ORGANOALUMINUM COMPOUNDS

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I. Introduction

Since about 1950, organoaluminum compounds have become of major importance in many technical processes, especially through the work of K. Ziegler. In addition to their use as catalyst components for polymerizing alkenes to plastic products (Ziegler catalysts), organoaluminum compounds are extensively applied as intermediate catalysts (e.g., for the oligomerization of ethylene) and also for syntheses of various other organic compounds. It is not surprising, therefore, that organoalanes, which attracted little notice for more than 80 years after their discovery (*42*, *85a*), have in recent times become the subject of lively interest throughout the world. This has resulted in intensive research on this class of compound. Some years ago K. Ziegler reviewed the scientific and technical results on organoaluminum compounds up to that time (*299*). Since then, however, so much new information has accumulated that a further review is certainly of interest, especially as only parts of the field have been covered in the interim (*4*, *80*, *117*, *243*).

In this article the chemistry of aluminum hydride will be dealt with only insofar as it is of interest for that of organoaluminum compounds (e.g., hydroalumination). Older classical work on the preparation and reactions of organoaluminum compounds will be dealt with only briefly, most attention being given to progress made since the appearance of Ziegler's article. In addition to new variations in the preparation of organoaluminum compounds, special mention will be made of improved processes for effecting their reactions with alkenes. In addition an account will be given of the synthesis of some novel organoaluminum compounds (e.g., Al heterocycles). Among other topics to be discussed are exchange reactions between the compounds of aluminum and those of other elements and, in considering organoaluminum complexes, their use in electrolytic processes. The article closes with a consideration of reactions with organic compounds in which stoichiometric amounts of organoaluminum compounds are used.

II. Preparation of Organoaluminum Compounds

A. SYNTHESES OF ALIPHATIC ORGANOALUMINUM COMPOUNDS

1. *From Aluminum, Hydrogen, and Alkenes*

Aluminum trialkyls (trialkyl alanes) are readily prepared from aluminum, hydrogen, and alkenes. The so-called "Direct Synthesis" of Ziegler and his co-workers (*292*, *298*) is particularly readily carried out with 1-alkenes:

$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H_2} + 3\mathrm{C}_n\mathrm{H}_{2n} \rightarrow \mathrm{Al}(\mathrm{C}_n\mathrm{H}_{2n+1})_3$$

The synthesis of trialkyl alanes may be performed in practice in two ways. Either the three components are allowed to react in the presence of preformed trialkyl alane (one-stage process), or one carries out the reaction in two separate stages. This is more advantageous in many cases. In the first stage 2 moles of trialkyl alane react with activated aluminum in the presence of hydrogen to give 3 moles of dialkyl aluminum hydride (dialkyl alane):

$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H_2} + 2\mathrm{AlR_3} \rightarrow 3\mathrm{R_2AlH}$$

This then reacts with the alkene in the second stage:

$$3\mathrm{R_2AlH} + 3\mathrm{C}_n\mathrm{H}_{2n} \rightarrow 3\mathrm{R_2AlC}_n\mathrm{H}_{2n+1}$$

Triethylalane is prepared mostly by the two-stage process; in the one-stage process ethylene and triethylalane react further forming a "growth" product (cf. Section V,C,1); only under strictly controlled conditions of temperature and pressure is extensive chain lengthening avoided (*112*). On the other hand, the one-stage process is suitable for preparing triisobutylalane, for example. Alkenes with the C═C double bond occupying an internal position in the chain also react with aluminum and hydrogen to form the corresponding alkyl alanes with secondary carbon atoms attached to aluminum. In spite of the use of excess of alkene only the di-*sec*-alkyl aluminum hydrides are obtained (*40, 95*).

The synthesis of organoaluminum compounds via aluminum hydrogen compounds has been somewhat extended recently. It is possible to use alkali hydrides to stabilize the aluminum hydride produced from aluminum and hydrogen in place of the trialkyl alane. Good yields of alkali aluminum hydrides, $MAlH_4$ (M = Li, Na, K, Cs), are obtained according to the general equation (*6, 14, 15, 44, 214, 275*):

$$M + Al + 2H_2 \rightarrow MAlH_4$$

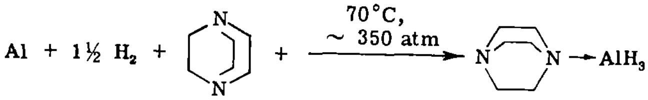
In place of the free alkali metal it is also possible to use its hydride to obtain alkali alanates:

$$MH + Al + \tfrac{3}{2}H_2 \rightarrow MAlH_4$$

Calcium alanate, $Ca(AlH_4)_2$, may also be prepared in this way (*44*).

The finely divided alkali metal or its hydride will react with activated aluminum at an elevated temperature in an autoclave under hydrogen pressure. The solvent plays a decisive role. While dialkyl ethers or polyethers are unsuitable, the synthesis goes particularly well in absolute tetrahydrofuran (*6, 15, 44, 214*). When using aliphatic or aromatic hydrocarbons it is necessary to add 5–10% aluminum triethyl to the reaction mixture (*6, 275*).

In the meantime it has also proved possible to synthesize an amine alane, triethylenediaminealane, directly (*8*):



Evidently the basicity of simple trialkylamines is insufficient to stabilize the AlH_3.

Since alkali aluminum hydrides with alkenes give alkali aluminum tetraalkyls (alkali tetraalkyl alanates) (*291, 293*), a further simple route to aliphatic organoaluminum compounds is opened up:

$$MAlH_4 + 4C_nH_{2n} \rightarrow MAl(C_nH_{2n+1})_4$$

1-Alkenes are particularly suitable for the addition of the Al—H bond of alkali alanates to the C═C double bond (hydroalumination). In addition to ethylene it is possible to use monosubstituted and unsymmetrically disubstituted alkenes, i.e., of the isobutene type. In the addition reaction, formation of compounds with primary carbon atoms on aluminum is favored. 1,2-Disubstituted alkenes, if they react at all, do so considerably more slowly than alkenes with a terminal double bond, and the reverse reaction (dehydroalumination) is appreciable in this case. In this way, using the hydroalumination-dehydroalumination equilibrium, it is possible to form 1-alkyl alanes from secondary alkyl alanes (isomerization) without a catalyst (*40*, *94*) or with salts of Zr(IV) and Ti(IV) as catalysts (*9*). In many cases (e.g., with cycloalkenes) only three of the four hydrogens of the alkali aluminum tetrahydride react with alkenes. Thus cycloalkenes with 5, 7, and 8 carbon atoms in the ring react with lithium alanate to form lithium tricycloalkyl alanate, according to the equation:

$$LiAlH_4 + 3\ \text{cycloalkene} \rightarrow LiAl(\text{cycloalkyl})_3H$$

There is virtually no reaction between cyclohexene and lithium aluminum hydride (*291*).

In addition to alkenes it is also possible to transform 1-alkynes readily into alkali tetraalkynyl alanates with splitting-off of hydrogen (*43*, *238*) (see Section IV,C,1,a):

$$MAlH_4 + 4HC{\equiv}CR \rightarrow MAl(C{\equiv}CR)_4 + 4H_2$$

Alkali metal cyclopentadienyl alanates may also be obtained (*285*):

$$MAlH_4 + 4C_5H_6 \rightarrow MAl(C_5H_5)_4 + 4H_2$$

A further possibility for the conversion of alkali metal alanates into organoaluminum compounds is the reaction with heptafluoropropyl iodide, from which perfluoropropylalanates are obtained (*93*).

2. From Tetraalkyl Alanates

Alkali tetraalkyl alanates, $M[AlR_4]$, provide a suitable starting point for the preparation of free trialkyl alanes. With aluminum halides (e.g., $AlCl_3$), alkali halides and trialkyl alanes are formed smoothly according to the equation (*117*, *291*):

$$MAlR_4 + \tfrac{1}{3}AlCl_3 \rightarrow \tfrac{4}{3}AlR_3 + MCl$$

Trialkyl alanes are also produced when mercury and metallic aluminum are stirred with molten sodium tetraalkyl alanate (*319*). Sodium amalgam is formed by the reaction

$$3NaAl(C_2H_5)_4 + 3xHg + Al \rightarrow 4Al(C_2H_5)_3 + 3Na(Hg)_x$$

until the sodium concentration reaches 0.7 wt%. It is best, therefore, to operate so that the sodium concentration is held under 0.7 wt% and the amalgam is continuously withdrawn with the addition of fresh mercury. This is analogous in principle to the direct synthesis (see Section II,A,1), using sodium and mercury as intermediates:

$$Al + 3Na + 1\tfrac{1}{2}H_2 + 3C_2H_4 + 3xHg \rightarrow Al(C_2H_5)_3 + 3Na(Hg)_x$$

One advantage of the process is that scrap aluminum can be used and it is unnecessary at any stage to work under high pressure. The process must clearly be operated in conjunction with some means of regenerating sodium from the amalgam, a problem which is being widely studied at present (*319*). Trialkyl alanes may also be liberated from their complex salts electrochemically (*319*) (see Section IV,C,3).

3. Preparation of Aliphatic Organoaluminum Compounds from Compounds of Other Elements

Following the introduction of the Direct Synthesis of trialkyl alanes and dialkyl aluminum hydrides, most of the older methods for preparing aliphatic organoaluminum compounds are now of historical interest only. This is particularly true of the synthesis of trialkyl alanes from mercury dialkyls and metallic aluminum (*42*). The very versatile methods based on the use of Grignard compounds (*299*) made separately or in a one-step reaction from Mg, RX, and AlX_3 (*199*) are also of practical significance only for preparing pure secondary or tertiary alkyl alanes. Only the direct reaction of metallic aluminum with alkyl halides is used often for preparing the alkyl aluminum sesquihalides (halide = Cl, Br), especially the methyl and ethyl compounds (*299*).

In order to prepare organoaluminum compounds with specific functional groups in the alkyl radical, reactions of aluminum halides with various metallic compounds are particularly important. Thus, vinyl magnesium halides and aluminum trichloride give unstable trivinylalane (see Section III,B,2) (*17, 288*):

$$3CH_2{=}CHMgX + AlCl_3 \rightarrow (CH_2{=}CH)_3Al + 3MgXCl$$

In the reaction with organomercury compounds it is possible to use either metallic aluminum or trialkylamine alanes, $AlH_3{-}NR_3$ (*17*). Tri(perfluorovinyl)alane has been prepared as the tetrahydrofuranate from $(CF_2{=}CF)_2Mg$ and $AlCl_3$ and, as the trimethylaminate, from $(CF_2{=}CF)_2Hg$ and $AlH_3{-}N(CH_3)_3$ (*18*). Similarly, $(CF_3)_2Hg$ and $AlH_3{-}N(CH_3)_3$ gave polymeric $CF_3AlH_2{-}N(CH_3)_3$ (*18, 26*). Further special methods for preparing organoaluminum compounds [e.g., Al heterocycles by alkyl and aryl exchange reactions (*135, 136*) (see Section V,A,1) or by pyrolysis (*64*); halomethylalanes (*97*) from $>AlX + CH_2N_2$ (see Section III,B,3)] can only be mentioned here.

The reaction of alkyl halides with metallic aluminum, which is analogous to the Grignard reaction, is not particularly versatile in its applications. In accordance with the equation

$$3RX + 2Al \rightarrow R_2AlX + RAlX_2$$

one obtains equimolar mixtures of dialkyl aluminum halide and monoalkyl aluminum dihalide (the so-called alkyl aluminum sesquihalides) (*85, 85a*) (see Section III,C). All alkyl iodides (*85a*) react in this way, but with chlorides and bromides in the absence of ether this reaction can be realized satisfactorily only with the methyl and ethyl compounds. Higher alkyl halides normally react with splitting off of alkenes and alkanes (presumably formed from alkyl radicals), and more highly halogenated aluminum compounds are formed simultaneously. As a result the corresponding alkyl aluminum halides can no longer be isolated (*299*). According to later work these difficulties can be avoided if the reaction is started with the methyl or ethyl halide and continued with the higher alkyl halide (*52*). 1-Propyl- and 1-butylaluminum sesquibromides may thus be prepared. When ethers are used as solvents the side reaction can be avoided, but the corresponding organoaluminum halides are obtained as etherates (*299*). Allyl and propargyl halides (chloride, bromide) also react with aluminum, but it has not yet been possible to isolate intermediate allyl- or propargylaluminum halides in a pure state (*186*).

B. Preparation of Aryl Alanes

Whereas the preparation of aliphatic aluminum compounds from appropriate element alkyls and aluminum halides is now of interest only in special cases (see Sections II,A,3 and IV,B), the route to aryl aluminum compounds from aryl magnesium halides and aluminum halides or from either aluminum or trialkylamine alanes and mercury diaryls is still useful (*174, 243*).

Very recently, a route has been worked out for the aryl series which links up with the Direct Synthesis of aliphatic organoaluminum compounds. Sodium tetraethylalanate and benzene react at over 150°C in a sort of exchange reaction to give sodium tetraphenylalanate and ethane:

$$Na[Al(C_2H_5)_4] + 4C_6H_6 \xrightarrow[\substack{NaOR\\(NaPh)}]{\sim 180^\circ\text{–}190^\circ C} NaAl(C_6H_5)_4 + 4C_2H_6$$

Ligand exchange is catalyzed by sodium alcoholate or sodium phenyl so that pure sodium tetraphenylalanate can be obtained in yields of about 75% (*156, 161, 232, 281*).

The preparation of certain Al heterocycles [e.g., triphenylbenzaluminole by heating the addition product from triphenylalane and tolane (*64*) (see Section V,C,2)] can only be mentioned here.

It has hitherto been assumed that only aryl iodides react with aluminum to form the corresponding aryl aluminum sesqui iodides (*246*). It has now been found, however, that aryl chlorides and bromides also react with aluminum. The latter are activated by dry milling at room temperature in the presence of aluminum chloride (*260*). Use of aluminum chloride is not essential if the reactants are brought together directly in a vibratory mill at an elevated temperature (ca. 100°C) in chlorobenzene (*171*). As in the case of alkyl halides and aluminum, an equimolar mixture of aryl aluminum dihalide and diaryl aluminum halide results:

$$2Al + 3C_6H_5Cl \rightarrow C_6H_5AlCl_2 + (C_6H_5)_2AlCl$$

The pure diphenylaluminum chloride may be prepared by adding the calculated amount of sodium chloride (*154*, *260*):

$$Ph_3Al_2X_3 + NaX \rightarrow Na(PhAlX_3) + Ph_2AlX$$

(where Ph = C_6H_5). An excess of sodium chloride is not desirable as it also forms a stable complex with diphenylaluminum chloride. On the other hand, lithium chlorides form only one stable complex, $Li(PhAlCl_3)$, so that the separation of the two phenylaluminum chlorides can be carried out without complication (*171*).

In dehalogenating the phenylaluminum chlorides with sodium it is best to work with xylene as solvent. The complex salts which are formed as an intermediate react further at above 100°C. Triphenylalane is obtained in high yield in this way from the corresponding phenylaluminum chlorides, but the compound usually contains some chlorine. A substantially better method for preparing pure triphenylalane is by the reaction of dimethylaluminum chloride with sodium phenyl: the resulting dimethylphenylalane disproportionates on distillation at reduced pressure to pure triphenylalane and trimethylalane (*171*):

$$3Al(CH_3)_2C_6H_5 \rightarrow Al(C_6H_5)_3 + 2Al(CH_3)_3$$

III. Properties of Organoaluminum Compounds

A. General Considerations

The four orbitals of the M shell of the aluminum atom are occupied by only three electrons ($3s^2,3p$), which give rise to the coordinatively unsaturated character of the element (sp^2 hybrid). For organoaluminum compounds (Lewis acids) the conversion to the stable rare gas configuration can occur by the acceptance of electrons from a donor molecule (e.g., in donor-acceptor complexes with ethers, amines, and the anions of alkali salts) (sp^3 hybrids of aluminum). Saturation of the aluminum valencies is also possible by bridge formation (with, for example, oxygen, nitrogen, or halogens in the bridge) or by bridges with electron-deficient bonds (e.g., with carbon in the form of AlC_2Al bridges). In the latter case there are three center bonds, as in diborane, and these are of special interest both from the point of view of valency theory and in preparative work. The relatively low electronegativity of aluminum results in Al—C and Al—H bonds being strongly polarized and therefore very reactive.

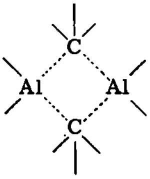
In keeping with the unsaturated character of organoaluminum compounds, only exceptionally are they monomers (e.g., trialkyl alanes with special groups attached to aluminum). As a rule, stable larger units are formed. If atoms or groups with free electron pairs are attached to aluminum (e.g., halogens, amino, or alkoxy groups), these are situated between two aluminum atoms and dimeric or trimeric organoaluminum compounds result. Hydride or alkyl groups can, however, also be located between two aluminum atoms. In the resulting electron-deficient or 3-centered bonds there are only four bonding electrons for the four atoms which are linked together. Such compounds exhibit an unsaturated character and their increased reactivity toward certain organic compounds is attributable to this cause.

Aluminum has 3*d* orbitals relatively accessible, and not only may the valency of aluminum rise above four, but some *d* character may be present in the bonds of the tetravalent and also in the bonds of the trivalent aluminum compounds. At present only few organic aluminum compounds with five- and six-coordinated aluminum are known (sp^3d and sp^3d^2 hybrids; see Sections III,D and IV,C). The differences between the behavior of aluminum and boron compounds can partially be explained by the possibility of formation of these structures (trigonal bipyramid, octahedron).

B. Organoaluminum Compounds with Three Al—C Bonds

1. *With Saturated Aliphatic and Aromatic Hydrocarbon Radicals*

Trialkyl alanes are, apart from some exceptions, associated through AlC_2Al bridges:

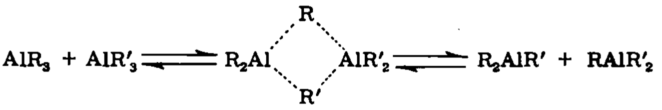


Trimethylalane and triethylalane are well known to be completely dimerized. Trialkyl alanes with bulky alkyl radicals, on the other hand, are practically unassociated. Among these are those of the isobutyl type, $Al(CH_2CHRR')_3$ (*103, 307*), and of the neopentyl type, $Al(CH_2CRR'R'')_3$ (*103, 299*), as well as tri-2-propylalane (*211*) and other alanes with secondary carbon atoms attached to aluminum. The latter compounds have not yet been fully studied because of their instability (for dehydroalumination, see Section V,B,1).

Simple Al heterocycles known at present [e.g., alumina-cyclopentane (*135*) and 1-aluminaindanes (*135*) or 1-aluminatetralins (*135*) are dimeric in benzene solution]. The so-called aluminaadamantanes (*259*) [e.g., $(CH_3)_6Al_6C_4(CH_3)_4$; cf. Section V,B,4] are monomeric in spite of their high aluminum content. The two aluminaadamantanes so far described (*235, 259*) also form no diethyl etherates, which is very surprising for organoaluminum compounds. It can readily be shown with the aid of a Dreiding model that the molecular framework is too rigid for a change in hybridization of aluminum from sp^2 to sp^3 to be possible. However, so long as it has not been demonstrated (e.g., by Al nuclear magnetic resonance or X-ray structural analysis) that all the aluminum atoms are bonded in the same way, the possibility is not excluded that the "Al adamantanes" have a quite different sort of structure. Bearing in mind the structure of certain organocarboranes (*137*), a structure of a "carbalane" type could also be considered.

Triphenylalane has been found to be about 80% dimeric by ebullioscopic measurements in benzene (*175*), although this is not supported by newer cryoscopic measurements on *p*-xylene (*171*). The degree of association of triphenylalane clearly is strongly dependent on the concentration and the solvent. Association with the aromatic hydrocarbons may also play a part.

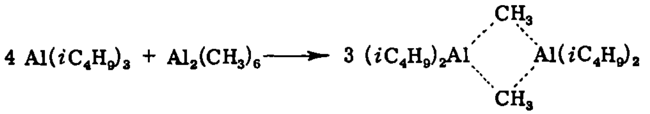
When any two trialkyl alanes are mixed, the alkyl groups undergo immediate exchange between the two aluminum atoms. The trialkyl alanes with different alkyl groups obtained in the equilibrium



$$AlR_3 + AlR'_3 \rightleftharpoons R_2Al\begin{array}{c}R\\ \\ R'\end{array}AlR'_2 \rightleftharpoons R_2AlR' + RAlR'_2$$

cannot usually be isolated in a pure form, as the energy of association in forming the bridges is in general very similar to that for the separate trialkyl alanes with the same radicals (*103, 307*). A similar rapid exchange of alkyl and aryl groups between trialkyl alanes and triphenylalanes is observed (*178*).

Detailed information on the nature and velocity of alkyl exchange may be obtained from cryscopic (*103*), calorimetric (*33*, *111*), infrared (*105*, *110*, *200*), Raman spectroscopic (*236*), and, particularly, nuclear magnetic resonance measurements (*84*, *104*, *106*, *185*, *263*, *264*). Particularly significant results (*111*) are obtained with mixtures of trialkylalanes, one of which in the pure form is a monomer [e.g., triisobutylalane (*103*, *307*), tri(1,3-dimethylcyclopentylmethyl)-alane (*139*)], and the other a dimer (trimethyl-, triethyl-, and tri-1-propylalane). Alkyl groups which are branched in the 2-position (e.g. 2-methyl-1-propyl) play practically no part in bridging two aluminum atoms. In addition, blocking groups of this kind on aluminum are also able to hinder dimerization by means of alkyl groups which are normally capable of forming bridges (e.g., CH_3, C_2H_5). Thus, whereas for $Al(CH_3)_3$ and $Al(iC_4H_9)_3$ all the methyl groups are built into the bridge as shown,



$$4\ Al(iC_4H_9)_3 + Al_2(CH_3)_6 \longrightarrow 3\ (iC_4H_9)_2Al(CH_3)_2Al(iC_4H_9)_2$$

association is greatly hindered in the mixed trialkyl alane derived from 2 moles of $Al(CH_3)_3$ and 4 moles of (1,3-dimethylcyclopentylmethyl)alane. Only dimethyl-1,3-dimethylcyclopentylmethylalane, $(CH_3)_2Al(iC_8H_{15})$, is fully dimerized. In mixtures of tri(1,3-dimethylcyclopentylmethyl)alane and higher trialkyl alanes (e.g., triethylalane, tri-1-propylalane) association may be completely suppressed; thus monomeric di(1,3-dimethylcyclopentylmethyl) alkyl alane is formed from dimeric trialkyl alanes. Alkyl exchange then takes place with loss of association energy, which shows itself as a measurable cooling effect on mixing (*33*, *111*). The driving force

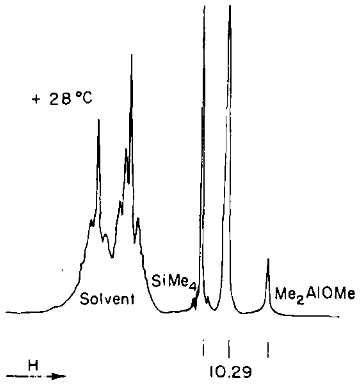


FIG. 1. H^1 NMR spectrum of $Al_2(CH_3)_6$ at +28°C in 40% solution in pentane; $[Al(CH_3)_2OCH_3]_3$ and $Si(CH_3)_4$ as internal standards. Only one signal for all the CH_3 protons of $[Al(CH_3)_3]_2$ [10.29 p.p.m. relative to $\tau = 0$ for $Si(CH_3)_4$] (*108*).

on the equilibrium which is established can therefore be only an increase in the entropy component.

The alkyl groups also exchange their position in the uniform trialkyl alanes. As a result, in studying the H^1 NMR spectra (Figs. 1 and 2), the two signals appropriate for the CH_2 or CH_3 groups in the AlC_2Al bridge and in terminal positions can be observed only in measurements at lower temperatures (−70° to −80°C); alkyl exchange is then practically frozen. At room temperature the signals for H^1 in CH_2 or CH_3 each combine to give one sharp signal. It follows that alkyl exchange must be very rapid. From the sharpness of the signal it is also possible to deduce that the life of a structural unit must be less than 10^{-3} sec (*84, 108, 109, 185, 263, 264*).

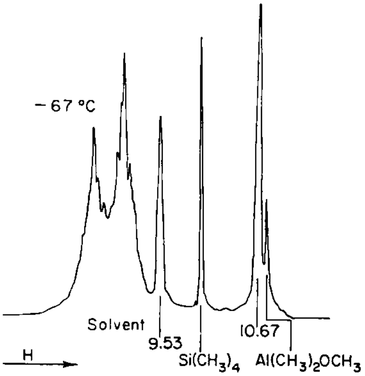
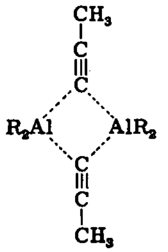


FIG. 2. H^1 NMR spectrum of $Al_2(CH_3)_6$ at −67°C in 40% solution in pentane; $[Al(CH_3)_2OCH_3]_3$ and $Si(CH_3)_4$ as internal standards. Two signals [10.67 p.p.m. for CH_3 bridge protons and 9.53 p.p.m. for other CH_3 protons of $[Al(CH_3)_3]_2$; $\tau = 0$ for $Si(CH_3)_4$] (*108*).

2. With Unsaturated Aliphatic Hydrocarbon Radicals

Bonding between two aluminum atoms through carbon bridges is very much stronger for unsaturated trialkyl alanes of the types $R_2AlCH{=}CHR'$ and $R_2AlC{\equiv}CR'$ than for saturated trialkyl alanes. These compounds must be strictly dimers, irrespective of the nature of R (*253, 259*):



H^1 nuclear magnetic resonance measurements have established that, at least for the dialkyl alkynyl alanes, bridge bonds are formed exclusively by the α-carbon atom of the alkynyl group (*30*). This bond is stronger for the alkynyl than for the alkenyl compounds. In accordance with this, the dialkylalkynyl alanes may be distilled at reduced pressure as dimers without decomposition, whereas the corresponding alkenyl compounds decompose when heated and then undergo further reaction, in which addition of the Al—C bond to the C=C double bond occurs. The resulting aluminum alkyls disproportionate subsequently to trialkylalane and polymeric compounds (*253*).

Dissociation of the dialkylalkenyl alanes clearly does not occur at lower temperatures (below 100°C) since the compounds are no longer able to undergo alkyl exchange. In the course of their preparation (from R_2AlH + $C\equiv C$) no $RAl(C{=}C)_2$ is found in addition to $R_2Al(C{=}C)$ even when excess alkyne is used. Dialkenylalkyl alanes and trialkenyl alanes must therefore be prepared by another route (cf. Section V,A,1). The fact that the dialkylalkenyl alanes are themselves associated means that they do not act as catalysts for alkyl exchange between different trialkyl boranes (*142*).

In some cases it has proved possible to isolate both possible *cis-trans* isomers of dialkyl-1-alkenyl alanes in a pure form. Triethylalane and acetylene yield the *cis*-butenyl compound (cf. Section V,C,2; for infrared spectrum see Fig. 3). Diethylaluminum hydride and 1-butyne, on the other hand, give the *trans*-butenyl compound (cf. Section V,B,4; for infrared spectrum see Fig. 4).

Deuterolysis gives the pure *cis*- or *trans*-1-deutero-1-butene (*102*, *254*). The differing behavior of the two isomeric diisobutyl-(4-methylpent-1-en-1-yl)-alanes on crystallization is particularly striking. The *cis* form is a crystalline compound with m.p. 59°–60°C, whereas the liquid *trans* form solidifies to a glass below 0°C (*235*, *259*). Interconversion of the *cis* and *trans* forms is impossible without dehydroalumination (*66*).

With increasing content of 1-unsaturated alkyl groups the stability of alkenyl and alkynyl alanes decreases. Trivinylalane is relatively unstable at room temperature; it polymerizes fairly rapidly to a glassy product. The lowest molecular weight found corresponds with a value between those for the dimer and trimer, and after standing for an hour the degree of polymerization increases 5–6-fold (*17*). Trialkynyl alanes and monoalkyldialkynyl alanes can be obtained only in the form of their 1:1 adducts with ethers, trialkylamines, or pyridine. The donor-free compounds decompose in the course of their preparation into dark-colored polymeric products, the structure of which has not yet been elucidated. The same is true of all ethynylalanes (including $R_2AlC\equiv CH$) (*235*, *259*).

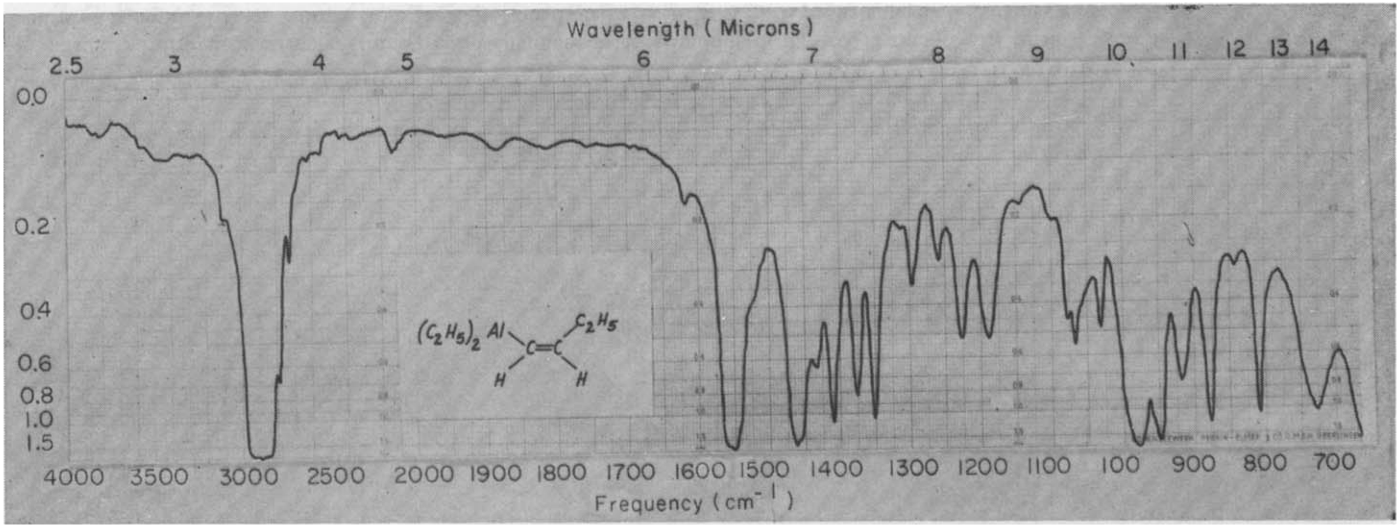


FIG. 3. Infrared-spectrum of *cis*-1-but-1-enyldiethylalane; undiluted, $d = 0.052$ mm (NaCl prism); ν_{max} (C=C): 1553 cm^{-1}; ν_{max} (CH=CH): 726 cm^{-1} (*235*).

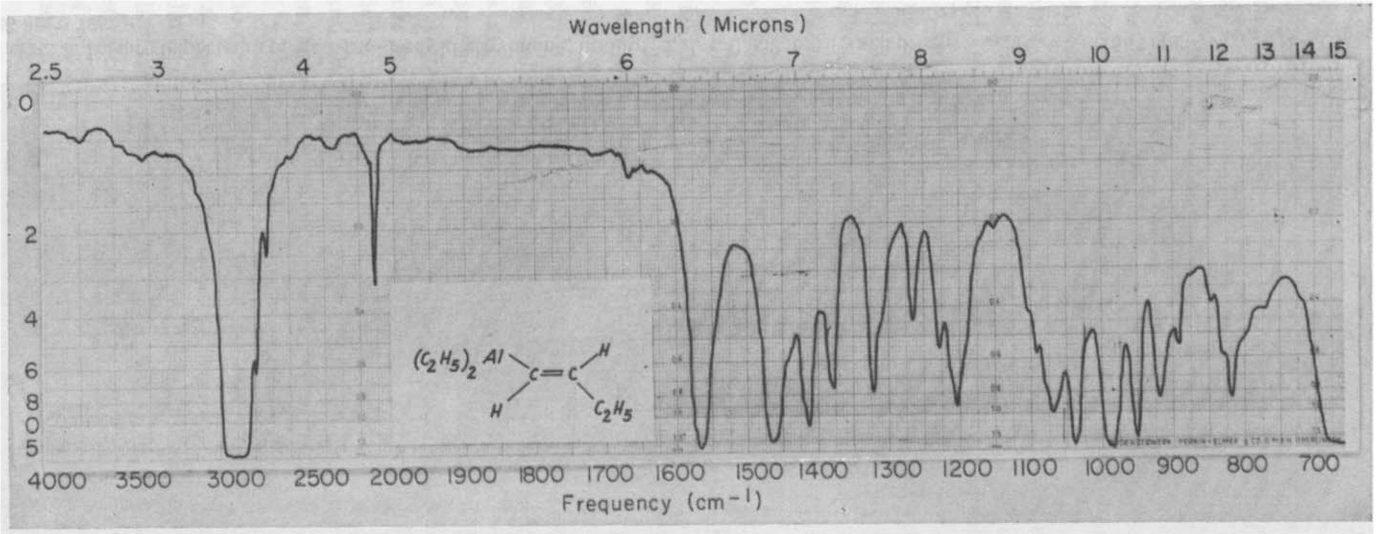


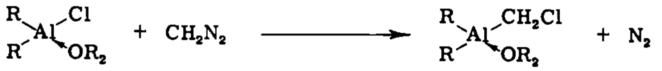
Fig. 4. Infrared-spectrum of *trans*-1-but-1-enyldiethylalane; undiluted, $d = 0.052$ mm (NaCl prism), ν_{max} (C=C): 1566 cm^{-1}. The infrared band at 2105 cm^{-1} arises from the C≡C bond of $(C_2H_5)_2AlC\equiv CC_2H_5$ present in small amount as impurity (*235*).

The special properties of the 1-unsaturated alkyl alanes are also very clearly recognizable in their infrared spectra. Because of the polarizing effect of aluminum the C═C vibration is shifted considerably to lower wavelengths and the band intensity is increased (for RCH═CHR, ν_{max} (C═C) = 1655 cm^{-1}; for $R_2AlCH{=}CHR'$, ν_{max} (C═C) = 1553 cm^{-1}) (*253*). The C≡C valency vibration for the free dialkylalkylethynyl alanes is at 2000–2030 cm^{-1}, and is lower by about 230 wave numbers than that for 1,2-dialkyl acetylenes (2240–2250 cm^{-1}). The infrared spectra of the following homologous diethyletherates illustrate the lowering effect of aluminum on the C≡C bond stretching frequency with increase in the number of alkynyl groups bonded to the metal (*259*):

Compound ($R' = C_2H_5$)	ν_{max}(C≡C stretching frequency) (cm^{-1})	
	R = H	$R = CH_3$
$(C_2H_5)_2AlC{\equiv}CR \leftarrow OR'_2$	1997	2150
$(C_2H_5)Al(C{\equiv}CR)_2 \leftarrow OR'_2$	2010	2150
$Al(C{\equiv}CR)_3 \leftarrow OR'_2$	2020	2165

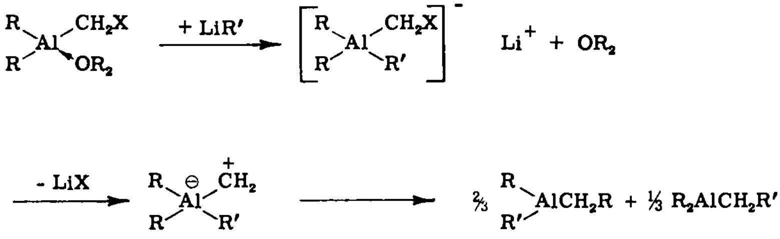
3. Alkyl Alanes Substituted in the Alkyl Chain

Substituents in the alkyl chain of alkyl aluminum compounds, such as halogens, alkoxy, alkylmercapto, or dialkylamino groups, have varying effects on the stability of the aluminum alkyls to extents which depend on the position of the group in relation to the aluminum. Interaction between the substituents and aluminum leads to activation of both the Al—C and the C-substituent bonds. If, in the case of dialkyl halomethylalanes, the substituent (Cl, Br, or I) and the aluminum are linked to the same carbon atom, the compound is especially reactive. These compounds, since their etherates are stable, may be prepared readily in ethereal solution from dialkyl aluminum halides and diazomethane (*97*, *98*):

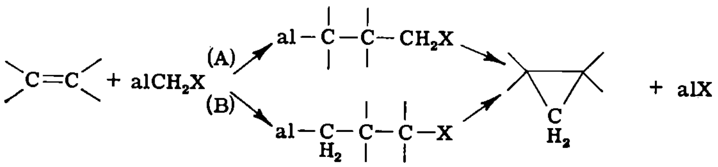


In the free state the compounds decompose at once into dialkyl aluminum halide and hydrocarbon (mainly ethylene with a little cyclopropane). But at very low temperatures (−80°C) it is possible to isolate, for example, iodomethyldiethylalane in hydrocarbon (pentane) solution (*97*, *98*).

A significant property of the halomethylalanes is their reaction with lithium alkyls: the complex salt formed from the etherate and a lithium alkyl immediately splits off lithium halide. Probably an "aluminumylide" is first formed and this stabilizes itself by migration of an alkyl group to the positively charged methylene group (*99*):



The Al—C bond in the halomethylalanes, in addition to the carbon-halogen bond, is highly reactive. Dialkyl halomethylalanes react with alkenes or alkynes even at room temperature with addition of the Al—C bond (route A, below) to the C=C double bond or the C≡C triple bond. Addition of the C—X bond (route B) is also possible, but has not yet been demonstrated with certainty. The resulting 3-halogenoalkyl alanes are unstable under the conditions of their formation and decompose to cyclopropane or cyclopropene and aluminum halide (*27*, *98*):

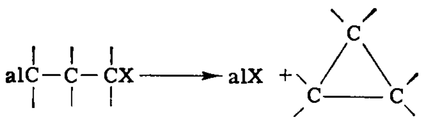


In the reactions of compounds of the halomethylalane type with compounds containing C=N double bonds (aldimines, ketimines, N heterocycles) both of these modes of reaction (A and B) have to be considered. So far, however, only the addition of CX to the C=N double bond has been detected with certainty (*99*).

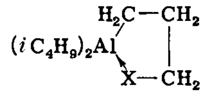
Alkyl alanes which are substituted at carbon-2 are likewise unstable in the free state. They undergo spontaneous decomposition with 1,2 elimination (*210*):

$$Al(iC_4H_9)_3 + (CH_3)_2CHCH_2OCH{=}CH_2 \xrightarrow[-iC_4H_8]{} (iC_4H_9)_2AlCH_2CH_2OCH_2CH(CH_3)_2 \xrightarrow[-C_2H_4]{} (iC_4H_9)_2AlOCH_2CH(CH_3)_2$$

The stability of alkyl alanes which are substituted in the 3-position depends very much on the nature of the substituent. Mention has already been made of 1,3 elimination of AlX from 3-halogenoalkyl alanes. Since the compounds are readily formed from the corresponding stable 3-halogeno-alkyl boranes by alkyl exchange, the decomposition to AlX and cyclopropane hydrocarbons:

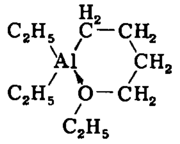


is demonstrated (*27*). In contrast to this, 3-alkoxy- and 3-dialkylaminoalkyl alanes are stable. Diisobutylaluminum hydride with allyl thioethers and allyl dimethylamines yields monomeric chelate compounds (with back-coordination), which have the following structure (*267*):

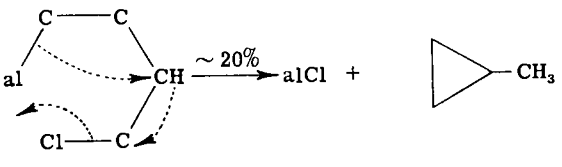


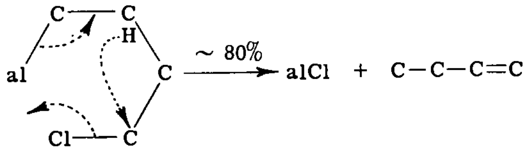
(where X = C_2H_5O, C_2H_5S, C_3H_7O, $(CH_3)_2N$). The 3-alkoxyalkyl alanes decompose at 190°–200°C to cyclopropane and alkoxy diisobutylalanes (*282*).

In the case of 4-ethyoxybutyldiethylalane the location of the substituents is so favorable that formation of a monomeric six-membered heterocyclic compound is preferred (*13*):



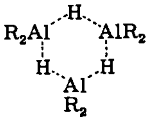
4-Chlorobutyldiethylalane, on the other hand, is far less stable. It decomposes even at 50°–60°C to $(C_2H_5)_2AlCl$, 1-butene (80%) and methylcyclopropane (20%). Cyclobutane, which might be expected, was not found, i.e., ring closure by 1,4 elimination is not favored. Consequently the molecule stabilizes itself by hydrogen migration (*27*):





C. ORGANOALUMINUM COMPOUNDS OF THE TYPES R_2AlX AND $RAlX_2$

Compounds of the type R_2AlX (X = H, halogen, OR, SR, NR_2) are usually strongly associated, the bond between two aluminum atoms being formed only by the substituents. The degree of association of such compounds depends on the nature of the substituents on the aluminum, and steric factors often play an important part. Dialkyl alanes, R_2AlH, in benzene solution are trimeric, irrespective of the alkyl groups bonded to aluminum (*103*, *247*). Some, such as di-1-alkyl aluminum hydrides, are also trimeric in phenanthrene at 100°C (*307*):

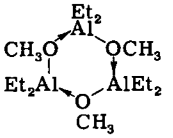


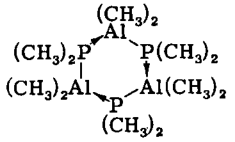
For diphenylalane, which was first made by the reaction

$$2Al(C_6H_5)_3 + AlH_3 \rightarrow 3(C_6H_5)_2AlH$$

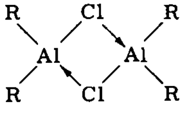
a degree of association of 2.4 in benzene solution was found (*244*).

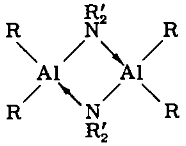
The following compounds are also trimeric (*56*, *103*):



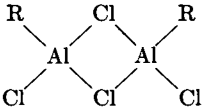


Dialkyl aluminum chlorides and dialkyl aluminum amides, R_2AlNR_2, are dimeric (*56*, *103*, *122*):

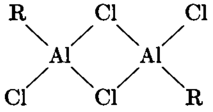




H¹ nuclear magnetic resonance studies show that the compounds known as "aluminum alkyl sesquichlorides" (*85*) occur at room temperature as association complexes of $RAlCl_2$ and R_2AlCl ($R = CH_3$, C_2H_5) with $AlCl_2Al$ bridging (*34*). It has, of course, not yet been possible to identify or even to separate the conceivable *cis* and *trans* forms of the $RAlCl_2$ dimers:



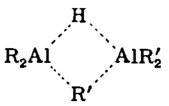
and

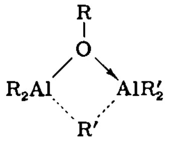


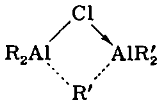
Evidently, the exchange equilibrium by means of the bridging is established too quickly.

Dimethylaluminum cyanide is tetrameric in benzene solution (*46*), while dimethylaluminum fluoride and diethylaluminum fluoride exhibit even higher degrees of association, which depend very much on the dilution (*294*).

When dialkyl aluminum hydride, chloride, or alcoholate is mixed with trialkyl alanes, rapid alkyl exchange takes place. This indicates that in such mixtures mixed association products such as



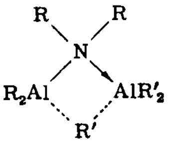




are present to a certain extent (*234*, *307*, *308*). With ethyl-ethoxyaluminum chloride, for example, it was possible to detect two different compounds which were in equilibrium (*233*):

At room temperature some 90% of the trimer (with AlOAl bridges) is present whereas, on heating, the dimer with Cl bridges becomes increasingly abundant. This example shows very elegantly the way in which different substituents are able to compete in bridge formation.

As a result of the exchange of substituents it is also possible, for example, to transform diethylaluminum chloride (*309*) and alcoholate (*310*) by ethylene addition into higher straight-chain dialkyl aluminum compounds. A small amount of trialkyl alane is added and this reacts with the ethylene. The long-chain alkyl groups are then transferred by alkyl exchange to the R_2AlCl or R_2AlOR. Synthetic reactions of this type are no longer possible with dialkyl aluminum alkylamides as mixed dimers of the type

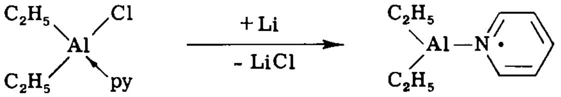


clearly cannot be formed. In this case association of the dialkyl aluminum alkylamide through AlN_2Al bridges predominates (*122, 308*).

D. FREE RADICALS OF ORGANOALUMINUM COMPOUNDS

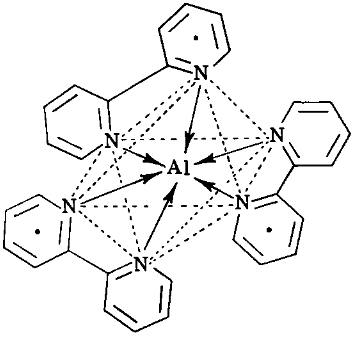
Free radicals of composition R_2AlX, where X = pyridine, 2,4,6-tri-*tert*-butylphenoxyl, can be obtained in various ways.

Very stable colored free radicals containing Al—N bonds are formed by the dehalogenation of, for example, pyridine-diethylchloralane in tetrahydrofuran with lithium at or below room temperature (*137*):



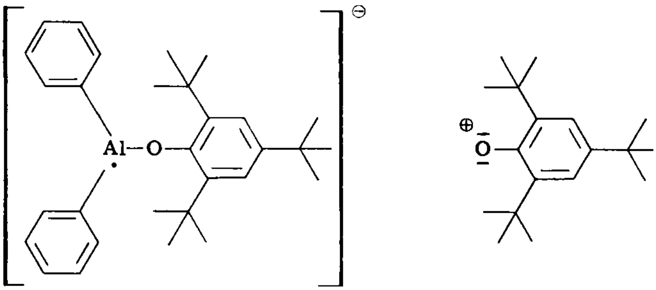
The compound is red-violet and gives an ESR signal with $g = 2.003$. By exchange between the corresponding BN free radical (diethylborylpyridine) and triethylalane, the diethylalanylpyridine radical is formed in good yield (*137*):

Similar free radicals with Al—N bonding but without hydrocarbon groups on the aluminum can be obtained either from the 3:1 adduct of 2,2′-dipyridyl and aluminum chloride by the action of dilithium-dipyridyl in tetrahydrofuran (*96*), or from lithium alanate and 2,2′-dipyridyl with spontaneous liberation of hydrogen (*96*). By analogy with the diethylalanylpyridine radical described above, the following structure for the complex $Al(dipyridyl)_3$ can be suggested:



The recently discovered AlO radicals (*183*) are markedly less stable than the AlN radicals; these are obtained, for example, from triphenylalane and the 2,4,6-tri-*tert*-butylphenoxyl radical in 1:2.01 molecular proportions.

Electron-spin resonance measurements indicate this product to be a radical complex for which isotopic investigations suggest the structure (*219*):

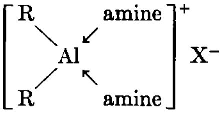


IV. Complex Compounds of Alkyl and Aryl Alanes

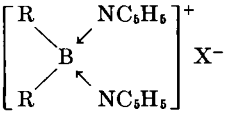
A. GENERAL CONSIDERATIONS

As compounds of coordinatively unsaturated trivalent aluminum, the organoaluminum compounds are Lewis acids and will combine with Lewis bases to form molecular compounds or complex anions.

Cations with complexed aluminum of the type known among organoboron compounds, e.g.,



analogous to



have not been described so far.*

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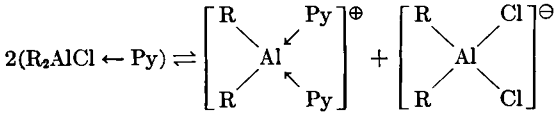
* Recently H. Lehmkuhl (Mülheim/Ruhr) has been able to prove the existence of such cations with aluminum by measuring transport number in the system $(C_2H_5)_2AlCl$/pyridine. He found that the 1:1 adduct dissociates according to the equation:

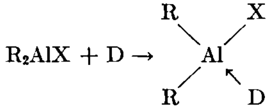


Suitable electron donators for organoalanes are amines (especially tertiary amines), ethers, or anions such as, for example, hydride, alkyl, alkoxy, or halogen. When organoaluminum compounds combine with these electron donors, compounds of tetravalent aluminum are formed. Stable anions with higher coordination numbers, i.e., analogs of $[AlF_6]^{3-}$, have not been observed so far among organoaluminum compounds.

As most alkyl alanes are dimers or trimers (cf. Section III,B,1), complex formation with Lewis bases must be preceded by dissociation of the association complex, or the latter process must at least occur simultaneously. The tendency to form a complex anion according to

$$R_2AlX + D^- \rightarrow [R_2AlXD]^-$$

or a neutral adduct according to



$$R_2AlX + D \rightarrow \begin{array}{ccc} R & & X \\ & Al & \\ R & & D \end{array}$$

increases with the strength of the Lewis acid (the monomeric aluminum alkyl R_2AlX) and with that of the Lewis base D or D^-. In forming the complex it is necessary to take into account at the same time the exchange equilibrium

$$R_2AlX + D^- \rightleftharpoons [R_2Al]^+ + X^- + D^- \rightleftharpoons R_2AlD + X^-$$

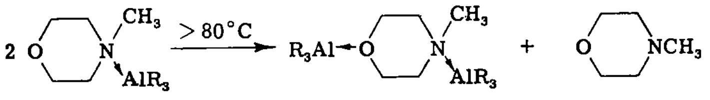
in which the hypothetical cation R_2Al^+ (*32*) unites with the negative substituents X^- or D^-. In general this will be combined with the strongest electron donors, and the acceptor properties of the resulting Lewis acid will then be weakened (*156*).

B. Neutral Addition Compounds

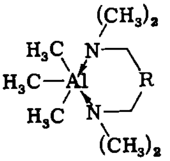
Trialkyl and triaryl alanes give stable 1:1 adducts with neutral donor molecules (e.g., ethers, thioethers, tertiary amines, tertiary phosphines):

$$R_3Al + D \longrightarrow R_3AlD$$

and these can in most cases be distilled (*304*). Bifunctional donors (e.g., dioxane, di-*tert*-amines, *N*-methyl-morpholine) usually add 2 moles of trialkyl alane (*30, 39*). At low temperatures a 1:1 complex may be made from *N*-methylmorpholine and triethylalane, but this decomposes on distillation into the 1:2 compound and free *N*-methylmorpholine (*30*):



The 1:1 adducts from trimethylalane and diamines, previously formulated:



[where R stands for —N=N—, $—CH_2—$, $—(CH_2)_n—$] with pentavalent aluminum (*74*, *75*), are, according to later findings, probably compounds with a tetravalent central atom (*177*):

$$(CH_3)_3Al \leftarrow N(CH_3)_2—R—N(CH_3)_2$$

The stability of 1:1 complexes with triethylalane decreases in the sequence (*304*):

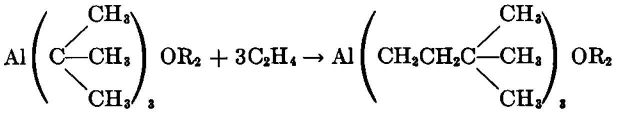
$$Me_3N > Me_3P > Me_2O > Me_2S > Me_2Se > Me_2Te$$

Accordingly, it is possible to displace a weaker donor by one which is stronger. Such exchange reactions have also been carried out with triphenylalane as acceptor (*175a*). The H^1 NMR spectra are measured for various complexes of triethylalane (*245*). New investigations of infrared spectra have been made (*122*).

The reactivity of the aluminum-carbon bonds is greatly reduced in the 1:1 adducts, and this may be utilized in preparing particularly labile organoaluminum compounds which cannot be isolated in the free form. Thus tri-*tert*-alkyl alanes, such as tri-*tert*-butylalane, may be prepared as etherates from tertiary butyl lithium in diethylether (*207*) or from the corresponding magnesium tertiary alkyls (*157*, *159*):

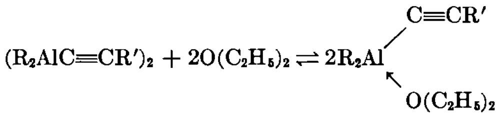
$$3(\textit{tert}\ C_4H_9)MgCl + AlCl_3 \xrightarrow{\text{ether}} (\textit{tert}\ C_4H_9)_3Al \leftarrow O(C_2H_5)_2 + 3MgCl_2$$

Triethynylalane and tripropynylalane were also prepared in this way from the corresponding sodium compounds as etherates (*43*, *219*). It may also be mentioned that the etherate of *tert*-butylalane adds ethylene smoothly at 100°C to give aluminum triisohexyl etherate without isomerization of the butyl group on aluminum (*159*) (cf. Section V,C,1):



$$Al\left(C(CH_3)_3\right)_3 OR_2 + 3C_2H_4 \rightarrow Al\left(CH_2CH_2C(CH_3)_3\right)_3 OR_2$$

Dialkyl aluminum hydrides and di- or monoalkyl aluminum halides (with the exception of dialkyl aluminum fluorides) also add the donors mentioned above; dialkyl aluminum alcoholates, on the other hand, form no adducts with ethers or amines (*101*, *304*). In some organoaluminum compounds the strength of the bridge bond in the associated form and of the coordinative bond in the etherate is about the same: in such cases the associated compound and the etherate will coexist in equilibrium. This situation exists for dialkyl aluminum hydrides (*304*) and also for dialkyl-1-alkenyl alanes and dialkyl-1-alkynyl alanes (*253*):



$$(R_2AlC{\equiv}CR')_2 + 2O(C_2H_5)_2 \rightleftharpoons 2R_2Al\begin{matrix} \diagup C{\equiv}CR' \\ \nwarrow O(C_2H_5)_2 \end{matrix}$$

In this case ether may be removed from the etherate by distillation at reduced pressure.

With other reactive donors such as alcohols, aldehydes, ketones, and carboxylic acids, organoaluminum compounds also form 1:1 adducts. Generally, however, these are not isolable, since the functional groups react further (cf. Section V,D). In a few cases, such 1:1 adducts can be identified, e.g., between triphenylalane and benzophenone (*176*) or benzonitrile (*175a*, *204*) at room temperature or between diethylaluminum bromide and alcohols, aldehydes, ketones, or carboxylic acids at −80°C (*217*).

C. SALTLIKE COMPLEXES WITH ALUMINUM IN THE ANION

1. Preparative Methods

a. Alkali Alkyl Alanates. The simplest method for preparing alkali alkyl alanates is the direct union of the components:

$$MX + AlR_3 \rightarrow M(AlR_3X)$$

(where X = H, CN (*149*), halogen, OR, R; M = alkali metal (*156*, *317*) NR'_4) (*59*). In the same way the complexes with anions $(R_2AlX_2)^{\ominus}$ (*299*) and $(RAlX_3)^{\ominus}$ (*237*, *299*) can be prepared. It is generally possible to operate without diluents, and temperatures up to about 100°C are usually adequate (*299*, *317*). A variant of this simple method is to prepare the alkali compound needed to form the complex (e.g., NaR) directly in the presence of the organoaluminum compounds. Thus methyl chloride and sodium with organoaluminum compounds $R_xAl(OR)_{3-x}$ ($x = 0$ to 2) in a suitable solvent (tetrahydrofuran, diethyleneglycol dimethyl ether) give the corresponding complex salt (*318*), eg.

$$2Na + CH_3Cl + AlR_2OR' \rightarrow Na[AlR_2ORCH_3] + NaCl$$

This reaction is unsuccessful with trialkyl alanes because the alkali metal reacts more rapidly with the aluminum compound than with the alkyl chloride, and as a result a quarter of the aluminum separates as metal:

$$4AlR_3 + 3Na \rightarrow 3NaAlR_4 + Al$$

Sodium tetramethylalanate may be prepared quite smoothly according to the equation

$$2Na(Hg) + CH_3Cl + Al(CH_3)_3 \xrightarrow{\text{diglyme, tetrahydrofuran}} NaAl(CH_3)_4 + NaCl + Hg$$

by using sodium amalgam in place of sodium and working in the presence of certain ethers. The sodium of the amalgam is unaffected by the diglyme— or tetrahydrofuran—trimethylalane but reacts with methyl chloride to give sodium methyl, which then combines with the trimethylalane (*160*, *323*). In preparing alkali metal tetraalkyl alanates, and particularly sodium tetraethylalanate, it is preferable to proceed by the roundabout route through the corresponding hydride complex, e.g., NaR_3AlH or $NaAlH_4$ (cf. Section II,A,1). These are readily transformed into the corresponding tetraalkyl alanates by the corresponding alkenes at 100°–150°C (*291*).

For the preparation of tetraalkylammonium trialkyl haloalanates, $(NR_4)^+ (AlR'_3X)^-$, an especially advantageous route has been described (*59*, *60*). Use is made in the direct reaction, e.g.,

$$(CH_3)_3N—Al(C_2H_5)_3 + C_6H_5CH_2F \rightarrow [(CH_3)_3NCH_2C_6H_5]^+[(C_2H_5)_3AlF]^-$$
$$(\text{m.p. } -50^\circ \text{ to } -47^\circ C)$$

of the energetically favorable interaction of the heterolytically cleaved compound and the donor-acceptor complex. The 1:2 complexes are formed directly by a corresponding reaction if excess of triethylalane is employed (*59*); as well as these, salts with nitrogen in the cation, phosphonium, stibonium, and telluronium complexes may be prepared (*60*).

Lithium tetravinylalanate may be prepared by a special method involving the reaction of lithium alanate with mercury divinyl (*17*).

It may be mentioned in this connection that complex compounds with aryl groups attached to aluminum may be made in the same way as for the alkyl series. Chlorobenzene and aluminum in the presence of sodium chloride yield a mixture of two complexes:

$$3C_6H_5Cl + Al + 2NaCl \rightarrow Na[AlC_6H_5Cl_3] + Na[Al(C_6H_5)_2Cl_2]$$

Unlike the corresponding alkyl compounds, the adduct of sodium chloride and the monochlorodiaryl alane is also stable (*171*, *260*) (cf. Section II,B).

Recently, numerous methods for the preparation of organoaluminum complexes have been published in which interconversion of the complex salts is brought about by displacement of the anion or cation (cf. Section IV,C,2). Mention may be made here of a synthesis which clearly is generally applicable to complex compounds with certain hydrocarbon radicals on aluminum. The acid hydrogen of 1-alkynes (*31*, *43*, *238*, *283*), acetylene (*31*, *127*), and for example, cyclopentadiene (*285*) reacts smoothly with the hydride of an organoaluminum complex (e.g., $MAlH_4$, $MAlR_3H$) with cleavage of hydrogen (cf. Section II,A,1); e.g.,

$$LiAlH_4 + 4HC{\equiv}CR' \xrightarrow[\text{catalyst}]{\text{amine as}} Li[Al(C{\equiv}CR')_4] + 4H_2$$

$$NaAlR_3H + 4CH{\equiv}CR' \rightarrow Na[AlR_3C{\equiv}CR'] + H_2$$

With acetylene both hydrogens are replaced by the R_3Al group:

$$2NaAlR_3H + HC{\equiv}CH \rightarrow Na_2[R_3AlC{\equiv}CAlR_3] + 2H_2$$

The reaction cannot be controlled so that it is arrested at the stage $Na[R_3AlC{\equiv}CH]$ (*31*).

At elevated temperatures the reaction may be applied to alkali tetraethylalanate and the alkali trialkylalkynyl alanate is formed with cleavage of alkane (*30*):

$$NaAlR_4 + HC{\equiv}CR' \rightarrow Na[AlR_3C{\equiv}CR'] + RH$$

A study of the complexes formed by alkali halides and hydrides with trialkyl alanes (*317*) has shown that the ease of formation increases with increasing radius of the alkali cation, but decreases with increase in size of the anion and increasing chain length of the alkyl radical linked to aluminum (cf. Figs. 5 and 6) (*156*).

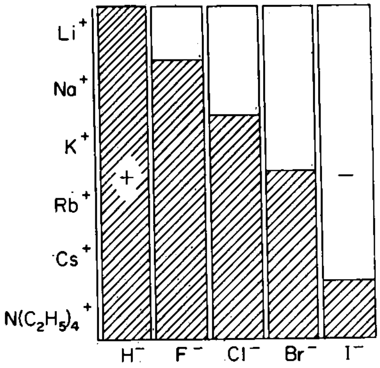


FIG. 5. The stability of complexes of alkali metal hydrides and halides with triethylalanes (*156*, *317*).

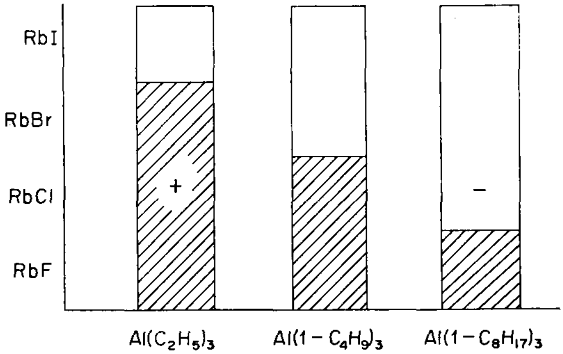


FIG. 6. The stability of complexes of rubidium halides with trialkyl alanes (*156*, *317*).

The decisive factor for a series of alkali halides with the same halogen is the decrease in lattice energy in passing from the lithium to the cesium halide. Account must also be taken of the reduction in the combination energy with increasing anion radius as halide ions are added to the alkylalane and with increasing length of the hydrocarbon chain of the trialkylalane (*156*, *294*, *317*).

Alkali halides or hydrides form two series of complexes with trialkyl alanes (*317*). As may be seen from Fig. 7, quite often the 1:1 complexes $M(AlR_3X)$ are able to add a further mole of the trialkyl alane complex to give 1:2 compounds of the type $M[Al_2R_6X]$ with X = H, F, Cl, Br, I, OC_6H_5. Trialkyl alanes no longer react with sodium fluoride to form stable 1:2 complexes if the alkyl radical has more than four carbon atoms. However, the fluorides of potassium, rubidium, and cesium are able to form

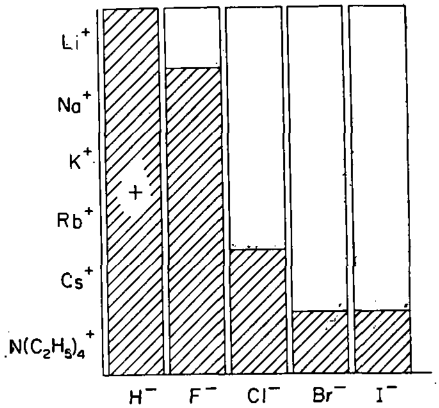


FIG. 7. The stability of the 1:2 complexes of alkali metal hydrides and halides with triethylalane (*156*, *317*).

1:2 complexes even with tri-1-octylalane (*317*). Definite complex compounds are also formed between some alkali pseudohalides and trialkyl alanes (e.g., triethylalane). In the system triethylalane–alkali cyanide (*317*) or triethylalane–alkali azide (*156*), however, the 1:1 compounds are not stable and only stable well-crystallized 1:2 complexes are found. The structure proposed originally for the 1:2 complex has in the meantime been verified by X-ray structural analyses (*2*, *187*)

Alkali alkyls or alcoholates and trialkyl alanes form only 1:1 complexes and no stable 2:1 compounds. On the other hand, various reactions indicate the formation of at least labile 2:1 complexes between triethylalane and sodium phenolate (*156*, *232*). The relationships become relatively complicated in mixtures with three different components, e.g., in the system alkali fluoride or hydride–triethylalane–diethylalane, in which up to 4 moles of aluminum compounds may combine with 1 mole of the alkali salt (*158*).

Thus lithium alanate forms stable 1:2, 1:3, and 1:4 adducts with triethylalane (*127*). The 1:2 adduct is crystalline (m.p. +29°C); the other compounds are liquids. On the other hand, if lithium alanate and triethylalane are mixed in 1:1 molecular proportions an alkyl-hydride exchange is the main result and a crystalline product of approximate composition $Li[(C_2H_5)AlH_3]$ is obtained (*127*).

The capacity to form complexes with alkali salts increases from triethylalane, through diethylaluminum chloride, to monoethylaluminum dichloride (cf. Fig. 8). With lithium chloride only the strongest Lewis acid in the series (ethylaluminum dichloride) forms a complex compound at room temperature, while potassium chloride forms a complex salt $K[Al(C_2H_5)_3Cl]$ even with aluminum triethyl; this can be isolated, even

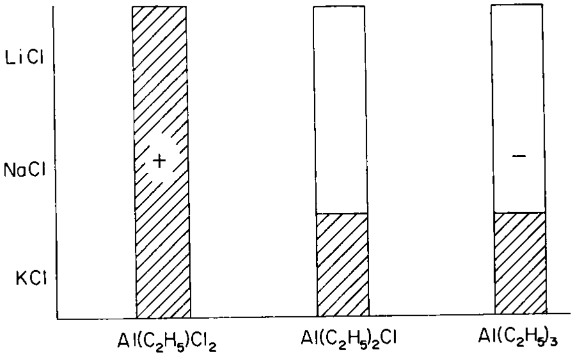


FIG. 8. The stability of the complexes of alkali metal chlorides with triethylalane and ethylchloroalanes (*156*).

though its stability is low (*317*). The adduct from KCl and $(C_2H_5)_2AlCl$ is relatively more stable, although it tends to disproportionate to potassium chloride, triethylalane, and the very stable potassium monoethyltrichloroalanate (*134*):

$$2K[Al(C_2H_5)_2Cl_2] \rightarrow KCl + K[Al(C_2H_5)Cl_3] + Al(C_2H_5)_3$$

Deviations from this general behavior are found with various alkyl aluminum alcoholates. Since alkoxy ions, OR′, are stronger Lewis bases than the halogen ions, the Lewis acidity of the dialkylalkoxy alanes formed with the hypothetical Lewis acid R_2Al^+ (*32*) is low, i.e., there is little tendency to form complexes with weak bases. Accordingly, diethylaluminum alcoholate forms stable salts with potassium and cesium fluoride but not with sodium fluoride. The tendency to form complexes (e.g., with KF and NaH) increases in going from R_2AlOR to $RAl(OR)_2$ (Fig. 9) (*156, 322*). Thus the smallest tendency to form complexes is found with dialkylalkoxy alanes (*156*). No plausible explanation of this has yet been advanced. A similar phenomenon is observed with the etherates and trialkylaminates of alkynyl alanes. The tendency to form stable addition compounds decreases from the trialkyl alane to the dialkylmonoalkynyl alane and then rises again in passing from the dialkynyl to the trialkynyl alane (*259*).

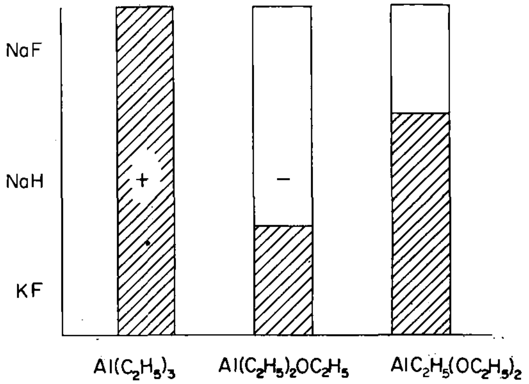


FIG. 9. The stability of the complexes of alkali metal hydrides and halides with triethylalane and ethylethoxyalanes (*156*).

b. Alkaline Earth Alkyl Alanates. In comparison with the complexes of trialkyl alanes with alkali halides and hydrides, little is known so far about the corresponding compounds of the alkaline earth halides with trialkyl alanes. According to recent investigations, the complexes from barium fluoride and hydride and triethylalane are stable (*158*). On the other hand, complex salts of all the alkaline earth alkyls and alcoholates with trialkyl alanes are known to exist. The alkyl magnesium complexes, $[RMg]^+[AlR_4]^-$ and $MR_2.2AlR_3$, have been known for a long time (*295*). In these the bond between the alkyl alane and the magnesium alkyl is only weak. The compounds are therefore split into their components [e.g., $Mg(C_2H_5)_2$ and $Al(C_2H_5)_3$] under reduced pressure at a little above 100°C. The same result is achieved by adding a suitable strong electron donor (triethylamine) (*83*, *295*).

Recently, the alkaline earth bis(tetraethylalanates) of calcium, strontium, and barium (see Table I) have been described (*155*). They are more stable thermally than the magnesium compounds, and those of calcium and strontium may be distilled without decomposition. The relatively high volatility of these substances indicates that they are less saltlike than the corresponding alkali compounds (*155*, *156*).

The alcoholates of calcium, strontium, and barium dissolve on warming in triethylalane in a manner analogous to that of the alcoholates of the alkalis, and compounds of the composition $M[Al(C_2H_5)_3OR]_2$ are obtained. When these viscous liquids are treated further with two moles of triethylalane per mole of the complex salt, diethylaluminum alcoholate is set free. The pure alkaline earth bis(tetraethylalanates) may thus be prepared according to the equation:

$$M[AlEt_3(OR)]_2 + 2AlEt_3 \rightarrow M[AlEt_4]_2 + 2Et_2AlOR$$

The more saltlike barium compound decomposes when distilled. Complete thermal breakdown of the alkaline earth bis(tetraethylalanates) gives triethylalane, ethylene, and alkaline earth hydride:

$$M[AlEt_4]_2 \xrightarrow[\text{10 torr}]{130^\circ\text{C}} MH_2 + 2C_2H_4 + 2AlEt_3$$

Hydride complexes $M[Al(C_2H_5)_3H]$ may possibly be formed as intermediates (*155*, *156*).

Although interaction of magnesium and mercury diethyl gives magnesium diethyl, analogous experiments with the remaining alkaline earth metals do not work. In the presence of triethylalane, however, it is possible to convert calcium, strontium, and barium into the complexes $M[Al(C_2H_5)_4]_2$ (*156*):

$$M + HgEt_2 + 2AlEt_3 \rightarrow M[AlEt_4]_2 + Hg$$

The alkaline earth metal bis(tetraethylalanates) are also formed in the following reaction:

$$MCl_2 + 2Na[AlEt_4] \rightleftharpoons M[AlEt_4]_2 + 2NaCl$$

This reaction does not go to completion. It can nevertheless be used for preparing the calcium and strontium compounds since these can be separated by utilizing their high solubility in cold benzene, in which sodium tetraethylalanate is insoluble (*156*).

Calcium bis(tetraethylalanate), which has little saltlike character, forms a stable crystalline adduct with 2 moles of tetrahydrofuran; its conductivity is 10^3 times greater than that of the ether-free compound. This probably arises from the fact that, when an electron donor is added, solvation of the cation to $[Ca(THF)_2]^{2+}$ takes place and this promotes ionization with the formation of $[Al(C_2H_5)_4]^-$ (*156*). It may be mentioned in this connection that the alkali tetraethylalanates from relatively stable 1:1 adducts with ethers [e.g., $K[Al(C_2H_4)_4]\cdot(C_2H_5)_2O$], whose conductivity is lower than the donor-free complex salt (*158*).

TABLE I
PROPERTIES OF SOME TETRAETHYLALANATES

Formula	Melting point (°C)	Remark	Crystal structure data (ref.)	H¹-NMR data (ref.)	Infrared data (ref.)
$LiAlEt_4$	~160 (*13a*)	Distillable	(*78*)	(*172*)	(*168*)
$NaAlEt_4$	126 (*319*)	Distillable with $AlEt_3$			(*168*)
$KAlEt_4$	72 (*71*)	—			
$CsAlEt_4$	112–114 (*158*)	—			
NEt_4AlEt_4	>160 decomposes (*156*)	—			
$Mg(AlEt_4)_2$	Liquid (*295*)	Decomposes			
$Ca(AlEt_4)_2$	41 (*155*)	Distillable			
$Sr(AlEt_4)_2$	109 (*155*)	Distillable			
$Ba(AlEt_4)_2$	138 (*155*)	Distillable and decomposes			

2. Exchange Reactions Involving Various Saltlike Organoaluminum Complex Compounds

a. Exchange Reactions of the Alanate Ion. (*i*) *General considerations.* As a result of equilibria involved in complex formation:

$$R_2AlX + Y^- \rightleftharpoons [R_2AlXY]^- \rightleftharpoons R_2AlY + X^-$$

on which may be superposed exchange processes such as:

$$R_2AlX + Y^- \rightleftharpoons R_2Al^+ + X^- + Y^- \rightleftharpoons R_2AlY + X^-$$

the interaction of Lewis acids (organoaluminum compounds) and Lewis bases (e.g., alkali compounds) in many cases does not lead to the formation of stable complex salts. Because of the substitution of one or more ligands on the aluminum, it is found in many cases that new aluminum compounds with a trivalent metal atom are formed.

There is always a tendency for the electron density on the aluminum to increase, and simultaneously for the acid character of the organoaluminum compounds to become weaker. In addition, the lattice energy of the alkali compounds and the association energy of the possible aluminum compounds involved in the equilibrium are of major significance (*156*).

For example, with the sodium salts, chlorine-fluorine exchange takes place (*294*) according to:

$$R_2AlCl + F^- \rightarrow [R_2AlClF]^- \rightarrow R_2AlF + Cl^-$$

Fluorine may also be displaced by alkoxy (*156*, *206*):

$$R_2AlF + OR^- \rightarrow R_2AlOR + F^-$$

Lithium salts differ in behavior from those of potassium, rubidium, and cesium. Thus in the case of lithium fluoride only chlorine-fluorine exchange takes place, whereas potassium, rubidium, and cesium fluorides add onto the alkyl aluminum fluorides and form stable complexes, $M[AlR_2F_2]$ (*294*). A similar complex is formed by sodium fluoride, but it breaks down at elevated temperatures ($>200°C$) to triethylalane and cryolite (*294*):

$$3Na[AlR_2F_2] \rightarrow Na_3AlF_6 + 2AlR_3$$

In the hydride-alkoxy system the sodium salts are only partly converted into NaH and $(C_2H_5)_2AlOR$ (*156*):

$$Et_2AlH + NaOR \rightarrow Na[Et_2Al(OR)H] \rightleftharpoons NaH + Et_2AlOR$$

Chloride attached to aluminum is readily replaced by hydride (*291*), and treatment of ethylethoxyaluminum chloride with sodium hydride leads to a replacement of this sort (*86*, *87*):

$$NaH + EtAlCl(OEt) \rightarrow EtAlHOEt + NaCl$$

Further hydride is then added to give the corresponding complex salt (*86*, *87*):

$$NaH + EtAlH(OEt) \rightarrow Na[EtAlH_2(OEt)]$$

The stability of these complex salts may be influenced by various added substances (e.g., ethers, tetrahydrofuran). Thus, although $Na[(C_2H_5)_2AlH(OR)]$ decomposes to NaH and $Al(C_2H_5)_2OR$, it is stable as the tetrahydrofuranate and may therefore be prepared readily from the components (*156*).

(*ii*) *Exchange of the alanate anion ligands.* Two different types of reaction may occur in exchange processes involving the anion of organoaluminum complex compounds, namely, displacements by Lewis acids (e.g., organoaluminum compounds) or Lewis bases (e.g., alkali compounds).

With Lewis acids: Displacement of an organoaluminum compound which is bound in a complex by a stronger Lewis acid may be used quite generally. Thus the more strongly acidic triethylalane may be incorporated quantitatively into the complex anion as shown in the equation (*156*, *319*):

$$M[AlEt_3OR'] + AlEt_3 \rightarrow M[AlEt_4] + Et_2AlOR'$$

(where $R' = C_2$ to C_{10}). In contrast to the diethylaluminum alcoholates, the acid character of diethylphenoxyalane and diethylaluminum *N*-methylanilide is similar to that of triethylalane and, as a result, reaction does not go to completion (*156*):

$$Na[AlEt_3OC_6H_5] + Et_3Al \rightleftharpoons Na[AlEt_4] + AlEt_2OC_6H_5$$

The 1:2 complex $Na[Al_2(C_2H_5)_6OC_6H_5]$ is also present in this equilibrium mixture (*156*), which may be displaced by distilling triethylalane, the most volatile component. Similar relationships exist in the system $Na[Al(C_2H_5)_4]$–$(C_2H_5)_2Al$–$NCH_3C_6H_5$ (*156*).

Similar exchange reactions are also possible between tetraalkyl alanates and trialkyl alanes. If the complexes $NaAlR_4$ and $NaAlR'_4$ have similar solubilities, all of the mixed compounds will be present. Otherwise exchange reactions will lead to separation of the complex salt with the lowest solubility. For example, reactions between sodium tetraethylalanate and trimethylalane or triphenylalane go practically to completion according to the equations (*319*):

$$3Na[Al(C_2H_5)_4] + 4Al(CH_3)_3 \rightarrow 3Na[Al(CH_3)_4] + 4Al(C_2H_5)_3$$
$$3Na[Al(C_2H_5)_4] + 4Al(C_6H_5)_3 \rightarrow 3Na[Al(C_6H_5)_4] + 4Al(C_2H_5)_3$$

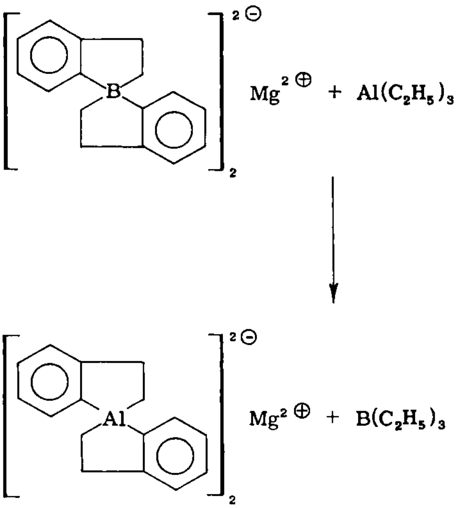
Trialkylalkynyl alanates are obtained from dialkylalkynyl alanes, which are more acidic than the trialkyl alanes (*30*):

$$Na[Al(C_2H_5)_4] + (C_2H_5)_2AlC{\equiv}CCH_3 \rightarrow Na[Al(C_2H_5)_3C{\equiv}CCH_3] + Al(C_2H_5)_3$$

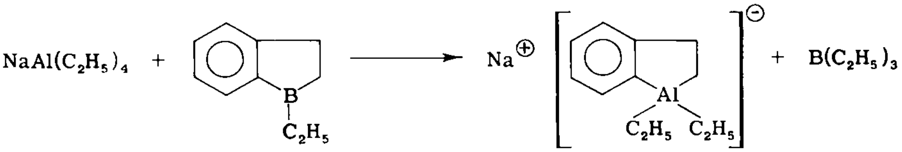
It is also possible to displace the weaker Lewis acid triethylborane from its complexes (*126*, *320*):

$$M[B(C_2H_5)_4] + Al(C_2H_5)_3 \rightarrow M[Al(C_2H_5)_4] + B(C_2H_5)_3$$

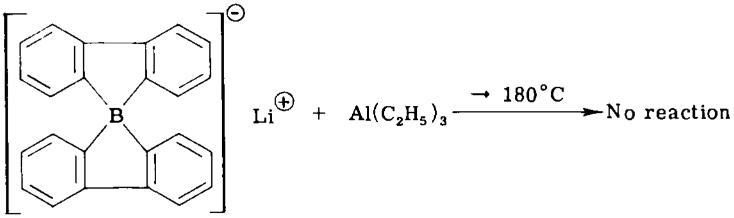
Sodium tetraphenylboranate reacts with triethylalane in the same manner (*126*, *138*). Also organospiroalanates can be made by alkyl exchange as shown in the following equation (*144*, *145*).



The exchange of boron and aluminum between boraindanes and NaAl-$(C_2H_5)_4$ is similar (*144, 145*).



In contrast to these reactions the lithium-bis(2,2′-diphenylyl)spiroboranate (*126, 262*) does not give the corresponding aluminum compound with triethylalane (*138*).



Alkali trialkylalkoxy alanates (*322*) react with trialkyl boranes to give alkali tetraalkyl boranates (*321*). In this case the weakly acidic dialkylalkoxy alane is displaced by the more acidic trialkyl borane:

$$\mathrm{Na[AlR_3OR']} + \mathrm{BR_3} \rightarrow \mathrm{NaBR_4} + \mathrm{R_2AlOR'}$$

The same result is obtained by starting with trialkyl alanes and sodium trialkylalkoxy boranates, which are readily made from NaOR and BR_3 (*29*):

$$Na[BR_3OCH_3] + AlR_3 \rightarrow NaBR_4 + R_2AlOCH_3$$

Exchange reactions are also known between two complexes containing aluminum [e.g., $NaAlH_4$ and $NaAl(C_2H_5)_4$]. Depending upon the reactant ratio employed, the mixed anions triethylalanate, $[Al(C_2H_5)_3H]^-$, and diethylalanate, $[Al(C_2H_5)_2H_2]^-$, are obtained, although monoethylalanates cannot be made in this way (*127*). Mixtures of sodium tetraethylalanate (m.p. 128°C) and sodium tetramethylalanate (m.p. 240°C) have only one eutectic (m.p. 83°C) at a 1:1 molar ratio (cf. Fig. 10). Dystectics do not occur. In spite of this, however, there seems to be no reason on general grounds why the formation of complexes with a mixture of alkyl groups should be excluded:

$$Na[Al(CH_3)_4] + Na[Al(C_2H_5)_4] \rightleftharpoons Na[Al(CH_3)_3(C_2H_5)] + Na[AlCH_3(C_2H_5)_3]$$

The melting point diagram (Fig. 10) indicates a rapid exchange process only for similar radicals (*319*).

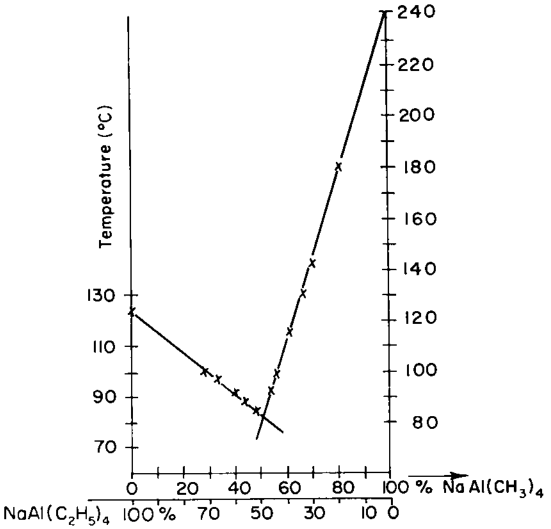


FIG. 10. Melting point diagram for $NaAl(CH_3)_4$–$NaAl(C_2H_5)_4$ system; eutectic at 83°C (1:1 mixture) (*319*).

With Lewis bases: Just as a Lewis acid (e.g., AlR_3, R_2AlOR) may be displaced from a complex, it is also possible to replace anions of a weaker electron donor X^- by those of a stronger donor Y^-:

$$[R_3Al \leftarrow X]^- + Y^- \rightleftharpoons [R_3Al \leftarrow Y]^- + X^-$$

Thus ether may be displaced from triethylalane etherate with sodium or potassium fluoride or amine from triethylalane aminate with potassium fluoride. Saltlike compounds of the type $M[Al(C_2H_5)_3F]$ are obtained and the fluoride can also be replaced readily by treating with the hydride of M:

$$Na[AlR_3F] + NaH \rightarrow Na[AlR_3H] + NaF$$

On the basis of many studies of such exchange reactions it has been possible to draw up an order of basicity for anions in their reaction with organoaluminum compounds (*156*):

$$I^- < Br^- < Cl^- < F^- < H^- \leq Et^- < OPh^- < (OC_nH_{2n+1})^-$$

It follows from this series that sodium alcoholate, for example, will be able to liberate sodium hydride (as the salt with the weaker basic hydride ion) from sodium triethylalanate (*156*):

$$Na[AlEt_3H] + NaOC_{10}H_{21} \rightarrow NaH + Na[AlEt_3OC_{10}H_{21}]$$

The basicity series also enables the preparation of sodium tetraphenylalanate from sodium tetraethylalanate (see Section II,B), in which NaOR or NaC_6H_5 is catalyst, to be explained (*156*, *232*, *281*).

b. Exchange of the Cation of Organoaluminum Complex Compounds. Cation exchange has been studied in detail (*156*) in the case of reaction between alkali tetraethylalanates and halides of other alkali metals. In the equilibrium

$$Na[Al(C_2H_5)_4] + KCl \rightleftharpoons KAl(C_2H_5)_4 + NaCl$$

the value of the quotient

$$\frac{[KAlEt_4][NaCl]}{[NaAlEt_4][KCl]}$$

is about 4–9. Cation exchange with a bulky univalent cation (e.g., $N(C_2H_5)_4^+$, $Sb(C_2H_5)_4^+$) goes almost to completion (*156*):

$$[ElEt_4]I + Na[AlEt_4] \rightarrow [ElEt_4][AlEt_4] + NaI$$

(where El = N, P, Sb). Exchange between complex salts and free alkali metals is also possible: alkali amalgams are used for preparative work. The reaction

$$NaAlEt_4 + K(Hg)_x \rightarrow Na(Hg)_x + KAlEt_4$$

may be used in the quantitative preparation of potassium tetraethylalanate from the sodium salt. If aluminum (inactivated form) is used instead of the alkali metal, all the ethyl groups of the alanate may be used to form triethylalane (*319*) (cf. Section II,A,2):

$$3NaAlEt_4 + 3xHg + Al \rightarrow 4AlEt_3 + 3Na(Hg)_x$$

The exchange reaction of the 1:2 adduct of NaF and $Al(C_2H_5)_3$ with potassium amalgam also proceeds smoothly to give the corresponding adduct of KF. On the other hand, the exchange involving the 1:1 complex $NaAl(C_2H_5)_3F$ is markedly less effective, and this is also true for exchange reactions in the system $NaAl(C_2H_5)_3OR/K(Hg)_x$ (*156*).

3. Uses of Organoaluminum Complex Compounds

Organoaluminum complexes have proved useful as electrolytes in the preparation of purest metallic aluminum (*59, 305*) and of the alkyls of various elements (e.g., HgR_2, PbR_4, SbR_3) from the metals (*324*). In the electrochemical synthesis of tetraethyllead (and in similar processes involving other metals), sodium serves as a carrier for ethyl groups in the reaction sequence Na → NaH → NaC_2H_5. Mixtures such as that of sodium tetraethylalanate and sodium triethylfluoroalanate are especially good electrolytes. The latter is transformed during electrolysis into the 1:2 complex $Na[Al_2(C_2H_5)_6F]$ as the ethyl sodium is used up:

$$NaAl(C_2H_5)_4 + pb(anode) + xHg(cathode) \xrightarrow{NaAlEt_3F} Na(Hg)_x + pbC_2H_5 + Na[Al_2(C_2H_5)_6F]$$

$$pb = \tfrac{1}{4}Pb$$

The ethyllead compound may be separated in this way from electrolytes which contain no free triethylalane (*299, 324*). Alkali tetraethylalanates are also very suitable for the preparation of the alkyls of various elements from their halides. Aluminum is present in the end product as alkali tetrachloroalanate (*117*). Quite often only MR in $MAlR_4$ exerts an alkylating action:

$$nNaAlR_4 + MX_n \rightarrow nNaX + nAlR_3 + MR_n$$

In many cases, of course, the corresponding AlR_3 also alkylates (see Section V,A,2). These reactions may also be carried out so that the actual reactants are formed in the mixture. The following variation has been proposed (*77, 228*):

$$NaAlEt_4 + EtCl + \tfrac{1}{4}Sn \rightarrow NaCl + AlEt_3 + \tfrac{1}{4}SnEt_4$$

V. Reactions of Organoaluminum Compounds

A. Reactions of Organoaluminum Compounds with Other Metal Compounds

1. Alkyl and Aryl Exchange Reactions

Exchange reactions between trialkyl or triaryl alanes and metal alkyls or aryls have been described for elements of the second (Mg), third (B), and fourth (Pb) main groups of the periodic system and also for the second subgroup (Zn, Cd, Hg). The intermediates in the ligand exchange must involve association between the trialkyl alanes and the alkyls of the elements in question. When exchange occurs rapidly it is necessary to suppose that the intermediate addition compounds which determine the exchange are relatively unstable, i.e., equilibrium between the alkyls of the element and of aluminum is established very rapidly:

$$R_3Al + R'El \rightleftharpoons R_2AlR' + REl$$

Trialkyl alanes also form association products with the alkyls of the alkali and alkaline earth metals, but these are very stable and some are saltlike complexes (cf. Section IV,C). An alkyl exchange such as

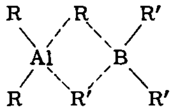
$$LiR' + AlR_3 \xrightarrow[20°C]{} Li[AlR'R_3] \nrightarrow LiR + AlR_2R'$$

does not therefore take place. In contrast to this, alkyls of zinc and cadmium exchange their alkyl groups with trialkyl alanes very rapidly. This may be detected by nuclear magnetic resonance spectroscopy (*166*). Exchange between hydride and ethyl has also been observed for diethylaluminum hydride and the ethyls of zinc, cadmium, mercury, and magnesium. The resulting hydrides of the first three metals decompose as shown (*278*):

$$2(C_2H_5)_2AlH + M(C_2H_5)_2 \rightarrow Al(C_2H_5)_3 + \underset{\displaystyle M + H_2}{\underset{\downarrow}{MH_2}}$$

Magnesium hydride, MgH_2, can be isolated.

Alkyl and aryl exchange reactions between trialkyl alanes and trialkyl or triaryl boranes have been very fully investigated (*133*). The exchange of ligands, which occurs very rapidly even at room temperature, occurs through the association products like:



The mixed associates cannot, however, be isolated and it is not yet known if the extent of association is sufficiently great to be detected by the usual methods (e.g., cryoscopy). To explain the readiness of exchange it is sufficient to assume that association occurs, although the equilibrium involved may correspond with almost complete dissociation. In connection with the exchange between alkyls (or aryls) of boron and aluminum, it may be noted that the trialkyl boranes, unlike the aluminum compounds, exist only as monomers. That they exchange alkyl radicals only with the aluminum compounds may be taken as conclusive proof that the trialkyl boranes are completely unassociated (i.e., not even below the limits of detection).

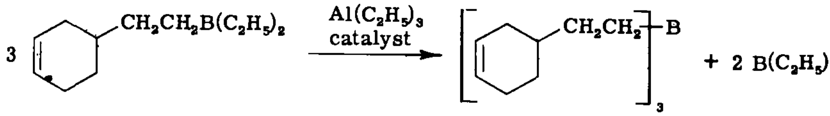
Some of the simple trialkyl alane–trialkyl borane systems have been studied fully with reference to the position of the exchange equilibria (*133*). It has been found, for example, that for an equimolar mixture of triethylalane and tri-1-butylborane, which reaches equilibrium very rapidly at or below room temperature, ethyl and butyl groups are equally distributed between the two elements. The fact that the equilibrium constant

$$K = \frac{[\mathrm{al}—1—C_4H_9][\mathrm{b}—C_2H_5]}{[\mathrm{al}—C_2H_5][\mathrm{b}—1—C_4H_9]}$$

is practically unity evidently depends on the close similarity of the ethyl and 1-butyl groups as units in the structures, and also on their other properties. The situation is different if the groups which compete for places around the central atoms are more dissimilar than those mentioned. Thus, with equimolar quantities of trimethylalane and tri-1-butylborane, the ratio of methyl to 1-butyl groups bonded to aluminum is about 3.5:1 ($K \sim 12$). In the system aluminum–boron–isobutyl–ethyl the equilibrium constant is about 3.5, which is connected with the different degrees of association of triethylalane (a dimer) and triisobutylalane (practically a monomer). When ethyl groups in this mixture transfer from boron to aluminum, there is a gain in association energy. The value of the equilibrium constant in the system aluminum–boron–methyl–1-butyl may be explained similarly. There are a number of indications that trimethylalanes are the most strongly associated of all the tri-1-alkyl alanes.

Exchange reactions between trialkyl alanes and either trialkyl or triaryl boranes and similar organoboron compounds have found various applications in both preparative and analytical chemistry. Triethylalane has been particularly useful since triethylborane produced in the exchange equilibrium may be removed very simply from the mixture by distillation. A convenient way of elucidating the constitution of unknown alkyl or aryl boranes is to carry out alkyl exchange with triethylalane and to follow this by hydrolysis (or deuterolysis) of the resulting organoaluminum compounds. In this way one obtains hydrocarbons (or deuterated hydrocarbons) which may be further studied by the usual analytical methods.

Trialkyl alanes may be used, like boron hydride derivatives (e.g., tetraalkyl diboranes), as catalysts for the alkyl exchange between two different trialkyl boranes (*133*). The AlR_3 compounds are particularly suitable for bringing about the disproportionation of mixed dialkylalkenyl boranes (e.g., diethylalkenyl boranes), which result from the partial hydroboronation of dienes with tetraethyldiboranes under the mildest possible conditions. The products are triethylborane and the trialkenyl boranes (*142*), e.g.,



If, however, the double bond is in the 1-position of the alkyl group, the trialkyl alane no longer catalyzes the exchange reaction because the completely dimerized dialkylalkenyl alane is formed at once (*29*):

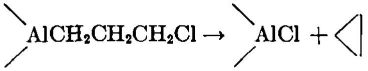
$$2R_2BC{=}C{-}R' + 2AlR_3 \rightarrow (R_2AlC{=}C{-}R')_2 + 2BR_3$$

Alkyl aluminum halides and alkyl aluminum alcoholates are also inactive as catalysts for the ligand exchange between trialkyl boranes (*133*).

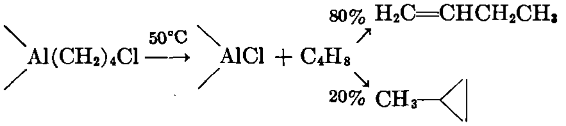
A large number of different types of organoaluminum compounds, either difficult or impossible to prepare by the usual methods, may be made by alkyl exchange with the more readily prepared organoboron compounds. In addition to trialkyl alanes (*133*) it is possible to obtain in this way cyclopropylalanes (*28*), halogenated alkyl alanes (*27*), and various organoaluminum heterocycles (*135*, *136*), e.g.,

$$Al(C_2H_5)_3 + (C_2H_5)_2BCH_2CH_2CH_2Cl \rightarrow (C_2H_5)_2AlCH_2CH_2CH_2Cl + B(C_2H_5)_3$$

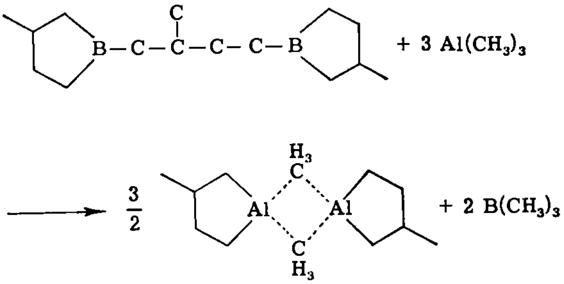
Exchange studies have shown, among other things, that the 3-chloropropylalanes are unstable even at room temperature. Spontaneous decomposition occurs to give cyclopropane and the aluminum halide:



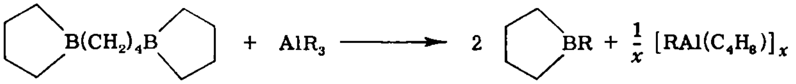
4-Chloro-1-butylaluminum compounds made in this way can, on the other hand, be isolated, although here also >Al—Cl splits off from the chloroalkyl aluminum group above 50°C. A mixture of 1-butene and methylcyclopropane is formed simultaneously (*27*):



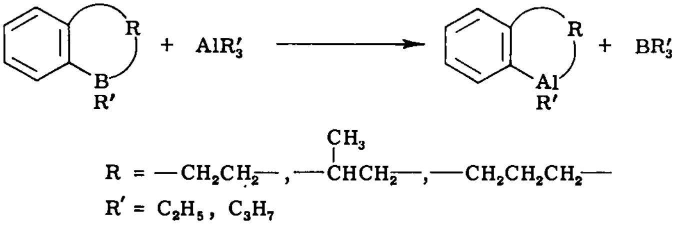
Alkyl exchange is also quite generally applicable to the preparation of 5- and 6-membered aluminum heterocycles. Thus, for example, bis-borolanyl alkanes and trialkyl alanes in a molar ratio of 1:3 to 1:4 react to form trialkyl boranes and 1-alkyl aluminacyclopentanes (*135*):



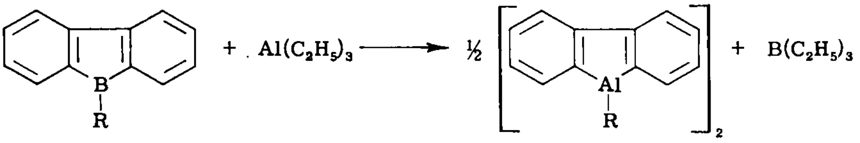
The aliphatic Al heterocycles are dimers changing above 100°C to high molecular weight compounds which are glasses at room temperature (*135*). When a bis-borolanyl alkane and a trialkyl alane are mixed in a 1:1 molar ratio, the products are the alkyl borolane and a high molecular weight aluminum compound which is bifunctional with respect to its hydrocarbon groups (*130*):



From 1 mole of 1-alkyl-boraindane or -tetralin (*131, 132, 141*) and 1 to 1.5 moles of trialkyl alane, distillation of the trialkyl borane gives an excellent yield of the well crystallized 1-alkyl-alumina-indanes or -tetralins (*135*):



Similarly, the yellow (monomeric) 9-alkyl or 9-aryl borafluorenes (*136, 141*) with triethylalane give (*136*) the colorless (dimeric) crystalline 9-alkyl or 9-aryl aluminafluorenes (*64, 136*):



1-Alkyl-alumina-indanes and -tetralins (see Table II) are dimers in solution (e.g., in benzene). They split off trialkyl alanes when heated to 120°–140°C at very low pressure. 1-Propylaluminatetralin gives tripropylalane and a crystalline compound with the empirical formula $C_{27}H_{30}Al_2$ (*135*). This is monomeric in benzene solution, and, since association by means of AlR_2Al bridges is assumed, must become saturated by means of intramolecular bonding: this is possible in the following way:

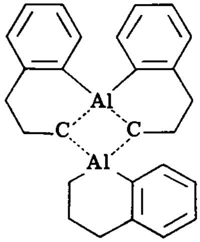


TABLE II

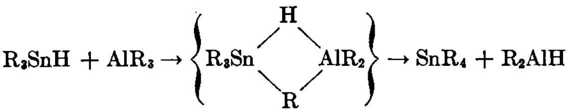
HETEROCYCLIC ORGANOALANES[a]

Compound	Melting point (°C)
1-Propyl-1-aluminaindane	52 (*135*)
1-Ethyl-3-methyl-1-aluminaindane	102 (*135*)
1-Propyl-3-methyl-1-aluminaindane	105.5 (*135, 143*)
1-Propyl-3-phenyl-1-aluminaindane	175 (*143*)
4-Propyl-cyclopenta[b]-4-aluminaindane	~25 (*143*)
5-Propyl-cyclohexa[b]-5-aluminaindane	Viscous liquid (*143*)
4-Propylcyclopenta[b]-4-aluminatetralin	Viscous liquid (*143*)
1-Propyl-1-aluminatetralin	Liquid (*135*)
Bis(1-aluminatetralinyl)propylbenzene	137–139 (*135*)
9-Phenyl-9-aluminafluorene	225–230 (*64, 136*)

[a] Numbers in parentheses indicate references.

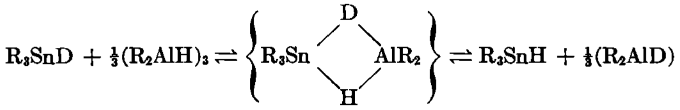
With the elements of the fourth main group of the periodic system, alkyl exchange at about 100°C has been detected so far with the aid of C^{14}-labeled alkyl groups between tetraethyllead and triethylalane (*189*). Ligand exchange also occurs to a small extent between tetraphenyl-tin or -lead and C^{14}-labeled triphenylalane (*190*). Such exchange processes have so far not been used on a preparative scale.

Trialkyl stannanes and trialkyl alanes react according to the equation:



$$R_3SnH + AlR_3 \rightarrow \left\{ R_3Sn\overset{H}{\underset{R}{\diamond}}AlR_2 \right\} \rightarrow SnR_4 + R_2AlH$$

Equilibrium lies completely over on the right-hand side, and the reaction has been used to accelerate the polar addition of 1-alkenes to the Sn—H bond (*198*). On the other hand, equilibrium is very rapidly established at 50°C between, for example, R_3SnD and R_2AlH. This must involve SnHDAl bridges, and hydrogen and deuterium are found to be distributed uniformly between the two metal atoms (*197*):



$$R_3SnD + \tfrac{1}{3}(R_2AlH)_3 \rightleftharpoons \left\{ R_3Sn \overset{D}{\underset{H}{\diamond}} AlR_2 \right\} \rightleftharpoons R_3SnH + \tfrac{1}{3}(R_2AlD)$$

2. *Alkylation and Arylation of Other Metal Compounds*

Alkyl derivatives of some elements of the second (Be), third (B, Ga, In, Te), fourth (Si, Ge, Sn, Pb), and fifth (P, As, Sb, Bi) main groups and of the second subgroup (Zn, Cd, Hg) of the periodic table may be prepared with alkyl alanes according to the general equation (*117*, *303*):

$$\text{al R} + \text{el X} \rightleftharpoons \text{el R} + \text{al X}$$

(where al = $\frac{1}{3}$Al; el = $\frac{1}{n}El^{(n)}$; X = halogen, OR). In some cases equilibria have been observed (e.g., El = Be, Si, Sn; X = Cl). In most cases (e.g., for Ga, In, Si, Sn) the chloride of the element in question is especially suitable. Fluorides have also been used (e.g., for B, Si). Oxides, on the other hand, are useful only in exceptional cases (e.g., boroxines, siloxanes) since they are often difficult to decompose (e.g., B_2O_3, SnO_2, SiO_2). In contrast to this, alcoholates of the elements are often quite useful for preparing alkyl compounds.

In considering the usefulness of this method of synthesizing alkyls from alkyl alanes, one factor which is often decisive is the number of alkyl groups on the aluminum compounds which are available for alkylation. The reactivity of an Al—R bond depends on the number and nature of the other substituents attached to aluminum. Reactions which occur smoothly with the first Al—R bond of the trialkyl alanes are often impossible with the second and third. Dialkyl aluminum halides, R_2AlX, and monoalkyl aluminum dihalides, $RAlX_2$, are substantially weaker alkylating agents than the trialkyl alanes. Similar gradations are also found in the reactivity of $El^{(n)}X_n$, $El^{(n)}RX_{n-1}$, and $El^{(n)}R_2X_{n-2}$ toward the same aluminum compound (e.g., AlR_3, R_2AlX).

The action of triethylalane on beryllium chloride leads to an equilibrium mixture:

$$Al(C_2H_5)_3 + BeCl_2 \rightleftharpoons (C_2H_5)_2AlCl + C_2H_5BeCl$$

The resulting ethylberyllium chloride can be converted into diethylberyllium by treatment with sodium hydride followed by ethylene (*181*):

$$C_2H_5BeCl \xrightarrow[-NaCl]{+NaH} C_2H_5BeH \xrightarrow{+C_2H_4} (C_2H_5)_2Be$$

Trialkyl boranes may be prepared readily from alkyl alanes [e.g., AlR_3, R_2AlX, $RAlX_2$, R_2AlOR', $RAl(OR')_2$] and various boron compounds [e.g., $NaBF_4$, $BF_3 \cdot OR_2$, BCl_3, $B(OR)_3$, $(RBO)_3$, $(ROBO)_3$]. This topic has already been dealt with in full (*117*, *303*). At this point reference will be made only to the particularly smooth synthesis of trialkyl boranes by allowing either B-trialkyl boroxines or B-trialkoxy boroxines to react with trialkyl alanes (*7*, *117*, *129*), according to the equations:

$$(RBO)_3 + 2AlR_3 \rightarrow 3BR_3 + Al_2O_3$$

$$(ROBO)_3 + 3AlR_3 \rightarrow 3BR_3 + (RO)_3Al + Al_2O_3$$

Since the boroxines are readily available from B_2O_3 and trialkyl boranes or trialkoxy boranes, they are in effect reactions of boron oxide with trialkyl alanes. Gallium tribromide and triethylalane give triethylgallane in over 80% yield, but only the first alkyl group on aluminum is involved in alkylation (*63*, *65*):

$$GaBr_3 + 3AlR_3 \rightarrow GaR_3 + 3R_2AlBr$$

The reaction between triethylalane and gallium chloride is analogous (*58*, *59*, *63*, *65*); in order to utilize the second ethyl group of the triethylalane for the ethylation of the gallium, a complex-forming agent (e.g., KCl) must be added. Thereby adducts from 1 mole $GaCl_3$ and 3 moles $(C_2H_5)_2AlCl$ (*65*), obtained according to the equation

$$3Al(C_2H_5)_3 + 2GaCl_3 \rightarrow Ga[(C_2H_5)_2AlCl_2]_3 + Ga(C_2H_5)_3$$

are also cleaved, and in the presence of potassium chloride the reaction

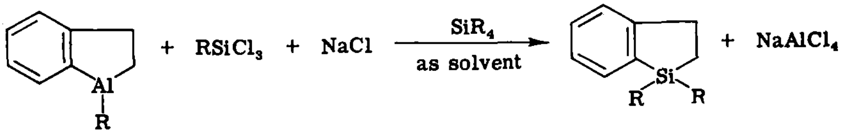
$$Ga[(C_2H_5)_2AlCl_2]_3 + 3KCl \rightarrow Ga(C_2H_5)_3 + 3K[AlCl_3(C_2H_5)]$$

leads to the formation of more triethylgallane (*63*, *65*).

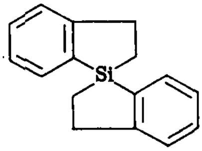
Indium halides behave similarly to gallium halides in their reaction with trialkyl alanes (*65*).

Little is known so far about the alkylation of thallium compounds with trialkyl alanes, although it has been reported that thallium trichloride gives good yields of dialkyl thallium chlorides with various trialkyl alanes (*268*).

The alkylation of various silicon compounds [e.g., Na_2SiF_6, $SiCl_4$, $Si(OR)_4$] by organoaluminum compounds has long been known (*117*, *303*). More information has become available recently on the methylation of silicon tetrachloride with methylaluminum sesquichloride (*162*). Also heterocyclic organoaluminum compounds [e.g., 1-alkyl-1-aluminaindanes, 1-alkyl-1-aluminatetralins (*135*)] react with alkylchlorosilanes [in presence of NaCl (*117*)] or with alkylfluorosilanes to the corresponding Si-heterocycles (*143*). Good yields (about 80%) of dialkylsilaindanes (R = C_2H_5; b.p.$_{15-16}$: 127°–129°C) result according to the equation,



if one uses tetraalkylsilanes as solvent. The spirosilane (b.p.$_{13}$: 219°C; m.p. 78°–79°C)



and higher molecular silicon compounds are formed when a solvent is not employed (*143*). Germanium tetrachloride and either triethyl- or triisobutylalane also give the corresponding tetraalkyl germanes in good yield (*272*).

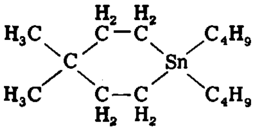
When tin tetrachloride is mixed with a trialkyl alane or an alkyl aluminum halide, mixtures of various highly alkylated tin and aluminum chlorides are formed, depending on the molar ratio of the two reactants. The reaction is complicated by the formation of complexes of the types $[R_2SnCl_2]^+[AlCl_4]^-$ and $[RSnCl_3]^+[AlCl_4]^-$, some of which are stable and may be isolated in a crystalline form (*194*, *196*). Addition of NaCl or NaF, however, affords a ready means of securing complete alkylation of the tin tetrachloride, according to the equation (*115*, *184*):

$$3SnCl_4 + 4AlR_3 + 4NaCl \rightarrow 3SnR_4 + 4NaAlCl_4$$

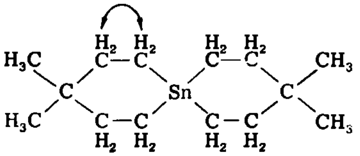
Alkali tetraalkyl alanates, e.g., $LiAl(C_2H_5)_4$, may be used in place of a mixture of NaCl and AlR_3 (*57*). The alkylation with alkali tetraalkyl alanates can also be carried out so that only one alkyl group reacts (*118*):

$$4MAlR_4 + SnCl_4 \rightarrow 4MCl + 4AlR_3 + SnR_4$$

In place of stannic chloride a mixture of alkyl chloride and metallic tin may be used (*228*). Complete alkylation of the tin is also often favored by the presence of ethers or tertiary amines, which are able to trap the strongest Lewis acid in the reaction mixture ($AlCl_3$) by forming a complex with it (*192*, *194*). In the same way cyclic alkylene stannanes of formula



and



may be made from the corresponding alkylene alanes (*212*, *213*), or tetraaryl stannanes from aryl aluminum sesquihalides (*261*). Removal of $AlCl_3$ from the reaction mixture as a complex (e.g., an etherate) also makes possible the preparation of the alkyl tin halides R_2SnCl_2 and R_3SnCl from $SnCl_4$ and the calculated amount of AlR_3 (*192*, *194*). Dialkyl tin oxides, R_2SnO, are likewise converted into tetraalkyl stannanes by trialkyl alanes (*169*). Only hydride-chloride exchange takes place on mixing dialkyl aluminum hydrides with alkyl tin chlorides at 0° to −20°,

$$R_3SnCl + R'_2AlH \rightarrow R_3SnH + R'_2AlCl$$
$$R_2SnCl_2 + 2R'_2AlH \rightarrow R_2SnH_2 + 2R'_2AlCl$$
$$RSnCl_3 + 3R'_2AlH \rightarrow RSnH_3 + 3R'_2AlCl$$

Such reactions are therefore very suitable for preparing the hitherto relatively inaccessible alkyl tin hydrides (*193*). Diisobutylaluminum hydride reduces and alkylates tin tetrachloride: isobutyltin(II) chloride results but $Sn(iC_4H_9)_2$ has so far not been made in this way (*239*).

The possibility of preparing tetraalkyl plumbanes from lead salts by alkylation with organoaluminum compounds has been very fully investigated over a considerable period because of the industrial importance of $Pb(CH_3)_4$ and $Pb(C_2H_5)_4$ (*303*). The attempted preparation of tetraethyllead from lead dichloride and triethylalane meet with difficulties because complete alkylation of the lead occurs only with the first $Al—C_2H_5$ group of the aluminum compound. Utilization of all three ethyl groups on the aluminum is, however, possible if $PbCl_2$ is replaced by PbO, PbS, or lead salts of carboxylic acids (*303*):

$$6PbS + 4AlEt_3 \rightarrow 3Pb + 3PbEt_4 + 2Al_2S_3$$

The lead which separates may be fully utilized in the synthesis of tetraethyllead by adding an organocadmium compound and ethyl iodide to the reaction mixture. The essential step in this multistage process clearly is ethylation of lead by cadmium diethyl:

$$\mathrm{Cd} \xrightarrow{\mathrm{RI}} \mathrm{C_2H_5CdI} \xrightarrow{\mathrm{AlR_3}} \mathrm{Cd(C_2H_5)_2}$$

according to the equation:

$$\mathrm{Pb + 2CdEt_2 \rightarrow PbEt_4 + 2Cd}$$

Cadmium thus acts as a carrier for ethyl groups from aluminum to lead. The material balance of the process is represented by

$$\mathrm{6PbAc_2 + 6AlEt_3 + 6EtI \rightarrow 6PbEt_4 + 4AlAc_3 + 2AlI_3}$$
$$\mathrm{(Ac = OCOCH_3)}$$

Inorganic lead(IV) compounds (e.g., K_2PbCl_6) with triethylalane give tetraethyllead in up to 50% yield. Metallic lead and ethyl chloride are secondary products because the intermediate $C_2H_5PbCl_3$ is unstable and decomposes according to the equation:

$$\mathrm{EtPbCl_3 \rightarrow EtCl + PbCl_2}$$

Better yields of tetraethyllead result from the use of organic lead(IV) compounds such as $Pb(OC_4H_9)_4$ or $Pb(OAc)_4$ (*76*).

Alkali tetraalkyl alanates have also been used successfully for the alkylation of lead salts. Sodium tetraethylalanate and other organoaluminum complexes (e.g., $Na[(C_2H_5)_3AlF]$, $Na[(C_2H_5)_3AlOCH_3]$) give tetraethyllead when treated with metallic lead and ethyl chloride (*77*):

$$\mathrm{2Na[Al(C_2H_5)_4] + Pb + 2C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 2NaCl + 2(C_2H_5)_3Al}$$

Only brief reference can be made here to the electrolytic process for preparing tetramethyl- or tetraethyllead, and mixed compounds (*160*) (see Section IV,C,3).

Alkyl compounds of all the elements of the fifth main group of the periodic table have been prepared by reaction with alkyl alanes. Thus phosphorus trichloride yields alkyl dichlorophosphines, dialkyl chlorophosphines, and trialkyl phosphines, according to the particular ratio of reactants employed (*250, 266*). Trialkyl phosphine oxides, on the other hand, are formed only in poor yield from $POCl_3$ and AlR_3 (*250, 303*), although dialkyl and trialkyl phosphine sulfides are readily made from $PSCl_3$ and AlR_3. Monoalkyl thiophosphonic dichlorides, which are important for the preparation of highly active insecticides, may also be obtained in good yield by the reaction (*170*):

$$\mathrm{PSCl_3 + RAlCl_2 \rightarrow RPSCl_2 + AlCl_3}$$

Arsenic, antimony, and bismuth trihalides (halogen = fluorine or chlorine) react with trialkyl alanes to give good yields of arsenic, antimony, and bismuth trialkyls. These reactions are carried out in ethers (*268*) or with the addition of NaCl to the reaction mixture to form a complex with the $AlCl_3$ which is produced (*116*). According to a new method, trialkyl arsines and stibines may be prepared satisfactorily by treating As_2O_3 or Sb_2O_3 with excess of trialkyl alanes:

$$2AlR_3 + M_2O_3 \rightleftharpoons \underset{\substack{(M\,=\,As,Sb)\\(R\,=\,alkyl)}}{(R_2M)_2O} + 2RAlO \xrightarrow{+AlR_3} 2MR_3 + 3RAlO$$

The pure trialkyl arsines and stibines are removed from the equilibrium mixtures by distillation at very low pressure (*240*).

Halides of zinc, cadmium, and mercury are readily alkylated by aluminum alkyls (*117*, *303*). All of the alkyl groups of the aluminum participate in the reaction with $HgCl_2$. But the alkylation does not proceed beyond the formation of alkyl mercury chlorides, RHgCl, except in the presence of a complexing agent (e.g., NaCl). Then complete alkylation to the mercury dialkyl occurs.

The chlorides of zinc and cadmium, on the other hand, react with only one alkyl group of the trialkyl alane and form zinc and cadmium dialkyls:

$$ZnCl_2 + 2AlR_3 \rightarrow ZnR_2 + 2R_2AlCl$$

Use of the fluorides in conjunction with a complexing agent (e.g., NaF) opens up the possibility of utilizing all the alkyl groups of AlR_3. The R_2AlF produced initially reacts with NaF as follows (*294*):

$$3R_2AlF + 3NaF \rightarrow 2AlR_3 + Na_3AlF_6$$

Alkyl alanes (e.g., AlR_3, R_2AlOR, R_2AlX) also react with various halides and alcoholates (e.g., acetylacetonates) of transition metals (e.g., titanium, nickel, and chromium) with exchange of the organo groups. Since, however, the organometallic derivatives of the transition elements formed initially are usually unstable, reduction occurs to give either the free metals or their compounds in lower oxidation states (*45*). When this occurs the alkyl groups appear as saturated and unsaturated hydrocarbons. In many cases it is actually possible to isolate alkyl or aryl compounds of the transition metal at very low temperatures [e.g., CH_3TiCl_3 (*21*, *22*), $C_6H_5CrCl_2$ (*150*)].

$$(C_6H_5)_3Al \leftarrow THF + CrCl_3 \xrightarrow[THF]{} \underset{\text{(green as THF adduct)}}{C_6H_5CrCl_2} + (C_6H_5)_2AlCl \leftarrow THF$$

Much has been published recently about the use of these substances (*24*, *25*, *35*, *45*, *228*, *258*) as catalysts for the polymerization of alkenes (*188*, *325*), but it is not proposed to go into details of this topic here.

B. REACTIONS OF THE Al—H BOND WITH UNSATURATED HYDROCARBONS

1. *Dialkyl Aluminum Hydrides, R_2AlH, and Alkenes*

Addition of dialkyl aluminum hydrides (dialkyl alanes) to C═C double bonds in alkenes (hydroalumination) leads to trialkyl alanes (*291*, *298*). For the preparation of higher trialkyl alanes it is proposed to add diethylalane to higher 1-alkenes and from the resulting ethyl-alkyl alane mixtures (analogous to the organoboron compounds) (*142*) to remove the ethyl groups as triethylalane by distillation (*241*):

$$3(C_2H_5)_2AlH + 3C{=}C{-}R \rightarrow 3(C_2H_5)_2AlCCH{-}R \rightarrow 2Al(C_2H_5)_3 + Al(CCH{-}R)_3$$

The breakdown of the Al—C bonds takes place at increased temperatures and gives the dialkyl aluminum hydride and alkene (dehydroalumination) (*293*). In the equilibrium

$$R_2AlH + C_nH_{2n} \rightleftharpoons R_2Al(C_nH_{2n+1})$$

the reaction from left to right is substantially faster than that in the reverse direction, particularly in the case of 1-alkenes. Up to 100°C, equilibrium lies almost completely over to the right. For alkyl alanes with certain alkyl groups which are branched in the 1- and 2-positions, however, considerable amounts of R_2AlH are present at equilibrium.

Comparative kinetic measurements for the hydroalumination have shown that with, for example, diethylalane and excess of a 1-alkene which is unbranched at carbon atom 2, reaction is half complete in 15 minutes at 65°C (*291*). In contrast to this, the time for 50% dehydroalumination with tripropylalane is 6 hours at 120°C (*307*) and 20 minutes at 160°C (*242*). Since hydroalumination proceeds only slowly at room temperature it is advantageous to work at about 50°C for preparative purposes. The rate of addition of the Al—H group to the C═C double bond decreases in the sequence

$$C{=}C \sim R{-}C{=}C > R_2C{=}C \gg R{-}C{=}C{-}R$$

1-Alkenes which are unbranched in the 2-position react twice as rapidly as alkenes substituted at carbon atom 2 (2,2-dialkyl ethylenes). Reaction is about 100 times slower for alkenes with C═C bonds occupying an internal position than for 1-alkenes. Addition of AlH to cyclohexene is extremely slow: the time for 50% reaction with this alkene is ca. 35 hours at 60°C (*291*).

Because of the two possible directions for the AlH addition, from 1-alkenes one obtains mixtures of 1-alkyl and 2-alkyl alanes. The proportion of primary to secondary alkyl groups is generally between 20:1 and 30:1

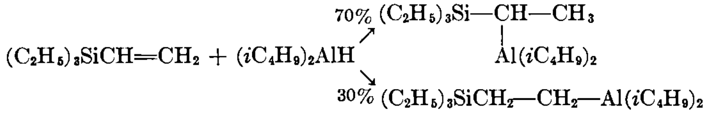
(*311*). When secondary alkyl alanes are heated above 100°C, equilibria are established which result in extensive isomerization to the 1-alkyl alanes (*40, 94*). The isomerization can be catalyzed by Ti(IV) or Zr(IV) salts (*9*). Since AlH addition to the C═C bond is more selective than for the corresponding organoboranes, it is possible to prepare 1-alkenes from alkenes with C═C bonds in an internal position. Simultaneously, however, the Al—C bond is able to react with the C═C double bond under these conditions (see Section V,C,1,a) i.e., synthetic reactions occur, which lead to considerable loss of the alkene used. With organoboranes this hardly occurs at all.

Addition of the Al—H bond to C═C double bonds in alkenes is greatly accelerated by catalytic quantities of certain titanium compounds [e.g., $TiCl_4$, $Ti(OC_4H_9)_4$]. For example, when propene is passed into dipropylaluminum hydride at room temperature no reaction is observed, whereas small amounts of $TiCl_4$ ($R_2AlH:TiCl_4$, 100:1) lead to rapid addition with the evolution of heat. Small amounts of polypropylene are formed simultaneously, but this can be avoided by using titanium(IV) butylate (*256*).

2. Dialkyl Aluminum Hydrides and Alkenes with Functional Groups

Dialkyl alanes may be added to a variety of substituted alkenes. Stable or unstable alkyl aluminum compounds are formed, depending upon the nature and location of the substituent in the alkene. An important part is also played by the direction of addition of the Al—H bond, which can be influenced by the substituents. Unstable alkyl alanes with functional groups mostly spontaneously go over as formed to alkenes and dialkyl aluminum compounds with the substituent directly bonded to the aluminum (e.g., R_2AlX, R_2AlOR') as a result of 1,*x* elimination.

Among the stable alkyl alanes with substituents in the alkyl group are the silylated compounds. In the compound formed from diisobutylalane and triethylvinylsilane, the dialkyl aluminum group is found to the extent of about 70% on the internal carbon atom (*70*):



$$(C_2H_5)_3SiCH{=}CH_2 + (iC_4H_9)_2AlH \left\{ \begin{array}{l} \nearrow 70\%\ (C_2H_5)_3Si{-}\underset{\displaystyle |\atop \displaystyle Al(iC_4H_9)_2}{CH}{-}CH_3 \\ \searrow 30\%\ (C_2H_5)_3SiCH_2{-}CH_2{-}Al(iC_4H_9)_2 \end{array} \right.$$

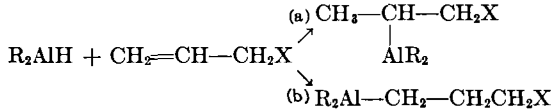
From 3-trimethylsilyl-1-propene and diisobutylalane one obtains correspondingly 3-(trimethylsilylpropyl)diisobutylalane. Nothing is known so far about the distribution of the R_2Al group between carbon atoms 1 and 2 (*276*).

5-Ethoxy-1-pentene, 4-ethoxy-1-butene, 3-ethoxy-1-propene, and the corresponding diethylamino alkenes react with diisobutylalane to form substituted 1-alkyl diisobutylalanes. In these cases the substituents have practically no influence on the direction of addition (*270*, *282*).

Allyl chloride or allyl bromide and dialkyl aluminum hydrides do not give halogenoalkyl alanes, the products being dialkyl aluminum monohalides and propene (*270*):

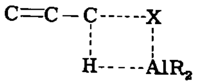
$$R_2AlH + CH_2{=}CH{-}CH_2X \rightarrow R_2AlX + CH_3CH{=}CH_2$$

The actual products in hydroalumination give no clear indication of the course of the reaction. Thus, considering the two possible directions of addition:



$$R_2AlH + CH_2{=}CH{-}CH_2X \begin{array}{l} \nearrow \text{(a)}\ CH_3{-}\underset{\displaystyle AlR_2}{\underset{|}{CH}}{-}CH_2X \\ \searrow \text{(b)}\ R_2Al{-}CH_2{-}CH_2CH_2X \end{array}$$

only reaction (a) is probable on the basis of the reaction product. The dialkyl 3-halogeno-1-propylalane to be expected from reaction (b) would decompose to dialkyl aluminum halide and cyclopropane (cf. Section III,B,3) (*27*). The complete absence of cyclopropane in the reaction products suggests that another type of reaction is taking place. If reaction occurs solely by addition of the Al—H bond to the C═C double bond, at least part of the aluminum of the AlH compound should be added to the terminal carbon atom of the allyl chloride. It must therefore be assumed that, prior to the addition, hydride-halide exchange takes place:



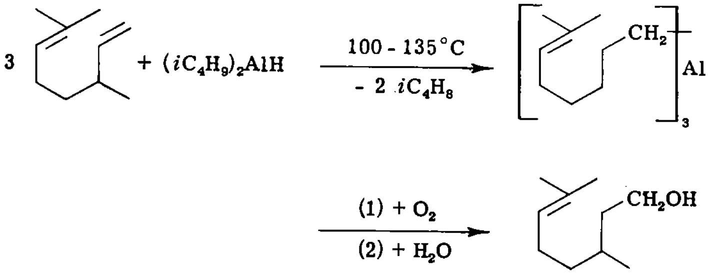
Between lithium alanate and allyl halides (*89*, *91*, *92*) or cyclic allyl halides (*82*) analogous reactions [H/X exchange without allyl rearrangement (*91*, *92*), allyl rearrangement (*89*), HX liberation (*89*, *90*)] are known.

From 4-chloro-1-butene and diisobutylalane one obtains not the anticipated addition product but diisobutylaluminum chloride and 1-butene (*228*). It seems very probable that diisobutyl-4-chloro-1-butylalane is formed as an intermediate. This decomposes under the conditions of the preparation (50°-60°C) as a result of 1,4 elimination (cf. Section III,B,3).

3. Dialkyl Alanes and Dienes

Addition of dialkyl alanes to the C═C double bonds of various dienes is of interest for the synthesis of bifunctional hydrocarbons. Because of the diversity of the reactions which are to be expected, it is necessary in carrying out such experiments to have a particularly precise knowledge of the mode of reaction of simple trialkyl alanes with alkenes. It is known that intramolecular transformations occur much more readily than intermolecular ones, i.e., alkenyl alanes ought to be unstable at least at elevated temperatures, depending on the type of C═C double bond.

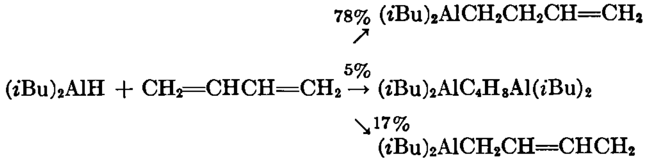
Selective partial hydroalumination of dienes and trienes or their mixtures is possible because of the differences in the rate of AlH addition to various sorts of C═C double bonds. Further transformations of the alkenyl alanes open the way to some interesting possibilities in preparative work. For example, by partial hydroalumination of 4-vinylcyclohexene or limonene, wherein the Al—H bond reacts with the terminal double bond, followed by air oxidation, it is possible to obtain cyclohexenylethanol or β-terpineol in good yield (*312*). A further example from terpene chemistry is the preparation of citronellol (*225*).



3,7-Dimethylocta-1,6-diene reacts with diisobutylalane hydride (or with triisobutylalane under displacement conditions) in such a way that addition of aluminum is exclusively at the terminal carbon atom. The large difference in reactivity between the terminal and internal double bond is apparent. Oxidation and hydrolysis of the organoaluminum compound gives citronellol in 60% yield. The optical activity of the starting material remains unchanged during the transformation (*225*).

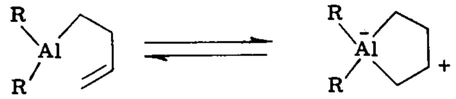
Complete hydroalumination of dienes with two separate C═C double bonds of the same type should give aluminum compounds of the type $R_2Al(CH_2)_nAlR_2$, which can then react with ethylene (cf. Section V,C,1) and thus be transformed into long-chain bifunctional compounds.

Attempts to bring about the reaction of the simplest diene (allene) with dialkyl aluminum hydrides led to no definite organoaluminum compounds (*123*). Little is known so far about the reaction of alkenes containing conjugated double bonds (butadiene (*290*), isopropene, etc.) with dialkyl alanes. Diisobutylalane and butadiene gave products whose hydrolysis yielded chiefly butenes (78% 1-butene, 17% 2-butene), together with a little butane (5%). Clearly 1,4 addition is occurring as well as 1,2 addition (*277*):



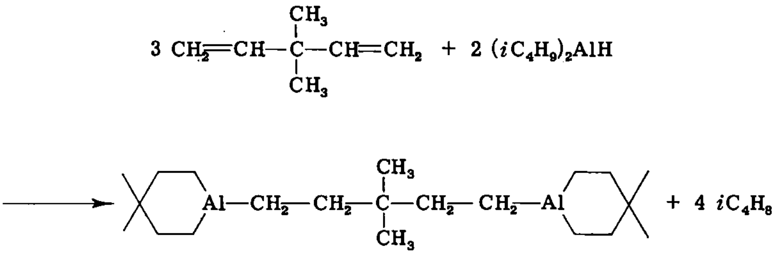
$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad 78\%\ (iBu)_2AlCH_2CH_2CH{=}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\nearrow \\ (iBu)_2AlH + CH_2{=}CHCH{=}CH_2 \xrightarrow{5\%} (iBu)_2AlC_4H_8Al(iBu)_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\searrow 17\% \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad (iBu)_2AlCH_2CH{=}CHCH_2 \end{array}$$

It is notable that reaction slows down at the alkenyl stage. This may be due to stabilization, perhaps by a sort of back-coordination (*62*):



This type of interaction between C=C double bonds of an alkenyl group and element of the third main group has been observed recently in the case of organoboranes (*145*, *146*, *147*).

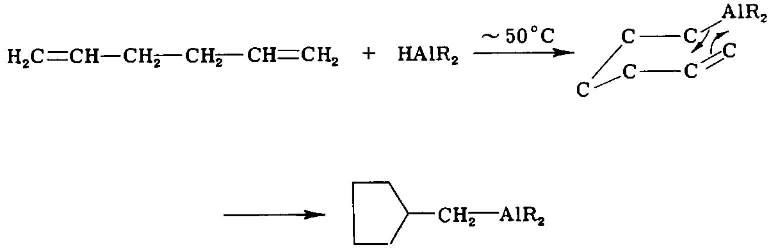
1,4-Pentadiene and dialkyl alanes give addition products from which only pentane is split off on hydrolysis (*88*). Nothing further is known yet about the constitution of these compounds, e.g., if aluminum heterocycles (6- or 5-ring compounds) are formed. Tris(3,3-dimethyl-pentamethylene) dialane is said to be formed from 3,3-dimethyl-1,4-pentadiene and di-isobutylaluminum hydride in 98% yield, even under forcing conditions at elevated temperatures (160°C). The compound distills at low pressures ($b.p._{10^{-4}}$: 132°–140°C) (*212*).



$$3\ CH_2{=}CH{-}C(CH_3)_2{-}CH{=}CH_2 + 2\ (iC_4H_9)_2AlH$$

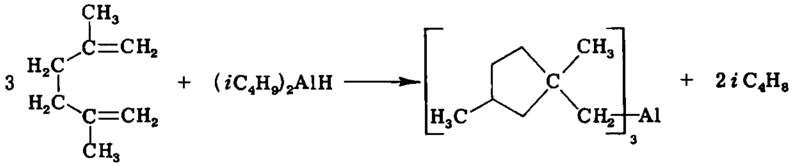
The high yield of a definite Al heterocycle seems, however, to be rather improbable since simple aliphatic Al heterocycles are transformed very readily above 100°C into viscous polymers (*135*).

The alkenyl compounds which can be prepared from 1,5-hexadiene and dialkyl alanes are unstable and undergo intramolecular addition of the Al—C bond to the C=C double bond, which is sterically well sited (*293*):



The products are cyclopentylmethylalanes, from which methylenecyclopentane may be split off with excess of diene.

With 2,5-dimethyl-1,5-hexadiene this reaction occurs quantitatively to give thermally stable organoaluminum compounds with a quaternary β-carbon atom (*139*):

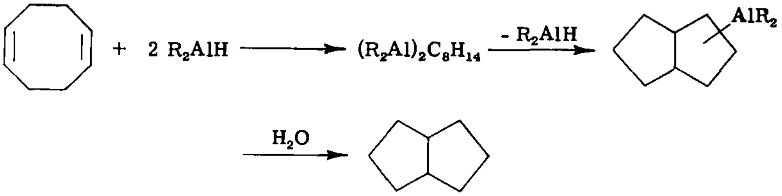


Dehydroalumination of the cyclic C_8 group in this case is no longer possible. In spite of its high molecular weight it is therefore possible to distill tris(1,3-dimethylcyclopentyl-1-methyl)alane under reduced pressure without decomposition (b.p. at 10^{-3} torr: 120°–125°C) (*139*).

Intramolecular AlC addition to the C=C double bond is also observed to a small extent (ca. 1%) in the hydroalumination of 1,6-heptadiene (*88*). Such C—C coupling hinders the synthesis of long-chain bifunctional compounds from low molecular dienes through organoaluminum intermediates. In contrast to this, 1,7-octadiene gives only the bis-hydroalumination products. With 1,7-octadiene (which may be prepared by pyrolysis of cyclooctene) (*226*) as the starting material, a route is available to the long-chain bifunctional bis-hydroalumination products and their derivatives (see Section V,C,1,a).

$$\mathrm{al{-}(CH_2)_8{-}al} + n\mathrm{CH_2{=}CH_2} \rightarrow \mathrm{al{-}(CH_2)_{8+2n}{-}al}$$

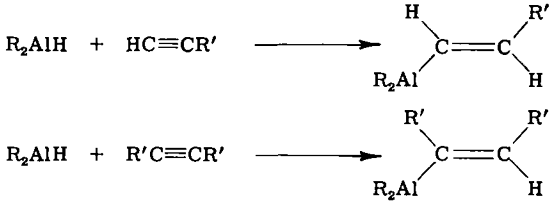
Among the cyclodienes, the reaction of cyclo-1,5-octadiene (*258*) with $(C_2H_5)_2AlH$ has been studied in detail (*255*). With 2 moles of diethylalane and 1 mole of diene a bis-hydroalumination product is first formed. This, on prolonged heating and subsequent hydrolysis, gives the bicyclic pentalane in high yield:



It is possible that the bicyclic compound is formed by a process of transannular dehydroalumination (*255*).

4. Dialkyl Aluminum Hydrides and Alkynes

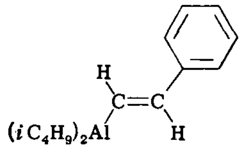
Hydroalumination of the terminal and internal C≡C triple bonds in alkynes with R_2AlH, which usually occurs quite smoothly, gives a *cis* product. One therefore obtains the following alkenyl alanes (*253*):



For alkynes with terminal acetylenic bonds, hydrogen cleavage is a competing reaction, dependent on the acidity of the C—H group, and this leads to alkynyl alanes (*68*, *209*, *235*):

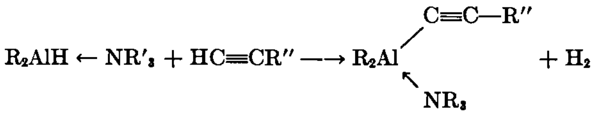
$$R_2AlH + HC{\equiv}CR' \rightarrow R_2AlC{\equiv}CR' + H_2$$

From diisobutylalalane and phenylacetylene one obtains, in addition to the product of hydroalumination (diisobutylphenylethenylalane):



up to 40% of diisobutylphenylethynylalane (*69*). Reaction between dialkyl alanes and acetylene itself is ill-defined and its cause has not yet been elucidated (*253*).

1-Alkynes and dialkyl alanes form dialkylalkynyl alanes almost quantitatively (with liberation of H_2) if one starts from the amine-dialkyl alane (e.g., the trialkylamine adduct) (*31*):



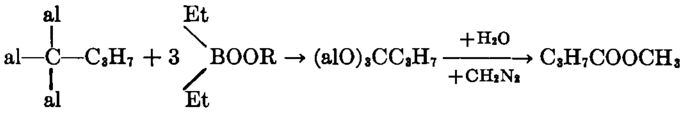
$$R_2AlH \leftarrow NR'_3 + HC{\equiv}CR'' \longrightarrow R_2Al\begin{matrix} \diagup C{\equiv}C{-}R'' \\ \nwarrow NR_3 \end{matrix} + H_2$$

Etherates occupy an intermediate position in the reaction with 1-alkynes. Below 100°C, dialkyl alane etherate does not react at all with monosubstituted acetylenes. Only at elevated temperatures (presumably after dissociation) is there predominantly an addition to the C≡C triple bond (*31*).

If 1-alkynes are reacted with 2 moles of R_2AlH or the dialkyl-1-alkenyl alanes with the addition of a further mole of dialkyl alane, compounds are obtained with two dialkyl aluminum groups on the terminal carbon atom. Likewise 1 mole of dialkylalkynyl alane and 2 moles of dialkyl alanes give tris(1,1,1-dialkylalanyl) alkanes. Deuterolysis of fully hydroaluminated propynylalane, for example, thus gives 1,1,1-trideuteropropane (*219*):

$$2Et_2AlH + Et_2AlC{\equiv}CMe \rightarrow (Et_2Al)_3C{-}CH_2Me \xrightarrow{+D_2O} 6EtD + D_3CCH_2CH_3 + Al(OD)_3$$

Oxidation with dialkylperoxyalkyl borane (*257*) produces carboxylic esters, e.g. (*259*),

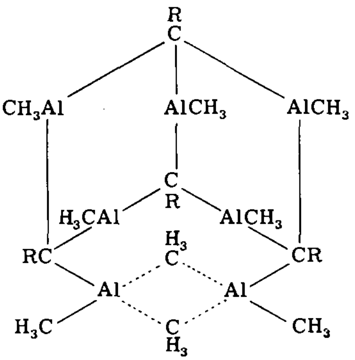


$$al{-}\underset{al}{\overset{al}{C}}{-}C_3H_7 + 3\begin{matrix} Et \\ \diagdown \\ \diagup \\ Et \end{matrix}BOOR \rightarrow (alO)_3CC_3H_7 \xrightarrow[+CH_2N_2]{+H_2O} C_3H_7COOCH_3$$

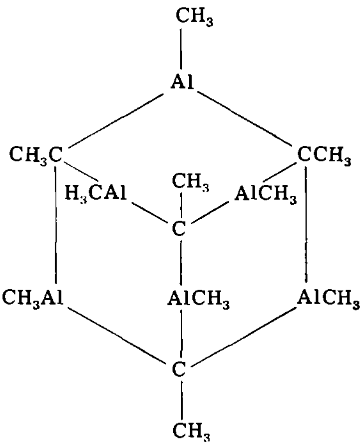
Organoaluminum compounds with 2 or 3 aluminum atoms on the same carbon atom disproportionate when distilled at low pressure. From tris-(diethylalanyl)propane, triethylalane is formed together with organic aluminum compounds which, from their properties, must be assigned an adamantane structure (*259*):

$$4(R_2Al)_3CR' \rightarrow (RAl)_6(CR')_4 + 6AlR_3$$

The compounds are crystalline and can be sublimed when R and R′ are methyl groups. The crystalline compound with adamantane structure which can be prepared from dimethylalane and dimethylpropynylalane has a framework containing AlR_2Al bridge bonds and may be called a pseudo-aluminaadamantane:



(where R = C_2H_5). Finally, use of dimethylethynylalane in place of dimethylpropynylalane has led to the successful synthesis of the so-called "aluminaadamantane" (*259*) (see also Section III,B,1):



C. Reactions of the Al—C Bond with Unsaturated Hydrocarbons

1. *With Alkenes*

a. Comparative Consideration of the Various Possible Reactions. The discovery of the addition of the Al—C bond in trialkyl alanes to C=C double bonds in ethylene and 1-alkenes was of fundamental significance in the development of organoaluminum chemistry. The most important possibilities arising from the resulting transformations effected on trialkyl alanes or unsaturated hydrocarbons have already been reviewed in detail by K. Ziegler (*289*, *293*, *302*), and in the following section only a summary of these results will be presented.

Tri-1-alkyl alanes react with ethylene at 100 atm and 90°–100°C to form unbranched long-chain alkyl alanes (the so-called "growth" reaction) (*289*):

$$\text{R—al} + n\text{C}_2\text{H}_4 \rightarrow \text{R(C}_2\text{H}_4)_n\text{—al}$$

Since all three Al—C bonds of the trialkyl alanes react equally quickly, the distribution of the alkyl groups in the product corresponds with Poisson's law (*249*):

$$x_p = \frac{n^p \cdot \mathrm{e}^{-n}}{p!}$$

where x_p denotes the molar fraction of $\text{al(C}_2\text{H}_4)_p\text{R}$ groups in the mixture of an average composition $\text{al(C}_2\text{H}_4)_n\text{R}$, n is the average number of moles of ethylene which have reacted with 1 mole of alR, and p is the number of C_2H_4 units in the individual hydrocarbon chains.

Triethylalane and ethylene yield higher trialkyl alanes with an even number of carbon atoms in the chain, while the tripropylalane gives compounds with odd numbers. Since dehydroalumination-hydroalumination reactions (see Section V,B,1) occur in the case of propylalane, resulting in the formation of alkyl alanes with even-numbered hydrocarbon radicals (e.g., triethyl alane), the reaction products do not consist entirely of the odd-numbered aluminum compounds.

This synthesis cannot be used for making aluminum derivatives with any desired chain length because dehydroalumination reactions cause chain rupture:

$$\text{al—CH}_2\text{—CH}_2\text{—R} \rightarrow \text{al—H} + \text{CH}_2\text{=CH—R}$$
$$\text{al—H} + \text{CH}_2\text{=CH}_2 \rightarrow \text{al—C}_2\text{H}_5$$

Even under the most favorable conditions (with as low a temperature as possible and a high C_2H_4 concentration, i.e., pressures of 100 atm or more) there is one chain-breaking reaction with alkene formation for about every one hundred steps in the synthesis. In spite of this, however, the synthesis may be used as it stands for making trialkyl alanes with even-numbered straight chains containing 4–30 carbon atoms.

The reactivity of alkenes toward the Al—H bond decreases in the sequence:

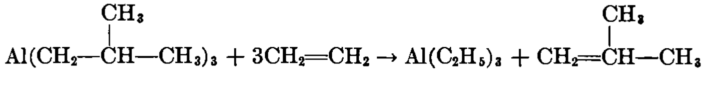
$$\text{CH}_2\text{=CH}_2 > \text{R—CH=CH}_2 > \text{R}_2\text{C=CH}_2 > \text{R—CH=CHR}$$

On the other hand, the rate of dehydroalumination depends on the nature of the alkyl groups attached to aluminum. The trialkyl alanes with radicals of the isobutyl type dissociate more easily into >AlH and alkenes than the tri-1-alkyl alanes with no branched chains. Comparable kinetic measurements have not yet been made. It follows that an alkene may be displaced from the organoaluminum compound by another which lies to the left in this series. For example, the equilibrium constant

$$K = \frac{(\mathrm{alR^{I}})(\mathrm{alkene^{II}})}{(\mathrm{alR^{II}})(\mathrm{alkene^{I}})}$$

is about 1600 for the reaction between triisobutylalane and ethylene, whereas for trialkyl alanes with α-branched alkyl chains and 1-alkenes it is about 40 (*306*, *307*).

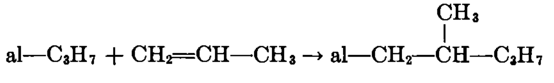
Closely related to these results is the fact that trialkyl alanes of the triisobutyl type give the growth reaction only partially with ethylene (*53*). The concurrent reaction is the displacement to give triethylalane and an alkene of the isobutylene type:



$$\mathrm{Al(CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3)_3 + 3CH_2{=}CH_2 \rightarrow Al(C_2H_5)_3 + CH_2{=}\overset{\overset{CH_3}{|}}{C}H{-}CH_3}$$

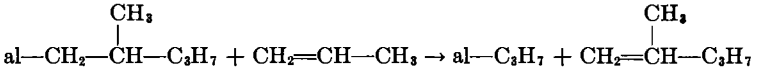
It was long believed that the isobutylalane does not give the "growth" reaction at all (*299*). This, however, was due to the fact that the reaction vessels employed always contained traces of a transition metal that catalyzed the displacement. With isoprene, isobutene is split off and polymeric alkyl aluminum compounds are formed which still contain some alkenyl groups. These are said to be less sensitive to air and moisture than the trialkyl alanes. The replacement is hastened by Ni as catalyst (*61*).

For the same reason 1-alkenes, unlike ethylene, react with trialkyl alanes to form practically exclusively the 2-alkyl-1-alkenes. Thus aluminum 2-methyl-1-pentyl, formed from tripropylalane and propene,



$$\mathrm{al{-}C_3H_7 + CH_2{=}CH{-}CH_3 \rightarrow al{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}C_3H_7}$$

is unstable in the presence of propene and undergoes displacement of a 6-carbon atom radical of the isobutyl type (*306*) as 2-methyl-1-pentene and simultaneous reformation of tripropylalane:

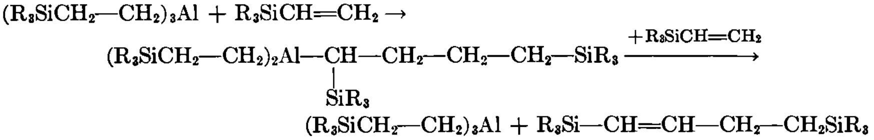


$$\mathrm{al{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}C_3H_7 + CH_2{=}CH{-}CH_3 \rightarrow al{-}C_3H_7 + CH_2{=}\overset{\overset{CH_3}{|}}{C}H{-}C_3H_7}$$

The transformation of propene to 2-methyl-1-pentene with catalytic quantities of tripropylalane has become important recently in the synthesis of isoprene. Following isomerization of the 2-methyl-1-pentene to 2-methyl-

2-pentene, pyrolysis of the isohexene gives isoprene and methane as cleavage products (*5, 11*).

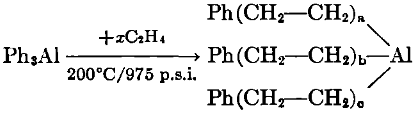
Similar considerations apply to reactions between tri-1-alkyl alanes and other 1-alkenes. Vinyl and allyl triorganosilanes may also be dimerized in this way. Dimerization of the allyl derivative proceeds normally, i.e., the aluminum atom adds on to the terminal carbon atom of the allyl group, but a trialkyl or triaryl silyl group directly adjacent to the C=C double bond appears to cause reversal of the direction of addition of the Al—C bond (*119*):



$$(R_3SiCH_2{-}CH_2)_3Al + R_3SiCH{=}CH_2 \rightarrow (R_3SiCH_2{-}CH_2)_2Al{-}\underset{SiR_3}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}CH_2{-}SiR_3 \xrightarrow{+R_3SiCH=CH_2} (R_3SiCH_2{-}CH_2)_3Al + R_3Si{-}CH{=}CH{-}CH_2{-}CH_2SiR_3$$

(where R = CH_3, C_2H_5, C_6H_5). A 1,4-triorganosilyl-1-butene is obtained in about 60% yield (*119*).

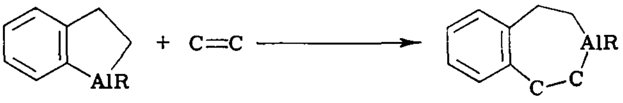
Very little is known so far about the addition of the $Al—C_{aryl}$ bond to C=C double bonds (e.g., $AlPh_3 + C_2H_4$). The addition reaction for triphenyl (*72*) and triaralkyl alanes (e.g., tribenzyl (*41*) triphenylethylalanes) using ethylene is described in a few publications (*41*, *72*):



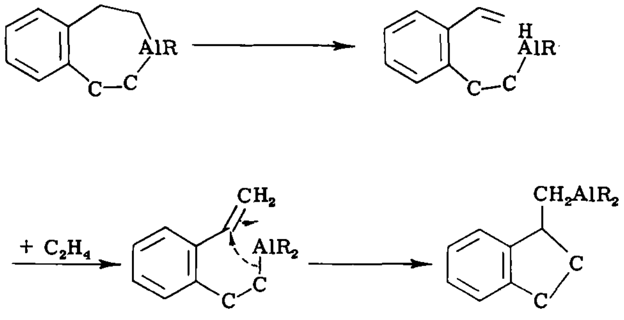
$$Ph_3Al \xrightarrow[200°C/975\ p.s.i.]{+xC_2H_4} \begin{matrix} Ph(CH_2{-}CH_2)_a \diagdown \\ Ph(CH_2{-}CH_2)_b{-}Al \\ Ph(CH_2{-}CH_2)_c \diagup \end{matrix}$$

No comparative studies of the reactivity of $Al—C_{alkyl}$ and $Al—C_{aryl}$ bonds have been published. Certain Al heterocycles (see Section V,A,1) would be very suitable for investigations of this sort, since many of these compounds (e.g., 1-aluminaindane) (*131*) with various Al—C bonds can be prepared pure. On the other hand, alkylaryl alanes R_2AlR' are unstable because of rapid ligand exchange (see Section V,A,1). Investigations on a mixture of mixed alkylaryl alanes were made with the object of studying differences in reactivity between $Al—C_{alkyl}$ and $Al—C_{aryl}$ bonds but were unrewarding, since the Lewis acidities of the various mixed compounds were different, so that the actual reaction which occurred reflected the tendency toward adduct formation from the alkene (alkyne) and organoaluminum compound.

Recent work has shown that reaction between 1-alkyl-alumina-indanes or -tetralins and alkenes (e.g., ethylene, propene, cyclohexene) occurs preferentially with the $Al—C_{aryl}$ bond (*140*):



The organoaluminum compound formed initially changes, as a result of dehydroalumination and subsequent intramolecular AlC addition to the terminal C=C bond, into indanylmethylalanes (*140*):



An important disadvantage in the stepwise addition of ethylene to trialkyl alanes is the relatively low rate of the process and the fact that it predominates only with highly pressurized ethylene. Addition of 1 mole of ethylene to 1 mole of trialkyl alane at 100°–110°C requires a high pressure of ethylene (ca. 100 atm) and about 1 hour, i.e., after 3 hours the triethylalane is transformed into a product with an over-all composition corresponding to tributylalane. It is not possible to use higher temperatures for the reaction because of various side reactions and subsequent changes (cleavage of alkene, alkene dimerization). In addition, care must be taken to remove the heat generated in the reaction. In view of these points it was a very great step forward when a way of operating the addition reaction was found by which alkyl alanes with long alkyl chains could be produced continuously. The mode of operation shows certain points of resemblance to the preparation of high pressure polyethylene. The operation is conducted in spiral copper reactors in which the temperature may be taken to 160°C because of the short residence time of the reactants (*326*). The products from trialkyl alanes and ethylene are mainly straight-chain higher alkyl alanes with only about 1–4% of branching in the alkyl groups. Reaction is considerably faster at the higher temperature. Instead of the earlier figure of 100–150 gm, it is possible to convert 500–1600 gm of ethylene per hour and per liter of reaction space. In fact, these carboalumination reactions are comparable in their rates with many long-established technical reactions (*314, 326*).

The rate of ethylene addition to alkyl alanes may also be increased considerably by diluting the aluminum compound with an inert solvent (e.g., a hydrocarbon) (*293*, *297*, *311*). This does not offer a useful route for preparing higher alkyl alanes on a large scale, but some indications of the mechanism of the synthesis are obtained. Measurements of the rate of absorption of ethylene by dissolved triethylalane show that the ratio of rates for 1 *M* and 0.01 *M* solutions was about 10:1. It follows that the rate of absorption per mole of (dimeric) triethylalane is proportional to the square root of its concentration. Corresponding results were obtained for the absorption of acetylene. With (monomeric) triisobutylalane, on the other hand, the same rate of absorption of acetylene was observed whatever the degree of dilution. Reaction with ethylene could not be measured in this case on account of the relatively rapid displacement reaction which occurred simultaneously (see preceding section). These experiments make it quite clear that the monomeric trialkyl alanes, and not the dimers, are the reactants in the addition process (*315*).

In contradiction to the above, it has been stated recently that the rate of formation of the isooctyl group from 1-hexene and triethylalane is proportional to the first power of the concentration of each reactant, i.e., the dimeric compound and not the monomer is taking part in the reaction with alkene. No explanation has been given so far of why experiments carried out in the same way can lead to such contrary conclusions (*3*).

b. Synthesis of Long-Chain Unbranched Alkenes from Ethylene Using Organoaluminum Compounds. The problem of synthesizing long-chain unbranched 1-alkenes from ethylene and triethylalane by using a combination of synthesis and displacement reactions was solved in principle a long time ago. In practice, however, difficulties have risen repeatedly and these have been overcome only very recently with the discovery of the so-called high temperature rapid displacement process (*314*, *326*).

In the one-stage process, in which the synthesis and displacement reactions are not separated, the product after reaction and distillation is a mixture of 1-alkenes with various numbers of C atoms and also α-branched 1-alkenes arising from AlC addition to alkenes which have already been formed:

$$\begin{array}{ll}
\text{(a)} & C_2H_5\text{—al} + (n-1)C_2H_4 \rightarrow C_2H_5\text{—}(C_2H_4)_{n-1}\text{—al} \\
\text{(b)} & C_2H_5\text{—}(C_2H_4)_{n-1}\text{—al} \rightarrow \text{al—H} + C_2H_5\text{—}(C_2H_4)_{n-2}\text{—CH}{=}\text{CH}_2 \\
\text{(c)} & \underline{\text{al—H} + C_2H_4 \rightarrow C_2H_5\text{—al}} \\
 & nC_2H_4 \rightarrow (C_2H_4)_n
\end{array}$$

(where alH = AlH in R_2AlH). The distribution of alkenes with various C numbers is substantially wider than would be calculated on the basis of Poisson's law (*302*, *314*). In spite of these disadvantages the one-stage process seems to be of some practical interest, because of its simplicity and the small amount of triethylalane needed. The growth and displacement reactions are also carried out as two separate steps (see the equations above). If the displacement reaction is accelerated by certain heavy metal catalysts (e.g., nickel compounds), the recovered triethylalane must subsequently be freed from catalyst (e.g., finely divided nickel) before it is returned to the synthesis stage. Nickel is known to interfere with the separation of alkenes from triethylalane because it catalyzes the regeneration of ethylene [reversal of Eqs. (b) and (c)] by the higher alkenes which have been produced. Separation of nickel from triethylalane has been worked out successfully, but the cost of carrying out the process is considerable (*302*, *316*).

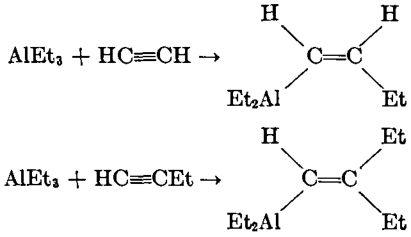
A marked improvement was effected when it was found that the displacement reaction could be operated with trialkyl alanes and ethylene or suitable 1-alkenes (propene, 1-butene, etc.) even at 300°–350°C, if the components were allowed to react for only a very short time at a moderate pressure of alkene. In spite of the high temperature, no decomposition of the trialkyl alanes to aluminum, hydrogen, and alkenes took place. Moreover, in the high temperature reaction with so short a reaction time there were practically no side reactions, i.e., α-branched alkenes and such compounds were hardly detected (*314*, *326*).

In carrying out the reaction under these conditions use was made of an apparatus consisting, for example, of an 18-meter long steel capillary (diameter about 15 mm) with its first and last quarters parallel to one another to even out the heat distribution. The heat exchanger and actual reaction space were enclosed in an aluminum block.

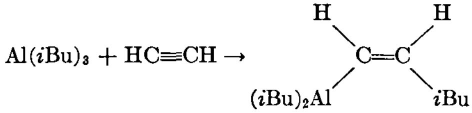
From the new process, which is particularly suitable for operation on a technical scale, it is possible to obtain from trialkyl alanes with long alkyl groups and ethylene about 95% of straight-chain alkenes, which may be separated quite easily by distillation. A certain amount of difficulty arises in the improved two-stage process because the trialkyl alanes formed (e.g., $AlEt_3$) distill over with alkenes with a certain chain length (e.g., dodecene). A special procedure has, however, been devised to deal with this problem. For details reference should be made to the original literature (*314*, *326*).

2. With Alkynes

Addition of an Al—C bond in tri-1-alkyl alanes to the C≡C triple bond of acetylene and 1-alkynes occurs as a rule under substantially milder conditions than the addition to double bonds of alkenes. Alkenyl alanes are formed from triethylalane and acetylene or 1-butyne at 40°–50°C with *cis* addition:



Triisobutylalane reacts similarly, e.g. (*253, 259*),



The difference in behavior of ethylene and acetylene with triisobutylalane is shown by the fact that, with ethylene, the isobutyl radical is removed very easily as isobutene.

In the reactions of trialkyl alanes with 1-alkynes or acetylene, reaction of the acidic hydrogen is not, in general, observed. Only in some cases, e.g.,

$$Al(CH_3)_3 + HC{\equiv}CR \rightarrow (CH_3)AlC{\equiv}CR + CH_4$$

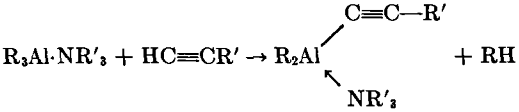
is alkane cleavage observed (*182*). The strongly acidic hydrogen atom in phenylacetylene or 1-naphthylacetylene is able to remove methane almost exclusively from trimethylalane, which is known to add on with difficulty to C—C multiple bonds (*311*). Alkynyl alanes are obtained in high yield (*182*). In the interaction of phenylacetylene with trialkyl alanes with longer alkyl groups, the quantity of alkane which is split off decreases sharply. Thus phenylacetylene and triethylalane at 100°–110°C give only 25–45% of the calculated amount of ethane (*30, 182*). On the other hand, the relatively weakly acidic hydrogen in 1-decyne is said to react with trimethylalane and to split off methane in 65% yield to give dimethyldecinylalane. In contradiction to earlier observations (*253*), triethylalane also yields 60% of diethyldecinylalane (*182*). The divergent results may be due to the experiments having been made at different temperatures. Addition reactions are already possible at 40°–50°C, whereas cleavage of alkane becomes rapid only above 100°C.

Triphenylalane also reacts with 1-hexyne or phenylacetylene at 50°C with formation of benzene (*67, 68, 180*):

$$(C_6H_5)_3Al + HC{\equiv}CR \rightarrow (C_6H_5)_2AlC{\equiv}CR + C_6H_6$$

(where R = C_4H_9, C_6H_5).

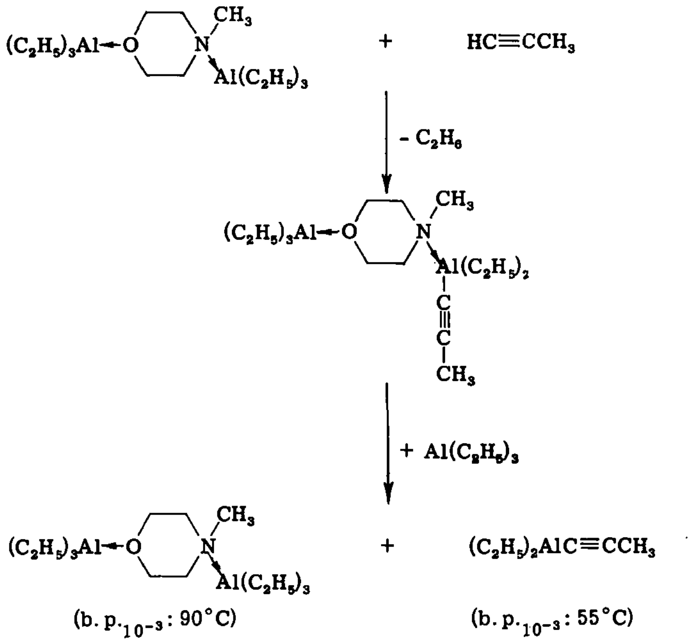
Reaction between 1-alkynes and trialkyl alanes goes uniquely in the sense of alkane cleavage if trialkylaminetrialkyl alanes are used. At 100°–120°C, trialkylaminedialkylalkynyl alanes are obtained in practically quantitative yield (*31*):



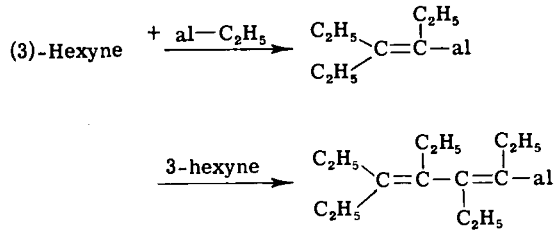
$$R_3Al{\cdot}NR'_3 + HC{\equiv}CR' \rightarrow R_2Al\begin{matrix}\nearrow C{\equiv}C{-}R' \\ \nwarrow NR'_3\end{matrix} + RH$$

Etherates of trialkyl alanes, on the other hand, do not react with 1-alkynes, even at elevated temperatures (*31*).

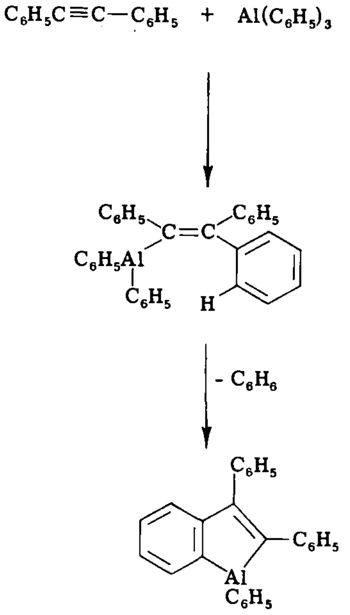
Free dialkylalkynyl alanes may be made through the trialkylamine-dialkylalkynyl alanes, which are accessible from $R_2AlH{-}NR_3$ and 1-alkynes (see Section V,B,4), by adding a mole of trialkyl alane. The reaction product may be separated by fractional distillation if a suitable trialkylamine is used. The following route (through the *N*-methylmorpholine adduct) has been found suitable for making diethylpropynyl- or 1-butynylalane (*131*):



Addition of AlC bonds in trialkyl alanes to the triple bond of 1,2-substituted alkynes occurs fairly rapidly above 100°C. At these temperatures a second mole of alkyne may be added to the alkenyl alane produced and an alkadienyl alane is formed (*253*):



The addition product from triphenylalane and tolane, which can be isolated, is transformed at 200°C with loss of benzene into an organoaluminum heterocycle (triphenylbenzaluminole) (*64*):



The ring closure takes place in an analogous manner from biphenylylphenylalanes. One obtains, for example, 9-phenyl-9-aluminafluorene (*64*), a dimeric colorless solid compound (*136*) (see Section V,A,1).

D. Reactions of Organoaluminum Compounds Involving Destruction of Al—C and Al—H Bonds

1. With Elements of Group VI (O,Se,Te) and Their Compounds

The oxidation of trialkyl alanes with molecular oxygen has long been known (*301, 312*). Aluminum alcoholates are formed, from which alcohols are readily obtained by hydrolysis:

$$AlR_3 \xrightarrow{+\frac{3}{2}O_2} Al(OR)_3 \xrightarrow{H_2O} 3HOR + Al(OH)_3$$

The first two Al—C bonds of the trialkyl alane react with oxygen appreciably faster than the third. Various side reactions may result (formation of ketones, dialkyl carbinols, etc.), and various modifications in the process for oxidizing the alane have therefore been proposed (*16*, *50*, *163*). The preparative possibilities of autoxidation, and particularly the preparation of long-chain fatty alcohols by a combination of the ethylene synthesis reaction and oxidation of the trialkyl alanes has been reported in detail (*301*, *312*).

Oxidation of triaryl alanes is less well defined than that of the aliphatic compounds. Tri-*p*-tolylalane, for example, gives only an 8% yield of *p*-cresol (*81*). The reaction in ether as solvent is even more involved as the diluent clearly participates in the reaction (*215*). Following oxidation of triphenylalane and hydrolysis, it was possible to isolate phenol, acetophenone, acetaldehyde, and benzene. The latter clearly arose from unreacted phenyl groups of the triphenylalane (*215*). Participation of the solvent in the reaction was also established in a study of the autoxidation of triphenylalane in C^{14}-labeled benzene, in which C^{14}-labeled phenol and biphenyl were isolated after hydrolysis (*216*).

Interaction of trialkyl alanes with elementary sulfur in equimolar amounts gives dialkyl-alkylmercapto alanes in relatively good yield. Attempts to introduce more sulfur into the organoaluminum compound gave no well-defined products. Hydrolysis of these compounds produced, in addition to thiols, hydrogen sulfide, dialkyl thioethers, and compounds with a higher sulfur content (dialkyl dithio and trithio ethers) (*114*, *271*). The products from the reaction of trialkyl alanes with selenium were of similar complexity (*271*).

By the interaction of sulfur dioxide and trialkyl alanes, when the Al—C bond is added across the S—O bond, alkyl sulfinates of aluminum are obtained (*231*, *313*). The analogous reaction with 3 moles of sulfur trioxide leads to alkyl sulfonates (*19*):

$$R_3Al + 3SO_3 \rightarrow Al(OSO_2R)_3$$

The sulfur trioxide is not used in the free state but in the form of an adduct with, e.g., pyridine, dimethylformamide, or dioxane; the yields of sodium alkyl sulfonates obtained after alkaline hydrolysis are up to about 70%.

Data for the reactions of trialkyl alanes (*20*, *248*) or dialkylalkoxy alanes (*248*) and dialkylhalogenoalanes with sulfuryl chloride are contradictory; in one case (*248*), after hydrolysis of the reaction products, alkyl sulfonyl chlorides, and in another alkyl chlorides (*20*), were obtained, despite the use of similar reaction conditions (temperature below 0°C, and hydrocarbon solvent).

2. With Protonic Acids

In general all Al—H and Al—C bonds in organoaluminum compounds react quantitatively at or below room temperature with water and alcohols to form compounds with Al—O bonds. Thus trialkyl alanes with alcohols produce aluminum alcoholates and alkanes. Reaction between water or most of the lower alcohols (methanol, ethanol) and trialkyl alanes with small alkyl groups is usually explosive if the undiluted components are mixed at room temperature. If certain safety precautions are observed, however, it is possible to carry out the hydrolysis (or deuterolysis for analytical purposes) so as to obtain the corresponding hydrocarbons. Ether solutions are particularly advantageous as the etherates of trialkyl alanes react less vigorously than the free compounds.

The reaction of trialkyl alanes with tertiary alcohols is worth mentioning in this connection, as only the first alkyl group is split off. The resulting dialkyl-*tert*-alkoxy alanes are particularly unreactive because of steric screening of the AlO_2Al bridge. They are also astonishingly stable to air oxidation (*106, 107*).

Ammonia, mono and dialkyl or mono and diaryl amines form 1:1 adducts with organoaluminum compounds AlR_3 (R = hydride, alkyl, aryl) at below 0°C and these split off hydrogen (from R_2AlH) or alkane (from R_3Al) on warming (*12, 56, 73, 151, 152, 153, 164, 230, 251*); e.g., the products are dialkyl(aryl)-dialkyl(aryl)amino alanes:

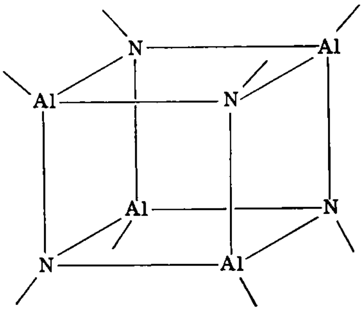
$$R_2AlR' + HNR''_2 \longrightarrow R_2AlR' \leftarrow NHR''_2 \longrightarrow R_2AlNR''_2 + R'H$$

(where R′ = H, alkyl, aryl). Cleavage of hydrogen from the AlH group occurs under appreciably milder conditions than that of alkane from the AlR group. Thus aluminum hydride reacts with amines at below 0°C and dialkyl aluminum hydrides, for example, with piperidine form dialkyl piperidinoalane quantitatively at about 40°C. Aminolysis of trialkyl alanes with piperidine, on the other hand, occurs only above 100°C. This difference in behavior has been recommended as a basis for the quantitative determination of dialkyl alanes, R_2AlH, in trialkyl alanes, R_3Al (*191*).

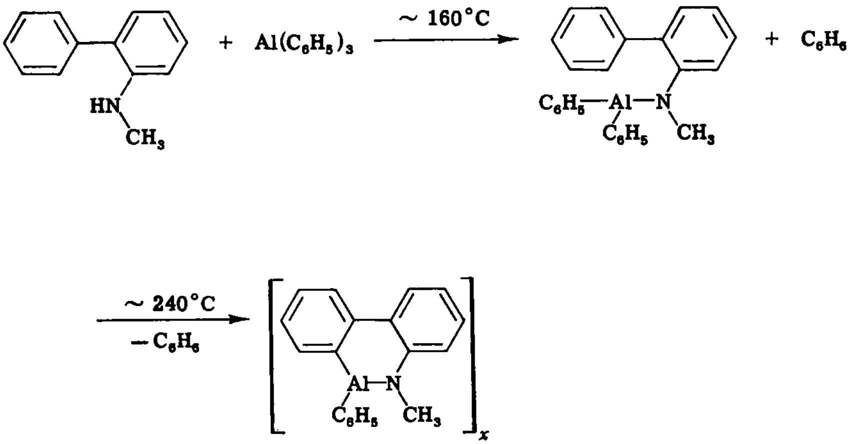
Dialkyl-monoalkylamino alanes, which are easily made from monoalkylamines and trialkyl or dialkyl alanes, lose one molecule of hydrocarbon under fairly energetic conditions (from about 180°C). The products are two- or three-dimensional structures of the empirical formula $(RNAlR')_n$, which usually have a high molecular weight. Only in special cases is it possible to make compounds of lower molecular weight. For example, triphenylalane and arylamines without substituents in the ortho position (e.g., aniline, *m*-toluidine, *p*-chloroaniline) split off 2 moles of benzene and give tetrameric AlN compounds (*120, 121, 167*):

$$4AlPh_3 + 4NH_2{-}Ph \rightarrow [Ph{-}Al{-}N{-}Ph]_4 + 8PhH$$

X-ray structural analysis shows the tetramer to have the "cubane" structure:



The heating of an equimolar melt of 2(methylamino)biphenyl- and triphenylalane at 160°C leads to the evolution of one equivalent of benzene. Further heating at 240°C produced about one more equivalent of benzene. The resulting pale amber-colored highly associated ($x > 1$) substance does not melt under 500°C and is insoluble in most aliphatic and aromatic hydrocarbons. The compound was identified as 9-methyl-10-phenyl-10,9-aluminazarophenanthrene (*69*).



The reaction of dialkyl(aryl) phosphines and arsines with trialkyl alanes is analogous to that for the corresponding nitrogen compounds. After splitting off 1 mole of alkane (with phosphines at ca. 140°–160°C; with arsines at 150°–170°C), dimeric dialkyl-dialkylphosphino or arseno alanes remain (*47*, *113*):

$$R_3Al + R'_2PH \rightarrow \frac{1}{2}[R_2AlPR'_2]_2 + RH$$

Various other compounds with acid hydrogens also split off hydrogen (or hydrocarbons) when they react with organoaluminum compounds and yield products of the type R_nAlX_{3-n} ($n = 0$–2). [For reactions with inorganic compounds (HCl, NaOH, etc.) see reference (*299*).] Hydrogen cyanide with trimethylalane gives the tetrameric dimethylaluminum cyanide (*46*). Finally, mention may be made of the reaction of trialkyl alanes with organic acids (e.g., propionic and methacrylic acids) from which dialkyl aluminum carboxylates may be isolated (*48*, *273*).

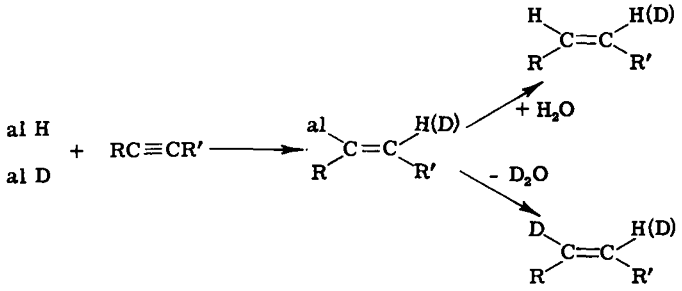
Various investigations have also been made recently on reactions of organoaluminum compounds with compounds containing acidic hydrogen bonded to carbon. Not only AlR_3 and R_2AlH but also their addition compounds with amines and also certain complex salts (e.g., $MAlR_4$, $MAlR_3H$, $MAlH_4$) have been examined. In some cases cleavage of H_2 or RH occurs practically quantitatively with the hydrocarbons (e.g., acetylene, 1-alkynes; cf. Section V,B,4). The exact experimental conditions (temperature, solvent) are often critical for securing a smooth reaction following a single route. With aliphatic unsaturated hydrocarbons, hydroalumination is the main reaction that competes with protonolysis. Other side reactions (e.g., dimerization of hydrocarbons) can also interfere. The reaction of trialkyl alanes with cyclopentadiene may be quoted as an example. The hydrocarbon does not react with the aluminum compound at low temperatures. If, however, elevated temperatures are used, dimerization of the hydrocarbon occurs and consequently no products of protonolysis are found but only addition products of the organoaluminum compound formed because of the hydrocarbon dimerization. The residual (strained) C=C double bond reacts relatively readily with the Al—C bond. If, however, gaseous cyclopentadiene diluted with nitrogen is led into trialkyl alane (e.g., triisobutylalane) heated to 140°–180°C in a reactor, the main product is said to be diisobutylcyclopentadienylalane in spite of the high temperature (*148*).

Cyclopentadiene also splits off hydrogen with the complex alkali alanates, $MAlH_4$, under certain conditions. It is stated that all the hydride hydrogen can be replaced by cyclopentadienyl groups (*285*). Furane and thiophene react with their acidic hydrogen in the 1-position (*284*).

3. Reduction of Organic Compounds

Dialkyl alanes, R_2AlH, are now widely used in place of lithium aluminum hydride as reducing agents because they are particularly readily prepared (see Section II,A,1) and may be used in the most varied solvents. A whole range of organic compounds with functional groups may be transformed by a process involving combination of reduction (hydroalumination) and hydrolysis.

a. Reduction of Unsaturated Hydrocarbons. The transformation of unsaturated to saturated hydrocarbons by hydroalumination and subsequent hydrolysis may be of interest because of the selectivity of the AlH addition. It has been possible to prepare definite deuterated hydrocarbons (*102*) by the following selective routes (*254*):



Dienes may be transformed into alkenes by partial hydroalumination followed by hydrolysis. The reactions occur particularly unambiguously and often with almost quantitative yields if the dienes contain certain types of C═C double bond (see Section V,B,3) [e.g., 4-vinylcyclohexene → 4-ethylcyclohexene; limonene → 1-methyl-4-isopropylcyclohexene (*296*); 2,6-dimethyl-2,7-octadiene → 2,6-dimethyl-2-octene (*227*)]. *Cis* hydroalumination of alkynes having C≡C triple bonds in the middle of the chain leads via the corresponding alkenyl alanes to 1,2-*cis*-disubstituted ethylenes (*252*).

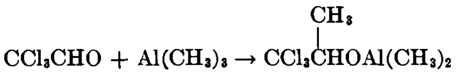
b. Reduction of Organic Compounds Containing Oxygen. The Al—H bond in dialkyl alanes, R_2AlH, reacts at room temperature with aldehydes, ketones, carboxylic acid esters, and epoxides to yield dialkylalkoxy alanes, from which the corresponding alcohols are readily obtained by hydrolysis (*174*, *296*). Only in exceptional cases can all three of the aluminum valencies be used for the reduction (after splitting off the alkene). From diethylalane (as well as from triethylalane) and chloral or bromal the corresponding trialkoxy alanes are formed after loss of 2 (or 3) moles of ethylene (*173*):

$$3Cl_3C{-}CHO + (C_2H_5)_2AlH \rightarrow (Cl_3C{-}CH_2{-}O)_3Al + 2C_2H_4$$

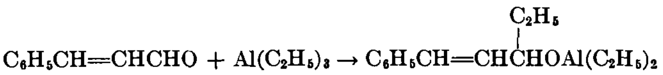
By using triisobutyl- and diisobutylalane such reductions may be extended to other aldehydes and ketones (*206*). Some benzaldehyde derivatives, furfural, and some azulene aldehydes are reduced without the occurrence of *C*-alkylation. Both 1,2-unsaturated aldehydes and ω-trichloroacetophenone give the corresponding alcoholates with triisobutylalane in a 3:1 molar ratio (*296*). Isobutylalanes and similar alkyl alanes with an alkyl group branched in the 2-position are of special significance, for with triethylalane only one aluminum valency is involved during the reaction with ω-trichloroacetophenone, benzophenone (*179*), and benzil, only 1 mole of C_2H_4 being split off (*296*):

$$Al(C_2H_5)_3 + (C_6H_5)_2CO \rightarrow (C_2H_5)_2AlOCH(C_6H_5)_2 + C_2H_4$$

With benzaldehyde, AlH reduction is accompanied by addition of the Al—C bond to the carbonyl group (*296*). Indeed, it is generally true to say that when organic carbonyl compounds react with tri-1-alkyl alanes or triaryl alanes, this addition of AlC to the carbonyl group is the main reaction. The following are some examples (*176*, *301*):



$$CCl_3CHO + Al(CH_3)_3 \rightarrow CCl_3\overset{CH_3}{\overset{|}{C}}HOAl(CH_3)_2$$



$$C_6H_5CH{=}CHCHO + Al(C_2H_5)_3 \rightarrow C_6H_5CH{=}CH\overset{C_2H_5}{\overset{|}{C}}HOAl(C_2H_5)_2$$

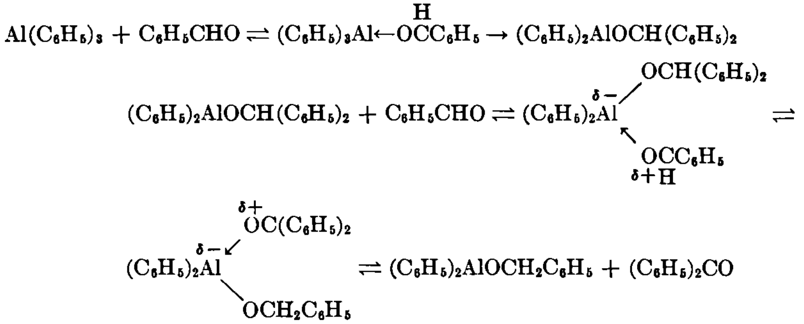
$$(C_6H_5)_2CO + Al(C_6H_5)_3 \rightarrow (C_6H_5)_3COAl(C_6H_5)_2$$

Formaldehyde (paraformaldehyde, trioxane) also undergoes a reaction with trialkyl alanes in which Al—C bonds add to the carbonyl group:

$$alR + CH_2O \rightarrow alOCH_2R$$

(where al = $\frac{1}{3}$Al). This reaction has been suggested for the conversion of long-chain trialkyl alanes to primary alcohols (*165*).

From the point of view of preparative reactions, alkylating reduction with trialkyl alanes is in no way comparable with the analogous reaction of organomagnesium compounds, since for the most part only one Al—C bond reacts with the carbonyl group. The remaining two alkyl groups are virtually lost. Moreover, side reactions interfere in many cases as, for example, when self-condensation of the carbonyl compound occurs or there are subsequent reactions involving the initial products (e.g., Meerwein-Ponndorf oxidation-reduction equilibria). As a result, a single reaction product is not obtained. With a 1:2 molar ratio of triphenylalane and benzaldehyde, for example, addition to the C—O bond and subsequent hydride transfer in a type of Meerwein-Ponndorf reaction results in the product after hydrolysis consisting of almost equimolar quantities of diphenylcarbinol, benzophenone, and benzyl alcohol (*176*):

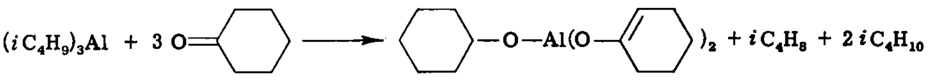


$$Al(C_6H_5)_3 + C_6H_5CHO \rightleftharpoons (C_6H_5)_3Al\leftarrow O\overset{H}{C}C_6H_5 \rightarrow (C_6H_5)_2AlOCH(C_6H_5)_2$$

$$(C_6H_5)_2AlOCH(C_6H_5)_2 + C_6H_5CHO \rightleftharpoons (C_6H_5)_2Al\begin{matrix} \overset{\delta-}{\diagup} OCH(C_6H_5)_2 \\ \nwarrow OCC_6H_5 \\ \delta{+}H \end{matrix} \rightleftharpoons$$

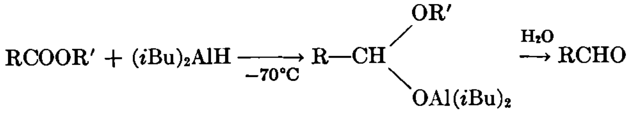
$$(C_6H_5)_2Al\begin{matrix} \overset{\delta+}{} OC(C_6H_5)_2 \\ \overset{\delta-}{\swarrow} \\ \diagdown OCH_2C_6H_5 \end{matrix} \rightleftharpoons (C_6H_5)_2AlOCH_2C_6H_5 + (C_6H_5)_2CO$$

Reaction of carbonyl compounds with triisobutylalane also is often not limited to reduction. Only 1 mole of isobutene is obtained with cyclohexanone and acetophenone because, following enolization of the ketone, isobutane is split off from the two last isobutyl groups (*274*):



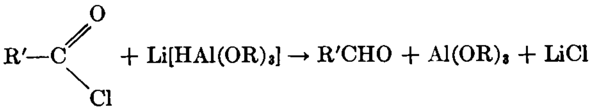
It is clear also that self-condensation of the carbonyl compounds cannot always be entirely avoided (*311*).

Aromatic and aliphatic *N*,*N*-dialkyl carboxylic acid amides, carboxylic esters, and free carboxylic acids are converted into aldehydes by diisobutylalane if reduction is carried out at low temperatures (0°C or −70°C) (*269*, *279*, *280*, *286*):



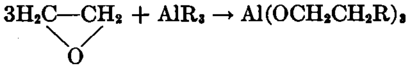
$$RCOOR' + (iBu)_2AlH \xrightarrow[-70^{\circ}C]{} R{-}CH\begin{matrix} \diagup OR' \\ \diagdown OAl(iBu)_2 \end{matrix} \xrightarrow{H_2O} RCHO$$

At higher temperatures reduction to the amine or alcohol stage takes place. The complex salt of sodium hydride and diisobutylalane may be used in place of the latter (*279*, *280*, *287*). It may also be mentioned in this connection that complex salts such as $Li[Al(OR)_3H]$, with $R = C_2H_5$ or *tert*-C_4H_9, may also act as selective reducing agents. Such compounds are used in reducing *N*,*N*-dialkyl carboxylic amides or carboxylic chlorides, when aldehydes are obtained (*36*, *37*):



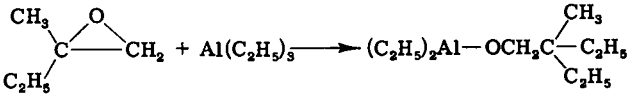
$$R'{-}C\begin{matrix} \diagup\!\!\diagup O \\ \diagdown Cl \end{matrix} + Li[HAl(OR)_3] \rightarrow R'CHO + Al(OR)_3 + LiCl$$

(where R = C_2H_5, *tert*-C_4H_9). Primary alcohols are also formed by reduction of epoxides and subsequent hydrolysis. With ethylene oxide the carbon chain of the original alkyl radical is lengthened by two CH_2 groups, and all the alkyl groups seem to be transformed into alkoxy groups (*10, 51, 229*):

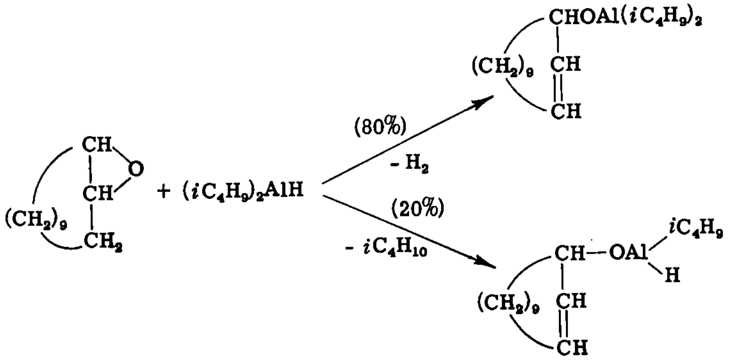


$$3H_2C{-}CH_2 + AlR_3 \rightarrow Al(OCH_2CH_2R)_3$$

With mono- or asymmetrically dialkylated ethylene oxides one obtains, in general, after hydrolysis of the products of alkylation, 2-substituted or 2,2-disubstituted primary alcohols. Only one alkyl group of the trialkyl alanes reacts with the epoxide function (*124*), e.g.,



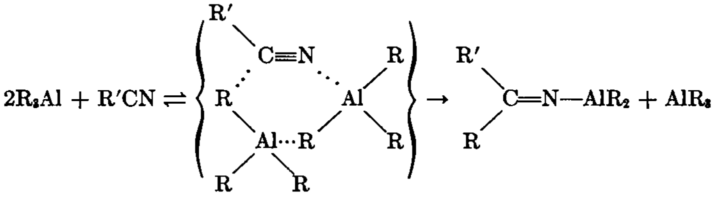
When dialkyl alanes are used in place of trialkyl alanes, the result is generally a mixture of alcohols, with R partly replaced by H. In certain special instances triisobutylalane, for example, reacts with epoxides and H_2 or RH is split off. 1,2-Epoxycyclododecane and 1,2-epoxycyclodeca-5,9-diene give, after hydrolysis, 1-hydroxycyclododeca-2-en (*125*) and 1-hydroxycyclododeca-2,5,9-triene (*125*):



c. Reductions of Organic Compounds Containing Nitrogen (Nitriles, Azomethines, Azides, Organocyanates, and Organothiocyanates). The reaction of organoaluminum compounds with nitrogen compounds is similar to that with those of oxygen. Azomethines [including the corresponding nitrogen heterocycles (*195*)] and nitriles (*79, 204, 205, 223, 265*) are reduced by dialkyl alanes or triisobutylalane with formation of isobutene and addition of an Al—H bond. Following hydrolysis either amines (from azomethines) or aldehydes (from nitriles) are obtained (*265*):

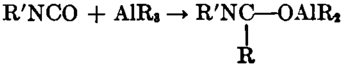
$$\mathrm{RCN + HAl(}i\mathrm{C_4H_9)_2 \rightarrow RCH{=}NAl(}i\mathrm{C_4H_9)_2 \xrightarrow{+H_2O} RCHO}$$

2 moles (not 1 mole!) triethylalane react with 1 mole alkylnitrile at 80°C to form aluminum derivatives of imines (*223*):



At elevated temperatures 2 moles of dialkyl alane react with nitriles up to the amine stage. The dialkyl-dialkylamino alanes, $R_2AlNR'(CH_2R'')$, resulting from azomethines form molecular compounds with strong donors. These are colored if the donor is an azomethine or an aromatic N heterocycle and may be used for the quantitative determination of AlH groups in organic aluminum compounds (*191*). Complex salts such as $Li[(RO)_3AlH]$ (*37, 38*) or $Na[(iC_4H_9)_2AlH_2]$ (*287*) may be used in the preparation of aldehydes instead of diisobutylalane (cf. Section V,D,3b).

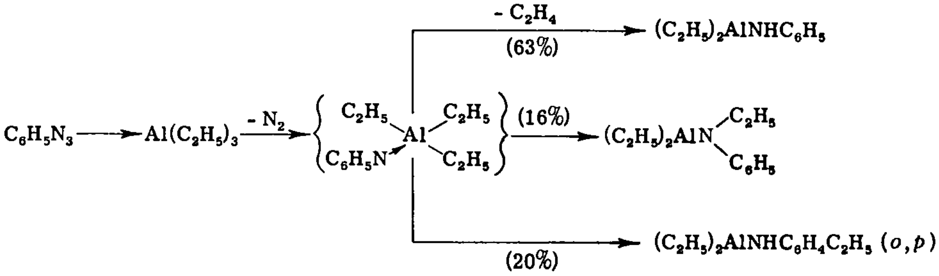
Trialkylalanes or, e.g., ethylaluminumsesquichlorides react with alkylisocyanates or alkylisothiocyanates to form the following products (*218, 223*):



$$\mathrm{R'NCO + AlR_3 \rightarrow R'N\underset{\underset{\textstyle R}{|}}{C}{-}OAlR_2}$$

The hydrolysis of these organoaluminum compounds results in the formation of *N*-alkylcarbonic amides R'NHCOR (*223*).

Phenyl azide forms a 1:1 adduct with triethylalane at −70°C; this decomposes when warmed to room temperature under nitrogen (*100*) and the formation of various products:



On decomposition of the 1:1 adduct of phenyl azide with both alkyl aluminum chlorides, the main reaction is *N*-ethylation with the formation of *N*-ethylanilides (*100*).

d. Reactions with Acid Chlorides and Halohydrocarbons. Organic compounds containing chlorine (e.g., carboxylic acid chlorides and chlorohydrocarbons) often react with organoaluminum compounds to form aluminum chlorides. Trialkyl alanes are not suitable for preparing ketones from carboxylic acid chlorides because of the high reactivity of the first Al—C bond. The corresponding ketones may, however, be made by using alkyl aluminum chlorides (*1, 201, 203, 220*). This is particularly true of the alkyl aluminum sesquichlorides, which are easily prepared from ethyl or methyl chloride and aluminum, and which give the corresponding ethyl or methyl ketone in excellent yield (*23*), e.g.

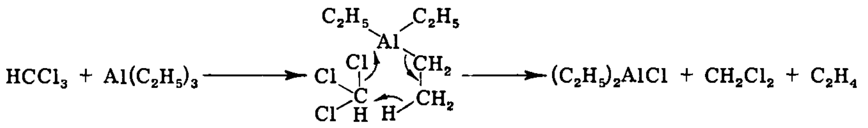
$$3RCOCl + (C_2H_5)_3Al_2Cl_3 \rightarrow 3RCOC_2H_5 + 2AlCl_3$$

Saturated hydrocarbons have been suggested as solvents. All the alkyl groups of the sesquichlorides can be used in forming ketone. Yields are smaller in aromatic hydrocarbons because of Friedel-Crafts acylation of the solvent. The use of complex salts of aluminum sesquichloride with sodium chloride in place of the free sesquichloride has also been suggested for converting carboxylic acid chlorides into ketones (*54*). Benzophenone and acetophenone may also be made from the corresponding acid chlorides by the use of lithium tetraphenylalanate (*262*). By adhering to particular reaction conditions it should also be possible to use the corresponding alkali tetraalkyl alanates for ketone synthesis.

In the reaction of alkyl alanes with chlorohydrocarbons (e.g., dichloromethane, carbon tetrachloride), various alkylated chlorohydrocarbons are formed in addition to aluminum-chlorine compounds (*174a, 221, 224*). Under some conditions the reactions may be explosive, particularly when using hydrocarbons containing several chlorine atoms (e.g., CCl_4) (*221, 224*). Such reactions appear to be quite complicated, with several successive steps. If, for example, a trialkyl alane is brought together with an alkyl halide, the relatively slow reaction

$$AlR_3 + R'Cl \rightarrow R_2AlCl + R—R'$$

is followed by a considerably faster reaction between the alkyl aluminum halide and alkyl halide. Under the influence of the Al—X bond, 1-alkyl halides are isomerized to *sec*-alkyl halides from which HX is then split off. The product is a mixture of dark-colored polymeric residues, hydrogen halide, and both saturated and unsaturated hydrocarbons (*55, 202, 208, 250*). Polychlorinated hydrocarbons are reduced rather than substituted by triethylalane (*174a, 221, 222*). Dichloromethane, for example, is transformed into methyl chloride, and chloroform into dichloromethane. The following mechanism has been suggested for such reactions:



Trialkyl alanes react differently with carbon tetrachloride, as is shown by the formation of ethyl chloride or butyl chloride, according to whether triethyl- or triisobutylalane is employed (*49*, *222*, *224*).

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