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The Etherates of Organoaluminium Compounds

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The literature data on the synthesis and chemical and physicochemical properties as well as the applications of the etherates of organoaluminium compounds are considered systematically and critically. The similarity and differences between the properties of the etherates and ether-free aluminium alkyls are demonstrated and the applications of the etherates of aluminium alkyls are discussed.
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I. INTRODUCTION

The application of organoaluminium compounds (OAC) have been greatly extended recently[1-6], but many difficulties arise in studies involving OAC due to their highly corrosive nature. A number of workers have found that many chemical reactions of OAC are characteristic of their etherates, which have been more readily available and are more convenient to handle and therefore can be used successfully instead of the ether-free OAC. Furthermore, examples are known where the use of etherates involves the manifestation by the latter of completely specific properties.

No attempts have been made to survey the literature data on OAC etherates, probably because the principal results concerning the specific features of these compounds have been obtained during the last ten years and their importance is still not adequately recognised[5,6]. The available reviews of OAC coordination complexes, including individual data on etherates, are based on results published up to the beginning of the 1960s [1,7-10] or are devoted to special problems (polymerisation[11,12], ligand exchange[13,14]). A monograph[15] deals with the literature up to 1966, mainly concerning various aspects of physicochemical studies on aluminium complexes; another publication[16] is descriptive.

The aim of the present review is to draw the attention of investigators to certain aspects of the chemistry of OAC etherates and to the possibility of their employment. The review deals systematically and critically with the literature data of the synthesis, physicochemical and chemical properties, and applications of the etherates of OAC complexes published mainly during the last decade. The properties of the etherates are compared with those for the ether-free aluminium alkyls. The influence of complex formation on OAC reactions is discussed. The tables present the constants of the most typical etherates among those which have not been included in the reviews mentioned above.

The conclusions reached can be used in considering many general problems of the chemistry of organometallic compounds, including the chemistry of complexes of aluminium alkyls with S-, N-, and P-organic donors.

II. THE ETHERATES OF ALUMINIUM TRIALKYLS

1. Composition and Structure

It has been established by various methods that the composition of the etherates usually corresponds to monomeric 1 : 1 complexes having the general formula $R_3Al.OR_2$. This composition is most likely for monofunctional ethers and aluminium alkyls with not unduly cumbersome side groups[7,8,17-23], but in the case of t-butyl compounds stoichiometry breaks down[23-25].

Bi- and poly-functional ethers can combine with several aluminium alkyl molecules. Dioxan[20-23,26], monoglyme[27,28], diglyme [28,29] and *p*-dimethoxybenzene[30] form stable 1 : 2 adducts; the 1 : 1 compounds are labile and exist in the presence of an excess of the donor. Acetals give rise to both 1 : 1 and 2 : 1 complexes[23,31]. The formation of complexes of triethylaluminium with dimethyl[29] and diethyl[31] ethers of ethylene glycol, the dimethyl ether of tetraethylene glycol[31], and polyethers with higher molecular weights[6,32,33] involves the attainment of an Al : O ratio of 1 : 1. However, the products formed are unstable and on heatin *in vacuo* split off part of their aluminium trialkyl and are converted into compounds of the type

$$-O-CH_2CH_2-O-CH_2CH_2-$$
$$\downarrow$$
$$AlEt_3$$

Complex formation with a single oxygen atom in such systems (ΔH = 10–10.5 kcal mole) reduces the electron donating properties of the neighbouring oxygen atom to such an extent that the next AlR_3 molecule is coordinated via at least one heteroatom, reducing still more the basicity of the oxygen which has not reacted[31,34]; this atom is the last to be coordinated (ΔH = −1.5–4 kcal mole^{-1} [31]).

Owing to steric hindrance, substituted poly(vinyl ethers) react with iso-Bu_3Al via only some of the ether groups[23]. Even in the presence of a triple excess of the acceptor, the degree of complex formation never reaches

50%. Furthermore, steric hindrance depends on the regularity of the polymer structure. It is noteworthy that, depending on the conditions (the state of aggregation, the concentration of the solution, temperature, etc.), polymeric ligands assume different conformations and possibilities are created for the occurrence of a wide variety of modes of coordination [23,32]. Systematic study of the formation of complexes by AlR_3 with polydentate ligands will assist in providing an answer to a number of questions concerning the specific features of the behaviour of such complexes in certain reactions (see, for example, Ivanov et al. [35]).

On the basis of spectroscopic data [17,18,36], the structure with C_S symmetry (as for $BF_3.OMe_2$) was postulated for the simplest etherate ($Me_2Al.OMe_2$). A number of infrared and Raman spectroscopic data [6,15] as well as X-ray diffraction [37] indicate an appreciable distortion of the tetrahedron in compounds of this kind. The molecule of triethylaluminium dioxanate has C_{2h} symmetry and the dioxan molecule exists in the chair form [38]. The coordination of the aluminium atom is closer to trigonal than tetrahedral, which can be accounted for by the electrostatic reduction of the electron pairs involved in the Al–C bond.

The coordination compounds of aluminium alkyls with electron-donating molecules, including ethers, readily conduct electricity [3,8,15,39] ($\kappa = 10^{-9}-10^{-7}$ m^{-1} cm^{-1} in solution in hydrocarbons and 10^{-6} in a pure state), which indicates the presence of the ionic complexes $[R_2Al.2OR_2]^+AlR_4^-$ as well as the neutral complex.

2. Methods of Synthesis

Etherates are obtained in high yields by the reactions

$$n\,RMgX + R_{3-n}AlX_n \xrightarrow{Et_2O} R_3Al \cdot OEt_2 + n\,MgX_2 \quad (n = 1-3)\ ^{1,6,7,40-42},$$

$$3LiR_3 + AlCl_3 \xrightarrow{Et_2O} R_3Al \cdot OEt_2 + 3LiCl\ ^{25,43,44}.$$

In principle, various ethers can be used as the solvent and the corresponding etherates can thus be obtained, but only the use of diethyl ether has been described. The etherates R_3Al (R = Me, Et, n-Pr, or n-Bu), [1,7,43,44] iso-Pr_3Al, [41] t-Bu_3Al, [24,25,41] $Al(CH_2SiMe_3)_3$, [42] and optically active tri-2-methylbutylaluminium etherate [5] have been obtained in this way.

The etherates are usually obtained by mixing trialkylaluminium with ether (exothermic reaction)—this was the method used to synthesise the adducts of Me_3Al, [17,18,29,36,45] Et_3Al, [18,20,21,46-48], and iso-Bu_3Al [22,46,48] with a series of dialkyl, alkylaryl, and cyclic ethers as well as $Et_2AlCH_2X.OEt_2$ (X = Cl, Br, or I) [49] and $(n\text{-}C_{10}H_{21})_3Al.iso\text{-}OPr_2$. [7]

When the etherate is acted upon by another ether which is a more powerful electron donor, a new complex is formed. The 2:1 adducts of trimethylaluminium with dioxan [26] and monoglyme [27] as well as compounds of triethyl-, [20,21] tripropyl-, and tributyl-aluminium [50] of various ethers have been obtained in this way.

According to patent data [5], the etherates of trimethyl- and triethyl-aluminium have been synthesised via the scheme

$$3NaAlR_4 + Al + 3Hg \xrightarrow{THF} 4R_3Al \cdot THF + 3NaHg.$$

A number of etherates have been obtained by adding the etherates of aluminium hydride to olefins on heating under pressure [1,6,7]:

$$AlH_3 \cdot Et_2O + 3CH_2{=}CHR \rightarrow (RCH_2{-}CH_2)_3Al \cdot OEt_2;$$
$$R = H,\ Me,\ Et,\ Pr,\ C_{10}H_{21}\ etc.$$

The above methods are simple in principle, but their application requires the availability of the organometallic compounds. A more convenient procedure involves treatment of alkyl halides in ether with metallic aluminium and magnesium:

$$2Al + 3Mg + 6RX \xrightarrow{ether} 2AlR_3 \cdot ether + 3MgX_2.$$

According to the latest data [51-56], the use of methods described previously [1,7] leads to the cleavage of the ether and the yield of the pure etherate is appreciably reduced [51,52]. Conditions preventing the ether cleavage have been found and triethylaluminium phenetolate has been obtained in 80% yields under these conditions [53,54]. However, a large excess of the ether is used to obtain a liquid reaction mixture and the final solution frequently contains organomagnesium compounds in addition to the OAC. It is more convenient to carry out this reaction in a hydrocarbon medium in the presence of 1.0 mole of ether per gram-atom of aluminium [21,50,55-57]. As a result, there is no need for vacuum distillation. The solution contains only the OAC and can be used directly, for example, in alkylation or polymerisation reactions, which greatly simplifies the experimental technique.

3. Physical and Chemical Properties

(a) Stability. With rare exceptions the etherates are colourless liquids which distil *in vacuo*. Compounds of the type $R_3Al.OR'_2$, where R, R' = Me or Et, can be distilled at atmospheric pressure. The adducts of trimethylaluminium and ethers containing more than one oxygen atom are solid crystalline substances soluble in hydrocarbons.

The heats of formation of the etherates can serve as an indication of their stability. Table 1 shows that, when complexes are formed by aluminium trialkyls with aliphatic ethers, the length of the groups linked to aluminium or oxygen has a small influence on the heat of formation. The stability of the complexes is greatly reduced on passing from aliphatic to aromatic ethers. In benzene [62] and toluene [63] Me_3Al does not form compounds with diphenyl ether. Experiments on the displacement of ethers from etherates [20] showed that the relative stability of the complexes with aluminium trialkyls increases in the sequence $Ph_2O < PhOR < R_2O <$ dioxan $<$ THF $< (PhCH_2)_2O$; if the position of dibenzyl ether is disregarded, this series is consistent with existing ideas concerning the electron-donating properties of ethers [64,65]. The displacement of tetrahydrofuran and dioxan by dibenzyl ether is associated with the high boiling point of the latter. According to ^1H NMR data for Et_3Al etherates at 20°C, the electron-donating capacity of dibenzyl ether is low (as for aromatic alkyl ethers [21]: $Ph_2O < (PhCH_2)_2O \leq PhOR < Bu_2O$. Ethers are readily displaced by nitrogen- and phosphorus-containing electron-donating molecules [26,43,66-69]. Exceptions are known, concerning mainly phenyl-containing donors [6,44,70] and sterically hindered aluminium alkyls [24].

The formation of the etherate stabilises the Al–C bond in straight-chain and branched aluminium trialkyls, which is reflected by a decrease of their tendency towards isomerisation [24] and racemisation [6] and also by an increase of their thermal stability (depending on the nature of the ether and the strength of the Al ← O bond, the decomposition temperature increases by 35–100°C). [22,48]

Apart from certain adducts with aromatic ethers [20,21,48,57,62] and polyethers [6,15,29,33], etherates do not usually dissociate into components. Dissociation is observed only

when the complexes are diluted by hydrocarbons [71]. On heating or irradiation, the etherates are cleaved, but the OAC undergoes further transformations under these conditions. The photochemical cleavage of etherates derived from aromatic ethers, aromatic alkyl ethers, and dioctyl ether [72] as well as thermal cleavage of etherates derived from dimethyl [53], diethyl [6,24], allyl propyl [17], and allyl phenyl [58] ethers, anisole [21,53-56,73] and its substituted derivatives [53], phenetole [21,53,54], diglyme [29], chlorex [58,74], tetrahydrofuran [24], and other cyclic ethers [4,75-77] have been described. The following reactions are therefore used to convert the etherates into free aluminium trialkyls [5,6,41]:

$$R_3Al \cdot OR_2 \longrightarrow \begin{cases} \xrightarrow[-R_2O]{BF_3 \cdot R_2O} R_2AlF \xrightarrow{RLi} R_3Al \\ \xrightarrow[-R_2O]{KF} (R_3Al)_2 \cdot KF \rightarrow AlR_3 \cdot KF + R_3Al \\ \qquad\qquad \uparrow \xrightarrow[R_3Al \cdot OR_2]{} \downarrow \\ \xrightarrow{AlCl_3} R_2AlCl \cdot R_2O \xrightarrow[-R_2O]{LiH} R_2AlH \xrightarrow{olefin} R_3Al \\ \xrightarrow[-R_2O]{Na} NaAlR_4 \xrightarrow{AlCl_3} R_3Al \end{cases}$$

Table 1. The heats of formation of the etherates R_3Al.ether in solution.

R	Ether	$-\Delta H$, kcal mole^{-1}*	Refs.
Et	Bu_2O	20.0	3,58
Et	$(C_7H_{15})_2O$	18.9	58
Et	$(ClCH_2CH_2)_2O$	16.3	58
Et	PhOEt	14.2	58
Et	Ph_2O	10.2	58
Et	$CH_2(OMe)_2$	31.5**	31
Et	1,4-dioxan	35.3**	31,58
Et	m-$(MeO)_2C_6H_4$	13.4***	31
Et	m-$(MeO)_2C_6H_4$	25.0**	31
Et	$EtO(CH_2CH_2O)_2Et$	18.0***	31
Et	$EtO(CH_2CH_2O)_3Et$	48.0****	31
Et	$MeO(CH_2CH_2O)_4Me$	77.3*****	31
Pr	Et_2O	19.5	59
n-Bu	THF	22.5	59
iso-Bu	THF	22.6	60
C_8H_{17}	Bu_2O	19.0	3

*Taking into account the energy of dissociation via the mechanism $R_6Al_2 \rightarrow 2R_3Al$. [59-61]
**2 : 1 adduct. ***1 : 1 adduct. ****3 : 1 adduct. *****5 : 1 adduct.

The free R_3Al can be isolated from the etherate also with the aid of transolvation with ethers of polyethylene glycols and subsequent thermal dissociation of the complexes formed [6,15].

(b) Physicochemical constants. More or less complete sets of physical properties (boiling and melting points, heats of evaporation and formation, etc.) are available only for isolated examples of aluminium trialkyl etherates [15,45,78]. The simplest constants, such as specific gravity and refractive index, are rarely encountered in the literature [22]. A large number of etherates have been described in the studies quoted (Tables 2 and 3); only the most typical examples are presented here.

In addition, there is some information about the infrared [6,15,18,26,27,36,79,80], NMR, [13,19,39,63,71,81-87] and NQR [88] spectra, luminescence spectra [32], electrical conductivity [22,28,39,59,82], magneto-optical properties [46,89,90], optical rotation [23,91,92], inversion [93,94], dipole moments [3,65], and thermodynamic characteristics [51,78,95-99].

Table 2. The properties of tri-isobutylaluminium etherates.

Ether	B.p., °C (mmHg)	n_D^{20}	d_{20}^4	Temp. of onset of decomp., °C	References
Et_2O	88 (2)	—	0.837	155	46, 48
iso- Pr_2O	59—60 (1.5)	1.4519	0.829	—	22
Bu_2O	103—105 (2)	1.4469	0.822	135	22, 46, 48
Dioxan	118—119 (1)	1.4620	0.868	—	22
PhOMe	73 (1)	1.4808	0.874	110	22, 48
PhOEt	80—81 (1.5)	1.4790	0.877	90	22, 48

Table 3. The properties of aluminium trialkyl etherates.

Alkyl	Ether	B.p., °C (mmHg)	d_4^{20}	References
Me	THF	54—55 (2)	—	18
Me	PhOMe	87 (2) *	—	51
Me	$(CD_3)_2O$	72—73 (42)	—	36
Et	Am_2O	109—110 (2)	0.825	58
Et	$(C_7H_{15})_2O$	141—143 (2)	0.828	58
Et	PhOEt	88—89 (1)	0.880	58
Et	Dioxan	111—113 (1)	—	20, 21, 48
Et	Cyclohexyl ethyl ether	90—91 (1)	—	20, 21, 56
Et	$(MeOCH_2)_2$	116—117 (2.5)	—	47
Pr	Bu_2O	103—107 (1.5)	—	21, 50
Pr	PhOEt	115—118 (5)	—	21, 50
Bu	Bu_2O	129—132 (2)	—	21, 50
Bu	PhOEt	123—126 (2)		21, 50
Me_3SiCH_2	Et_2O	64 (0.02)	—	42

*Colourless needles at −78 °C.

(c) Reactions with inorganic compounds. Me_3Al does not usually react with alkali metals, but in the presence of ether or tetrahydrofuran (THF) the reaction proceeds smoothly with formation of $MAlMe_4$. [5] Other R_3Al readily react both in ether and in a hydrocarbon. The etherates react in a very unusual manner with alkali metals or magnesium in the presence of unsaturated hydrocarbons. In this case interesting cyclic OAC are formed together with $MAlR_4$, [100-104] for example:

$$2Na + 2R_3Al \cdot OR_2 + \text{naphthalene} \xrightarrow{R_2O} Na\left[\text{naphthalene}\right]AlR_2 \cdot OR_2 + NaAlR_4 .$$

Free aluminium trialkyls react very vigorously with water (explosively); on the other hand, the corresponding etherates interact quietly [105], particularly in the presence of a solvent, an alkane and aluminium hydroxide being produced. For the molar ratio R_3Al : water = 2 : 1, hydrolysis at room temperature leads to the etherates of alkyl aluminoxanes [106]:

$$2R_3Al \cdot Et_2O + H_2O \rightarrow (R_2Al)_2O \cdot Et_2O + 2RH + Et_2O .$$

The yield of tetra-alkylaluminoxanes formed from the etherates is much higher (90%) than in the hydrolysis of free R_3Al (25–30%).

Aluminium trialkyl diethyl etherates begin to react with carbon dioxide at 100–120 °C. The final product is the dialkylaluminium salt, which readily hydrolyses to a

carboxylic acid[24,107-109]. When etherates are treated with CO_2 under pressure, a second Al–C bond is involved in the reaction[6,7]. R_3Al diethyl etherates react with sulphur dioxide to form the corresponding sulphinic acids. The reaction proceeds readily at −50°C via the three Al–C bonds; the yield of highly pure aluminium trisulphinate is quantitative[109,110]. The yields of carboxylic and sulphinic acids in reactions involving etherates are much higher than for ether-free aluminium trialkyls, since the etherates do not undergo side reactions.

Alkali metal hydrides and fluorides (except LiF) react with R_3Al and their etherates to form complexes of the type $M[AlR_3X]$, where X = H or F;[5,6] they do not react with chlorides and bromides. Ethers accelerate the reaction of lithium hydroxide with Me_3Al, which leads, depending on the reactant ratio to $[Me_2AlOLi].AlMe_3$ or $Me_2AlOLi.R_2O$. The ability to accelerate this reaction decreases with enhancement of the electron-donating properties: PhOMe > Et_2O > THF.[111] Triethylaluminium and its tetrahydrofuranate do not react with CaH_2; treatment with BaH_2 leads to $Ba[AlEt_3H]_2$.[112]

On interaction with the acid derivatives of many metals and metalloids, the OAC exchange the organic group for the acid residue with formation of organoelemental compounds:

$$R_3Al \cdot OR'_2 + EX_n \rightarrow ER_n + X_3Al \cdot OR'_2 \quad .$$

In these reactions the etherates are as a rule more effective than ether-free aluminium alkyls. The synthesis of trialkylboranes (yield 87–98%),[1,7] alkylmercury compounds (80%),[7,113] dialkylthallium chlorides (57–63%),[7] mixtures of ethylsilanes (85%),[5,6,14] and trialkyl derivatives or gallium[114], antimony, and bismuth[1] has been described. The etherates are particularly effective in the synthesis of alkyl derivatives of phosphorus[6,7], lead[6], and tin[115,116].

Transition metal salts, which do not form stable alkyl compounds, are reduced by etherates to lower-valence compounds or to the free metal[51,117-119]. The reaction proceeds in general at a high rate and to a higher extent than in the case of ether-free trialkylaluminium[21,120-122]. In the presence of stabilising ligands (phosphines, 2,2-bipyridyl, olefins, etc.) it is possible to isolate the intermediates[5,123]. A multiplicity of transition metal compounds have been synthesised in this way, for example: $(Ph_3P)_3Co(N_2)H$;[5] $MeCu(PPh_3)_3.0.5Et_2O$;[124,125] $(Ph_3P)_2Ni.(C{\equiv}CPh)H$;[126] $R_2M(bipy)_2$[125] (M = Fe, Co, or Ni); $(Ph_3P)_4RuH_2$;[5] $MnAl_2Et_4L_4.4THF$;[127] $RCrCl_2.3THF$.[128,129]

The reduction of chromium, molybdenum, tungsten, and manganese salts by aluminium alkyls in an ethereal medium in the presence of carbon monoxide has been proposed for the synthesis of the corresponding metal carbonyls (yield 85–86%),[3] which are otherwise difficult to obtain.

(d) Reactions with organic compounds. In contrast to the free tri-n-alkyl derivatives of aluminium, their diethyl etherates do not add to olefins. However, the etherates of aluminium trialkyls containing branched groups react with ethylene (under certain conditions, the yield of the product is quantitative)[24]:

$$(Me_3C)_3Al \cdot OEt_2 + 3C_2H_4 \rightarrow (Me_3C{-}CH_2{-}CH_2)_3Al \cdot OEt_2 \quad .$$

Like aluminium trialkyls, the etherates catalyse the migration of the double bond in olefins when it is present in the centre of the chain[130]. Under the influence of $Et_3Al.OEt_2$, dodec-6-ene is converted into dodec-5-ene and dodec-4-ene. Hex-2-ene isomerises to hex-1-ene with a much higher yield than in the presence of ether-free aluminium alkyls[131]. The etherates inhibit the *cis–trans* isomerisation of straight-chain octenes, which proceeds under the influence of γ-rays in the presence of aluminium alkyls[132]. When ethylene and triethylaluminium are heated together, a mixture of olefins is formed; in this reaction the etherate gives rise predominantly to α-olefins[6].

Etherates react with molecules containing an active hydrogen atom similarly to free R_3Al (with liberation of RH) but more smoothly[5,133-135]. The reactions of etherates with imines[5] and carboxylic[109], thiocarboxylic[136], dithiocarboxylic[137], dimethylarsinic, and dimethylphosphinic[109,138] acids are therefore used to synthesise the corresponding dialkylaluminium derivatives. The reaction of trimethylaluminium with an excess of MeSH in pentane gives rise to $(MeS)_2AlMe$, while in ether the product is $(MeS)_3Al$ in a yield of approximately 100%.[139]

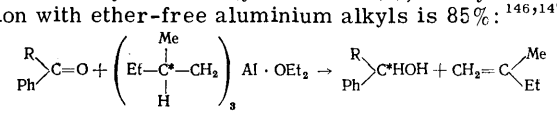
Strong electron donors displace the ethers from etherates, forming complexes with aluminium trialkyls:

$$R_3Al \cdot OR'_2 + D \rightarrow R_3Al \cdot D + R'_2O.$$

A number of such reactions have been achieved, where the donors (D) were NMe_3, PMe_3, and C_5H_5N,[1,7] *N*,*N*,*N*′,*N*′-tetra-alkylethylenediamines[27,66], 2,2′-bipyridyl[26,66,140], 1,10-phenanthroline[26,66], *N*-methylmorpholine and *N*,*N*′-dimethylpiperazine[26], *N*,*N*-dimethylaminomethoxyethane[27], iminotriphenylphosphine[67], R_nEO (E = S, N, or P),[43] and R_3EnPR_3 (E = Si, Sn, or Ge).[44,68,69] The electron-donating capacity of compounds and the rate of displacement decrease in the following sequence[43,68]: $Me_3NO > Me_3PO > Me_2SO > Et_2O$; $Me_3GeNPEt_3 > Me_3GeNPMe_3 > Et_2O \simeq Me_3SiNPMe_3 > Me_2SiPPh_3$.

Aluminium trialkyls in ether do not react with alkyl halides and the reaction with $ClCH_2OMe$ gives a low yield of ethers[141]. In the presence of ether (ether : $R_3Al < 1$) the above reactions proceed readily[74]. Etherates react with CCl_4 to form free radicals and vinyl chloride introduced into this mixture is converted quantitatively into a polymer[142].

The diethyl etherates of R_3Al behave in many instances as effective reducing agents for aldehydes and ketones. Chloral is reduced to trichloroethanol in 89% yield, cinnamaldehyde is converted into ethylstyrylmethanol (95%)[7] and benzophenone is converted into diphenylmethanol (94%).[143] Various alkyl methyl ketones react with $Et_3Al.OEt_2$, forming mainly tertiary alcohols, while free Et_3Al gives a mixture of secondary and tertiary alcohols[144]. The dialkyl etherates of triethylaluminium interact with benzylideneacetophenone via a 1,2-addition mechanism, the yield of the addition product being higher (82%) in the reaction of the di-isopropyl etherate than in the reaction of Et_3Al (69%).[145] The etherates of chiral aluminium trialkyls reduce alkyl phenyl ketones, forming optically active secondary alcohols (yield 91–97%); the yield in the reaction with ether-free aluminium alkyls is 85%:[146,147]



It has been established that, when optically active ethers are used, the aluminium alkyl does not lose the coordinated ligand in this reaction and gives rise to a six-membered transition complex with a pentacoordinate aluminium atom[147]. The nature of the solvent, aluminium alkyl, ether, carbonyl compound, etc. plays a major role in reactions of this type[148-156]. As a rule, on passing to THF and stronger electron donors (amines), the

yields diminish or the reaction does not take place at all [147,153,157-159]. Aluminium trialkyls behave differently in the reactions with anhydrides. The yield of ketene formed from $(CH_3CO)_2O$ increases when the diethyl etherate and particularly the tributylaminate is used instead of free R_3Al. [160]

In a mixture with HCN the etheral aluminium alkyls behave as stereoselective agents for the hydrocyanation of α,β-unsaturated ketones [161-163], for example, cholestenones. The same mixture cleaves the epoxy-groups of steroids, giving high yields of diaxial products. Etherates readily convert epoxyalkanes into the corresponding alcohols [76,150,151]; under certain conditions, triethylaluminium in ether condenses epoxyalkanes to 1,4-dioxan derivatives [164,165]. In contrast to aluminium trialkyls, the etherates interact only insignificantly with the oxygen–oxygen bonds of peroxides [166,167]. The reaction with hydroperoxides [40] proceeds even at 0–20°C, involving the active hydrogen atom and giving rise to organoaluminium peroxides, which are stable in solution for several hours. The diethyl etherate of tri-isobutylaluminium reduces benzonitrile exclusively to benzaldehyde, while free iso-Bu_3Al gives a mixture of the aldehyde and a ketone [168].

III. THE ETHERATES OF ALKYLALUMINIUM HALIDES

With the exception of fluorine-containing OAC, which do not form complexes with ethers [5,10,41], alkylaluminium halides form etherates with a stronger donor–acceptor bond than do aluminium trialkyls. The tendency towards complex formation increases with increasing electronegativity of aluminium: $Et_3Al < Et_2AlCl < Et_2AlBr < EtAlCl_2$. Using the ^1H NMR, [83] cryoscopic [62], conductimetric, and calorimetric [87] methods, a somewhat different OAC acidity series was found: $Et_2AlCl < Et_3Al < EtAlCl_2$; this is associated with the fact that Ph_2O is too weak a base to cleave the diethylaluminium chloride dimer. Diethylaluminium bromide and iodide, which exhibit a greater tendency towards dissociation, add to diphenyl ether [21,87].

Synthesis. These complexes can be obtained by the reaction involving a redistribution of ligands between the alkyl derivatives of sodium [3,169], magnesium [1], or aluminium [1,24] and aluminium halides in ether, for example:

$$n\,RNa + AlCl_3 \xrightarrow{Et_2O} R_nAlCl_{3-n}\cdot OEt_2 + n\,NaCl\ ;$$

$$n\,R_3Al + AlCl_3 \xrightarrow{Et_2O} R_nAlCl_{3-n}\cdot OEt_2\ ;$$

R=Et, Bu, or t-Bu

If the reaction of aluminium with alkyl halides is carried out in ether, a mixture of etherates is formed [21,57]:

$$2Al + 3RX \xrightarrow{R'_2O} R_2AlX\cdot OR'_2 + RAlX_2\cdot OR'_2\ .$$

Higher alkyl halides are cleaved during the synthesis [6,8]. Since ethers retard the cleavage reaction, it is possible to synthesise propyl- and butyl-aluminium sesquichlorides [5], propyl- and isopentyl-aluminium sesqui-iodides, and octyl-aluminium sesquibromides [1] in diethyl ether. Hydrocarbon solutions of diethylaluminium bromide and diethylaluminium iodide etherates have been obtained in 65–90% yield and by the reaction [21,55-57]:

$$2Al + Mg + 4EtX + 2D \rightarrow 2Et_2AlX\cdot D + MgX_2\ ;$$

D = Ph_2O, MeOPh, or EtOPh.

A number of etherates of alkyl aluminium halides have been synthesised by mixing the components and subsequent distillation [15,16,18,48,170] or crystallisation [29,171,172]. In the synthesis of their components account must be taken of the tendency of alkylaluminium dihalides towards disproportionation [173-175]; this tendency increases in the sequence $RAlI_2 < RAlBr_2 < RAlCl_2$: [172,174]

$$2RAlX_2 + \text{ether} \rightarrow R_2AlX + AlCl_3.\text{ether}.$$

The optimum Al : ether ratio can be various and is determined by the nature of the ether [6,172,176]. In this connection it was impossible to obtain the diphenyl etherate [176] and dioxanate [172] of ethylaluminium dichloride in paraffinic hydrocarbons. The dioxanates of ethylaluminium dihalides can be readily obtained from ethylaluminium sesquihalides [172]:

$$2Et_3Al_2X_3 + C_4H_8O_2 \rightarrow [EtAlX_2]_2\cdot C_4H_8O_2 + 2Et_2AlX\ .$$

The formation of Et_2AlX disproves the possibility of disproportionation. The method is of interest, because it makes it possible to obtain the individual compounds from the readily available mixture of alkylaluminium halides.

Table 4. The properties of alkylaluminium halide etherates*.

Etherate	B.p., °C (mmHg)	Other properties	References
$Me_2AlCl\cdot Et_2O$	73—74 (2.5)	—	18
$[Me_2AlCl]_2\cdot[MeOCH_2CH_2]_2O$	—	m.p. 75°	29
$Cl_2AlCH_2AlCl_2\cdot 2Et_2O$	—	m.p. 34-37°	171
$Et_2AlCl\cdot Et_2O$	92—93 (3.5)	d_4^{20} 0.9403	18, 170
$Et_2AlCl\cdot PhOMe$	86 (2)	decomp. temp. 135°	48
$[Et_2AlCl]_2\cdot C_4H_8O_2$	143—146 (3)	m.p. 97-98°	172
$EtAlCl_2\cdot Et_2O$	100—105 (3)	d_4^{20} 1·0779	18, 170
$[EtAlCl_2]_2\cdot C_4H_8O_2$	135—137 (2)	m.p. 118-120°	172
$Et_2AlBr\cdot Ph_2O$	102—106 (4)**	—	21, 56, 57
$[Et_2AlBr]_2\cdot C_4H_8O_2$	—	m.p. 123°	172
$EtAlBr_2\cdot C_4H_8O_2$	—	m.p. 28-30°	172
$Et_2AlI\cdot PhOMe$	99—102 (0.5—1)**	—	21, 56
$Et_2AlI\cdot Ph_2O$	104—105 (1)**	—	21, 56, 57
$[Et_2AlI]_2\cdot C_4H_8O_2$	—	m.p. 127-128°	172
$Et_2AlI\cdot C_4H_8O_2$	—	m.p. ~ 10°	172
$EtAlI_2\cdot C_4H_8O_2$	—	m.p. 46-48°	172
$Bu_2AlCl.Et_2O$	128—130 (0.5)	—	169
$t\text{-}Bu_2AlCl.0.7Et_2O$	70 (10^{-3})	—	21

*The boiling points quoted by Gallais [46,170] (see also Alpatova et al. [15]) are somewhat high compared with the data of other workers.
**With decomposition.

Properties. The majority of the compounds obtained are colourless liquids which can be distilled *in vacuo* and which do not ignite in air; the 2 : 1 complexes with dioxan and monoglyme are crystalline substances (Table 4). According to cryoscopic measurements [18], the etherates of alkylaluminium halides are monomeric. The 1 : 1 compounds of methyl- and ethyl-aluminium halides with di- and poly-functional ethers (dioxan [172], diglyme [29]) are more stable than the R_3Al compounds, and on heating *in vacuo* they split half the ether and are converted into 2 : 1 complexes. Diethylaluminium chloride adds to polyethylene glycol up to the ratio Al : O = 1 : 1, the organic molecule passing from the skew to the transoid conformation in the process [177-179]. 2 : 1 complexes are also

formed under certain conditions [178]. Owing to the presence of the CH_3 side group, polypropylene glycol is incapable of being fully "saturated" by the acceptor. The methylenealuminium compounds $C_2Al-CH_2-AlCl_2$ and $Cl_2Al-CH_2-Al(Cl)-CH_2-AlCl_2$ form complexes with two and three diethyl ether molecules respectively [171,180-182]; on heating above 120°C *in vacuo*, these complexes split off part of the ether with simultaneous disproportionation and polymerisation [171]. The physical properties of the etherates of alkylaluminium halides have been investigated to an even lesser extent than for the etherates of R_3Al. Apart from the data presented in Table 4, there is isolated information about the heats of formation [3,87,177,178], infrared spectra [15,18,178,179], NMR spectra [13,83,171,181-183], and magneto-optical properties [170].

The etherates of alkylaluminium halides show a tendency towards rupturing the C–O ether bond with liberation of the alkyl halide and the formation of alkoxy-compounds of aluminium. Allyl [184] and alkyl phenyl [53-56,73,118] ethers are particularly readily cleaved, while dialkyl ethers [53] and diglyme [29,185] are cleaved with more difficulty. The "stabilising effect" of dialkyl ethers is therefore less pronounced than in the case of R_3Al (the Et_2AlCl decomposition temperature increases from 160° to 170–180°C on formation of the complex with Bu_2O and Et_2O; on the other hand, alkyl phenyl ethers reduce this temperature to 130–135°C [48]). The tendency towards cleavage in the series of aluminium alkyls increases with increase of their acidity: $R_3Al < R_2AlX < RAlX_2$, [73,184] while for different X the tendency increases in the sequence $Cl < Br < I$. [21]

In contrast to free R_2AlCl and $RAlCl_2$, the diethyl etherates of alkylaluminium chlorides do not react with ethyl chloride and vinyl chloride [186], while their reaction with NaF and LiH (in the case of $R_2AlCl.Et_2O$) results in the formation of dialkylaluminium fluorides and hydrides respectively [1]. Alkali metals dehalogenate the etherates of R_2AlCl, sometimes with the cleavage of the ether and liberation of aluminium. The presence of aromatic hydrocarbons rules out side processes, which leads to the formation of the etherates of aromatic alkyl compounds of aluminium [6,187,188]. The etherates of alkylaluminium halides react with tin dichloride and tetrachloride to give a high yield of dialkylstannanes [189] and tetra-alkylstannanes [115] as well as dialkyltin dichlorides [6]. These etherates are used to synthesise various aluminoxanes [106,190,191], including aluminosiloxanes [192]:

$$2R_2AlCl \cdot Et_2O + H_2O \rightarrow (RAlCl)_2O \cdot Et_2O + 2RH + Et_2O \ ;$$
$$R_2AlCl \cdot THF + R_2AlOLi \rightarrow (R_2Al)_2O \cdot THF + LiCl \ ;$$
$$RAlCl_2 \cdot Et_2O + 2R_3SiONa \rightarrow (R_3SiO)_2AlR + 2NaCl \ .$$

The interaction of methylenedialuminium compounds with aldehydes in tetrahydrofuran has been suggested as a method of synthesising olefins [193]:

$$RCHO + Br_2Al-CH_2-AlBr_2 \xrightarrow{THF} RCH=CH_2 \ .$$

Styrene, nitrostyrene, and vinylnaphthalene have been obtained in yields of 65, 60, and 80% respectively.

In contrast to hydrocarbon solutions of OAC and pure R_3Al, which give rise to a maximum in electrical conductivity on mixing with electron-donating molecules in proportions of 1 : 1, pure Et_2AlCl and $EtAlCl_2$ mixed with diethyl ether and tetrahydrofuran exhibit a maximum corresponding to the ratio Al-alkyl : ether 2 : 1. [39] On subsequent dilution with a hydrocarbon, the position of the maximum shifts, tending towards the 1 : 1 ratio. These results have not been explained satisfactorily.

IV. THE ETHERATES OF ORGANOALUMINIUM COMPOUNDS OF THE TYPE R_2AlY (Y = H, OR, NR_2, ETC.)

The etherates of these compounds are less stable than those described above; this is due to the competing interaction of R_2AlY molecules with one another, forming extremely stable associated species. Dialkylaluminium hydrides do not form stable adducts with ethers for this reason [62], but the existence of such compounds has been demonstrated by infrared spectroscopy [6,15] and calorimetric measurements [59].

Like the R_2AlH, their etherates readily add to multiple bonds, but in many instances this entails the formation of other products [194-199]. Thus the etheradduct Et_2AlH reacts with hexa-1,5-diene to form the etherate of diethylhex-5-enylaluminium [196]:

$$(H_2C=CH-CH_2)_2 + Et_2AlH \cdot Et_2O \rightarrow Et_2Al(CH_2)_4CH=CH_2 \cdot Et_2O \ .$$

In the absence of ether, a cyclic OAC is formed, giving rise to methylcyclopentane after hydrolysis [197,198]. In the presence of ether 1,1-dimethylindene interacts stereospecifically with di-isobutylaluminium hydride, forming a product with the *cis*-configuration, while in the absence of ether a molar mixture of the *cis*- and *trans*-isomers is obtained [200]. The reaction of the etherates of dialkylaluminium hydrides with alkenylacetylenes proceeds via two pathways: addition (as for the free R_2AlH) and metallation (as for the aminates of R_2AlH). [201] Two moles of OAC add to alkynes of the type HC≡CR in ethers [202,203]:

$$R'_2AlH + HC \equiv CR \rightarrow R'_2Al-CH=CHR \xrightarrow{R'_2AlH} (R'_2Al)_2CH-CH_2R \ .$$

With increasing basicity of ethers, the yield of product rises [203]. In octane and toluene only the first stage of this reaction occurs, while in triethylamine metallation takes place.

The introduction of a donor alters the reactivity of dialkylaluminium hydrides, probably as a result of the loosening of the Al–H bond, which increases with increasing strength of the donor [6,204]. In the absence of an ether, diazomethane reacts more effectively with the less associated R_3Al than with R_2AlH. In the presence of an ether, the Al–H bond is preferentially involved in the reaction [205]. Apparently this is why R_2AlH are frequently used as reductants in the form of etheral solutions. The alkyl and alkyl halide derivatives of certain elements (Be, Si, Sn, etc.) are reduced by dialkylaluminium hydrides in ether to the hydrides of these elements [6,206,207]. The reduction of optically active R_3SiX by the etherate of iso-Bu_2AlH takes place without change of configuration (X = OMe or OPh) or with its inversion (X = F, Cl, or SMe), depending on the nature of X. [208,209]

The diethyl etherate of di-isobutylaluminium hydride reduces epoxides quantitatively to primary and secondary alcohols [210]. The presence of stronger electron donors leads to an increase of the yield of the secondary alcohol, while pure iso-Bu_2AlH gives preferentially the primary alcohol. Di-isobutylaluminium hydride in ether reduces nitriles, carboxylic acids, esters, and *N*,*N*-disubstituted amides [6,211] to the corresponding aldehydes. In the presence of an excess of iso-Bu_2AlH amides are readily reduced to the amines. Ethereal solutions of R_2AlH can be used to hydrogenate nitrogen-containing heterocycles, for example, quinoline [211]. The reduction proceeds much more readily and in a higher yield than in the case of $LiAlH_4$.

On heating, dialkylaluminium hydrides cleave dialkyl ethers[53], tetrahydrofuran[75,212] and other cyclic ethers[75], diglyme[29], anisole[53], phenetole, and benzyl ethyl and allyl phenyl ethers[5,7] with formation of compounds of the type R_2AlOR'. Diphenyl ether[53] is cleaved above 200°C, while α,β-unsaturated ethers[213] are cleaved at temperatures as low as 25–35°C. Iso-Bu_2AlH reacts with alkyl allyl ethers as a rule at the double bond, giving rise to inner complexes[5].

The presence of a bond between aluminium and O, N, P, and S atoms greatly reduces the electron-accepting properties of aluminium alkyls, but does not eliminate the possibility of the formation of complexes by these compounds with ethers in many instances. Compounds having the composition $Et_2AlPPh_2.Et_2O$,[5,6] $Et_2AlN_2.THF$,[214] and several adducts of the type $R_2AlNR'_2$.ether[59,215] have been described. A number of etherates of alkylaluminoxanes (Table 5), which undergo polycondensation with formation of polyalkylaluminoxanes on heating, have been synthesised and characterised (Table 5).

Table 5. Alkylaluminoxane etherates.

Etherate	Yield, %	d_4^{20}	Molecular weight		Refs.
			found	calc.	
$(MeAlCl)_2O\cdot Et_2O$	—	—	444	245	190
$(Me_2Al)_2O\cdot THF$	90	—	—	—	191
$Me_3Cl_2Al_2O\cdot Et_2O$	—	—	237–324	224.5	216
$(Me_2Al)_2O\cdot PhOMe$ *	—	—	—	—	191
$(Et_2Al)_2O\cdot Et_2O$	90	0.8576	248	260	106
$(EtAlCl)_2O\cdot Et_2O$	90	1.0880	268	273	106
$(iso\text{-}Bu_2Al)_2O\cdot Et_2O$	85	0.8766	390	372	106
$[(C_8H_{17})_2Al]_2O\cdot Et_2O$	100	1.1332	—	—	106

*M.p. −50°C.

$(Me_2AlCN)_2.THF$,[214] $Et_2AlBH_4.Et_2O$,[217] $EtAlC_2B_9H_{11}.2THF$,[218,219] $(Ph_3Si)_3Al_2Et_6.8THF$,[220] iso-$Bu_2AlMC_5H_5(CO)_3.C_4H_8O_2$ (M = W or Mo),[221] $Me_2AlOLi.E$ (E = Et_2O, THF, or PhOMe),[111] $R_2AlOM(THF)AlR_3$ (M = Li, Na, or K; R = Me, Et, or iso-Bu),[157,222] and $Et_2AlHNi(CDT).Et_2O$ (CDT = cyclododecatriene)[223] should be assigned to the same class of compounds.

V. THE ETHERATES OF UNSATURATED ORGANOALUMINIUM COMPOUNDS

Unsaturated OAC were discovered comparatively recently. Their synthesis in the form of etherates or aminates constitutes frequently the only possibility of isolating them in a pure form; many studies dealing with compounds of the vinyl, acetylene, allyl, and other series have been published.

The direct proximity of a C=C or C≡C bond to aluminium greatly reduces the electron accepting properties of aluminium alkyls owing to the interaction of the π electrons of the multiple bond with the vacant p orbitals of the aluminium atoms in a second molecule, which leads to the formation of a complex with a relatively high dissociation energy[224,225]. On the other hand, aluminium trialkynyls form very stable etherates, sometimes with two ether molecules[224,226]. This is due to a uniform distribution of electron density in the molecule, as a result of which each individual bond has a low polarity; for this reason, the associated species are unstable and are readily cleaved by ether. The foregoing considerations have been confirmed by infrared[227,228] and ^1H NMR[227–231] spectroscopy.

The principal methods for the synthesis of the etherates of unsaturated OAC involve the interaction of alkyl halides and aluminium trihalides with alkenylmagnesium halides[224,229,230,232], alkenyl-lithium[229,230], or sodium acetylides[224,227,228,233,234] in ether. In addition, the reactions of aluminium with vinyl[224] and acetylenic[3] organomercury compounds as well as complex acetylides of the type $MAl(C\equiv CR)_4$ (M = Li or Na) and $NaAlR_n(C\equiv CR)_{4-n}$ are used[224,226]. The etherates of aluminium acetylides are sometimes synthesised by displacing one ether by another in the sequence $Et_2O \rightarrow THF \rightarrow$ dioxan[227] and also by the exchange reaction of $Al(C\equiv CR)_3$ with triethylaluminium or aluminium trichloride in ether[233]. The synthesis of the etherates of allyl-, crotyl, and propargyl-aluminium sesquibromides from aluminium and the corresponding organic bromides has been described[5,232]. The dibutyl etherate and anisolate of but-3-enylaluminium have been synthesised from the Al/Mg alloy and 1-bromobutene[3] in butyl ether or anisole[232]. A method has been patented for the synthesis of the dioxanates, tetrahydrofuranates, and diethyl etherates of a wide variety of cycloalkenylaluminium compounds by the reaction of aluminium, dialkylaluminium hydrides (or $NaAlR_4$), and a conjugated diene in an ethereal medium[235–241].

With the exception of allyl derivatives[6,229,230,232], the etherates of unsaturated OAC are relatively unstable (Table 6). As a rule, compounds with a double bond are mobile liquids, while acetylides are solid crystalline substances. The triacetylides are monomeric in dioxan, while in benzene the molecular weight of $Al(C\equiv CBu)_3.C_4H_8O_2$ varies with concentration (the association factor of 0.7–1% solutions is 1.3–1.5).[224] The molecular weight of the diethyl etherate of trivinylaluminium corresponds to the monomeric form.

Table 6. Etherates of unsaturated organoaluminium compounds.

Etherate	Yield, %	Properties	Refs.
$(CH_2=CH-CH_2-CH_2)_3Al\cdot Bu_2O$	69	b.p. 113 (1)	232
$(CH_2=CH-CH_2-CH_2)_3Al\cdot MeOPh$	—	b.p. 110–115 (1)*	232
$[CH_2=CH-(CH_2)_3]_3Al\cdot Et_2O$	80	b.p. 96–98 (1)	232
$(PhC\equiv C)_3Al.THF$	90	does not melt	224, 226
$(PhC\equiv C)_3Al.2THF$	85	decomp. > 100°	224, 226
$(C_6H_9C\equiv C)_3Al\cdot Et_2O$ **	47	m.p. 78–81°*	227
$EtAl(C\equiv CBu\text{-}t)_2\cdot THF$	85	liquid, decomp. > 140°	224, 226
$Et_2Al-C\equiv CPh\cdot THF$	96	liquid, decomp. > 120°	224, 226
$HC\equiv C-AlCl_2\cdot$dioxan	87	—	233
$Ph_2Al-C\equiv CMe\cdot Et_2O$	81	m.p. 69–73°*	228

*With decomposition.
**C_6H_9 = cyclohexenyl.

The chemical properties of the etherates of unsaturated OAC are somewhat unusual, but in general they resemble those of the etherates of aluminium alkyls. They are unstable in air and are explosively decomposed by water[228,242]. The dioxanate of the triacetylide[224] is inert with respect to CO_2 up to 100°C, condenses with acetone and mesityl oxide, does not react with dimethyl sulphate and ethylene, but initiates the polymerisation of

olefins in combination with $TiCl_4$.[233] The etherates of unsaturated OAC react with various aldehydes and ketones to give the corresponding alcohols[6,227,228,243-245]. In contrast to the etherates of aluminium trialkyls, the etherates of allylaluminium compounds add readily (at 25 to 100°C) to olefins, forming 1 : 1 adducts[229,230].

By virtue of the electron-accepting effect of the vinyl and ethynyl groups, the polarity of the Al–R bond in compounds of the type $R_2AlC{\equiv}CR'$ and $R_2AlCR'{=}CHR''$ diminishes, which entails a diminution of its nucleophilic properties. The vinyl and ethynyl groups are therefore more reactive in the reactions of vinyl- and ethynyl-alkyl mixed compounds with carbonyl compounds[169,226,228,244,246], CO_2, alcohols[226,246], and halogens[246,247], which makes it possible to carry out the reactions selectively with the unsaturated group without affecting the alkyl group. Furthermore, the vinyl group in the compounds $R_2AlCR'{=}CHR''$ is more reactive than the alkyl group in R_3Al.[246] The reactivity of the ethynyl group depends on the nature of the reactants: the ethynyl group reacts more readily with bromine and isopropyl alcohol, while the alkyl group reacts more readily with iodine and CO_2. The reactivity of the groups usually increases in the sequence alkyl < alkynyl < alkenyl. Compounds of the type $R_2AlC{\equiv}CR'$ are partly associated even in the presence of an ether, while the ethynyl group is in the bridging position, which lowers its reactivity compared with the vinyl group.

VI. THE ETHERATES OF OTHER ORGANOALUMINIUM COMPOUNDS

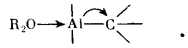
In the first place mention should be made of the etherates of aromatic organoaluminium compounds for which there are about twenty publications. However, since in many chemical reactions (with I_2, alkyl halides, carboxylic acids, metal salts, ketones, aldehydes, nitriles, and esters) these compounds resemble alkyl analogues with rare exceptions (the reactions with α,β-unsaturated ketones[4] and diphenylacetylene[248]) and the data can merely supplement those described above, there is no point in presenting them here.

An extensive class of compounds $M[AlR_4]$.ether, where M is an alkali or alkaline earth metal and R = alkyl, alkenyl, alkynyl, H, OR, etc., is also known. The ether in these compounds is coordinated to the other metal cation and not to aluminium[112,249], but the coordination is significantly influenced also by the group linked to aluminium[224,250]. A series of such compounds, many of which are valuable alkylating and reducing agents, have been obtained and investigated[5-7,15,16,35,224,233,250-253].

VII. THE REACTIVITY OF ETHERATES

When OAC etherates are used instead of ether-free aluminium alkyls in various reactions, the characteristic features of the etherates are manifested: (a) the yield of the desired product is in many instances increased; (b) the reaction frequently proceeds via another pathway and many reactions are characteristic solely of etherates; (c) the reactivity of etherates depends on the strength of the donor–acceptor bond.

It has been shown frequently that coordination of the type of *at*-complexes leads to a weakening of the metal–carbon bonds[254], which is usually attributed to an increase of the amount of their ionic character (the carbanionic mobility of the alkyl groups[15,255-266]), which leads in its turn to an increase of the reactivity of the metal alkyl. An extensive generalisation of this postulate is apparently not feasible, since, together with an increase of the polarity of the Li–C,[256-258] Mg–C,[259,260] Hg–C,[261-263] and certain other bonds[263,264], coordination has been found to entail an acceleration of the homolytic rupture of the Ti–C[267-270] and V–C[271] bonds. Furthermore, it is known that the presence of electron-donating molecules stabilises transition metal–carbon bonds[272,273], but in many instances the opposite effect has been observed[268,274]. The results of ^1H NMR studies on OAC (enhancement of the electropositive nature of the aluminium atom)[63,82,83,275] and of conductimetric studies (a sharp increase of conductivity)[21,22,39] suggest the "ionic loosening" of the Al–C bond:



On the other hand, infrared spectra[30,36,228] and X-ray diffraction[38] indicate only a slight change in the nature of this bond.

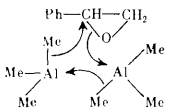
In order to explain processes involving organometallic compounds, it is insufficient to take into account only the polarity of the metal–ligand bond[256,276]. In most cases metal alkyls are associated, the associated species ranging from dimers to hexamers. Coordination to molecules of other compounds, accompanied by changes in the geometry of the organometallic compound, leads to the dissociation of the associated metal alkyls, the nature of which depends on the nature of the alkyls[256,259,277]. Furthermore, many metal alkyls have several comparatively readily accessible vacant orbitals, so that their complexes are capable of being coordinated to the reacting molecule, which results in a decrease of the activation energy in the transition state. Consequently the decisive factor in a particular reaction may not be the amount of ionic character, but the state of the coordination sphere of the metal. Having combined with the electron-donating molecule, the OAC lose or undergo a sharp reduction in their capacity for further coordination (the *d* orbital of aluminium is not readily accessible), so that certain reactions of the etherates of aluminium alkyls are slower or are altogether ruled out. These include primarily the reactions with CO_2, halogens, alkyl halides, H_2S, O_2, olefins, certain carbonyl compounds, nitriles, and all possible ligand exchange processes. However, the decrease of reactivity frequently entails an increase of the yield of the desired product[6,106,107-110,131,144,278]. For example, the presence of an ether or another electron donor has a favourable influence on the alkylation of the salts of various elements by organometallic compounds, which is usually attributed to the enhanced nucleophilic properties of the latter[255]. We believe that a more significant factor in the case of OAC is that the ether neutralises the strong Lewis acid (usually $AlCl_3$) arising during synthesis, reducing its dealkylating and electron accepting capacities, for example[115]:

$$4R_3Al.ether + 3SnCl_4 \rightarrow 3R_4Sn + 4AlCl_3.ether.$$

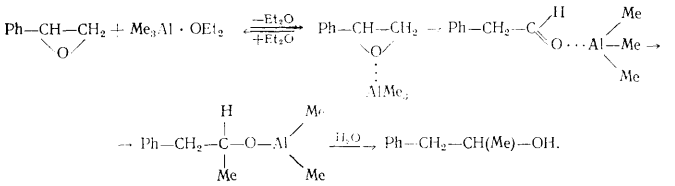
Without the involvement of an ether in this reaction, a mixture of organotin compounds alkylated to different extents is formed, since $AlCl_3$ forms stable complexes of the type $AlCl_3.R_nSnCl_{4-n}$, which prevent further alkylation of tin. This is confirmed by the finding that diphenyl ether, which has only a weak influence on the Al–C bond but forms stable complexes with $AlCl_3$, is effective in this reaction, and this is also true of tetrahydrofuran.

The different types of behaviour of etherates and ether-free OAC are frequently due to the different structures of these compounds[161,167,194,197,198,202,246]. In a pure state and

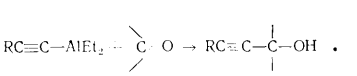
in solution in hydrocarbons aluminium alkyls as a rule exist in a dimeric form [3]. In this form they attack various molecules (aldehydes, ketones, α-olefins, etc.), forming many-centre intermediate complexes [143,148,167,279], for example, the complex of phenyloxiran (styrene oxide) and trimethylaluminium [150,151]:



A further transformation of this complex leads to the primary alcohol $PhCH(Me)CH_2OH$. Etherates, which are saturated monomeric molecules, are effective in such reactions when the ether is displaced by the reacting molecule. The resulting coordination complex reacts further in a manner which depends on the structure of the components. Thus phenyloxiran isomerises to phenylacetaldehyde and, reacting via the carbonyl group, gives rise to a secondary alcohol:

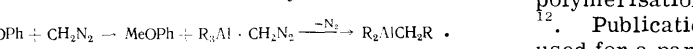


In mixed alkenyl- and alkynyl-alkyl compounds of aluminium the most reactive group (the unsaturated group) is in the bridging position in the absence of an ether [225,246] which lowers its reactivity. In complex formation the reactivity of the unsaturated group increases, so that, for example, the reactions with carbonyl compounds proceed more effectively in ether than in hexane and benzene [169]:

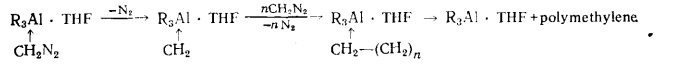


Thus acetone gives the corresponding alcohol in ether with a yield twice as great as in a hydrocarbon, while 2-methylcyclohexanone gives 96% of 2-methyl-1-propynylcyclohexanol in THF and 87% in benzene.

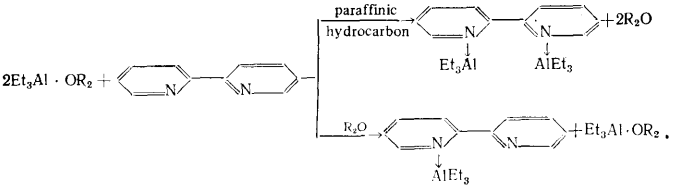
The properties of the whole class of various OAC etherates cannot be judged on the basis of individual instances (for example, $Et_3Al.OEt_2$). Apart from all other factors, the properties of etherates depend on the strength of the Al ← O bond [12,21,151]. For example, on reacting with the anisolate of R_3Al, diazomethane displaces anisole and the resulting adduct rearranges as in the case of the ether-free aluminium alkyl [205]:



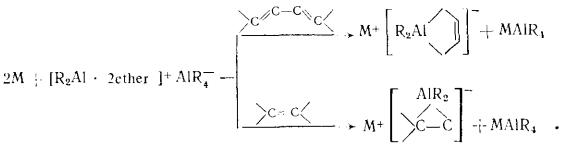
The reaction with $R_3Al.THF$ takes place differently, because tetrahydrofuran is a stronger donor than diazomethane. As a result, diazomethane coordinates via the free *d* orbital (the fifth coordination site of aluminium) with its subsequent polymerisation via the mechanism



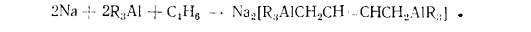
Apart from the strength of the donor–acceptor bond, the reactivity of etherates is influenced by the presence of an excess of the ether [7,140]. One must therefore treat with much caution conclusions concerning the reactivity of etherates if the study has been carried out in an ethereal solution. Thus the claim that the etherates cannot be used to synthesise the 2:1 complex of triethylaluminium with 2,2′-bipyridyl has been disproved [140]:



Finally, in connection with the tendency of the etherates of R_3Al to dissociate into the ions $[R_2Al.2ether]^+$ and AlR_4^-, a large group of reactions characteristic of such ions, with participation of alkali metals or magnesium and unsaturated compounds (aromatic hydrocarbons, olefins, and conjugated diolefins), has been observed [100–103]:



Ether-free R_3Al react quite differently, for example, in the case of butadiene we have



In the presence of stronger solvating agents (diglyme, hexamethylphosphoramide) the formation of butadienes polymerisation products was observed.

Thus the difference between the reactivities of etherates and ether-free OAC is due to the following factors: (a) the decrease of the degree of association of the aluminium alkyl; (b) the change in its geometry; (c) the increase in the degree of electrolytic dissociation; (d) the change in the polarity of the Al–C bond; (d) the ability of the ether to bind side products. The results of the reaction may depend on energy of the Al ← O bond in the etherate. Although some of these factors are interrelated and their effects overlap, in many cases individual factors are decisive. The problem of the dominant influence of one or several of the above factors must be solved in each specific instance, taking into account the specific features of the mechanism of the given reaction and the structure of the intermediate complex.

VIII. THE APPLICATIONS OF ETHERATES

The application of OAC etherates as components of polymerisation catalysts have been reported in reviews [11, 12]. Publications [48,280–285] recommending that etherates be used for a particular purpose in the polymerisation process have now appeared. The use of Et_2AlCl etherates [286,287] or of an ethereal solution of Et_3Al [288] to polymerise ϵ-caprolactam has been described. The ether adducts of aluminium trialkyls are promising in the polymerisation of epoxy-compounds [289–291], as catalysts [292,293], and as reagents [102] for selective hydrogenation and hydroalumination [200,294].

Etherates are fairly mild alkylating agents and this feature permits their employment in the synthesis of incompletely alkylated compounds of various elements: R_2Sn [189] and $RECl_2$ [295] (E = As, B, or P), the yield being appreciably higher than in the case of ether-free aluminium alkyls. Apart from the examples presented in the preceding sections, the use of the ether adducts of OAC

for the synthesis of organic derivatives of beryllium [14], cadmium [295], boron [14,296], aluminium [297-299], niobium and tantalum [42], and titanium [300] and also for the synthesis of alkylcylcopropanes [301], cyclopentanes [299], a wide variety of olefins [235-239,295], alcohols [4-7,224,239-241,302,303], ketones [4,158,304], and carboxylic, sulphinic, and sulphonic acids and their aluminium salts [5,305,306] is of interest.

Etherates are frequently used as the starting materials in the synthesis of other complexes. Many such examples are known among alkyl [24,26,27,43,44,66-69,140,190,307], alkenyl [232], alkynyl [224,227], and phenyl [308,309] OAC. The free aluminium alkyls can also be obtained from the etherates. It has been shown that iso-Pr_3Al and t-Bu_3Al can be most-simply synthesised from their etherates [41].

The heat treatment of various etherates is used to obtain high-purity aluminium (>99.99%), [310] diethylaluminium arylalkoxides [311], and organoaluminium polymers used as components of rocket fuels [312,313]. The employment of etherates makes it possible to increase the yield and purity of polyalkylaluminoxanes [314]. Finally, the formation of stable complexes by aluminium alkyls with ethers is used for their separation [172,315], analysis [3,105,316], and isolation from various hydrocarbon mixtures [317-321].

REFERENCES

1. A. F. Zhigach and D. S. Stasinevich, Symposium, "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods of Investigation of Organic Compounds), GKhI, Moscow, 1961, Book 10, p. 209.
2. J. H. Harwood, "Industrial Applications of the Organometallic Compounds: A Literature Survey" (Translated into Russian), Izd. Khimiya, Moscow, 1970, p. 71.
3. N. N. Korneev, A. F. Popov, and B. A. Krentsel', "Kompleksnye Metalloorganicheskie Katalizatory" (Complex Organometallic Catalysts), Izd. Khimiya, Moscow, 1969.
4. H. Reinheckel, K. Haage, and D. Jahnke, Organometal. Chem. Rev., 4, 47 (1969).
5. T. Mole and E. A. Jeffery, "Organoaluminium Compounds", Elsevier Publ., Amsterdam, 1972.
6. Houben-Weyl, "Methoden der organischen Chemie", Thieme Verlag, Stuttgart, 1970, Vol. 13/4.
7. A. N. Nesmeyanov and R. A. Sokolik, "Metody Elementoorganicheskoi Khimii. Bor, Alyuminii, Galii, Indii, Tallii" (Methods of Organoelemental Chemistry. Boron, Aluminium, Gallium, Indium, and Thallium), Izd. Nauka, Moscow, 1964, p. 283.
8. K. Ziegler, in "Organometallic Chemistry" (Edited by H. H. Zeiss) (Translated into Russian), Izd. Mir, Moscow, 1964, p. 231.
9. R. Köster and P. Binger, in "Advances in Inorganic Chemistry and Radiochemistry" (Edited by H. J. Emeleus and A. G. Sharpe), Acad. Press, New York–London, 1965, Vol. 7, p. 263.
10. V. Fic, Chem. Listy, 59, 685 (1965).
11. A. D. Pomogailo and P. E. Matkovskii, Trudy Inst. Khim. Nefti. i Prirodnykh Solei Akad. Nauk Kazakh SSR, No. 1, 214 (1970).
12. V. P. Mardykin, A. M. Antipova, and P. N. Gaponik, Usepkhi Khim., 40, 24 (1971) [Russ. Chem. Rev., No. 1 (1971)].
13. N. S. Ham and T. Mole, in "Progress in Nuclear Magnetic Resonance Spectroscopy" (Edited by J. W. Emsley), Pergamon Press, Oxford, 1969, Vol. 4, p. 91.
14. T. Mole, in "Organometallic Reactions" (Edited by E. I. Becker and M. Tsutsui), Wiley-Intersci., New York, 1970, Vol. 1, p. 1.
15. N. M. Alpatova, V. V. Gavrilenko, Yu. M. Kessler, O. R. Osipov, and D. N. Maslin, "Kompleksy Metalloorganicheskikh, Gidridnykh i Galoidnykh Soedinenii Alyuminiya" (Complexes of Organometallic, Hydride, and Halide Compounds of Aluminium), Izd. Nauka, Moscow, 1970.
16. G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds", Methuen, London, 1967, Vol. 1, p. 295.
17. R. Tarao, Bull. Chem. Soc. Japan, 39, 725 (1966).
18. S. Takeda and R. Tarao, Bull. Chem. Soc. Japan, 38, 1568 (1965).
19. J. P. Marchal, D. Canet, P. Bonnet, and J. Barriol, Org. Magn. Reson., 6, 322 (1974).
20. V. P. Mardykin and P. N. Gaponik, Zhur. Obshch. Khim., 38, 2479 (1968).
21. P. N. Gaponik, Candidate's Thesis, Belorussian State University, Minsk, 1970.
22. V. P. Mardykin, P. N. Gaponik, and D. D. Skorobogatov, Zhur. Obshch. Khim., 42, 2213 (1972).
23. P. Pino, P. Salvadori, G. P. Lorenti, E. Chiellini, L. Lardicci, G. Consiglio, O. Bonsignori, and L. Lepri, Chimica e Industria, 55, 182 (1973).
24. H. Lehmkuhl, Annalen, 719, 40 (1968).
25. J. Paul and T. D. Smith, J. Chem. Soc., 2770 (1964).
26. K. H. Thiele, H. K. Müller, and W. Brüser, Z. anorg. Chem., 348, 179 (1966).
27. K. H. Thiele, H. K. Müller, and W. Brüser, Z. anorg. Chem., 345, 194 (1966).
28. R. D. Bushik and R. S. Stearns, J. Polymer Sci., A4, 215 (1966).
29. H. Lehmkuhl and H. Schäfer, Annalen, 705, 23 (1967).
30. K. Starowieyski, S. Pasynkiewicz, and E. Jankowska, J. Organometal. Chem., 22, 283 (1970).
31. P. N. Gaponik, O. M. Baranov, and V. P. Mardykin, "XII Vsesoyuznoe Chugaevskoe Soveshchanie po Khimii Kompleksnykh Soedinenii. Tezisy Dokladov" (The XIIth All-Union Chugaev Conference on the Chemistry of Complexes. Abstracts of Reports). Novosibirsk, 1975, p. 118.
32. M. G. Kolomeer, E. V. Stovbun, V. F. Gachkovskii, and E. F. Vainshtein, Dokl. Akad. Nauk SSSR, 212, 403 (1973).
33. US P. 3 499 057 (1970).
34. E. V. Stovbun, E. F. Vainshtein, N. G. Taganov, and S. G. Entelis, Vysokomol. Soed., A16, 2087 (1974).
35. L. L. Ivanov, S. Ya. Zavizion, and L. I. Zakharkin, Zhur. Obshch. Khim., 43, 2265 (1973).
36. R. Tarao, Bull. Chem. Soc. Japan, 39, 2126 (1966).
37. Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, Chem. Comm., 1243 (1970).
38. J. L. Atwood and G. D. Stucky, J. Amer. Chem. Soc., 89, 5362 (1967).
39. H. Lehmkuhl and K. D. Kobs, Annalen, 719, 11 (1968).
40. G. A. Razuvaev, L. P. Stepovik, and V. A. Dodonov, Zhur. Obshch. Khim., 40, 1800 (1970).
41. H. Lehmkuhl, O. Olbrysch, and H. Nehl, Annalen, 709 (1973).

42. S. Moorhouse and G. Wilkinson, J. Chem. Soc., Dalton Trans., 2187 (1974).
43. H. Schmidbaur and F. Schindler, Chem. Ber., **100**, 3655 (1967).
44. H. Schmidbaur and W. Wolfsberger, Chem. Ber., **100**, 1000 (1967).
45. C. H. Heinrickson, D. Duffy, and D. P. Eyman, Inorg. Chem., **7**, 1047 (1968).
46. F. Gallais and P. Loth, Compt. rend., **C255**, 2755 (1962).
47. Japanese P. 22 051 (1967); Ref. Zhur. Khim., 22S269 (1968).
48. A. F. Popov, M. P. Forost, R. N. Kurbatova, N. N. Korneev, and V. K. Badaev, Zhur. Prikl. Khim., **46**, 142 (1973).
49. H. Hoberg, Annalen, **703**, 1 (1967).
50. V. P. Mardykin, P. N. Gaponik, N. V. Voronina, and L. V. Gaponik, Zhur. Obshch. Khim., **39**, 2475 (1969).
51. A. Tröber and H. Täubert, Wiss. Z. Techn. Hochschule Chem. Leuna–Merseburg, **8**, 34 (1966).
52. A. Tröber and C. Stricker, Wiss. Z. Techn. Hochschule Chem. Leuna–Merseburg, **8**, 283 (1966).
53. A. Tröber, G. Gladiau, B. Richter, W. Drechsel, and D. Topf, J. prakt. Chem., **311**, 942 (1969).
54. DDR P. 67 427 (1969).
55. V. P. Mardykin, P. N. Gaponik, and V. K. Saevich, Zhur. Obshch. Khim., **36**, 2162 (1966).
56. V. P. Mardykin and P. N. Gaponik, Izv. Vys. Ucheb. Zabed., Khim. i Khim. Tekhnol., **12**, 963 (1969).
57. V. P. Mardykin, P. N. Gaponik, and E. I. Kvasyuk, Zhur. Obshch. Khim., **38**, 109 (1968).
58. P. N. Gaponik, O. M. Baranov, and V. P. Mardykin, Vestnik Beloruss. Univ., Ser. 2, No. 3, 7 (1974).
59. W. P. Neumann, Habilitationschrift, Universität Gissen, 1959.
60. M. B. Smith, J. Organometal. Chem., **22**, 273 (1970).
61. M. B. Smith, J. Organometal. Chem., **70**, 13 (1974).
62. G. H. Smith and F. J. Hamilton, J. Phys. Chem., **72**, 3567 (1968).
63. K. Hatada and H. Yuki, Tetrahedron Letters, 213 (1968).
64. M. E. Vol'pin (Editor), "Sovremennye Problemy Fizicheskoi Organicheskoi Khimii" (Modern Problems of Physical Organic Chemistry), Izd. Mir, Moscow, 1967, p. 246.
65. E. N. Gur'yanova, I. P. Gol'dshtein, and I. P. Romm, "Donorno-Aktseptornaya Svyaz'" (The Donor–Acceptor Bond), Izd. Khimiya, Moscow, 1973.
66. K. H. Thiele and W. Brüser, Z. anorg. Chem., **349**, 33 (1967).
67. H. Schmidbauer and G. Jonas, Chem. Ber., **101**, 1271 (1968).
68. W. Wolfsberger, Dissertation, Universität Würzburg, 1968.
69. W. Wolfsberger and H. Schmidbaur, J. Organometal. Chem., **17**, 41 (1969).
70. J. Chatt, R. H. Crabtree, E. A. Jeffery, and R. L. Richards, J. Chem. Soc., Dalton Trans., 1167 (1973).
71. V. M. Denisov, E. B. Toporkova, L. V. Alferova, and A. I. Kol'tsov, Izv. Akad. Nauk SSSR, Ser. Khim., 157 (1975).
72. J. Furukawa, K. Omura, O. Yamamoto, and K. Ishikawa, Chem. Comm., 77 (1974).
73. K. Starowieyski and S. Pasynkiewicz, J. Organometal Chem., **19**, 249 (1969).
74. D. B. Miller, J. Org. Chem., **31**, 908 (1966).
75. D. B. Miller, J. Organometal. Chem., **14**, 253 (1968).
76. A. J. Lundeen and A. C. Oehlschlager, J. Organometal. Chem., **25**, 337 (1970).
77. W. Kuran, S. Pasynkiewicz, and J. Serzyko, J. Organometal. Chem., **73**, 187 (1974).
78. A. Tröber and A. Gerstmeyer, Wiss. Z. Techn. Hochschule Chem. Leuna–Merseburg, **13**, 327 (1971).
79. Yu. A. Gorin, L. S. Skripova, K. N. Charskaya, and E. Zh. Menligaziev, Zhur. Prikl. Spektrosk., **15**, 67 (1971).
80. E. Benedetti and G. Zerbi, Spectrochim. Acta, **25A**, 1449 (1969).
81. H. Koiti, J. Synth. Org. Chem. Japan, **25**, 843 (1967); Ref. Zhur. Khim., 9B284 (1967).
82. Y. Takashi, Bull. Chem. Soc. Japan, **40**, 612 (1967).
83. T. Takeshita and W. E. Frankle, Tetrahedron Letters, 5913 (1968).
84. H. Haraguti, Kagaku-no ryoiki, **24**, 689, 802 (1970); Ref. Zhur. Khim., 11B68 (1971).
85. T. L. Brown and L. L. Murrell, J. Amer. Chem. Soc., 94, 378 (1972).
86. S. I. Vinogradova, V. M. Denisov, and A. I. Kol'tsov, Zhur. Obshch. Khim., **42**, 1031 (1972).
87. V. P. Mardykin, P. N. Gaponik, and O. M. Baranov, Vestnik Beloruss. Univ. Ser. 2, No. 3, 17 (1975).
88. M. J. S. Dewar, D. B. Patterson, and W. I. Simpson, J. Chem. Soc., Dalton Trans., 2381 (1973).
89. P. Loth, These doct. sci. phys. Univ. Toulouse, 1967; Ref. Zhur. Khim., 10B482 (1970).
90. J. F. Labarre and F. Gallais, Uspekhi Khim., **40**, 654 (1971) [Russ. Chem. Rev., No. 4 (1971)].
91. P. Salvadori, L. Lardicci, G. Consiglio, and P. Pino, Tetrahedron Letters, 5343 (1966).
92. P. Pino, G. P. Lorenzi, and E. Chiellini, J. Polymer Sci., C, 3279 (1968).
93. G. Fraenkel, D. T. Dix, and M. Carlson, Tetrahedron Letters, 579 (1968).
94. M. Witanowski and J. D. Roberts, J. Amer. Chem. Soc., **88**, 737 (1966).
95. T. Uchijima, N. Nojiri, and Y. Yokeda, Nippon Kagaku Kaishi, 1210 (1972).
96. P. E. M. Allen, A. E. Byers, and R. M. Lough, J. Chem. Soc., Dalton Trans., 479 (1972).
97. A. P. Batalov, Zhur. Org. Khim., **7**, 861 (1971).
98. E. L. Kopp, O. S. Mikhailycheva, and E. B. Milovskaya, Vysokomol. Soed., **14A**, 2653 (1972).
99. E. V. Stovbun, E. F. Vainshtein, and S. G. Entelis, Zhur. Obshch. Khim., **44**, 1622 (1974).
100. H. Lehmkuhl, Annalen, **719**, 20 (1968).
101. H. Lehmkuhl, Chimia (Switz.), **24**, 182 (1970).
102. H. Lehmkuhl, J. Culikovic, and H. Nehl, Annalen, 666 (1973).
103. H. Lehmkuhl and H. Nehl, Annalen, 659 (1973).
104. D. J. Brauer and G. D. Stucky, J. Organometal. Chem., **37**, 217 (1972).
105. D. F. Hagen, D. G. Biechler, W. D. Leslie, and D. E. Jordan, Analyt. Chim. Acta, **41**, 557 (1968).
106. G. B. Sakharovskaya, N. N. Korneev, A. F. Popov, Yu. V. Kissin, S. M. Mezhikovskii, and E. V. Kristalnyi, Zhur. Obshch. Khim., **39**, 788 (1969).
107. J. Weidlein, J. Organometal. Chem., **16**, P33 (1969).

108. J. Weidlein, Z. anorg. Chem., **378**, 245 (1970).
109. J. Weidlein, J. Organometal. Chem., **49**, 257 (1973).
110. J. Weidlein, J. Organometal. Chem., **24**, 63 (1970).
111. T. Aoyagi, T. Araki, N. Oguni, M. Mikumo, and H. Tani, Inorg. Chem., **12**, 2702 (1973).
112. H. Lehmkuhl and W. Eisenbach, Annalen, **705**, 42 (1967).
113. L. G. Makarova and A. N. Nesmeyanov, "Metody Elementoorganicheskoi Khimii, Rtut'" (Methods of Organoelemental Chemistry. Mercury), Izd. Nauka, Moscow, 1965, p. 38.
114. B. P. 98 685 (1965); Organometal. Comp., **6**, 111 (1965).
115. V. P. Mardykin and P. N. Gaponik, Zhur. Obshch. Khim., **39**, 2046 (1969).
116. K. A. Kocheshkov, N. N. Zemlyanskii, N. I. Sheverdina, and E. M. Panov, "Metody Elementoorganicheskoi Khimii, Germanii, Olovo, Svinets" (Methods of Organoelemental Chemistry. Germanium, Tin, and Lead), Izd. Nauka, Moscow, 1968, p. 256.
117. M. J. Prince and K. Weiss, J. Organometal. Chem., **2**, 166 (1966).
118. R. E. Cunningham and R. A. Dove, J. Polymer Sci., **A-1**, 6, 1751 (1968).
119. J. Peyroche, R. Laputte, and A. Guyot, Makromolek. Chem., **136**, 11 (1970).
120. V. P. Mardykin, V. K. Badaev, and P. N. Gaponik, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., **10**, 1259 (1967).
121. W. Cooper, R. K. Smith, and A. Stokes, J. Polymer Sci., **B4**, 309 (1966).
122. A. Zambelli, J. Pasquon, R. Signorini, and G. Natta, Makromolek. Chem., **112**, 160 (1968).
123. A. E. Jeffery, Austral. J. Chem., **26**, 219 (1973).
124. J. F. Normant, Synthesis, No. 2, 63 180 (1972).
125. A. Yamamoto, T. Yamamoto, Y. Kubo, A. Miyashita, and S. Ikeda, "V Mezhdunarodnyi Kongress po Metalloorganicheskoi Khimii, Tezisy Dokladov" (The Vth International Congress on Organometallic Chemistry. Abstracts of Reports), Moscow, 1971, Vol. 1, p. 113.
126. G. A. Chukhadzhyan, Z. K. Evoyan, and G. A. Gevorkyan, "V Mezhdunarodnyi Kongress po Metalloorganicheskoi Khimii, Tezisy Dokladov" (The Vth International Congress on Organometallic Chemistry. Abstracts of Reports), Moscow, 1971, Vol. 1, p. 185.
127. A. Yamamoto, K. Kato, and S. Ikeda, J. Organometal. Chem., **60**, 139 (1973).
128. K. Nishimura, H. Kuribayashi, A. Yamamoto, and S. Ideka, J. Organometal. Chem., **37**, 317 (1972).
129. V. V. Mazurek, "Polimerizatsiya pod Deistviem Soedinenii Perekhodnykh Metallov" (Polymerisation Under the Influence of Transition Metal Compounds), Izd. Nauka, Leningrad, 1974, pp. 28, 51.
130. K. Ziegler, H. G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Soell, and W. R. Kroll, Symposium, "Alyuminiiorganicheskie Soedineniya" (Organoaluminium Compounds) (Translated into Russian), Inostr. Lit., Moscow, 1962, p. 151.
131. US P. 3 384 677 (1968).
132. S. Warmel, H. P. Hemmerich, and F. Asinger, Chem. Ber., **105**, 88 (1972).
133. H. Schmidbaur, K. Kuhr, and U. Kruger, Angew. Chem., **77**, 169, 866 (1965).
134. S. Tadeo and U. Takashi, Inorg. Chem., **6**, 1679 (1967).
135. J. Z. Nyati, J. M. Ressner, and J. D. Smith, J. Organometal. Chem., **70**, 35 (1974).
136. J. Weidlein, J. Organometal. Chem., **32**, 181 (1971).
137. J. Weidlein, Z. anorg. Chem., **386**, 129 (1971).
138. H. Olapinski, B. Schaible, and J. Weidlein, J. Organometal. Chem., **43**, 107 (1972).
139. J. M. Lalancette, Y. Beauregard, and M. Bhereur, Canad. J. Chem., **48**, 1093 (1970).
140. P. N. Gaponik, O. M. Baranov, and V. P. Mardykin, Zhur. Obshch. Khim., **45**, 1516 (1975).
141. F. A. Cermeno, An. Real. Soc. esp. fis. y quim., **B60**, 753 (1964); Ref. Zhur. Khim., 13Zh. 101 (1966).
142. D. S. Breslow, D. L. Christman, H. H. Espy, and C. A. Lukach, J. Appl. Polymer Sci., **11**, 73 (1967).
143. E. C. Ashby and H. Simon, J. Org. Chem., **35**, 1034 (1970).
144. Y. Baba, Bull. Chem. Soc. Japan, **41**, 2173 (1968).
145. Y. Baba, Bull. Chem. Soc. Japan, **41**, 928 (1968).
146. R. A. Kretchmer, J. Org. Chem., **37**, 801 (1972).
147. G. Giacomelli, R. Menicagli, and L. Lardicci, J. Org. Chem., **38**, 2370 (1973).
148. E. C. Ashby and J. T. Laemmle, J. Org. Chem., **33**, 3398 (1968).
149. J. Namy, E. Henry-Basch, and P. Freon, Compt. rend., **C268**, 287, 1601 (1969).
150. J. Namy, E. Henry-Basch, and P. Freon, Compt. rend., **269**, 1222 (1970).
151. J. Namy, E. Henry-Basch, and P. Freon, Bull. Soc. chim. France, 2249 (1970).
152. J. Namy, These doct. sci. phys. Univ. Paris-Sud, 1972; Ref. Zhur. Khim., 18Zh69 (1974).
153. E. C. Ashby, S. H. Yu, and P. V. Roling, J. Org. Chem., **37**, 1918 (1972).
154. G. E. Heinsohn and E. C. Ashby, J. Org. Chem., **38**, 4232 (1973).
155. H. M. Neumann, J. Laemmle, and E. C. Ashby, J. Amer. Chem. Soc., **95**, 2597 (1973).
156. G. Giacomelli, R. Menicagli, and L. Lardicci, J. Org. Chem., **39**, 1757 (1974).
157. T. Araki, K. Hayakawa, T. Aoyagi, Y. Nakano, and H. Tani, J. Org. Chem., **38**, 1130 (1973).
158. J. Hooz and R. B. Layton, J. Amer. Chem. Soc., **93**, 7320 (1971).
159. D. Guillerm-Dron, M. L. Capmau, and W. Chodkiewicz, Tetrahedron Letters, 479 (1972).
160. S. Warmel and H. Schiffers, J. Organometal. Chem., **97**, 21 (1975).
161. W. Nagata, M. Yoshioka, S. Hirai, J. Amer. Chem. Soc., **94**, 4635 (1972).
162. W. Nagata, M. Yoshioka, and M. Murakami, J. Amer. Chem. Soc., **94**, 4644, 4654 (1972).
163. W. Nagata, M. Yoshioka, and T. Terasawa, J. Amer. Chem. Soc., **94**, 4672 (1972).
164. K. Weissermel and E. Nolken, Makromolek. Chem., **68**, 140 (1963).
165. G. Ceccarelli, A. Pesca, and F. Andruzzi, Izv. Akad. Nauk SSSR, Ser. Khim., 2188 (1972).
166. L. P. Stepovik, V. A. Dodonov, and L. A. Malygina, Zhur. Obshch. Khim., **39**, 2043 (1969).
167. E. V. Milovskaya, Symposium, "Uspekhi Khimii Organicheskikh Perekisnykh Soedinenii i Autookisleniya" (Advances in the Chemistry of Organic Peroxide Compounds and Autoxidation), Izd. Khimiya, Moscow, 1969, p. 256.
168. L. Lardicci and G. P. Giacomelli, J. Organometal. Chem., **33**, 293 (1971).
169. H. Demarne and P. Cadiot, Bull. Soc. chim. France, 205 (1968).

170. F. Gallais and P. Loth, Compt. rend., C, 259, 785 (1964).
171. H. Lehmkuhl and R. Schäfer, Tetrahedron Letters, 2315 (1966).
172. V. P. Mardykin, P. N. Gaponik, and O. M. Baranov, Zhur. Obshch. Khim., 42, 1996 (1972).
173. A. Zambelli, A. L. Serge, A. Marinangelli, and G. Gatti, Chimica e Industriya, 48, 1, 333 (1966).
174. A. Zambelli, G. M. Giongo, and A. L. Serge, Chimica e Industriya, 50, 1185 (1968).
175. R. Tarao and S. Takeda, Bull. Chem. Soc. Japan, 40, 650 (1967),
176. P. N. Gaponik, O. M. Baranov, and V. P. Mardykin, Zhur. Obshch. Khim., 45, 1514 (1975).
177. A. A. Popov, E. F. Vainshtein, and S. G. Entelis, Reakts. Sposobn. Org. Soed., 7, 825 (1970).
178. A. A. Popov, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1971.
179. A. A. Popov, E. F. Vainshtein, and S. G. Entelis, Dokl. Akad. Nauk SSSR, 198, 1124 (1971).
180. US P. 3 577 450 (1971).
181. E. H. Mottus and M. R. Ort, J. Electrochem. Soc., 117, 885 (1970).
182. M. R. Ort and E. H. Mottus, J. Organometal. Chem., 50, 47 (1973).
183. A. C. M. Wanders and E. Konijnenberg, Tetrahedron Letters, 2081 (1967).
184. F. M. Sonnenberg, J. Org. Chem., 35, 3166 (1970).
185. F. Glockling and J. R. Light, J. Chem. Soc. A, 623 (1967).
186. S. Pasynkiewicz and W. Kuran, J. Organometal. Chem., 15, 307 (1968).
187. H. Lehmkuhl and J. Culjkovic, Angew. Chem., 81, 928 (1969).
188. Dutch P. 6 609 375 (1967); Chem. Abs., 67, 64 518 (1967).
189. US P. 3 454 569 (1969).
190. M. Boleslawski, S. Pasynkiewicz, A. Minorska, and W. Hryniow, J. Organometal. Chem., 65, 165 (1974).
191. N. Ueyama, T. Araki, and H. Tani, Inorg. Chem., 12, 2218 (1973).
192. H. Schmidbaur, B. Armer, and M. Bergfeld, Z. Chem., 8, 254 (1968).
193. A. Bongini, D. Savoia, and A. Umani-Ronchi, J. Organometal. Chem., 72, C4 (1974).
194. G. Fritz and M. Hähnke, Z. anorg. Chem., 377, 48 (1970).
195. T. W. Dolzine and J. P. Oliver, J. Organometal. Chem., 78, 165 (1974).
196. J. J. Eisch and G. R. Huck, J. Organometal. Chem., 64, 41 (1974).
197. R. Rienacker and G. F. Cotel, Angew. Chem., 79, 862 (1967).
198. US P. 3 325 524 (1967).
199. G. F. Brodovskaya, Candidate's Thesis, INKhS, Moscow, 1974.
200. J. J. Eisch and K. C. Fichter, J. Amer. Chem. Soc., 96, 6815 (1974).
201. V. V. Markova, V. A. Kormer, and A. A. Petrov, Zhur. Obshch. Khim., 37, 226 (1967).
202. V. V. Gavrilenko, V. A. Palei, and L. I. Zakharkin, Izv. Akad. Nauk SSSR, Ser. Khim., 910 (1968).
203. L. I. Zakharkin, V. V. Gavrilenko, L. L. Ivanov, B. A. Palei, V. S. Kolesov, and M. P. Semenova, "IV Vsesoyuznaya Konferentsiya po Khimii Atsetilena, Doklady" (The IVth All-Union Conference on the Chemistry of Acetylene. Reports), Alma-Ata, 1972, Vol. 2, p. 90.
204. Y. Senda, S. Mitsui, R. Cno, and S. Hosokawa, Bull. Chem. Soc. Japan, 44, 2737 (1971).
205. H. Hoberg, Annalen, 695, 1 (1966).
206. BRD P. 1 288 089 (1969); Organometal. Comp., 14, 168 (1969).
207. B. P. 1 175 825 (1970); Organometal. Comp., 16, 58 (1970).
208. L. H. Sommer, J. McLick, and C. M. Golino, J. Amer. Chem. Soc., 94, 669 (1972).
209. L. H. Sommer, C. M. Golino, D. N. Roark, and R. D. Bush, J. Organometal. Chem., 49, C3 (1973).
210. L. I. Zakharkin and I. M. Khorlina, Izv. Akad. Nauk SSSR, Ser. Khim., 862 (1965).
211. A. Hajos, "Complex Hydrides in Organic Chemistry" [Organic Preparation Methods Vol. 4, Berlin, Deut. Verlag Wissenschaften, 1966] (Translated into Russian), Izd. Khimiya, Leningrad, 1971, p. 340.
212. L. I. Zakharkin and V. V. Gavrilenko, Izv. Akad. Nauk SSSR, Ser. Khim., 664 (1965).
213. P. Pino and G. P. Lorenzi, J. Org. Chem., 31, 329 (1966).
214. J. S. Thayer and R. West, in "Advances in Organometallic Chemistry" (Edited by F. G. A. Stone and R. West), Acad. Press, New York–London, 1967, p. 169.
215. J. E. Rie and J. P. Oliver, J. Organometal. Chem., 80, 219 (1974).
216. M. Boleslawski, S. Pasynkiewicz, K. Jaworski, and A. Sadovnik, J. Organometal. Chem., 97, 15 (1975).
217. N. Davies, C. A. Smith, and M. G. H. Wallbridge, J. Chem. Soc. A, 342 (1970).
218. B. M. Mikhailov and T. V. Potapova, Izv. Akad. Nauk SSSR, Ser. Khim., 1153 (1968).
219. D. Young, R. Wiersema, and M. Hawthorne, J. Amer. Chem. Soc., 93, 5687 (1971).
220. G. A. Razuvaev, I. V. Lomakova, and L. P. Stepovik, Zhur. Obshch. Khim., 43, 2416 (1973).
221. US P. 3 644 445 (1972).
222. T. Aoyagi, T. Araki, N. Oguni, and H. Tani, Inorg. Chem., 12, 817 (1973).
223. K. Fischer, K. Jonas, P. Misbach, R. Stabba, and G. Wilke, Angew. Chem., 85, 1002 (1973).
224. L. L. Ivanov, Candidate's Thesis, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1966.
225. E. A. Jeffery, T. Mole, and J. K. Saunders, Austral. J. Chem., 21, 137 (1968).
226. L. I. Zakharkin, V. V. Gavrilenko, and L. L. Ivanov, Zhur. Obshch. Khim., 37, 992 (1967).
227. H. Demarne and P. Cadiot, Bull. Soc. chim. France, 211 (1968).
228. H. Demarne and P. Cadiot, Bull. Soc. chim. France, 216 (1968).
229. H. Lehmkuhl and D. Reinehr, J. Organometal. Chem., 23, C25 (1970).
230. D. Reinder, Dissertation, Universität Bochum, 1971.
231. G. Zweifel and G. M. Clark, J. Organometal. Chem., 39, C33 (1972).
232. L. I. Zakharkin and L. A. Savina, Izv. Akad. Nauk SSSR, Ser. Khim., 1222 (1964).
233. BRD P. 1 154 476 (1964).
234. M. E. Davidson and M. C. Henry, Chem. Rev., 67, 73 (1967).
235. US P. 3 631 065 (1971).
236. US P. 3 634 482 (1972).
237. US P. 3 641 084 (1972).

238. US P. 3 755 400 (1973).
239. US P. 3 761 528 (1973).
240. US P. 3 669 990 (1972).
241. US P. 3 773 714 (1973).
242. S. Czernecki, C. Georgoulis, B. Gross, and C. Prevost, Compt. rend., C, **266**, 1617 (1968).
243. D. Plouin, S. Jacquet, and R. Glenat, Compt. rend., C, **268**, 190 (1969).
244. H. Newman, Tetrahedron Letters, 4571 (1971).
245. F. Gerard and P. Miginiac, Compt. rend., C, **275**, 1129 (1972).
246. B. A. Palei, V. V. Gavrilenko, and L. I. Zakharkin, Izv. Akad. Nauk SSSR, Ser. Khim., 2760 (1962).
247. G. Zweifel and C. C. Whitney, J. Amer. Chem. Soc., **89**, 2753 (1967).
248. J. J. Eisch and J. M. Biedermann, J. Organometal. Chem., **30**, 167 (1971).
249. J. L. Atwood and G. D. Stucky, J. Organometal. Chem., **13**, 53 (1968).
250. L. L. Ivanov, S. Ya. Zavizion, and L. I. Zakharkin, Zhur. Obshch. Khim., **45**, 1060 (1975).
251. US P. 3 262 959 (1966).
252. US P. 3 262 958 (1966).
253. J. F. Ross and J. P. Oliver, J. Organometal. Chem., **22**, 505 (1970).
254. J. J. Eisch, "The Chemistry of Organometallic Compounds. The Main Group Elements", Macmillan, New York, 1967, p. 61.
255. O. Yu. Okhlobystin, Uspekhi Khim., **36**, 34 (1967) [Russ. Chem. Rev., No. 1 (1967)].
256. E. A. Kovrizhnykh and A. I. Shatenshtein, Uspekhi Khim., **37**, 1836 (1968) [Russ. Chem. Rev., No. 10 (1968)].
257. G. M. Khvostik, I. Ya. Poddubnyi, V. N. Sokolov, and O. N. Babkina, Zhur. Fiz. Khim., **44**, 2642 (1970) [Russ. J. Phys. Chem., No. 10 (1970)].
258. A. P. Batalov and G. A. Rostokin, Zhur. Obshch. Khim., **44**, 2019 (1974).
259. B. J. Wakefield, Organometallic Chem. Rev., **1**, 131 (1966).
260. H. F. Ebel and B. O. Wagner, Chem. Ber., **104**, 307, 320 (1971).
261. L. A. Fedorov and E. I. Fedin, Dokl. Akad. Nauk SSSR, **195**, 856 (1970).
262. A. N. Nesmeyanov, N. S. Kochetkova, L. A. Fedorov, and G. B. Materikova, Dokl. Akad. Nauk SSSR, **199**, 361 (1971).
263. V. S. Petrosyan, A. S. Voyakin, and O. A. Reutov, Zhur. Org. Khim., **6**, 889 (1970).
264. V. S. Petrosyan, N. S. Yashima, V. I. Bakhmutov, A. B. Permin, and O. A. Reutov, J. Organometal. Chem., **72**, 71 (1974).
265. S. Pasynkiewocz and T. Diem, Makromolek. Chem., **136**, 137 (1970).
266. V. S. Petrosyan and O. A. Reutov, J. Organometal. Chem., **52**, 307 (1973).
267. F. S. D'yachkovskii, N. E. Khrushch, and A. E. Shilov, Kinetika i Kataliz, **9**, 1006 (1968).
268. K. H. Thiele, P. Zdunneck, and D. Baumgart, Z. anorg. Chem., **378**, 62 (1970).
269. O. S. Rasshchupkina, N. E. Khrushch, F. S. D'yachkovskii, and Yu. G. Borod'ko, Zhur. Fiz. Khim., **45**, 1329 (1971) [Russ. J. Phys. Chem., No. 5 (1971)].
270. E. B. Mikovskaya, L. V. Zamoiskaya, and E. L. Konn, Uspekhi Khim., **38**, 928 (1969) [Russ. Chem. Rev., No. 5 (1969)].
271. F. S. D'yachkovskii, N. E. Khrushch, and A. E. Shilov, Kinetika i Kataliz, **8**, 1230 (1967).
272. G. A. Baranova, L. L. Stotskaya, and B. A. Krentsel', Kinetika i Kataliz, **8**, 24 (1967).
273. J. Müller and K. H. Thiele, Z. anorg. Chem., **362**, 120 (1968).
274. K. H. Thiele, Uspekhi Khim., **41**, 1180 (1972) [Russ. Chem. Rev., No. 7 (1972)].
275. B. Sen and G. L. White, J. Inorg. Nuclear Chem., **35**, 2207 (1973).
276. A. A. Korotkov and A. F. Podol'skii, "Kataliticheskaya Polimerizatsiya Vinilovykh Monomerov" (Catalytic Polymerisation of Vinyl Monomers), Izd. Nauka, Leningrad, 1973.
277. H. L. Lewis and T. L. Brown, J. Amer. Chem. Soc., **92**, 4664 (1970).
278. W. R. Kroll and W. Naegele, J. Organometal. Chem., **19**, 439 (1969).
279. J. Namy, Compt. rend., C, **272**, 1334 (1971).
280. E. Chiellini, G. Montagnoli, and P. Pino, J. Polymer Sci., B7, 121 (1969).
281. V. P. Mardykin and K. B. Martinovich, Vestnik Beloruss. Univ., Ser. 2, No. 2, 22 (1975).
282. Austrian P. 264 124 (1968).
283. US P. 3 380 977 (1968).
284. Japanese P. 36 513 (1970).
285. Dutch P. 131 225 (1971).
286. I. V. Kulevskaya, Ya. M. Paushkin, V. P. Mardykin, M. A. Zil'bergleit, and G. A. Gimpel', USSR P. 431 192 (1974); Byul. Izobret., No. 21, 89 (1974).
287. I. V. Kulevskaya, V. P. Mardykin, M. A. Zil'bergleit, and Ya. M. Paushin, Dokl. Akad. Nauk Beloruss. SSR, **19**, 532 (1975).
288. T. Konomi and H. Tani, J. Polymer Sci., A-1, **7**, 2255, 2269 (1969).
289. Japanese P. 11 509 (1972); Ref. Zhur. Khim., 5S357 (1973).
290. US P. 3 644 224 (1972).
291. Y. Masuda and H. Hani, J. Polymer Sci., Polymer Chem. Ed., **11**, 3101 (1973).
292. W. R. Kroel, J. Catalysis, **15**, 281 (1969).
293. B. P. 1 325 153 (1973).
294. G. Zweifel and R. L. Miller, J. Amer. Chem. Soc., **92**, 6678 (1970).
295. O. Yu. Okhlobystin, Candidate's Thesis, Moscow State University, Moscow, 1961.
296. B. M. Mikhailov and K. L. Cherkasova, Zhur. Obshch. Khim., **41**, 2578 (1971).
297. US P. 350 938 (1971).
298. G. V. Zenina, N. I. Sheverdina, and K. A. Kocheshkov, Dokl. Akad. Nauk SSSR, **195**, 96 (1970).
299. G. Zweifel, G. M. Clark, and R. Lynd, Chem. Comm., 1593 (1971).
300. US P. 3 173 902 (1965).
301. G. Zweifel, G. M. Clark, and C. C. Whitney, J. Amer. Chem. Soc., **93**, 1305 (1971).
302. US P. 3 642 825 (1972); Organometal. Comp., **20**, 210 (1972).
303. US P. 3 692 847 (1972); Organometal. Comp., **22**, 6 (1973).
304. G. W. Kabalka and R. F. Daley, J. Amer. Chem. Soc., **95**, 4428 (1973).
305. US P. 3 872 144 (1975); Organometal. Comp., **27**, 3 (1975).
306. US P. 3 311 650 (1967); Chem. Abs., **67**, 53 680 (1967).
307. P. N. Gaponik, O. M. Baranov, and V. P. Mardykin, Zhur. Obshch. Khim., **44**, 2789 (1974).

308. J. E. Lloyd and K. Wade, J. Chem. Soc., 2662, 5083 (1965).
309. R. D. Chambers and J. A. Cunningham, J. Chem. Soc., 2185 (1967).
310. B. P. 956 990 (1964); Chem. Abs., **61**, 2774 (1964).
311. US P. 3 313 836 (1967).
312. US P. 3 280 088 (1966).
313. US P. 3 429 754 (1969).
314. G. B. Sakharovskaya, N. N. Korneev, A. F. Popov, A. F. Zhigach, G. I. Medvetskaya, and M. V. Sobolevskii, USSR P. 209 746 (1968); Byul. Izobret., No. 5, 104 (1968).
315. V. P. Mardykin, P. N. Gaponik, and E. I. Kvasyuk, USSR P. 281 470 (1970); Byul. Izobret., No. 29, 39 (1970).
316. V. P. Mardykin, E. I. Kvasyuk, and P. N. Gaponik, Zhur. Prikl. Khim., **42**, 947 (1969).
317. US P. 3 326 957 (1967).
318. US P. 3 352 894 (1967):
319. US P. 3 363 021 (1968).
320. Swiss P. 484 197 (1970).
321. US P. 3 499 057 (1970).

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