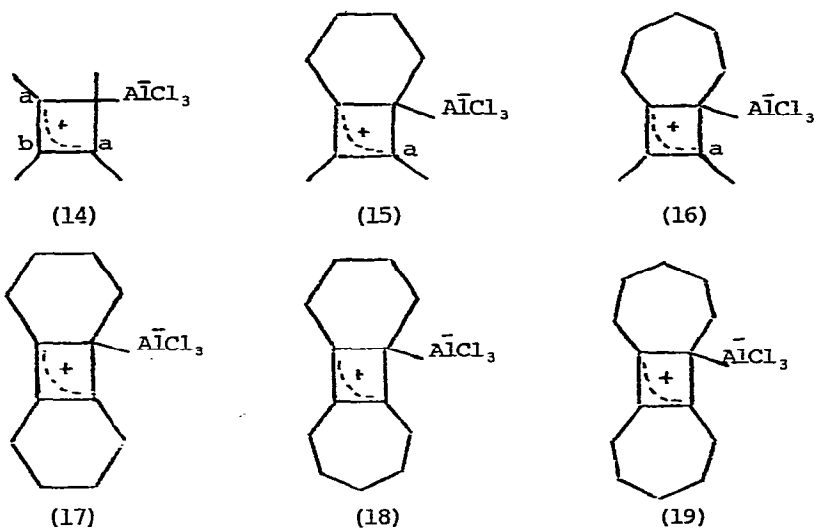
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Alkyl groups are easily cleaved from alkylaluminium halides by chlorine with formation of chloroalkanes [45]. This reaction may be used to obtain a mixture of $\text{C}_4\text{-C}_{28}$ chloroalkanes with the same distribution of

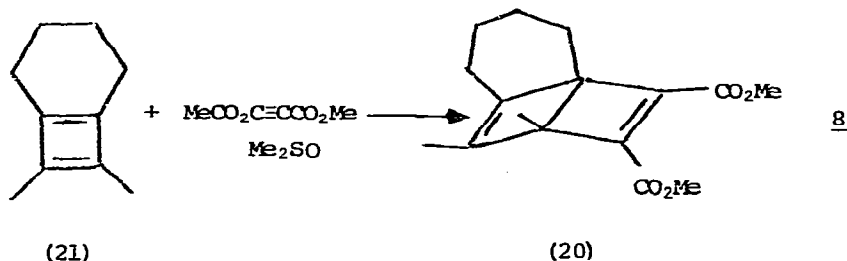
alkyl groups as in the dialkylaluminium chlorides made by addition of ethylene to diethylaluminium chloride. [68]. Some bromoalkanes are formed in chlorination of dialkylaluminium bromides.

Alkylaluminium halides may also serve as reducing agents. Thus copper(II) chloride as an impurity in copper(I) chloride may be reduced with the halides Et_2AlCl or EtAlCl_2 [46].

Complexes between aluminium(III) chloride and cyclobutadienes have been described in previous surveys. The complexes (14)-(19) have now



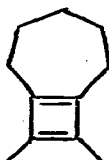
been made by adding the appropriate diyne [e.g. 1,7-cyclododecadiyne for (17)] to a suspension of aluminium(III) chloride in $\text{CH}_2\text{Cl}_2/\text{CHCl}_2\text{CHCl}_2$, and the migration of the AlCl_3 fragment round the cyclobutadiene ring has been studied by ^1H and ^{13}C NMR spectroscopy [47]. It is shown, for example, that the AlCl_3 may move to position a much more readily in (14) than in (15). The Diels-Alder reaction of compound (14) with $\text{MeCO}_2\text{C}=\text{CCO}_2\text{Me}$ / Me_2SO gives only compound (20) (Equation 8) showing that the predominant valence structure of the intermediate cyclobutadiene is (21) in which the double bond is in the six-membered ring.



The corresponding reaction with (16) gives products from both (22) and (23). The tetramethyl compound (14) also reacts with dienophiles $\text{MeC}=\text{OMe}$ or $\text{MeCO}_2\text{C}=\text{OMe}$ to form Dewar benzenes. Both (14) and (15) react with ethyl cyanofomate to give pyridine derivatives; with sulphur dioxide (14) gives, after basic hydrolysis, the sulphonic acid (24).

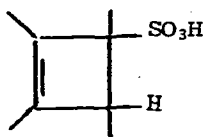


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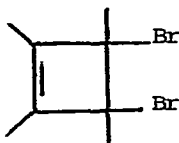


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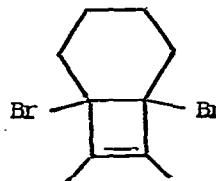
In the presence of an excess of sulphur dioxide the bromo-compounds analogous to (14) and (15) yield the dibromo derivatives (25) and (26), which may be useful precursors for cyclobutadiene- $\text{Fe}(\text{CO})_3$ complexes [48].



(24)



(25)



(26)

A theoretical paper [49] describes the complex equilibria involving alkyl-aluminium and -gallium halides in the $\text{Me}_3\text{Al}/\text{GaCl}_3$ system. Measured heats of mixing are given in Table 2.

Table 2 Heats of mixing (kJ mol^{-1}) at 1:1 mole ratio at 50°C [50].

	GaCl_3	GaMeCl_2	GaMe_2Cl	GaMe_3
Me_2AlCl	-83.7	-55.6	-26.8	-5.4
Me_3Al	-143.9	-77.0	-31.0	-1.8

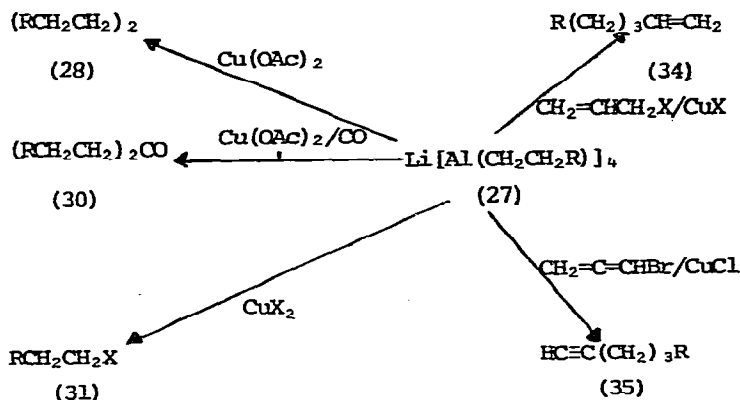
5. ALKYLALUMINIUM HYDRIDES

A patent [51] describes the preparation of diethylaluminium hydride by pyrolysis of diethyl(isobutyl)aluminium and the formation of dimethylaluminium hydride from diisobutylaluminium hydride and trimethylaluminium. The compounds HMgAlH_3R ($\text{R} = \text{Et}, \text{Bu}^t$ or Ph) may be made from RMgH and aluminium hydride in THF; when $\text{R} = \text{Me}$, however, the product disproportionates into MgH_2 and $\text{Mg}(\text{AlH}_3\text{Me})_2$ [52]. The Ge-Ge or Si-Si bonds of aryl-digermanes or -disilanes may be cleaved by reduction with lithium aluminium hydride with formation of compounds with Al-Si or Al-Ge bonds (See also ref. [30]). One of these, $\text{Li}[\text{AlH}_3(\text{GePh}_3)]$, THF, has been isolated. [53].

Diphenylaluminium borohydride may be made from triphenylaluminium and aluminium tris(tetrahydroborate) [54], but the pure monophenyl derivative $\text{PhAl}(\text{BH}_4)_2$ has not been isolated. The solid dimeric compound $\text{Ph}_2\text{Al}-\text{BH}_4$ slowly evolves hydrogen on standing in vacuum. It forms solid adducts with diethyl ether or trimethylamine but $\text{Ph}_2\text{AlBH}_4 \cdot \text{NMe}_3$ decomposes within a few hours at 25°C to give Ph_2AlH and $\text{H}_3\text{B} \cdot \text{NMe}_3$. The reaction between diethylaluminium hydride and aluminium tris(tetrahydroborate) gives the volatile compounds $\text{Al}(\text{BH}_4)_{3-x}\text{Et}_x$ ($x = 1$ or 2) and a residue which appears to be $\text{Al}(\text{BH}_4)_{3-x}\text{H}_x$ ($x = 1$ or 2). The compound $\text{Al}(\text{BH}_4)_2\text{H}$ reacts slowly with ethylene in diethyl ether to give the etherate $\text{Al}(\text{BH}_4)_2\text{Et} \cdot \text{OEt}_2$ [55].

6. REACTIONS WITH CARBON-CARBON DOUBLE BONDS

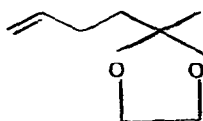
There have been several papers and a patent [56] on applications of hydroalumination in organic synthesis.



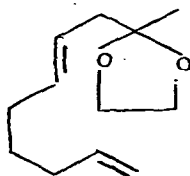
The tetraalkylaluminates (27) are readily available by the TiCl_4 -catalysed reaction of lithium aluminium hydride with alkenes, as described in last year's survey. They may be used *in situ* for preparation of alkanes or dienes (28) ($\text{R} = \text{Bu}, \text{CH}_2\text{CH}=\text{CHCH}_3, \text{CH}_2\text{CH}_2\text{OMe}=\text{CH}_2$, or 4-cyclohexenyl) by reaction with copper(II) acetate. The compound (29)

may be converted to 2,11-dodecandione. In a carbon monoxide atmosphere the products are ketones (30) ($R = \text{Pr}^n, \text{Bu}^n$ or $\text{CH}_2\text{CH}=\text{CMe}$) suggesting that alkyl-copper intermediates may be involved. Cross-coupled products i.e. with two different groups R^1 and R^2 may also be obtained; the reaction may be useful for making unsaturated ketones since alkenylaluminium compounds (27) may be easily obtained [57].

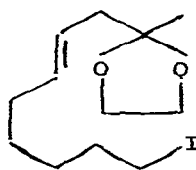
With copper(II) chlorides or bromides the compounds (27) give good yields of the halides (31) ($R = \text{Bu}^n, \text{CH}_2\text{CH}=\text{CMe}, \text{CH}_2\text{CH}_2\text{CMe}=\text{CH}_2, 4\text{-cyclohexenyl}$) [58]. An example of the application of this reaction in the



(29)



(32)



(33)

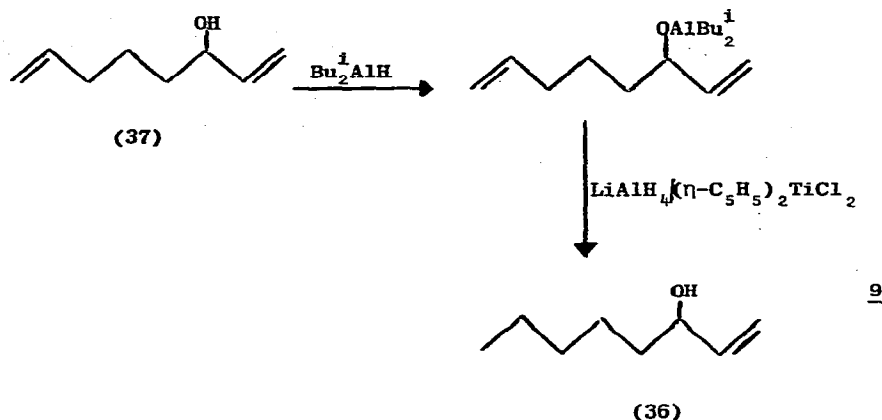
syntheses of a natural product is the conversion of the diene (32) to the iodide (33). [59]. With a catalytic amount of copper(I) halide the compounds (27) couple with 3-chloroprop-1-ene to give the alkenes (34): (Yields in parentheses) $R = \text{H}$ (70%), Me (65%), Bu (80%), $\text{MeCH}=\text{CHCH}_2$ (68%), $\text{CH}_2=\text{CMeCH}_2\text{CH}_2$ (63%), 4-cyclohexenyl (77%) [60]. Other examples of the reaction of compounds (27) $R = \text{Bu}^n$ are given in Table 3. With bromopropadiene $\text{CH}_2=\text{C}=\text{CHBr}$ the compounds (27) react to give terminal alkynes $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{R}$ (35): (Yields in parentheses) $R = \text{H}$ (43%), Pr (49%), Bu (50%), $\text{MeCH}=\text{CHCH}_2$ (52%), $\text{CH}_2=\text{CMeCH}_2\text{CH}_2$ (55%), 4-cyclohexenyl (50%), or $\text{MeOCOCH}_2\text{CH}_2$. For the last case, there is reaction also at the carbonyl function so the product is $\text{MeCH}(\text{OH})(\text{CH}_2)_5\text{C}\equiv\text{CH}$ (52%) [61].

Similar results have been reported [62] by another Japanese group using trihydroaluminates LiAlH_3R made from alkenes and lithium aluminium hydride in the presence of catalytic amounts of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$. From alkenes $\text{R}^1\text{HC}=\text{CH}_2$ and $\text{R}^2\text{HC}=\text{CH}_2$, alkanes $\text{R}^1(\text{CH}_2)_4\text{R}^1$, $\text{R}^2(\text{CH}_2)_4\text{R}^2$ and $\text{R}^1(\text{CH}_2)_4\text{R}^2$ are obtained in statistical proportions; products $\text{RHC}=\text{CH}_2$ ($\text{R} = \text{C}_6\text{H}_{13}$ or C_9H_{19}) or $\text{C}_8\text{H}_{17}\text{CHPhCH}=\text{CH}_2$, from alkyl-allyl coupling have also been described.

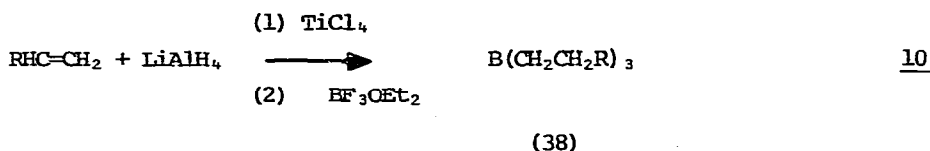
Table 3 Reactions of $\text{LiAl}(\text{C}_6\text{H}_{13})_4$ with allylic chlorides [60]

Chloride	Product	Yield (%)
	(65%)	47
	(35%)	
	(>99%)	66
		57
		68
		66

In the synthesis of the naturally occurring alcohol oct-1-en-3-ol (36), using $[(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2]$ -catalysed reduction of (37) by lithium aluminium hydride, diisobutylaluminium has been used as a protecting group (Equation 9). Under these circumstances the double bond at the 1-position is not attacked [63]. It is often not possible to prepare tris(alkenyl)-boranes (38) by direct interaction of diborane and unconjugated dienes



since both double bonds are usually reactive. They may, however, be made from alkenylaluminates (27) (Equation 10).



Good yields have been obtained for $\text{R} = \text{CH}_2\text{CH}=\text{CHMe}, \text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2, 4\text{-cyclohexenyl}, \text{CH}_2\text{CH}=\text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2,$ or $(\text{CH}_2)_4\text{CH}=\text{CH}_2$ [64].

The photochemically initiated hydroalumination of octenes by diisobutylaluminium hydride in the presence of triphenylphosphine has been studied [65]. The products after oxidation and hydrolysis show that there is no isomerisation in the process. The reaction rate decreases as the double bond is moved towards the centre of the molecule.

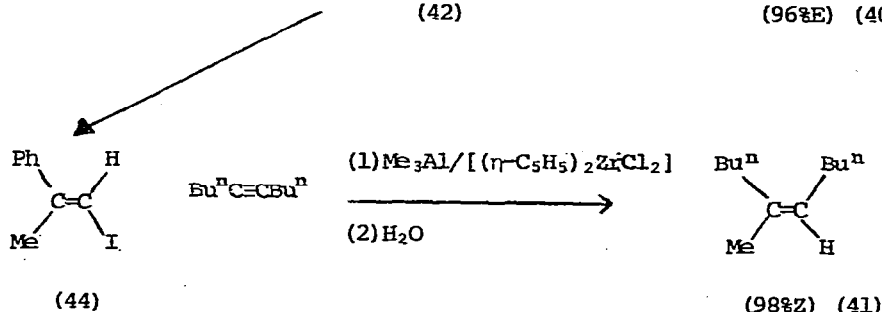
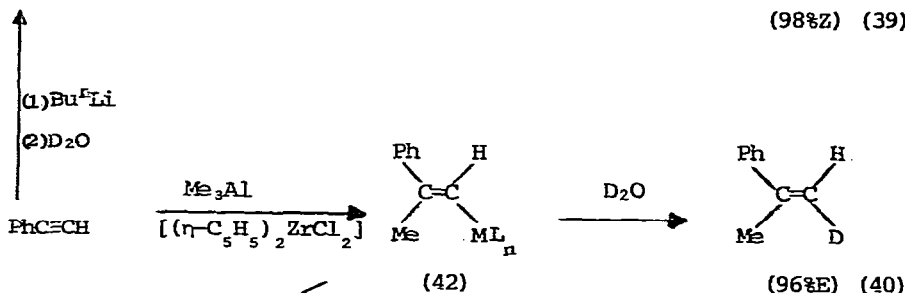
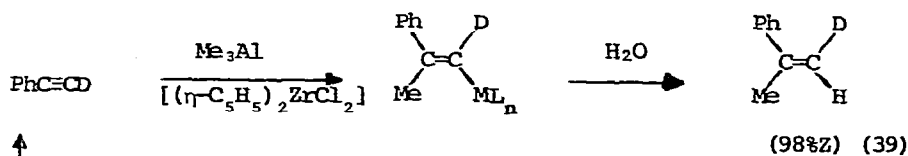
The alkylation of alkynols in the presence of titanium catalysts was described last year. Two further papers [66,67] discuss alkylation of but-3-en-1-ol. This is converted to $\text{R}_2\text{AlOCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ or $\text{RCIAlOCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ($\text{R} = \text{Me}$ or Et) which is then treated with a stoichiometric amount of titanium(IV) chloride. The main products with diethylaluminium chloride are hexan-1-ol, 3-methylpentan-1-ol, trans-hex-3-en-1-ol and butan-1-ol. Presumably, the C_4 products and trans-hex-3-en-1-ol arise from β -elimination reactions. The yields are maximum when the ROH/Al/Ti ratio is 1/2/1. Triethylaluminium gives no C_6 (alkylation) products, perhaps because it reduces the Ti(IV) to Ti(III) . Reactions with Me_2AlCl and Me_3Al are slower than those with ethylaluminium compounds; the effectiveness of Me_3Al in methylation may reflect its poorer capability as a reducing agent.

Diethylaluminium chloride is resistant towards addition of ethylene

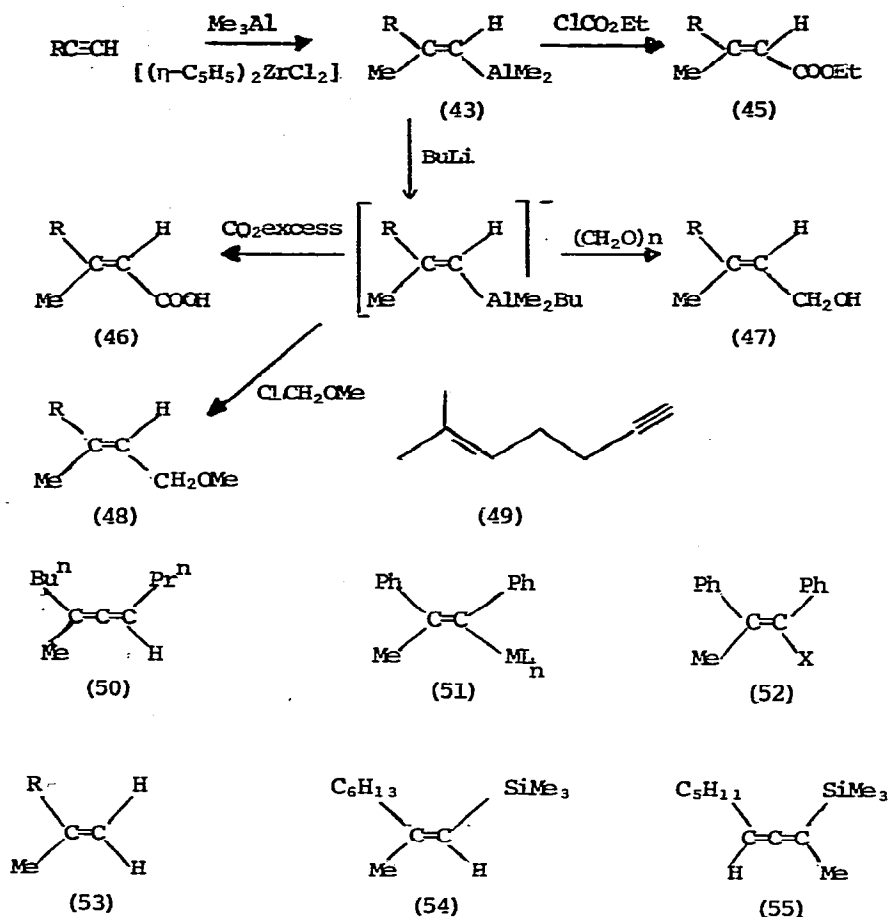
to give compounds with C₄-C₂₀ alkyl groups. In the presence of titanium-(IV) chloride, however, the reaction is effected smoothly at 1 atm. Aromatic solvents are much better than aliphatic, and xylene appears to be the best of those studied. Diethylaluminium bromide and alkoxides are less effective at promoting the multiple addition and zirconium(IV) chloride is less effective than is TiCl₄, [68]. Compare ref. [84].

7. REACTIONS WITH CARBON-CARBON TRIPLE BONDS: ALKENYLALUMINIUM COMPOUNDS

Alkynes R¹C≡CR² may be converted in one-pot reactions to stereo- and regio-defined alkenes e.g. (39)-(41) [69]. Carbometallation involves



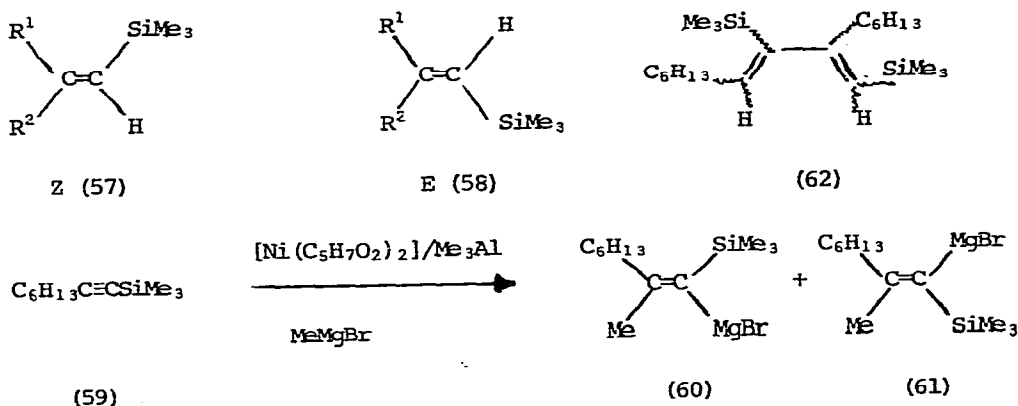
cis-addition and the intermediates (42) or (43) may be cleanly transformed in further steps e.g. to iodides (44), esters (45), acids (46), alcohols (47) or ethers (48) [70]. Reactions leading to (44)-(48) have been explored for R = C₅H₁₁ and their potential in organic synthesis is illustrated by the preparation of geraniol (47, R = Me₂C=CH(CH₂)₂) or ethyl geranate (45 R = Me₂C=CH(CH₂)₂) from the alkyne (49). The nature of the alkylating species in formation of the compounds (42)-(43) is not established but NMR measurements show formation of organozirconium species with fast exchange of methyl groups with trimethylaluminium. It is interesting that there appear to be no complications from abstraction of the terminal hydrogen atoms of the alkynes.



The use of $[(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2]$ in place of the zirconium compound results in more side reactions. For example, the main product from dec-5-yne is (50) and terminal alkynes give only low yields of mono-carbonmetallated products. However, titanium is sometimes superior to zirconium [71]. Diphenylacetylene may be stereoselectively converted by $\text{Me}_3\text{Al} / [(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2]$ in CH_2Cl_2 at 20°C into the alkenyl derivative (51) which may be transformed to the Z α -methylstilbene (52, X = H) or 1-iodo-1,2-diphenylpropene (52, X = I). Organometallic compounds $\text{R}^n\text{C}\equiv\text{CML}_n$ ($\text{ML}_n = \text{ZnCl}$, BR_2^2 or ALR_2^2) with $\text{Me}_3\text{Al} / [(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2]$ give good yields of (53) after hydrolysis but $\text{C}_6\text{H}_{13}\text{C}\equiv\text{CSiMe}_3$ gives a 70:30 mixture of (54) and (55). Carbonmetallation of silanes $\text{R}^1\text{C}\equiv\text{CSiMe}_3$ (56) with $[(\eta\text{-C}_2\text{H}_5)_2\text{TiCl}_2]$ and $\text{R}_n^2\text{AlCl}_{3-n}$ ($\text{R}^2 = \text{Me}$ or Et ; $n = 0-2$) has been studied by another research group [72], and the proportions of the Z and E products (57) and (58) have been determined. Alkyltitanium rather than alkylaluminium intermediates are responsible for the carbonmetallation reaction since the compounds $\text{R}_n^2\text{AlCl}_{3-n}$ without titanium species give little reaction. When the groups R^1

in (56) are saturated, e.g. $n\text{-C}_6\text{H}_{13}$ or $\text{cyclo-C}_6\text{H}_{11}$, the products (57,58) are predominantly E, i.e., the carbometallation is trans. When the groups R^1 in (56) are unsaturated $\alpha\beta$ to the $\text{C}\equiv\text{C}$ bond ($\text{R}^1 = \text{Ph}$ or 1-cyclohexenyl) the carbometallation is regiospecific but non-stereospecific, i.e., equal amounts of Z and E products (57,58) are obtained.

As described in previous surveys, carbometallation may be catalysed by compounds of the late transition metals. The mixture $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2] / \text{Me}_3\text{Al}[\text{C}_5\text{H}_7\text{O}_2 = \text{pentan-2,4-dionato}]$ catalyses the addition of methylmagnesium bromide to trimethylsilyloct-1-yne (59) to give (60) which slowly isomerises to a mixture of (60) and (61) (Equation 11). The Grignard reagents



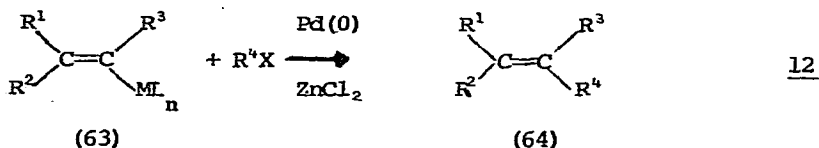
11

(60) and (61) may be converted into a wide range of derivatives. The reactive species in carbometallation is not established: a mixture of $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2]$ (1 mol) and Me_3Al (1.5 mol) does not react and methylmagnesium bromide seems to be necessary. A similar reaction between ethylmagnesium bromide and (59) catalysed by $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2] / \text{Bu}_2\text{AlH}$ gives, after quenching with water, a 50% yield of a 95:5 mixture of (57) and (58) ($\text{R}^1 = \text{C}_6\text{H}_{13}$, $\text{R}^2 = \text{H}$) and a 30% yield of (62).

The conversion of the alkenyl-metal derivatives (63) (R^1, R^2 or $\text{R}^3 = \text{H}$ or alkyl, $\text{ML}_n = \text{AlR}_2$ or $\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}$) to tetrasubstituted alkenes (64) by reactions with halides R^4X ($\text{R}^4 = \text{alkenyl, aryl or alkynyl}$; $\text{X} = \text{Br or I}$) in the presence of $\text{Pd}(\text{PPh}_3)_4$ and ZnCl_2 (Equation 12) neatly shows how catalysis by several different metal species may be applied [74] [75].

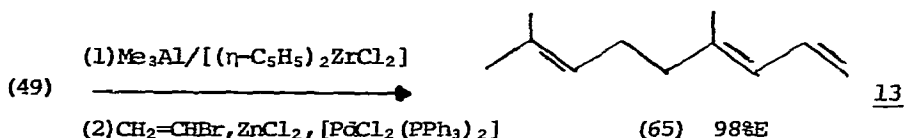
As a specific example, the stereoselective one-pot conversion of the alkyne (49) into the triene (65) is shown in Equation 13.

The products obtained from the reaction between triisobutylaluminium and alkynes $RC\equiv CH$ ($R = Bu^i, Et, CMe$) may be varied by changing the transition

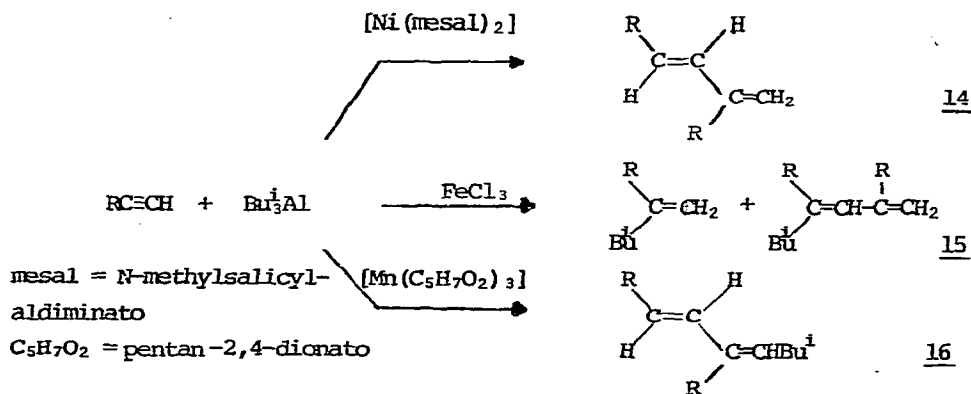


metal used as catalyst. The principal products are summarised in equations 14 to 16. Small amounts of 1,2,4- and 1,3,5-trialkylbenzenes are also found [76].

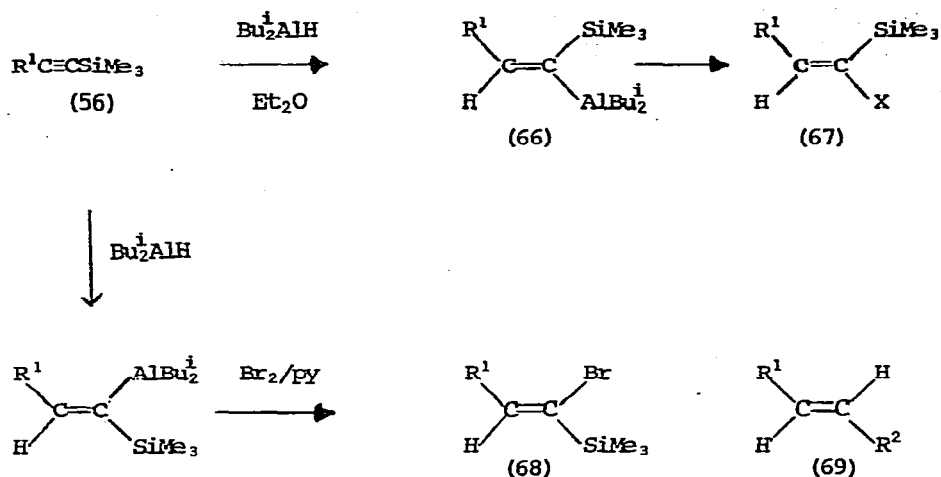
Stereoselective hydroalumination of alkynes has also been described [77]. Thus the compounds (66) made from silanes (56) ($R^1 = Bu^t$ or cyclo- C_6H_{11}) and diisobutylaluminium hydride in ether give E halides (67) by



treatment with N-chlorosuccinimide ($X = Cl$), bromine ($X = Br$) or iodine ($X = I$). The Z bromide (68) may be obtained either by photochemical isomerisation of the E compound (67) or from the hydroalumination of (56) by diisobutylaluminium hydride without solvent.

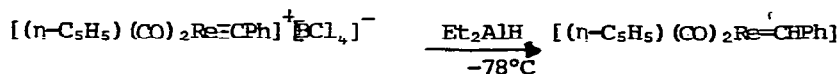


Coupling of alkenylaluminium compounds with aryl halides R^2X to give compounds (69) was described in the 1976 Survey. The analogous reaction with alkenylzirconium compounds (63) ($R^{2-3} = H, ML_n = Zr(\eta-C_5H_5)_2Cl$) is now reported [75,78]. The coupling reaction of (63) with aryl halides

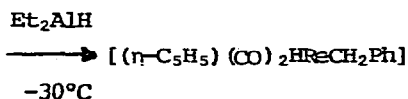


R^4X to give (64) is catalysed by $\text{Ni}(\text{PPh}_3)_4$ prepared in situ by reaction of $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2]$ with Bu_2^iAlH and Ph_3P . Similarly the compounds (63) react with alkenyl halides R^4X in the presence of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and Bu_2^iAlH to give the dienes (64) ($\text{R}^2 = \text{H}$, $\text{R}^4 = \text{alkenyl}$) [75].

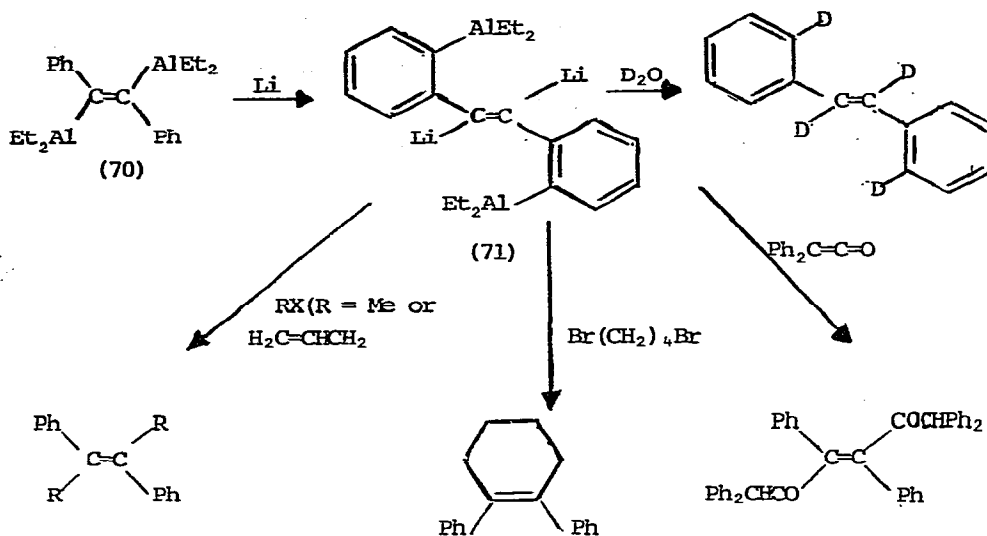
The first example of the stepwise reduction of a metal-carbon triple bond by diethylaluminium hydride has been reported [79] (Equation 17).



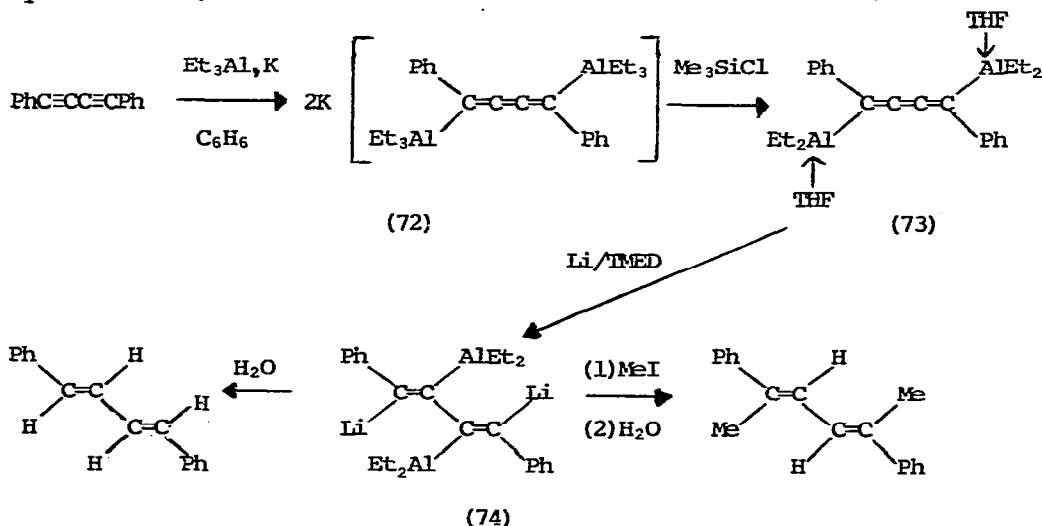
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The compound (70), made from diphenylacetylene, lithium and diethylaluminium chloride in donor solvents [Et_2O , THF or $\text{NNN}'\text{N}'$ -tetramethylethylenediamine (TMED)], was described last year. With lithium metal it gives a substance formulated on the basis of its reactions as (71) [80]. Diphenylbutadiyne reacts with triethylaluminium in benzene to yield a complex thought to be (72) [81]. With trimethylchlorosilane this gives a substance, formulated as (73), which reacts with lithium in TMED to give



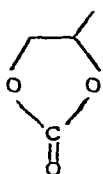
a butadiene (74). Four positions in this compound appear to be metallated. The hydrolysis of (74) and its reactions with iodomethane suggest that in the conversion from (73) to (74) the aluminium atoms have shifted from the 1,4- to the 2,3-positions [82]. Further evidence has been published [83] suggesting that the blue compound obtained in low yield from pentaphenylaluminacyclopentadiene, lithium and nickel(II) bromide is bis(tetraphenylcyclobutadiene)nickel.



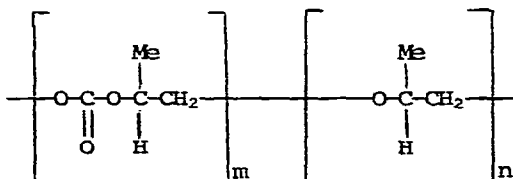
8. REACTIONS WITH CARBONYL COMPOUNDS

The carbonylation of long chain alkylaluminium compounds R_3Al and R_2AlCl by carbon dioxide has been investigated [84]. The reaction is catalysed by titanium (IV) chloride or butoxide (4-6 mole %), so that

good yields of carboxylic acids may be obtained at 1 atm. pressure. Trialkylamines reduce the yield of carbonylation products from R_2AlCl but apparently increase the yield from R_3Al . A variety of solvents has been studied; diglyme seems to be best. The reaction of tetraphenylporphin (TPPH₂) with triethylaluminium to give a compound (TPPAEt) was described last year. This reacts with methanol to give TPPAlOMe which absorbs carbon dioxide reversibly in the presence of 1-methylimidazole. This reaction, unlike that between TPPAEt and CO₂, is observed even in the dark. The absorbed carbon dioxide reacts with 1,2-epoxypropane to give propylene carbonate (75); in the absence of imidazole, the CO₂ and 1,2-epoxypropane are copolymerised to (76). The catalyst system from tetraphenylporphin and diethylaluminium chloride polymerises propylene oxide much more rapidly than does diethylaluminium chloride alone. Homopolymeric (OCHMeCH₂)_n without copolymer (76) is formed in the presence of carbon dioxide [86].

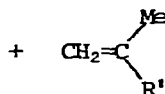
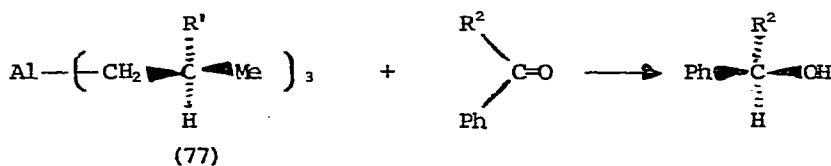
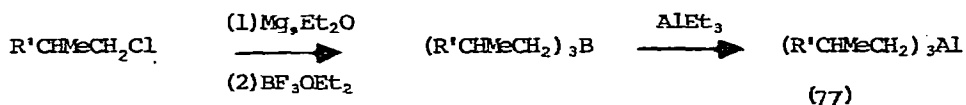


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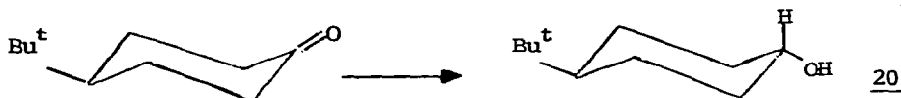
(76)

Several papers describe reactions of organoaluminium compounds with ketones. Optically active organoaluminium compounds (77) ($R^1 = Et, Pr^1$ or Bu^t) have been made by the route shown in equation 18 and used for asymmetric reduction of alkyl phenyl ketones as shown in equation 19.

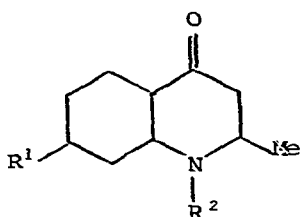
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The extent of asymmetric reduction of EtPhCO increases for $R^1: Et < Pr^1 < Bu^t$, but that of Bu^tPhCO decreases for the same sequence. Selectivity of reduction of Pr^1PhCO is maximum when $R^1 = Pr^1$. Subtle and complicated

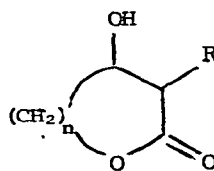
steric and electronic effects are apparent [87]. The stereoselectivity in reduction of 4-t-butyl-,3,3,5-trimethyl-, 2,2,6-trimethyl-cyclohexanones, camphor and norcamphor by trisobutylaluminium is increased by the addition of various amines. For example, from 4-t-butyl-cyclohexanone, yields of 91-98% of the trans-alcohol may be obtained (Equation 20).



Experiments with a variety of amines seem to indicate that the stereoselectivity is greatest when the ketone displaces amine from the trisobutylaluminium-amine complex. Amines which complex weakly (e.g., Ph₂NH) or too strongly (e.g., piperidine) or easily form aluminium amides (e.g. C₆H₁₁NH₂) are ineffective [88]. Reactions between triethylaluminium and quinolinones (78, R¹ = H or Me, R² = Me or Bu^t) having methyl substituents in the 2-position have been studied [89].

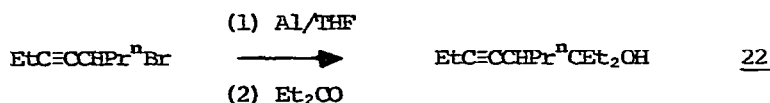
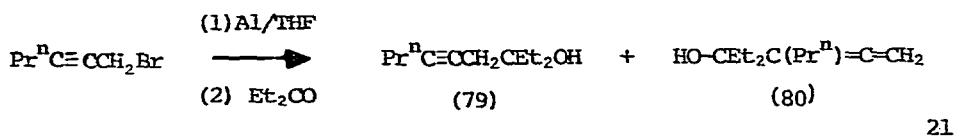


(78)



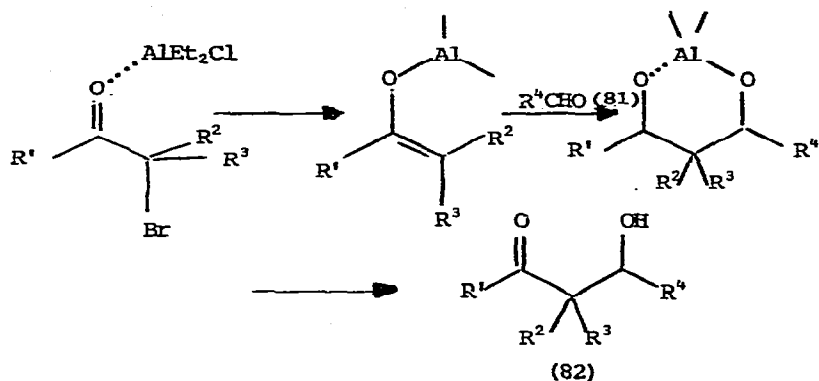
(83)

Alkynylaluminium compounds have been used in syntheses of branched alkynols [90]. The products (79) and (80) are obtained in the ratio 1:3 (Equations 21 and 22).



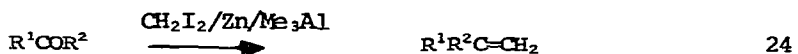
Another application of organoaluminium compounds has been to aldol synthesis, represented by the sequence of equation 23. By simultaneously adding the α -haloketone and carbonyl compound (31) to a mixture of zinc (1.5 equiv.), copper(I) bromide (0.05 equiv.) and diethylaluminium chloride

(1.1 equiv.) in THF at -20°C the β -hydroxycarbonyl compounds (82) may be

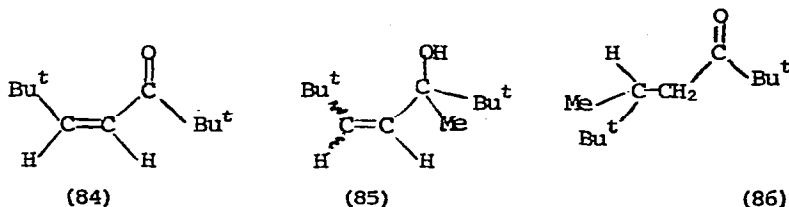


23

obtained in yields of over 90% after work-up [91]. The bromoketones used have included PhCOCH_2Br , 2-bromocyclohexanone, 2-bromocamphor, ethyl bromoacetate or $\text{BrCH}_2\text{CH}=\text{CHCO}_2\text{Me}$, and the carbonyl compounds PhCHO , Me_2CHCHO , $\text{PhCH}=\text{CHCHO}$, Me_2CO and cyclohexanone. The method is easily adapted to the synthesis of large ring lactones e.g. (83 $n = 9-11$) from the compounds $\text{BrCH}_2\text{CO}_2(\text{CH}_2)_n\text{CHO}$ ($R = \text{Me}$ or H). A similar combination of reagents is used in a new method [92] for conversion of carbonyl compounds R^1COR^2 ($R = \text{Ph}, \text{PhCH}=\text{CH}$, or n -alkyl; $R^2 = \text{H}$ or n -alkyl) into alkenes $\text{R}^1\text{R}^2\text{C}=\text{CH}_2$ (Equation 24). This serves as an alternative to the Wittig reaction.



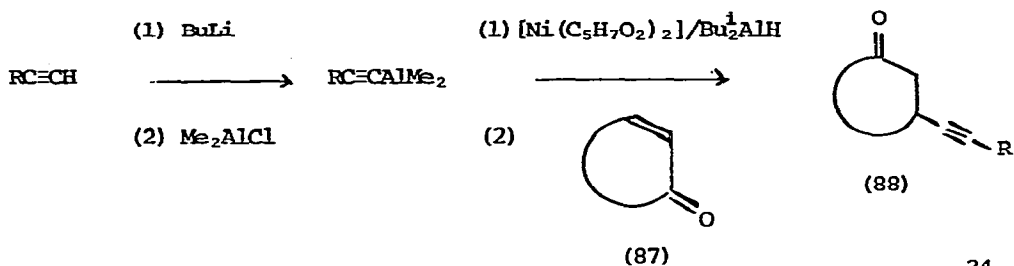
As part of an extensive programme to find out whether reactions between organometallic compounds and ketones involve polar or radical intermediates, the reaction between 2,2,6,6-tetramethylhept-4-en-3-one (84) and trimethylaluminium has been studied [93]. It is assumed that



Polar reactions of the cis-isomer give only cis-products. However, any reaction involving transfer of an electron to the enone results in rapid isomerisation of the cis- to the trans-isomer so both cis- and trans-products are formed. Considerable care must be exercised in the interpretation of the results. Trimethylaluminium in ether reacts with the trans-enone but not with the cis-isomer (84) except in the presence of transition metal impurities, which presumably catalyse the cis \rightarrow trans.

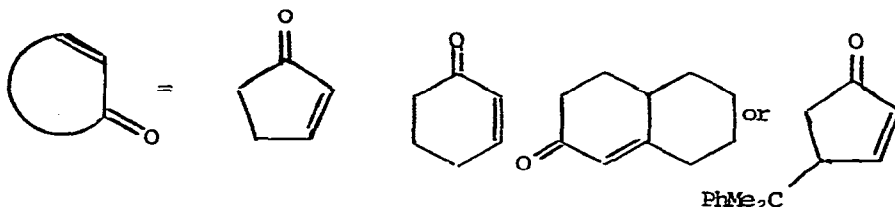
conversion. Polar intermediates are probably involved. In benzene, however, the products are 70% cis and trans (85) from 1,2-addition and 30% (86) from 1,4-addition. At some stage there is isomerisation and it is possible that a single electron transfer is involved.

The $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2] - \text{Bu}_2^1\text{AlH}$ catalyst described in Section 7 has been exploited for the conjugate addition of terminal alkynyl units to α,β -unsaturated ketones (87) (Equation 24). The compounds (88, R = H) are best



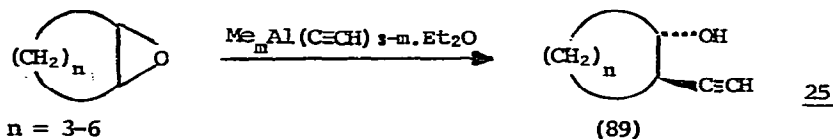
R = H, Buⁿ, Bu^t, SiMe₃

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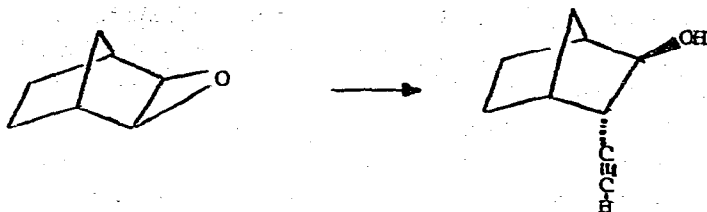


made by treatment of (88, R = SiMe₃) with potassium fluoride. An excess of the aluminium acetylide is necessary to prevent aldol condensation of the initially formed aluminium enolate with excess of enone [94].

Organoaluminium compounds react with epoxides to give products which are hydrolysed to alcohols. Triisobutylaluminium or diisobutylaluminium hydride react with 1,2-epoxy-3-phenoxypropane to give mainly PhOCH₂CH(OH)Me together with some products from addition. Diisobutylaluminium chloride gives 60% yield of PhOCH₂CH(OH)CH₂Cl [95]. Ring opening of epoxides has been exploited for synthesis of trans-2-ethynyl substituted alcohols [96] (Equation 25). A reproducible reagent is made from methylaluminium

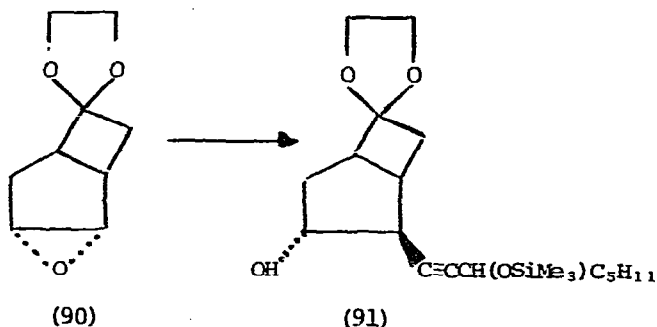


sesquichloride and NaC≡CH in ether: this is sometimes able to effect conversions which are not observed with LiC≡CH/NH₂CH₂CH₂NH₂, e.g. that in Equation 26. The compounds (89) are important precursors in the synthesis of a number of natural products. The transformation of the epoxide

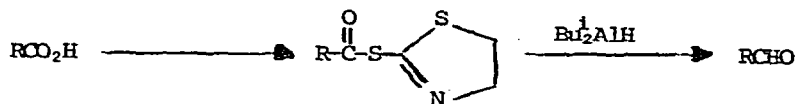


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(90) into the alcohol (91) by treatment with $\text{Me}_2\text{AlC}\equiv\text{CCH}(\text{OSiMe}_3)\text{C}_5\text{H}_{11}$ is an application of this reaction in the preparation of prostaglandins [97].

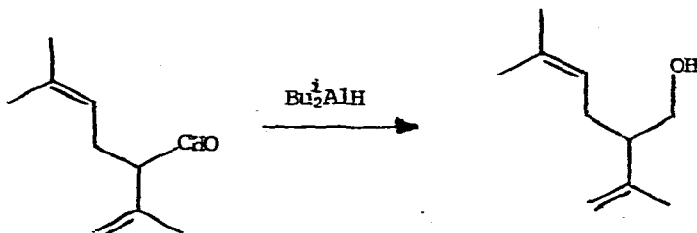


Diisobutylaluminum hydride has found many uses as a reducing agent, e.g., for the conversion of acids to aldehydes [98] (Equation 27), for the further reduction of aldehydes to alcohols [99] (Equation 28) or for the



[$\text{R} = \text{Ph}, n\text{-C}_{15}\text{H}_{31}, n\text{-C}_9\text{H}_{19}, n\text{-C}_5\text{H}_{11}, \text{PhCH}=\text{CH}, \text{MeCO}_2(\text{CH}_2)_7$]

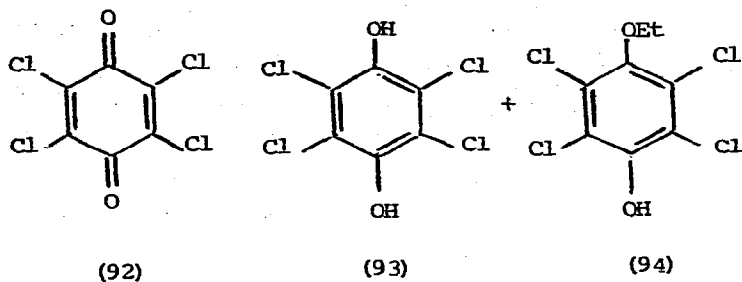
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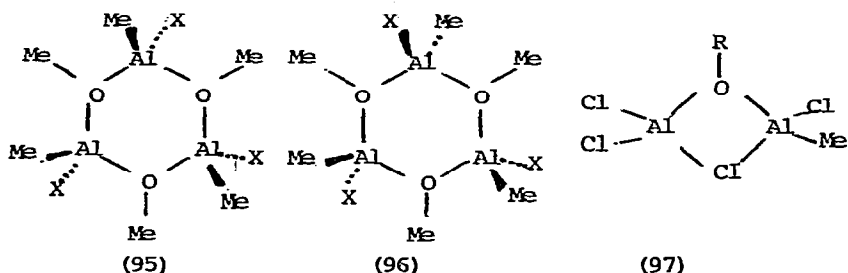
reduction of lactones in prostaglandin synthesis [100 - 105].

The products from the reaction between ethylaluminum chlorides and chloranil (92) are (93) and (94). A detailed analysis of biproducts suggest that they arise via radical intermediates or via hydride transfer from ethyl groups attached to aluminum to the carbonyl carbon of the quinone [106].



9. ALKYLALUMINIUM ALKOXIDES, ALUMINOXANES AND RELATED COMPOUNDS

The ^1H NMR spectra of methylmethoxyaluminium chloride and iodide have been interpreted [107] in terms of the trimeric structure found in 1973 for $(\text{Me}_2\text{AlOMe})_3$ by electron diffraction. Isomers (95) and (96) ($\text{X} = \text{Cl}$ or I) are indicated in solution. Alkoxyaluminium dichlorides ROAlCl_2 react autocatalytically with methylaluminium dichloride at $170\text{--}180^\circ\text{C}$ with formation of hydrocarbons and aluminoxane ($>\text{Al-O-Al}<$) systems [108] [109]. The rate of reaction decreases for $\text{R:Bu}^t > \text{Pr}^i > \text{Bu}^n > \text{Pr}^n > \text{Et} > \text{Me}$ and it is suggested that the products may be derived from

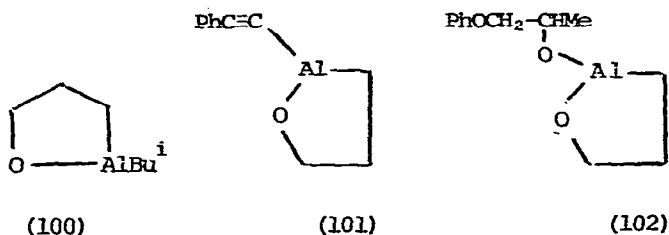


carbocations R^+ formed from intermediates (97). Reactions between methoxyaluminium compounds $\text{Me}_x(\text{OMe})\text{AlCl}_{2-x}$ ($x = 0, 1, 2$) and methylaluminium chlorides $\text{Me}_y\text{AlCl}_{3-y}$ ($y = 1, 2, 3$) have been studied in considerable detail. The rate depends more on the compound (99) than on the methoxy-compound (98) and decreases with decreasing Lewis acidity of (99). NMR studies of mixtures of (98) and (99) show incomplete exchange between methyl groups and chlorine atoms attached to aluminium.

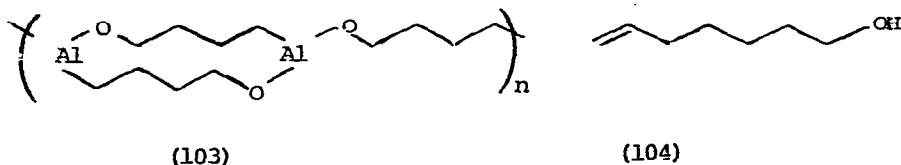
Dimethylaluminium phenoxide may be obtained either as dimer, by sublimation, or as trimer by recrystallisation from heptane. Mass spectra of each of these species have been recorded [110]. In the spectrum of the trimer there are weak peaks containing at least five aluminium atoms which are assumed to come from intermediates in the trimer \rightarrow dimer conversion. 2,6-Di-*t*-butyl-4-methylphenoxyaluminium ($\text{ArOAl}<$) compounds were reported in a preliminary communication in 1975. More details have now been given [111] of $\text{MeAl}(\text{OAr})_2$, $\text{Bu}_2^i\text{AlOAr}$, $\text{Bu}^i\text{Al}(\text{OAr})_2$, which are mono-

meric in freezing benzene, and of $[\text{MeAlCl}(\text{OAr})]_2$. The compound Me_2AlOAr disproportionates in solution to $\text{MeAl}(\text{OAr})_2$ and Me_3Al_2 ; $\text{MeC}\equiv\text{C}(\text{Me})\text{AlOAr}$ is also apparently unstable in solution and gives a complex mixture of species.

Cyclic alkoxides have been described in two papers. The reactions of 2-isobutyl-1,2-oxaluminolan (100) with bromine, carbon dioxide, phenylacetylene and phenoxymethyloxiran all show that the exocyclic Al-C bond

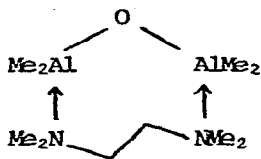


is more reactive than the cyclic one. The reaction with phenylacetylene gives, after hydrolysis with D_2O , products $\text{PhC}\equiv\text{CD}$ and $\text{CH}_2\text{DCH}_2\text{CH}_2\text{OD}$ from an intermediate (101) formed by metallation, without any further addition or reduction. The products $\text{PhOCH}_2\text{CHOHMe}$ and Pr^nOH obtained from the epoxide after hydrolysis with water show that the only reaction is reduction giving the intermediate (102) [112]. When aluminium turnings are heated in THF in the presence of a catalyst of HgCl_2 (2 mol %)/ Me I (4 mol %)/ ZnCl_2 (4 mol %), the organoaluminium compound (103) is obtained in 93% yield [113]. Similar derivatives may be made from 2-methyl- and

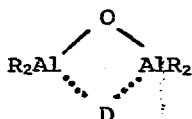


2,5-dimethyl-THF, tetrahydropyran (THF), 2-methyl-THF, oxepan, ^{and} 7-oxabicyclo [2.2.1] heptane. These compounds react with D_2O to give d_2 -alcohols, with allyl halides in the presence of copper(II) bromide to give unsaturated alcohols e.g. (104) from (103) and $\text{CH}_2=\text{CHCH}_2\text{Br}$, and with chloral to give 2,2,2-trichloroethanol.

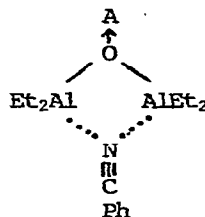
There have been several more papers on the preparation and properties of aluminoxanes which are important as components of Ziegler-Natta catalysts [166]. Triethylaluminium reacts with water in the presence of TMED to form the monomeric volatile complex (105) [114]. Similar complexes (106) ($\text{R} = \text{Et}$ or Bu^i) are apparently formed with $\text{D} = \text{PhCN}$, NMe_2Ph or $\text{Bu}^n\text{N}=\text{CPh}$ but where the groups R or D are small association to oligomers is observed.



(105)



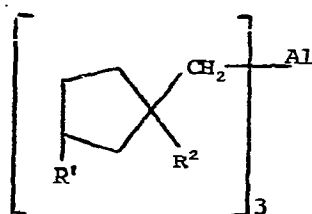
(106)



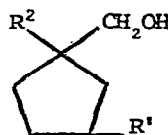
(107)

An electron-deficient nitrogen bridge is postulated in (106) [115]. The oxygen atom in (106 R = Et, D = PhCN) is sufficiently basic to form complexes (107) with A = Et₂AlCl, EtAlCl₂ or Et₃Al but not Me₂Zn or Et₂Zn [116]. The hydrolysis of ethylaluminum chlorides has been studied in considerable detail and spectroscopic evidence has been obtained for a number of intermediates [117,118]. Diethylaluminum chloride reacts with water (from CuSO₄ · 5H₂O) to give the aluminoxane (EtClAl)₂O and then the complex (106 R₂ = EtCl, D = H₂O); the reaction is slower in benzene than in heptane. The product (106 R₂ = EtCl, D = Et₂O), formed in ether, may be distilled without decomposition. The hydrolysis of ethylaluminum dichloride in benzene or ether proceeds similarly with formation of complexes (106 R₂ = Cl₂ or EtCl; D = H₂O or Et₂O). In heptane, however, it is possible to detect the complex EtAlCl₂ · H₂O. The complexed water cannot be displaced by ether and apparently does not react with sodium, but the compound EtAlCl₂ · H₂O is decomposed by dioxygen to give (EtOClAl)₂O and by ethanol to give EtOAlCl₂. Controlled hydrolysis of tri- or tetraalkylaluminates NaHAlR₃ or NaAlR₄ in ethers yields the crystalline compounds Na₂[R₂AlOAlR₃](R = Me, Et, or Buⁱ), which may be considered as 2:1 adducts of alkali metal alkyls and aluminoxanes [119]. Compare also ref. [134].

The oxidation of the cycloalkylaluminum compounds (108) to cyclopentanemethanols (109) (R¹, R² = H or Me) has been described [120]. Trimethylamine N-oxide oxidises trialkyl- or triarylaluminums R₃Al smoothly at 140° in xylene giving, after hydrolysis, alcohols or phenols ROH (R = Me, Prⁿ, Buⁱ, n-C₈H₁₇, C₁₀H₂₁, Ph) in good yield [121]. Vinylaluminum compounds are not oxidised under these conditions and ethylaluminum chlorides are converted into tars.

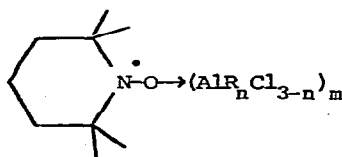


(108)

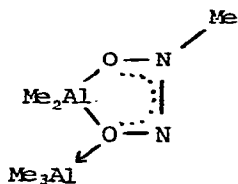


(109)

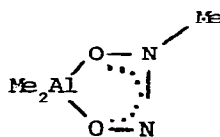
The compound 2,2,6,6-tetramethylpiperidin-1-oxyl reacts with alkyl-aluminium chlorides to give complexes (110) ($R = \text{Me}, \text{Et}, \text{Pr}^n, \text{Bu}^i$ or $n\text{-C}_8\text{H}_{17}$; $n = 1, 2$ or 3 ; $m = 1$ or 2) characterised by ESR spectra. The most stable



(110)



(111)



(112)

complexes are obtained when the Lewis acidity of the aluminium-containing fragment is greatest [122]. The main decomposition products are alkanes, alkenes, 2,2,6,6-tetramethyl-1-hydroxy- and -1-alkoxy-piperidines and reduction products, and it is suggested that these result from displacement of alkyl groups from aluminium by the piperidinoxyl [123]. Nitric oxide reacts with trimethylaluminium to form compounds (111) and (112) which are derivatives of N-methyl-N-nitrosohydroxylamine [124].

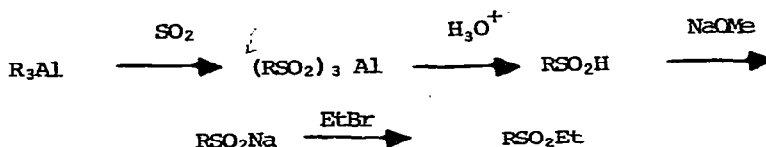
The white powders obtained by the reaction between trimethylaluminium and cesium salts of sulphur oxyacids have been formulated as $\text{Cs}_2\text{SO}_4 \cdot 4\text{AlMe}_3$ and $\text{Cs}_2\text{S}_2\text{O}_3 \cdot 4\text{AlMe}_3$, with AlMe_3 attached to all terminal oxygen or sulphur atoms. In $\text{Cs}_2\text{S}_2\text{O}_6 \cdot 4\text{AlMe}_3$ only four of the six terminal atoms of the oxyanion are coordinated to aluminium [125].

10. ORGANOALUMINIUM SULPHIDES AND SELENIDES

The reagent $\text{Me}_2\text{AlS}^t\text{Bu}^t$ made in situ from trimethylaluminium and t-butyl mercaptan converts a wide range of esters $\text{R}'\text{COOR}^2$ into t-butyl thioesters $\text{R}'\text{COS}^t\text{Bu}^t$ ($\text{Ph}, \text{C}_{17}\text{H}_{35}, \text{PhCH}_2, \text{cyclo-C}_6\text{H}_{11}, \text{PhCHOH}, 2\text{-furyl}$). Lactones are converted to ω -hydroxy t-butyl thioesters [126]. Phenyl thioesters are readily obtained in good yield using aluminium thiophenoxide $\text{Al}(\text{Sph})_3$, made from trimethylaluminium and thiophenol [127].

The compound $\text{Me}_2\text{AlSe}^t\text{Me}^t$, made from trimethylaluminium and selenium metal in toluene under reflux, may be used similarly as an acyl transfer agent. A wide variety of carboxylic esters, including a number having functional groups, may be converted to compounds $\text{R}'\text{COSe}^t\text{Me}^t$ from which the derivatives $\text{R}'\text{COOH}, \text{R}'\text{COOMe},$ or $\text{R}'\text{CONHR}^2$ may be easily prepared [128].

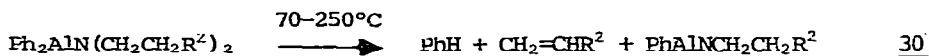
Organoaluminium compounds have also been suggested as useful for the synthesis of sulphones RSO_2Et [$\text{R} = 2\text{-(cyclohex-3-en-1-yl)ethyl}, \text{PhCH}_2\text{-CH}_2$ or PhCHMe] by the sequence of equation 29 [129].



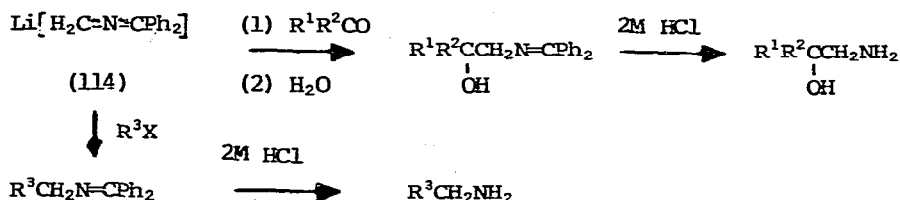
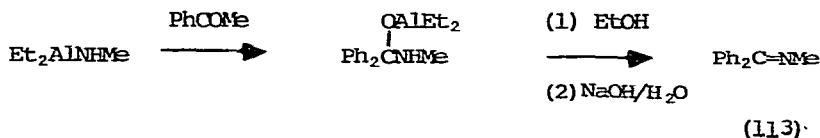
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11. NITROGEN AND PHOSPHORUS DERIVATIVES

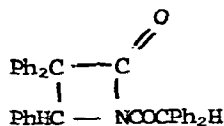
As part of a study to develop a convenient stereospecific method for conversion of secondary to primary amines the thermal decomposition of organo-magnesium, -zinc and -aluminium amides has been investigated [130]. Aluminium compounds $Ph_2AlNR_2^1$ ($R^1 = Et, Pr, Bu^i$ or cyclo- C_6H_{11}) have been isolated with various proportions of toluene of crystallisation. After this is removed on heating the decomposition follows reaction 30 except when $R^1 = Bu^i$. The primary amine $R^2CH_2CH_2NH_2$ may be obtained by hydrolysis



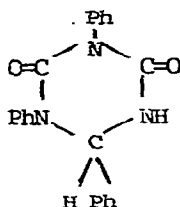
of the residue. The amide $(Et_2AlNHMe)_3$ has been used in the synthesis of N-methyl-diphenylketimine (113) for aminomethylation reactions. On treatment with $LiNPr_2^i$, (113) gives the reagent $Li^+[H_2C=N=CPh_2]^-$ (114), which reacts with ketones to give alkylidenamino-alcohols, or with alkyl halides to give amines [131]. The compounds $Et_2AlN=CHPh$ or $Na^+[Et_3AlN=CHPh]^-$ have proved useful for the synthesis of a number of cyclic species [132]. Diphenylketene, for example, is converted to (115) and phenylisocyanide to (116). The carbo-diimide $R^1N=C=NR^1$ ($R^1 = cyclo-C_6H_{11}$) gives (117) but the product from $PhN=C=NPh$ is the four-membered ring compound (118). The derivatives (119), easily made from tris (3-trimethylsilylpropyl)-aluminium and aliphatic nitriles ($R = Me, Et, n-C_{11}H_{23}$) may be hydrolysed



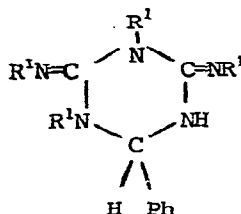
to ketones $Me_3Si(CH_2)_3COR$. When $R = Ph$, however, the trimethylsilylalkyl group is eliminated, even at 20° , with formation of $Me_3SiCH_2CH=CH_2$ and only benzaldehyde is obtained on hydrolysis [133].



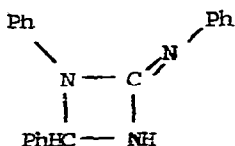
(115)



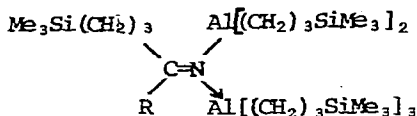
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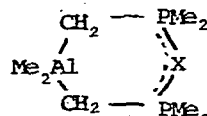
(117)



(118)



(119)



(120)

The formation of the compounds $\text{Na}_2[\text{R}_3\text{AlOAlR}_3]$ by hydrolysis of $\text{Na}[\text{AlHR}_3]$ is described in Section 9 above. The compounds $\text{Na}_2[\text{R}_3\text{AlNMeAlR}_3]$ ($\text{R} = \text{Me}$ or Et) may be made similarly from $\text{Na}[\text{AlHR}_3]$ and methylamine in THF [134]. Analytical data have been given but there is no further structural information.

Vibrational spectra of the derivatives $(\text{R}_2\text{M}=\text{NMe}=\text{CMe}=\text{NMe})_2$ ($\text{M} = \text{Al}$, Ga or In , $\text{R} = \text{Me}$ or Et) have been discussed in terms of the centrosymmetrical C_{2h} structure (8) [135]. Both triethylaluminium and the imido compound $[(\text{HAlNPr}^1)_6]$ react with caprolactam to give a series of derivatives in which Al-H or Al-Et groups are successively replaced. The product formed by replacement of all groups attached to aluminium is said from IR, NMR and molecular weight measurements to consist of a monomer and dimer with eight-membered rings having Al-N-C=O-Al linkages [136].

The double ylide complex (120 $\text{X} = \text{CH}$) was described in last year's survey. The isoelectronic compound (120 $\text{X} = \text{N}$) has been mentioned in a patent [137] and the boron derivative (120 $\text{X} = \text{BH}_2$) has been obtained from the reaction between LiAlMe_4 and $[(\text{Me}_3\text{P})_2\text{BH}_2]^+\text{Br}^-$ [138].

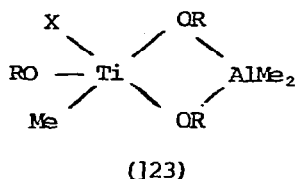
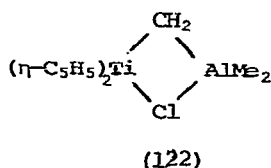
12 SYSTEMS INVOLVING ORGANOALUMINIUM COMPOUNDS AND OTHER METALS

This section covers papers describing the interaction of organoaluminium compounds and compounds of other metals. Many such interactions have been considered in previous sections dealing with specific reactions; [13-16, 29, 56-64, 66-76, 78, 93-94]; others are dealt with in the following section on catalysis.

The reaction between potassium and triisobutylaluminium in a non-polar solvent, e.g., hexane at 20°C , gives a brown product which may be recrystallised from toluene. This has been formulated as $\text{K}_2[\text{Bu}_3^1\text{Al}-\text{AlBu}_3^1]$. 0.2PhMe (121) with a σ -bond between the two aluminium atoms. The evi-

dence comes from hydrolysis with $\text{Bu}^n\text{CHCHEtCH}_2\text{OD}$, which gives $\text{D}_2 + 6\text{BuD}$, and from conductivity measurements, but it would be interesting to have confirmation by diffraction methods. With trimethylchlorosilane the compound (121) gives Me_3SiBu^i , KCl and a product said to be $[\text{Bu}_2^i\text{Al}-\text{AlBu}_2^i, 2\text{THF}]$; with allyl bromide, it yields $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}=\text{CH}_2$, KBr and triisobutylaluminium [139].

The formation of compounds with Zr-C-C-Al bridges from the reaction between $(\eta\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ and Et_3Al was described in 1975. The reaction between $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ and Me_3Al has now been shown to yield methane and a reddish-orange compound (122) which appears to have a methylene bridge between aluminium and titanium [140]. Similarly, $(\eta\text{-C}_5\text{H}_5)_2\text{TiMe}_2$ reacts with trimethylaluminium to give $(\eta\text{-C}_5\text{H}_5)_2\text{TiCH}_2\text{AlMe}_3$, presumed to have a structure like (122) but with a methyl instead of a chlorine bridge.



NMR spectra show that in mixtures of (122) and aluminium alkyls AlY_3 ($\text{Y} = \text{CD}_3$ or Bu^i) alkyl groups are statistically distributed between the two types of species, and $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\eta\text{-CH}_2)(\mu\text{-Cl})\text{AlBu}_2^i$ may be obtained by repeated exchange with an excess of AlBu_3^i . With ethylene, compound (122) gives propene, and with propene 2-methylpropene; with C_2D_4 , the products are $\text{CD}_3\text{CD}=\text{CH}_2$ and $\text{CH}_2\text{DCD}=\text{CD}_2$, suggesting that the CH_2 group is transferred. With carbonyl compounds $\text{R}^1\text{R}^2\text{CO}$ ($\text{R}^1\text{R}^2 = \text{Ph}_2, \text{PhH}, \text{Me}$ (OEt) or cyclo- $(\text{CH}_2)_5$) the alkenes $\text{R}^1\text{R}^2\text{C}=\text{CH}_2$ are obtained, so the compound (122) serves as a methylene transfer agent with chemistry like that of compounds $\text{L}_n\text{Ta}=\text{CR}^1\text{R}^2$. A series of titanium derivatives $(\text{R}^1\text{R}^2\text{R}^3\text{SiCH}_2)_n\text{TiCl}_{4-n}$ ($\text{R}^1, \text{R}^2, \text{R}^3 = \text{H}, \text{C}_{1-10}$ alkyl or cycloalkyl, $n = 1-3$), which are polymerisation catalysts for alkenes, e.g. butadiene, may be made from the appropriate alkylaluminium compounds and titanium (IV) chloride [141]. The reaction between titanium (IV) chloride and diethylaluminium chloride in a mixture of benzene and hexamethylbenzene yields the black crystalline compound $[\text{C}_6\text{Me}_6\text{TiCl}_2][\text{AlCl}_4]$. The hexafluorophosphate(V) salt has also been isolated [142]. Trimethylaluminium converts a number of titanium alkoxides $\text{XTi}(\text{OR})_3$ ($\text{X} = \eta^5\text{-C}_5\text{H}_5$, OR or Me; $\text{R} = \text{Et}$ or Bu^i) to titanium-methyl compounds formulated as (123). [143].

The black slurry formed from tris(pentan-2,4-dionato)cobalt and triisobutylaluminium in the presence of triphenylphosphine shows a higher

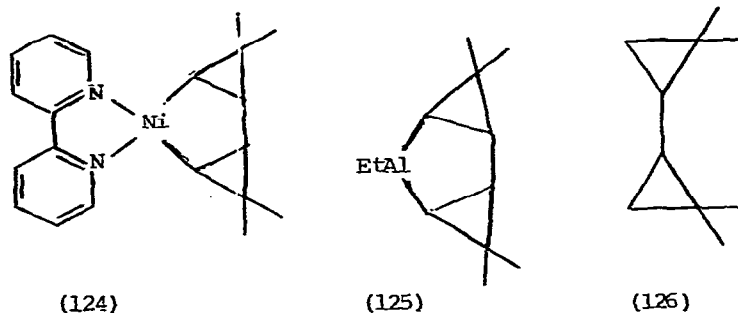
hydrogenating activity than does the catalyst made without phosphine [144]. In cobalt-catalysed syntheses of pyridines from alkynes and nitriles, added organoaluminium compounds serve as reducing agents rather than as integral parts of the catalyst. [145]. Several papers refer to the interaction between organoaluminium compounds and nickel derivatives.

Bis(pentan-2,4-dionato)nickel reacts with trimethyl- or triethylaluminium to give a complex mixture of gaseous products which includes not only ethane and ethylene but also various C_3 and C_4 hydrocarbons. The products are explained by assuming that alkyl radicals from decomposition of alkyl-nickel intermediates react with the excess of trialkylaluminium [146]. In the presence of butadiene and 1,3-pentadiene, mixtures of nickel(II) chloride and triisobutylaluminium give π -allyl nickel compounds $R[C_nH_{2n-2}]_m NiCl$ ($R = Bu^i$ or H) with the alkenyl group an oligomer of the diene. These appear to react only slowly with $M HCl$ so that the aluminium compounds may be easily washed out [147]. Similar reactions are observed with $CoCl_2$ but the resulting organocobalt compounds are more easily hydrolysed. In the presence of triphenyl phosphite and butadiene, $Ni(C_5H_7O_2)_2$ and triethylaluminium give an organonickel compound which is rapidly decomposed to metallic nickel [148]. However, the complex $[(Me_3SiCH_2)_3Al, OEt_2]$ or the alkoxides $[(Me_3SiCH_2)_n Al(OEt)_{3-n}]$, in the presence of an excess of bipyridyl (bipy) react with bis(pentan-2,4-dionato)nickel to give the dark green, almost black, compound $[(Me_3SiCH_2)_2Ni(bipy)]$ [149]. With the etherate Ph_3Al, OEt_2 , in the presence of an excess of phosphine, displacement of the pentan-2,4-dionato ligands is incomplete and the products are $[NiPh(C_5H_7O_2)(PR_3)_n]$ ($R = Ph$, $cyclo-C_6H_{11}$; $n = 1$; $R = Et$; $n = 2$). With a stoichiometric quantity of triethylphosphine, the compound $[NiPh(C_5H_7O_2)(PEt_3)]$ is obtained. Reactions of these compounds with alkyl halides or alkenes have been documented [150]. Similarly, the chromium compound $[CrPh(C_5H_7O_2)_2]$ may be made from $[Cr(C_5H_7O_2)_3]$ and $[Ph_3Al, OEt_2]$ [151]. The reaction between $[Pd(C_5H_7O_2)_2]$ and dialkylaluminium alkoxides R_2^1AlOEt ($R^1 = Me, Et, or Pr^i$) and tertiary phosphines gives the characterisable complexes $[PdR_2L_2]$ $L = PEt_3, PPh_2Me$ or $\frac{1}{2} Ph_2PCH_2CH_2PPh_2$ [152]. Bipyridyl(cycloocta-1,5-diene)nickel(0) reacts with 3,3-dimethylcyclopropane to give the complex (124). With triethylaluminium, this gives (besides ethane, ethylene and metallic nickel from ethyl-nickel compounds) a residue which appears to contain the aluminium compound (125) since it yields the hydrocarbon (126) quantitatively on hydrolysis [153].

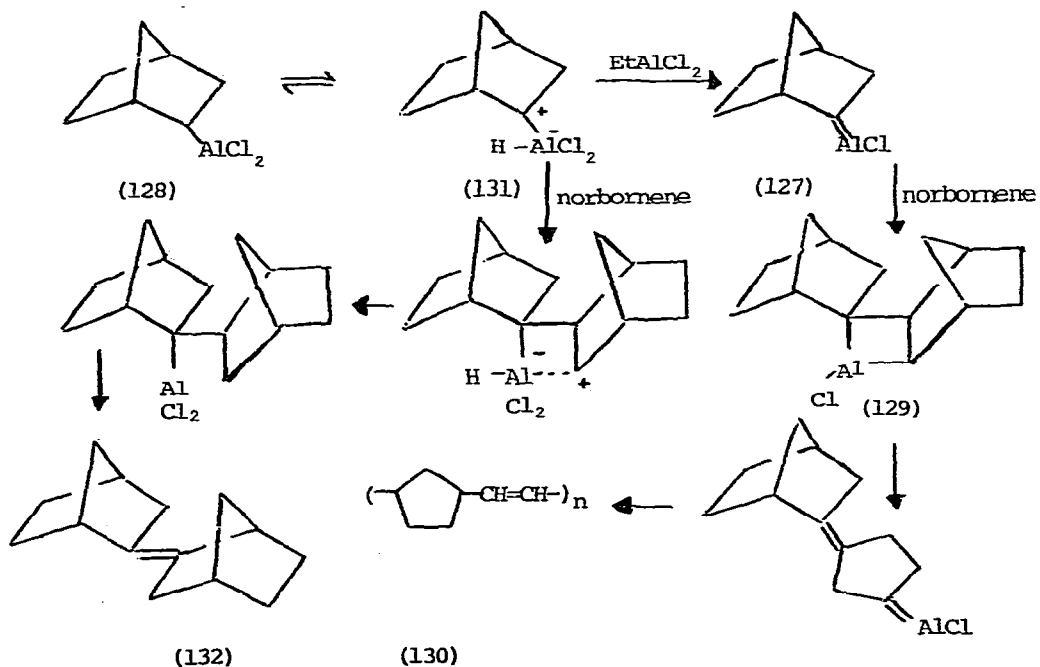
13 CATALYSIS

In this section, two papers dealing with the mechanism of catalytic processes are summarised in detail. Others covering polymerisation of

alkenes and vinyl monomers, alkene metathesis and hydrosilylation are surveyed only briefly. An introductory account of the use of organo-aluminium compounds in polymer chemistry has appeared [154] but a full discussion of this topic is not attempted here.

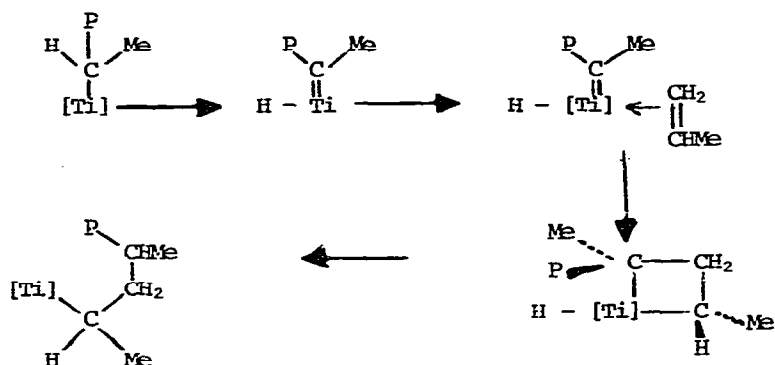


The ring-opening polymerisation of norbornene may, under certain circumstances, be catalysed by ethylaluminium chloride, in the absence of transition-metal compounds. It has been suggested [155] that the process may involve carbene species (127) generated by a hydride shift from



precursor (128). The carbenes may then give metallocycles (129) which eventually give polymer (130). Alternatively the intermediates (131)

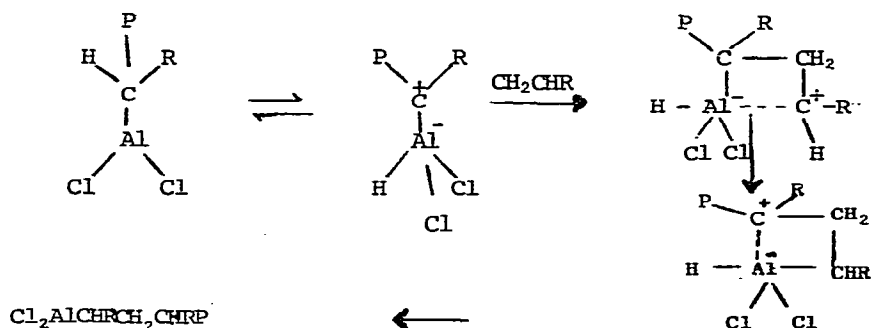
may be converted to oligomers such as [132]. Since ring opening polymerisation of norbornene is a kind of alkene metathesis, this work emphasises the similarity between Ziegler-Natta and alkene metathesis catalysts and leads to the postulate [156] that Ziegler-Natta catalysis may proceed (Equation 30) via titanium carbenes and metallocycles, instead of by the more widely assumed mechanism involving insertion of an alkene into a Ti-C bond, a reaction for which there is almost no independent evidence.



P = polymer

30

It is also interesting to speculate [156] that the well-established oligomerisation of alkenes by organoaluminium compounds may proceed by an analogous sequence (Equation 31).



$\text{Cl}_2\text{AlCHRCH}_2\text{CHRP}$

31

A patent [157] claims the use of a catalyst system $\text{TiCl}_4/\text{R}^1\text{AlCl}_{3-n}/\text{R}^2\text{R}^3\text{R}^4\text{OCl}$, $\text{R}^1 = \text{C}_1\text{-C}_4$ alkyl, $\text{R}^{2-4} =$ alkyl or aryl, for the cyclic trimerisation of butadiene to cyclododeca-1,5,9-triene. As in previous years, there are many papers describing detailed studies on the polymerisation of alkenes with Ziegler-Natta catalysts using organoaluminium compounds [158-166]. Various polymers have been obtained from substituted

allenes [167]; for example, polymerisation of alkoxyallenes using NiCl_2 or $\text{CoCl}_2/\text{AlEt}_3$ gives $\{-\text{C}(=\text{CHOR})-\text{CH}_2-\}_n$ ($\text{R} = \text{Me}$ or Et) and polymerisation using Ziegler-Natta catalysts TiCl_4 , VOCl_3 or $\text{FeCl}_3/\text{AlEt}_3$ gives $\{-\text{C}(=\text{CH}_2)-\text{CH}(\text{OR})-\}_n$ [168].

In papers describing the use of organoaluminium compounds in catalytic systems for polymerisation of various vinyl monomers, attention has focussed on the function of the aluminium compound as Lewis acid [4] or as chain transfer agent in termination processes, on competition between ionic and radical reactions and on competition between homopolymerisation and alternating copolymerisation. Specific processes described during 1978 are as follows: the polymerisation of methyl methacrylate using triethylaluminium-2,2'-dipyridyl [169], polymerisation of but-2-ene using t-butyl chloride/trivinylaluminium [170], the formation of phenyl methacrylate-styrene copolymers using diethylaluminium chloride as catalyst [171], copolymerisation of benzfurans and various acrylic monomers with various organoaluminium compounds [172], copolymerisation of acrylonitrile and butadiene [173], and of styrene and acrylic monomers [174] with a range of organometallic catalysts, copolymerisation of but-2-ene and methyl methacrylate using a peroxide-ethylaluminium sesquichloride initiator [175], copolymerisation of carbon dioxide and propylene sulphide in the presence of a catalyst derived from triethylaluminium and pyrogallol [176] and copolymerisation of carbon dioxide and propylene oxide [86].

Another group of papers describes alkene metathesis [11-12, 177-181].

The use of the catalytic systems $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2]/\text{AlEt}_3$ (with or without Ph_3P) or $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2/\text{AlEt}_3$ for the hydrosilylation of alkenes or dienes has been described in the 1976 and 1977 surveys. Further hydrosilylations using alkyl or arylsilanes [182] or trichlorosilane [183] have been studied. Linear cooligomerisation of vinylsilanes with 1,3-dienes using $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2]/\text{AlEt}_3/\text{Ph}_3\text{P}$ is shown in Table 4 [184] [185]. The course of the reaction has been followed by deuteration studies. The products (133) and (134) from the reaction between trimethyl(vinyl)silane and butadiene react with molybdenum (V) chloride to give deca-1,4,9-triene and with diisobutylaluminium hydride to give the silanes (135) and (136). The same catalyst $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2]/\text{AlEt}_3/\text{PPh}_3$ promotes the linear oligomerisation of ethynyl-

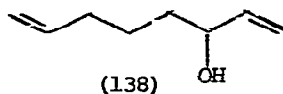





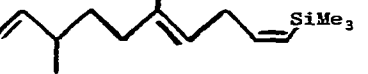

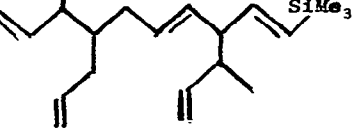
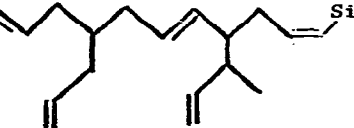






Table 4 Products from the reaction between trimethyl(vinyl)silane and various polyenes.

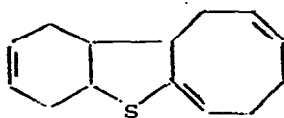
Polyene	Product
	 (133)  (134)
	 
	 
	
	
(135)	(136)

trimethylsilane, giving a 1:1 mixture of $\text{Me}_3\text{SiCH}=\text{CH}=\text{CSiMe}_3$ and $\text{Me}_3\text{SiCH}=\text{CH}(\text{SiMe}_3)=\text{CH}=\text{CSiMe}_3$ [186]. For reactions of Me_2SiH_2 (Table 5) the catalyst is $[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2]/\text{PPh}_3/\text{cyclododecane-1,5,9-triylaluminum}$. Under the conditions used (8h at 100°C) only one Si-H bond is reactive. The products on the right of Table 5 e.g. $\text{Me}_2\text{HSiCH}_2\text{CH}_2\text{OBU}^n$ react with butadiene to give compounds such as $\text{MeCH}=\text{CHCH}_2\text{SiMe}_2(\text{CH}_2)_2\text{OBU}^n$. [187].

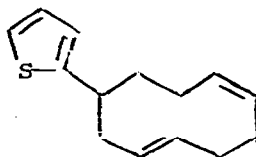
Table 5 Products from the reaction between dimethylsilane and various substrates [187].

Reactant	Product
$H_2C=CHX$ (X = CN or CO_2Me)	$Me_2SiHCHMeHX$
$H_2C=CMeX$ (X = CO_2Me or $OCOMe$)	Me_2SiHCH_2CMeHX
$H_2C=CHX$ (X = $OCOMe$ or OBu^t)	$Me_2SiHCH_2CH_2X$
$(H_2C=CHCH_2)_2O$	$\{Me_2SiH(CH_2)_3\}_2O +$ $\{Me_2SiHCHMeCH_2\}_2O$

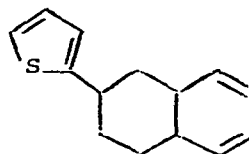
A method has been described [188] for the conversion of butadiene into the alcohols (137) and (138) using $[Pd(C_5H_7O_2)_2]/PPh_3/AlEt_3$ in aqueous boric acid and toluene. It is not clear how the catalyst survives the reaction conditions described unless the active species is an organopalladium compound which is stable with respect to hydrolysis. Butadiene also reacts with 2-vinylthiophene with $[Ni(C_5H_7O_2)_2]/P(OPh)_3/AlEt_3$ as catalyst to yield the compounds (139) and (140) converted on heating to (141) [189].



(139)



(140)



(141)

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