ORGANOALUMINUM CHEMISTRY

I. OXIDATIVE DEGRADATION OF ALUMINUM ALKYLS WITH METAL HALIDES

MARTIN I. PRINCE AND KARL WEISS*
William H. Nichols Chemical Laboratory and Department of Chemical Engineering, New York University, New York (U.S.A.)

(Received September 11th, 1963)

Aluminum alkyls are readily oxidized by transition metal salts. Thus triethylaluminum with titanium halides gives gaseous products and Ziegler-type polymerization catalysts, and much effort has been devoted to elucidating the structure, mechanism of formation, and mode of operation of the catalytically active species[1,2] (Ref. 1 cites most of the pertinent literature.) Other transition metal halides have been variously reported to yield complex compounds which are also polymerization catalysts[3], lower valence states salts[4], and the corresponding metals in finely divided form[5]. These reactions have been utilized for the preparation of metal carbonyls[5]. A formal analogy appears to exist with the reduction of metal halides by Grignard compounds[6], and with the cobaltous chloride catalyzed reactions of these reagents which have been postulated to generate radicals[7].

With the exception noted[1], no detailed study of the fate of the alkyl groups in the oxidation of aluminum alkyls has been made. The reactions may proceed according to equations 1 and 2 (al = 1/3 Al), or may lead to intermediate oxidation states and

$$\mathrm{alC_2H_5} + \frac{1}{n}\mathrm{MX}_n \longrightarrow \frac{1}{n}\mathrm{M}^0 + \mathrm{alX} + \frac{1}{2}\mathrm{C_2H_4} + \frac{1}{2}\mathrm{C_2H_6}\ \left(\text{or } \frac{1}{2}\mathrm{C_4H_{10}}\right) \qquad (1)$$

$$\mathrm{alR} + \frac{2}{n}\mathrm{MX}_n \longrightarrow \frac{2}{n}\mathrm{M}^0 + \mathrm{alX} + \mathrm{RX} \qquad (2)$$

new organometallic compounds. Further, intermediates generated in the formation of these products may be diverted by interaction with the solvent. In this paper we report some observations on the scope and mechanism of these oxidations.

RESULTS

Triethylaluminum

The oxidations were carried out under standardized conditions in refluxing methylcyclohexane at 105°, in which the amount of finely divided, anhydrous metal halide demanded by equation 1 was suspended. The total gas evolution was measured, and the composition of the gaseous mixture was determined by gas–liquid chromato-

---

* To whom enquiries should be addressed: Department of Chemistry, Northeastern University, Boston 15, Massachusetts.

graphy or mass spectrometry. Since the vigorous nature of the reaction in many cases made it desirable to add the metal alkyl slowly, only qualitative observations regarding the relative rates could be made.

Pertinant results are presented in Table 1. Metal corresponding to the metal halide was produced in every reaction. Thus the precipitated solids from the cobalt, nickel, and iron chlorides showed ferromagnetic properties. Analysis of the solid from a cobalt chloride experiment showed it to contain at least 97 % cobalt. Complete decomposition of the alkyl evidently requires an excess of halide, as illustrated by the behavior of cobalt chloride.

TABLE 1

OXIDATION OF TRIETHYLALUMINUM WITH METAL HALIDES[a]

Halide (mmoles)	*Gas evolved by reaction*					*Ethyl groups % recovery*[c]
	moles/mole $Al(C_2H_5)_3$	*Composition %*				
		C_2H_4	C_2H_6	C_4H_{10}	*other*[b]	
$CoCl_2$[d] 10	2.7	30	69	1.0	C_3, C_4H_8	98
$CoCl_2$ 10	2.1	31.5	67.5	1.0		95
$CoBr_2$ 10	1.5	35	60	5.0		103
CuCl 20	1.2	39.5	58.5	2.0	C_2H_5Cl[f]	72
$CuCl_2$ 10	0.93	33	58	9.0	C_2H_5Cl[f]	73
$NiCl_2$ 10	2.2	24	75	1.0	C_3	93
$FeCl_3$ 6.7	2.0	39	60.5	0.2	0.3 C_3H_8	102
AgCl[e] 10	1.7	15	62	23	C_2H_5Cl[e]	77

[a] 6.7 mmole triethylaluminum in 20 ml of methylcyclohexane unless otherwise indicated. [b] Trace quantities present, unless otherwise indicated. [c] Based on gas produced during reaction and subsequent hydrolysis. [d] 4.7 mmoles triethylaluminum; therefore excess $CoCl_2$. [e] 3.3 mmoles triethylaluminum. [f] Detected in gas and liquid.

In the reactions with the cobalt, nickel, and iron salts, hydrolysis of the mixture after cessation of gas evolution furnished quantities of ethane which, together with the reaction gas, accounted for 90–100 % of the ethyl groups. Ethyl chloride is produced (equation 2) with both copper chlorides and with silver chloride. The appearance of this additional product which, with the gas collection system employed could not be estimated*, made it impossible to obtain an ethyl balance in these cases. Every metal halide examined produced a sizable excess of ethane over ethylene. From the essentially complete recovery of ethyl groups in those reactions which could be completely analyzed, it may be inferred that the ethane to ethylene ratio is not due to loss of ethylene by polymerization. These metal halide–aluminum alkyl reactions thus differ markedly from those involving titanium halides[1,3]. Solvent participation, in this case by hydrogen donation, is clearly indicated. The composition of the gas can therefore be expected to be solvent-dependent (*vide infra*).

The reaction with ferric chloride appears to proceed in two stages. No metallic iron is produced in the initial, relatively rapid stage during which an amount of gas approximately equivalent to the reduction of ferric to ferrous chloride is evolved. Gas continues to be produced slowly, and the metal is formed. This contrasts with the

---

* The solubility of ethyl chloride in water, over which the gas was collected, is *ca.* 0.1 mole/liter at 20°.

behavior of cupric chloride, which is converted directly to the metal. Complete reduction to metal occurs with both copper salts, indicating extensive reaction according to equation 2.

n-Butane is formed in every case, but in significant amounts only with cupric chloride and silver chloride. Further, not only the metal but also the anion influence the product distribution. This is illustrated by the behavior of cobalt bromide, which furnishes significantly more butane than the chloride.

Effect of solvent

The reaction of cobalt chloride with triethylaluminum was carried out in the solvents and solutions listed in Table 2, either at the boiling point of the solution or at a maximum temperature of 120°. Predominantly C_2 hydrocarbons were evolved in all cases. Cyclohexane, benzene, cumene, and chlorobenzene, like methylcyclohexane give more ethane than ethylene, but the ratio is reversed with the simple alkenes and with benzyl chloride in ether.

TABLE 2

OXIDATION OF TRIETHYLALUMINUM WITH COBALT CHLORIDE IN VARIOUS SOLVENTS

Solvent	*Mole Ratio* $CoCl_2/Al(C_2H_5)_3$	*Gas evolved by reaction*[a]					*Ethyl groups, % Recovery*[b]
		(moles/mole $CoCl_2$*)*	*Composition, %*				
			C_2H_4	C_2H_6	C_4H_{10}	*Other*[c]	
Ether	1.5	1.5	48	51.5	0.5		
Ether[d]	0.25	2.3	54	46			
Ether[e]	0.10	4.0	76.5	16.5	5.5	1.5 C_3H_8	91
Cyclohexane	0.25	1.05	42	58			
Benzene	1.5	0.56	25.5	73.5	1.0		
Methylcyclohexane	1.5	1.4	31.5	67.5	1.0	C_3, C_4H_8	95
Cumene	1.5	1.2	33	64	3.0	0.3 C_3	90
1-Hexene	1.5	1.15	77.5	22.5			68
1-Octene	1.5	1.35	62.5	35.5	1.7	C_3	79
1-Decene	1.5	1.3	64	34.5	1.0	C_3, C_4H_8	84
Styrene	1.5	1.0					101
α-Methylstyrene	1.5	0.83	52	47	0.8		42
Ethyl Bromide	0.25	7.2	46.5	51.5	2.0		
Chlorobenzene	0.10	9.9	37	61.5	0.6	0.9 C_4H_8	95

[a] Complete reaction to ethane and ethylene according to equation 1 requires 2.0 moles gas/mole $CoCl_2$. [b] Based on gas produced during reaction and subsequent hydrolysis. [c] Traces detected, unless otherwise indicated. [d] 1.50 molar in ethyl bromide. [e] 1.35 molar in benzyl chloride.

Especially significant results were obtained in experiments with halogen-containing compounds, which evidently participate in the reaction by regenerating the metal halide or by producing another oxidizing agent. In ether (ethane:ethylene *ca.* 1:1) the alkyl consumes about 75 % of the metal salt. When ether containing ethyl bromide was used (line 2, Table 2) with only 17 % of the stoichiometric amount of cobalt chloride based on equation 1, the gas composition changed little but more gas was produced than expected from the amount of metal salt. In ethyl bromide as solvent the gas ratio remained essentially unchanged, but almost four times the theoretical quantity of gas based on equation 1 was evolved. The participation of organic halides is shown even more strikingly in an experiment in which an excess of the alkyl was reacted in chlorobenzene. About 5.5 times the amount of gas expected from the oxidizing agent was obtained, and a sizable quantity of biphenyl was formed. Under similar conditions using ether containing 270 mmoles of benzyl chloride (line 3, Table 2), twice the expected quantity of gas was produced, and toluene (41 mmoles), benzene* (13 mmoles), and bibenzyl (16 mmoles) were isolated by distillation. Benzyl chloride as solvent, or in methylcyclohexane resulted in sudden and violent decomposition which was accompanied by copious hydrogen chloride evolution and the formation of a red polymer.

The reactions in olefinic solvents were marked by a significant decrease in the number of ethyl groups recoverable as gaseous reaction and hydrolysis products. The only exception was styrene, in which the recovery was complete. In α-methylstyrene no gas was produced by hydrolysis, and the reaction accounted for less than half the original ethyl groups. The loss was less extensive in the terminal olefins, and it decreased with increasing molecular weight of the solvent.

1-Hexene, 1-octene, and 1-decene were completely converted into other compounds. With hexene and octene about 50% of higher molecular weight materials were obtained. The former furnished about 20% non-volatile residue and two fractions which, based on their analysis and molecular weight, are unsaturated trimer and tetramer of the starting olefin. The octene gave a dimer and unidentified higher polymers. The infrared spectra indicate *trans* configuration for these products. In both cases, the starting olefins were completely isomerized to *trans* compounds. This conversion is remarkable clean, and only a single isomer (*trans*-3-hexene and *trans*-4-octene) is produced as evidenced by gas chromatographic analysis. With decene, the products were not isolated, but the infrared spectrum showed the absence of terminal methylene groups and a *trans* band at 10.41 μ.

These olefin conversions appear to be a direct consequence of the oxidation reaction. In separate experiments neither 1-hexene nor 1-octene reacted with triethylaluminum under otherwise identical conditions. Exchange reactions (equation 3), which have been shown to take place in the dimerization of terminal olefins[8], are thus

$$\text{alC}_2\text{H}_5 + \text{RCH}{=}\text{CH}_2 \rightleftharpoons \text{CH}_2{=}\text{CH}_2 + \text{alCH}_2\text{CH}_2\text{R} \qquad (3)$$

eliminated. Although the left side of this equation is favored by a factor of about 40 (ref. 9), the large excess of olefin (*ca.* 70:1) made this mode of reaction a distinct possibility. The observed results differ markedly from those reported for the reactions of aluminum alkyls with terminal olefins in the absence of metal salts. At higher temperature (145–195°) triethylaluminum and 1-octene produce C_{10} and C_{16} hydrocarbons which have been postulated to arise from a series of addition and exchange steps[10]. Tri-*n*-propylaluminum and propene give 2-methyl-1-pentene and a very small amount of trimer. Similarly, triisobutylaluminum reacts with 1-hexene and with 1-octene by displacement of isobutene and forms 2-butyl-1-octene and 2-hexyl-1-decene respectively with only minor amounts of higher polymers[8]. In the oxidizing system, on the other hand, polymerization proceeds past the dimer stage. The isomerization of starting olefin, and the exclusive production of internal double bonds may undoubtedly be ascribed to the colloidal cobalt produced in the reaction. Cobalt

---

* The benzene is undoubtedly formed from the toluene by an aluminum compound catalyzed dealkylation.

TABLE 3

OXIDATION OF ALUMINUM ALKYLS WITH COBALT CHLORIDE

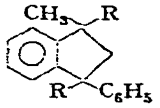
Alkyl	*Solvent*[b]	*moles/mole* AlR_3	*Gas evolved by reaction*[a]							*Alkyl groups, % Recovery*[c]
			Composition %							
			CH_4	C_2H_4	C_2H_6	iso-C_4H_8	iso-C_4H_{10}	n-C_4H_{10}	*Other*	
$(CH_3)_3Al$	E	0.50	84.5		14			0.6	1.0 C_3	
$(CH_3)_3Al \cdot (C_2H_5)_3Al$	E	0.95	62	13	24				0.8 C_3	
(iso-$C_4H_9)_3Al$	MC	1.3[d]				23	77			80
$(CH_3)_3Al \cdot 2$(iso-$C_4H_9)_3Al$	MC	1.8	46	4	6.5	18.5	24.5			98
$(C_2H_5)_3Al \cdot O(C_2H_5)_2$	MC	2.0		11	88.5			0.3		94
$(C_2H_5)_3Al \cdot N(C_2H_5)_3$	MC	2.2		14	86			[e]		89
$KAl(C_2H_5)_3Cl$	MC	2.3		32.5	66			1.4	0.1 C_3	105

---

[a] 6.7 mmoles of alkyl and 10 mmoles of cobalt chloride in 20 ml of solvent. [b] E = diethyl ether, MC = methylcyclohexane. [c] Based on gas produced during reaction and subsequent hydrolysis. [d] Analysis by mass spectrometer. [e] Trace detected.

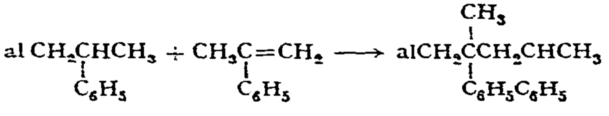
chloride is without effect, and the ability of nickel to act in this manner has been reported[8,11].

In α-methylstyrene a large amount of polymer was formed, and about 40 % of 1,1,3-trimethyl-3-phenylidane (I, R = CH_3). Styrene was converted predominantly into ether-insoluble polymer and about 1 % of 1-methyl-3-phenylindane (I, R = H).



(I)

This behavior again contrasts with the reported reactions of these olefins with aluminum alkyls alone. Excess α-methylstyrene and triisobutylaluminum yields exclusively tris(2-phenyl-1-propyl)aluminum[11]. Similarly, styrene is converted into a mixture of tris(1-phenylethyl)aluminum and tris(2-phenylethyl)aluminum[12]. Further reaction (equation 4) is not favored[13], and in any case the product (II) is not a likely precursor of (I). It was confirmed that α-methylstyrene and aluminum chloride yield only



$$\mathrm{al\,CH_2\underset{\displaystyle C_6H_5}{\underset{|}{C}}HCH_3 + CH_3\underset{\displaystyle C_6H_5}{\underset{|}{C}}{=}CH_2 \longrightarrow alCH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle C_6H_5C_6H_5}{\underset{|}{C}}}}CH_2CHCH_3} \qquad (4)$$

(II)

polymer, although this reagent converts the unsaturated dimer, 2,4-diphenyl-4-methyl-2-pentene, to (I) (ref. 14).

The reaction in cumene, which was expected to furnish bicumyl (2,3-diphenyl-2,3-dimethylbutane) instead gave much polymeric material, benzene, diisopropylbenzenes (10 % *ortho*, 42 % *meta*, and 48 % *para*), and other alkylated benzenes possibly including ethylisopropyl compounds. The dealkylation–alkylation reactions of alkylbenzenes with Friedel-Crafts catalysts are well-known, and the results differed from those obtained with aluminum chloride only in that a larger amount of *para* isomer was formed[15]. In benzene, the reaction ceased when about one quarter of the alkyl had been consumed, and almost three times as much ethane as ethylene was produced. The liquid, after hydrolysis, contained a small amount of ethylbenzene, which suggests that at least part of the ethane excess may be due to the removal of ethylene in alkylation reactions.

Other aluminum compounds

The oxidation of a number of other aluminum compounds with cobalt chloride was examined under standardized conditions (Table 3). Trimethylaluminum in ether reacts only one quarter as extensively as triethylaluminum (Table 2). The major product, methane, undoubtedly arises by hydrogen abstraction from the solvent, yet no new components were detected in the liquid even in a large-scale run. This parallels the experience of Kharash *et al.*[16], who were unable to isolate products from the interaction of methyl radicals with ether.

TABLE 4

OXIDATION OF R_2AlR' WITH COBALT CHLORIDE

R	*R'*	*Mole Ratio* $CoCl_2/R_2AlR'$	*Solvent*[a]	*Gas evolved by reaction* moles/mole R_2AlR'	*Composition %* C_2H_4				*Alkyl groups, % Recovery*[b]
					C_2H_4	C_2H_6	n-C_4H_{10}	*Other*[c]	
C_2H_5	Cl	1.0	E	0.07					
C_2H_5	Cl	1.0	MC	1.2	45.5	54	0.2	C_3, C_2H_5Cl	90
Cl	C_2H_5	2.0[d]	E	0.13					
Cl	C_2H_5	0.5	MC	0.13	7.5	92	0.6	C_2H_5Cl	
C_2H_5	Br	1.0	MC	0.55	36	60	3.1	0.5 C_3	106[e]
C_2H_5	OC_2H_5	1.0	MC	1.4	13	80.5	0.8	C_3	
C_2H_5	$N(C_2H_5)_2$	1.0	MC	0.52	21	74.5	4.0	0.5 C_3	93
CH_3	NH_2	1.0	MC	0.61	3.5	9.5	0.5	87 CH_4	93
C_2H_5	H	1.5	E	0.82[e]	0.5	18.5		79 H_2, 2.0 CH_4	
C_2H_5	$CH=CHC_2H_5$	1.5	E	0.57	60	13.5	0.8	19 1-C_4H_8, 5.5 2-C_4H_8	
C_2H_5	$C≡CC_2H_5$	1.5	E	0.17	60	38.5	0.2	0.3 1-C_4H_8	
iso-C_4H_9	$CH=CHC_4H_9$-iso	1.5	E	0.09				[f]	

[a] E = Diethyl ether, MC = methylcyclohexane. [b] Based on gas produced during reaction and subsequent hydrolysis. [c] Traces unless otherwise indicated. [d] 4-fold excess of cobalt chloride. [e] Analysis by mass spectrometer. [f] Gas consisted of isobutane and isobutene only.

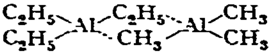
TABLE 5

OXIDATION OF ETHYLALUMINUM CHLORIDES WITH COBALT CHLORIDE

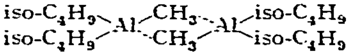
Ratio C_2H_5/Cl $CoCl_2$	*Mmoles*[a]			*Method*[b]	*Gas evolved by reaction*					*Ethyl groups, % Recovery*[c]
					moles/mole C_2H_5	*Composition %*				
	$(C_2H_5)_3Al$	$AlCl_3$	$CoCl_2$			C_2H_4	C_2H_6	n-C_4H_{10}	*Other*[d]	
0.5	3.3	6.7	15[e]	(*B*)	0.58	21.5	70.5	6.5	1.5 C_3	101
1.4	4.65	3.3	14[e]	(*A*)	0.67	19	80	0.5	C_3	102
2.0	6.7	3.3	10	(*C*)	0.82	30.5	69	0.2	0.3 C_3	99
4.0	3.3	[c]	10[e]	(*D*)	0.58	25	74.5	0.5	C_3	96
5.0	8.4	1.7	12.5	(*A*)	0.69	37.5	61.5	0.8	C_3	85
11.0	11.0	1.0	16.5	(*A*)	0.84	31.5	67.5	0.8	C_3	94

[a] In 20 ml of methylcyclohexane at reflux. [b] See text. [c] Based on gas produced during reaction and subsequent hydrolysis. [d] Traces present unless otherwise indicated. [e] Excess cobalt chloride.

Revealing results were obtained with mixed alkyls. Aluminum alkyls, other than those having only isoalkyl groups are dimeric, and mixtures of different alkyls generate mixed dimers by exchange of alkyl groups. [This exchange is very rapid (*cf.* ref. 17) and extends to compounds of the type R_2AlX, where X is not an alkyl group[18].] An equimolar mixture of trimethylaluminum and triethylaluminum would therefore contain structures of which (III) may be considered representative. Oxidation produced gas corresponding to one third of the alkyl groups, showing that reaction proceeds further than with trimethylaluminum but less than with the triethyl compound. The methane to ethane + ethylene ratios (1.7:1 from reaction and 0.7:1 from hydrolysis) indicate a greater reactivity for methyl than ethyl groups. This may be considered evidence for methyl–ethyl interactions (see DISCUSSION), although no conclusions can be drawn from the formation of propane since small amounts of this alkane are also produced from triethylaluminum alone. Triisobutylaluminum in methylcyclohexane is significantly less reactive than the ethyl compound, but the product distribution (3.3:1 isobutane to isobutene) again shows solvent interaction. Due to alkyl exchange, a 2:1 mixture of triisobutylaluminum and trimethylaluminum may be represented by structure (IV) (ref. 19). The oxidation of this compound affords a comparison of the reactivity of bridging and non-bridging groups.



(III)



(IV)

The product distribution accounts for complete reaction of the methyl groups and for about half of the isobutyl groups. This was supported by hydrolysis of the mixture after reaction, which furnished only isobutane. The oxidation therefore ceased with the formation of isobutylaluminum dichloride; separate experiments showed this type of compound to be substantially less reactive than the alkyls. In this case methyl–isobutyl interactions are indicated not only by the decrease in the isobutane–isobutene ratio (1.3:1 compared to 3.3:1 with triisobutylaluminum), but also by the detection of a small amount of 2-methylbutane in the liquid after hydrolysis.

In methylcyclohexane, the coordination of triethylaluminum with electron donors such as diethyl ether, triethylamine, and chloride ion produces little change in the total gas yield (*cf.* Table 3 and line 2, Table 2). The product distribution is substantially unchanged with the potassium chloride complex, but a large increase in the ethane–ethylene ratio (from 2:1 to 6:1 and 8:1, respectively) results from coordination with the amine and ether. This is particularly remarkable when compared with the 1:1 ratio obtained in ether as solvent.

A series of alkyls of type R_2AlR' were also oxidized with cobalt chloride, with the results shown in Table 4. Diethylaluminum chloride shows a pronounced solvent effect; hardly any reaction occurs in ether, yet two-thirds of the ethyl groups are removed in methylcyclohexane. Ethylaluminum dichloride is unreactive in both solvents. In general, electron-donating substituents appear to decrease the extent of reaction, and to lead to increased ethane formation. With diethylaluminum hydride the hydrogen, which is the bridging group[17], reacts preferentially as shown by the 4:1 hydrogen to C_2 ratio. The 40-fold excess of ethane over ethylene strongly suggests that the aluminum compound acts as a hydrogen donor. The unsaturated aluminum compounds gave gas predominantly derived from the alkyl groups*. As in the reactions with the terminal olefins as solvents, a sizable excess of ethylene over ethane was produced from the ethylaluminum compounds.

A relation between the product distribution and the number of alkyl groups is apparent from the behavior of the ethylaluminum chlorides. This point was explored further in experiments with mixtures of aluminum compounds corresponding to compositions $(C_2H_5)_nAlCl_m$ in which the ratio m/n was varied from 0.5 to 11 (Table 5). Several methods were employed to run these reactions: (*A*) the premixed solution of the aluminum compounds was added to the cobalt chloride; (*B*) the triethyl was added to the cobalt salt first, and was followed by a suspension of aluminum chloride; (*C*) the cobalt salt, triethyl, and aluminum chloride were mixed at —78° and warmed to reflux; (*D*) same as (*B*), except that a solution of the triethyl was added to a mixture of ethylaluminum dichloride and cobalt chloride. Under comparable conditions (method *A*), increasing the C_2H_5:Cl ratio gave increased gas yields and a decreased ethane to ethylene ratio which finally approaches that of the triethyl. Distilled ethylaluminum dichloride reacts hardly at all (line 4, Table 4) yet when it was prepared by method (*B*) about 60 % of the ethyl groups appeared as gaseous products. Further, the ethane:ethylene ratio was much smaller under the latter conditions. Similarly, diethylaluminum chloride reacted by method (*C*) yielded gaseous products characteristic of triethylaluminum (*cf.* line 2, Table 1, and line 2, Table 4). The monochloride prepared by method (*D*) resulted in yet another product ratio, which is between that of the triethyl and the dichloride. These results indicate that a fraction of the alkyl initially mixed with the cobalt salt reacts as such without undergoing extensive ethyl–chlorine exchange. Since these exchange reactions are practically instantaneous[17,18], it is reasonable to infer that the reaction is preceeded by an interaction of the alkyl with the cobalt chloride surface which approaches the strength of the Al–Cl–Al bridging bond.

Comparison with boron compounds

Triethylboron is quite unreactive under conditions which result in facile oxidation of triethylaluminum. There was no reaction with cupric chloride and nickel chloride. Cobalt chloride and silver chloride furnished 0.17 and 0.05 moles/mole alkyl of gas respectively. The cobalt chloride reaction was completely inhibited by coordinating the triethylboron with pyridine. The complex salt $LiB(C_2H_5)_3C_4H_9$ gave 0.6 moles of gas per mole of compound, composed of 78 % C_2 and 22 % C_4 hydrocarbons. This distribution correlates approximately with the abundance of the corresponding alkyl groups in the compound. These results contrast with the reactions of trialkylboranes with the oxides of silver and gold in alkaline medium, which result in high yields of coupling products[21].

---

* The liquid products from these systems are discussed in detail in ref. 20.

DISCUSSION

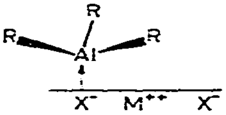
The results of the metal halide oxidations of aluminum alkyls may be summarized as follows. (*1*) The extent of reaction and the proportions of gaseous hydrocarbons vary with different metal salts when the reactant ratio is based on equation (1). Under these conditions, none of the reactions involving cobalt chloride proceed much beyond the stage which leaves one aluminum-bound alkyl group. Triethylaluminum in methylcyclohexane produces more ethane than ethylene with all the salts. Substantial ethyl chloride formation is evident with copper and silver chlorides. (*2*) The solvent exerts appreciable influence. Hydrogen abstraction occurs in most cases, and solvent-derived polymers are formed in unsaturated solvents. Reactions in the latter are marked by a loss of ethyl groups recoverable as gaseous products, and by a decreased ethane:ethylene ratio. (*3*) Alkyl and aryl halides are capable of increasing the extent of oxidation expected from equation (1) when used with an excess of triethylaluminum. (*4*) The reactivity varies with the alkyl group of the trialkyls, *e.g.* ethyl > methyl in ether and ethyl > isobutyl in methylcyclohexane. (*5*) In mixed alkyls, the distribution of gaseous products and the reactivity of a given alkyl group depends on the number and identity of the other substituents. (*6*) A strong interaction between the alkyl and metal halide surface appears to preceed the actual oxidation.

An exact interpretation of the reaction is obviously complicated by the heterogeneity of the system, and by the changing composition of the aluminum compound and accompanying slow collapse of the metal halide crystal to the metal as the oxidation proceeds. However, the experimental observations are in accord with the formation of radicals, which then undergo secondary changes characteristic of these species. The commercially available aluminum alkyls thus provide a convenient means of generating radicals.

The reaction of metal monoalkyls with heavy metal salts gives gaseous products[22] which have been postulated by Gilman and Jones to arise from initially generated alkyl radicals[23] by disproportionation, dimerization, or hydrogen abstraction from the solvent. More recently, Eden and Feilchenfeld[1] have presented evidence that the decomposition of polyalkylmetals by heavy metal chlorides involves hydrogen abstraction from metal-bound alkyl groups. Specifically these authors found that the reaction of titanium tetrachloride with triethylaluminum in carbon tetrachloride produces primarily ethane and not ethyl chloride which would be expected from "free" radicals. Our results confirm that aluminum-bound alkyl groups constitute a source of hydrogen atoms which can compete effectively with the solvent. Without the participation of these groups, the product distribution from a given alkyl group would be expected to be essentially independent of the nature of the other attached groups. It was demonstrated with several examples that this is not the case. However, in a number of the experiments with ethylaluminum compounds, the ethyl group balance and excess of ethane over ethylene indicate that part of the hydrogen comes from the solvent.

Disproportionation as a source of alkenes also deserves some comment. In gas phase reactions, the disproportionation to dimerization ratio is small for the radicals of interest[24]; the ratio is even smaller for cross-disproportionation, *e.g.* $CH_3^{\bullet} + C_2H_5^{\bullet} \rightarrow CH_4 + C_2H_4$. It has also been reported that alkyl radicals do not disproportionate in the liquid phase[25]. The large excess of monomeric hydrocarbons over dimers observed in the present study thus casts considerable doubt on this mode of alkene production. Based on the finding that ethylaluminum chloride yields almost solely ethane whereas triethylaluminum yields about 30 % ethylene, it is suggested that the alkene arises from radical attack on metal–alkyl groups.

A mechanism which adequately summarizes these considerations for triethylaluminum is presented in Chart 1. The first step is postulated to be dissociation of the aluminum alkyl dimer by interaction with the surface, resulting in a surface complex (V) which is formulated in analogy to the known compounds with alkali metal halides[26]. Electron transfer to the metal ion then results in a lower oxidation state



(structure VI) and an alkyl radical. It is a moot point whether transition metal alkyls are involved in this step, since these would not be stable at the temperature of the reaction (*cf.* ref. 27. However, in coordinating solvents transient stability may be possible. See ref. 28). Reaction of intermediate (VII) along path *a* only results in a 1:1

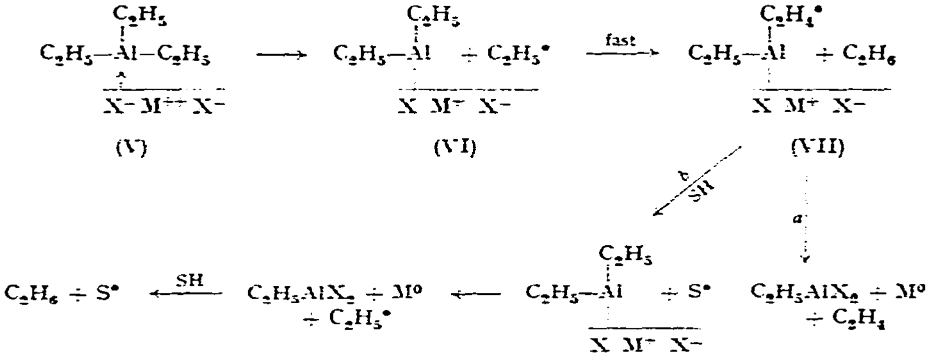
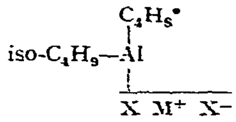


Chart 1

ratio of ethane to ethylene, which appears to be the case with diethyl ether (see, however, ref. 7, p. 124, and also ref. 16). If part of the system decomposes via path *b* (SH is solvent), excess ethane is produced as is observed with methylcyclohexane. The ethylene to ethane ratio therefore becomes a function of the rate parameters of paths *a* and *b*. The enhanced reactivity of the methyl groups in the mixed methylethylaluminum compound tends to support the suggestion that the formation of (VII) from (VI) is very rapid[1]. It is further proposed that the oxidation of an alkyl molecule is accomplished by one particular metal ion. Thus intermediate oxidation products, such as the monochloride from triethylaluminum, do not leave the surface but follow the sequence shown in the Chart. The observed cessation of the reaction close to the alkylaluminum dichloride stage is in agreement with this view. This corresponds to the consumption of one mole of metal halide, as demanded by equation 6. At this point the products fall away from the surface, and the dichloride is stabilized in solution as its dimer[19]. The oxidation of the unsaturated aluminum compounds gives further support for this picture. Here the reaction predominantly involves the unsaturated groups and gives rise to liquid products[20]. Owing to the relative inertness of the solvent (ether) the large excess of ethylene in the gaseous products must result from the attack of ethyl and unsaturated radicals on ethyl groups.

$$(C_2H_5)_3Al + MCl_2 \longrightarrow C_2H_5AlCl_2 + M^0 + 2C_2H_5 \qquad (6)$$

According to the mechanism of Chart 1, the methylisobutyl compound (IV) and the triisobutylaluminum both furnish the same intermediate (VIII), with the formation of methane and isobutane respectively. The proportions of isobutene and isobutane (43 % and 57 % respectively, according to Table 3) from the mixed alkyl reflect the further reaction of (VIII) along the two paths. The calculated product



$$\begin{array}{c} C_4H_8^{\bullet} \\ | \\ \text{iso-}C_4H_9\text{—}Al \\ | \\ \overline{X\ M^+\ X^-} \end{array}$$

(VIII)

distribution for triisobutylaluminum based on these figures (21.5 % isobutene and 78.5 % isobutane) is in good agreement with the values found (23 % isobutene and 77 % isobutane).

The predominant production of ethane in methylcyclohexane when triethylaluminum is coordinated with ether or triethylamine may be due to the donor remaining weakly bonded to the surface complex. This either blocks access between adjacent alkyl groups or changes the geometry sufficiently to make hydrogen abstraction from the solvent the preferred mode of reaction. The same spatial arguments would apply to the reaction in ether, but here interaction with the solvent is evidently intrinsically less favored (see, however, ref. 7, p. 124, and also ref. 16.)

Eden and Feilchenfeld[1] ascribe butane formation to the rearrangement of (VII) to $C_4H_9Al^{\bullet}Cl$, which is presumably oxidized further. Our results are not at variance with this suggestion, although the higher proportion of butane formed with some metal halides (AgCl) remains to be explained. Ethyl chloride, which was produced in sizable quantities with the copper chlorides and silver chloride, must arise from the further oxidation of radicals by the metal halide (equation 7). This reaction, which has ample

$$M^{++} + C_2H_5^{\bullet} \longrightarrow M^{+} + C_2H_5^{+} \xrightarrow{Cl^-} C_2H_5Cl \qquad (7)$$

precedent (*cf.* ref. 29), also occurs in the reaction of titanium tetrachloride with ethylaluminum compounds[30]. The generation of an oxidizing species by organic halides has been observed in Grignard reagent–cobalt chloride reactions[7,31]. The aluminum alkyl system behaves analogously, and the products (biphenyl from chlorobenzene, and bibenzyl and toluene from benzyl chloride) are those expected from phenyl and benzyl radicals respectively. Our results in ethyl bromide are apparently not in agreement with the work of Batalov and Korshunov[32]. These authors studied ethyl group exchange with triethylaluminum using ^{14}C-labelled ethyl bromide and catalytic amounts of metal salts including ferric chloride, cupric chloride, cobaltous chloride, silver bromide, and nickel chloride. With the possible exception of the latter salt, which invariably caused explosions, no gas evolution was observed. While this discrepancy can undoubtedly be traced to differences in experimental conditions, the sparse published details do not allow a meaningful comparison to be made.

The secondary reactions of the solvent are the least well understood aspects of these systems. With methylcyclohexane, gas chromatographic examination of the liquid after reaction revealed no new volatile components. Further, the evolved gases often contained small quantities of C_3 hydrocarbons, suggesting methyl as well as hydrogen abstraction. It must be assumed that the resulting solvent radicals are ultimately converted into higher molecular weight compounds. The results with cumene shed some light on this problem. The formation of bicumyl from this compound by hydrogen abstraction has been used to detect radical intermediates in other reactions (*cf.* ref. 33). The aluminum alkyl oxidation in this solvent showed hydrogen abstraction (ethane to ethylene 2:1), and one can only surmise that the dimethylbenzyl radicals are converted to α-methylstyrene* which polymerizes.

EXPERIMENTAL

All melting points and boiling points are uncorrected. Carbon–hydrogen analyses and molecular weight determinations were made by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y.

Materials

a) *Aluminum alkyls.* These were obtained from the Ethyl Corporation, New York, N. Y., and were purified by fractional distillation under vacuum where feasible. Triethylaluminum had b.p. 72° (0.6 mm). (Found: Al, 24.0. $C_6H_{15}Al$ calcd.: Al, 23.6%.) Diethylaluminum hydride, b.p. 67° (0.6 mm) was obtained by distillation of its 60:40 mixture with triethylaluminum. (Found: Al, 30.7; gas 2.9 mole/mole. $C_4H_{11}Al$ calcd.: Al, 31.4%; gas, 3.0 mole/mole.) Trimethylaluminum (assay 99.2%) was used without further purification. Triisobutylaluminum (assay 93%) was also used without purification since attempted distillation resulted in gross decomposition.

Diethylaluminum chloride had b.p. 39° (0.5 mm). (Found: Al, 22.3. $C_4H_{10}AlCl$ calcd.: Al, 22.4%.) Ethylaluminum dichloride, b.p. 40° (0.25 mm), had an assay of 95.3%.

1-Butenyldiethylaluminum[35], (4-methyl-1-pentenyl)diisobutylaluminum[35], and potassium triethylaluminum chloride[36] were prepared according to the literature. Dimethylaluminum amide** and diethylaluminum bromide*** were obtained from other laboratories.

b) *Solvents.* All the solvents were of C.P. grade. They were redistilled and, where possible, dried and stored over sodium wire. Diethyl ether was distilled from calcium hydride, and triethylamine from barium oxide. Purity was checked by gas chromatographic analysis.

---

* α-Methylstyrene, as well as bicumyl, are produced in the irradiation of phenanthrenequinone in cumene. See ref. 34.

** Dr. M. TSUTSUI, New York University.

*** Dr. A. L. SEARLES, College of Mount St. Vincent.

c) Metal salts. Cobaltous chloride was prepared from the hexahydrate by direct dehydration[36] at 136°, and by reaction with thionyl chloride[37]. Both samples yielded identical results in the oxidation reaction. Cobaltous bromide was obtained from its hexahydrate by first heating under hydrogen bromide and then under nitrogen at 130°. Cuprous chloride was prepared from the cupric salt and sodium sulfite[38]. Reagent grade samples of anhydrous cupric chloride, ferric chloride, silver chloride, and nickelous chloride were used without purification after drying in vacuum over phosphorous pentoxide for eight hours. All the salts were stored under nitrogen over potassium hydroxide.

Analysis

Aluminum was determined gravimetrically with 8-hydroxyquinoline[39]. Consistent results were obtained by washing the digested precipitate with hot water, and drying at 130° for 5 h. Determination of the alkyl content of aluminum alkyls was accomplished by hydrolysis and volumetric measurement of the alkane evolved (equation 8). The apparatus used is described in Texas Alkyls Bulletin T 69-5, Stauffer Chemical Co. This procedure was used in lieu of, or in conjunction with, aluminum analysis for assaying purposes.

$$R_3Al + 3H_3O^+ \longrightarrow 3RH + Al^{3+} + 3H_2O \qquad (8)$$

Gas chromatographic analysis of the gaseous and liquid reaction and hydrolysis products was carried out with Perkin-Elmer Model 154 and F & M Model 500 instruments. Columns found useful were (12 feet × 1/4" diameter copper tubing packed with "Chromosorb" containing 20% substrate) "Ucon" 525 for higher olefins, "Carbowax" 1500 for C_4–C_8 hydrocarbons, diisooctyl isosebacate for C_8–C_{20} hydrocarbons and aromatics, and silicone gum rubber for very high boiling materials. The C_1–C_4 hydrocarbons were analyzed at room temperature with a 50-feet long diethyl glutarate column. Some samples, including all those containing hydrogen, were analyzed on a Consolidated Electrodynamic Type 21-103C mass spectrometer.

General procedure

All glass apparatus was dried for several hours at 130° prior to use. The standard reactions were carried out in 100-ml flasks provided with a "Teflon"-coated magnetic stirring bar, an efficient condenser, and a pressure-equalizing dropping funnel. A gas inlet tube and mercury valve protected exit allowed the assembly to be purged with General Electric Lamp Grade nitrogen (total impurities *ca.* 5 ppm) for the removal of air and for protection during additions. Gas evolution was measured by displacement of water from a reservoir which was isolated from the system by a one-way mercury valve and a "Drierite" tube. Tests of this arrangement showed that no hydrolysis of the alkyls by back-diffusion of water vapor takes place, and that the composition of the gas is the same on both sides of the valve. For very small volumes, a mercury-filled gas burette was used. The same assembly, with larger vessels, served for larger-scale experiments.

In a typical experiment the reaction flask was charged with half of the solvent and the required amount of metal halide was added. A solution of the alkyl in the remaining solvent was placed in the funnel. The alkyl was conveniently weighed in a hypodermic syringe, the tip of which was protected by insertion into a rubber stopper.

The mixture was brought to reflux or 120° by a thermostatically controlled oil bath, and the addition of the alkyl solution was started when there was no further volume change due to expansion. The reactions were always allowed to proceed until no more gas was evolved. The time required for this varied from 2–18 h. Samples of gas for analysis were withdrawn by syringe through a serum cap covered outlet. In most cases the mixtures were hydrolyzed after reaction, and the hydrolysis gas was measured and analyzed. From repeat measurements it is estimated that the gas yield and composition are reliable to ± 5 %.

Since most of the reactions ran very similar courses, only those with unique features are described further.

Reactions of triethylaluminum

a) With cobalt chloride. Triethylaluminum (0.76 g, 6.7 mmoles) in 10 ml of methylcyclohexane was added dropwise to a suspension of cobalt chloride (1.30 g, 10 mmoles) in 10 ml of refluxing solvent. The solid became dark immediately, and 18 mmoles of gas was evolved overnight. The solid was separated, washed, and dried (0.61 g). Hydrolysis of the filtrate gave another 1.1 mmoles of gas, so that 95 % of the ethyl groups were accounted for.

The solid was dissolved in acid, and the solution was diluted to 500 ml after adjusting the pH to 5. Aliquots were treated with excess EDTA solution at pH 10 and back-titrated with standard zinc sulfate solution using Eriochrome Black T as indicator. In this manner the solid was shown to contain 97 % cobalt.

b) With cupric chloride. The reaction was carried out as above with 6.7 mmoles of triethylaluminum and 10 mmoles of cupric chloride. Gas evolution ceased after producing 6.2 mmoles of gas. The orange-yellow solid was insoluble in water and proved to be copper. Gas chromatography showed that both gas and liquid contained ethyl chloride.

c) In α-methylstyrene. Triethylaluminum (6.7 mmoles), cobalt chloride (10 mmoles) were reacted in 20 ml of α-methylstyrene at 120°. Gas (8.3 mmoles) was evolved in 2 h. Hydrolysis of the mixture produced no further gas. The mixture was extracted with ether, and the dried extract was distilled. A sizable non-volatile residue was obtained, and 8.0 g of clear liquid, b.p. 122–124° (0.5 mm), n_D^{20} 1.5649, which crystallized, m.p. 48–51°, after recrystallization from ethanol, $\lambda_{max}^{n\text{-}PrOH}$ 258.5, 264.7, and 271.6 mμ (characteristic of indane derivatives, *cf.* ref. 40). The m.p. reported[14] for 1,1,3-trimethyl-3-phenylindane (I, R = CH_3) is 51–52°. (Found: C, 91.4; H, 8.5; mol.wt., 242. $C_{18}H_{20}$ calcd.: C, 91.5; H, 8.5 %; mol. wt., 236.)

d) In styrene. The same quantities of reagents as above were reacted in 20 ml of styrene at 120°. Gas (10 mmoles) was evolved in 6 h, and hydrolysis furnished another 10 mmoles, so that all the ethyl groups were accounted for. Addition of ether gave much insoluble solid and a yellow extract from which 0.25 g of clear liquid, b.p. 40° (0.1 mm), was obtained by distillation. The ultraviolet spectrum ($\lambda_{max}^{n\text{-}PrOH}$ 254.0, 259.1, 264.9, and 272.8 mμ) identified this material as 1-methyl-3-phenylindane (I, R = H)[41].

e) In cumene. A suspension of cobalt chloride (19.5 g, 0.15 mole) in 70 ml of cumene was reacted with triethylaluminum (11.4 g, 0.10 mole) at 120°. The reaction, which was over in 1 h gave 0.175 mole of gas and hydrolysis produced another 0.092 mole. Extraction with ether and distillation gave four fractions, (*1*) 6.5 g, b.p. 81–83°

(760 mm), (*2*) 17.4 g, b.p. 152–5° (760 mm), (*3*) 15.0 g, b.p. 52–55° (13 mm), (*4*) 1.8 g, b.p. 65–100° (13–3 mm), and a polymeric residue. Three fractions were identified by gas chromatography, using authentic compounds for comparison*, as follows: (*1*) Benzene, (*2*) cumene, and (*3*) a 10:42:48 mixture of *ortho*-, *meta*-, and *para*-diisopropylbenzenes. The last fraction, which presumably consists of higher alkylbenzenes, contained no 2,3-dimethyl-2,3-diphenylbutane.

f) *In 1-hexene.* A mixture of cobalt chloride (0.15 mole), triethylaluminum (0.10 mole), and 1-hexene (200 ml) was refluxed overnight. The reaction produced 0.17 mole of gas, and hydrolysis another 0.033 mole. The usual isolation procedure gave four fractions: (*1*) 38.0 g, b.p. 67–70° (6.4 mm), (*2*) 9.7 g, b.p. 72–6° (6.4 mm), (*3*) 14.0 g, b.p. 84° (0.1 mm), (*4*) 15.8 g, b.p. 120–140° (0.1 mm), *ca.* 6 g of interfractions, and a non-volatile residue of 26 g.

Fraction (*1*) was identified as *trans*-3-hexene by gas chromatography and its infrared spectrum**. Fractions (*2*) and (*3*) gave positive unsaturation tests and showed infrared bands at 10.36 μ and 10.27 μ respectively.

Fraction (*2*): (Found: C, 85.5; H, 14.6; mol. wt., 235. $C_{18}H_{36}$ calcd.: C, 85.7; H, 14.3 %; mol. wt., 252.)

Fraction (*3*): (Found: C, 85.7; H, 14.5; mol. wt., 353. $C_{24}H_{48}$ calcd.: C, 85.7; H, 14.3 %; mol. wt., 336.)

Refluxing a solution of 6.7 mmoles triethylaluminum in 20 ml of 1-hexene overnight gave no gas. Hydrolysis gave 20 mmoles of gas, accounting for all the alkyl. Gas chromatography of the liquid showed only 1-hexene.

g) *In 1-octene.* The reaction of 6.7 mmoles of triethylaluminum with 10 mmoles of cobalt chloride in 20 ml of 1-octene gave 13.5 mmoles of gas during reaction and 1.7 mmoles on hydrolysis. Distillation afforded *trans*-4-octene, b.p. 94–96° (760 mm), identified by its infrared spectrum and retention time on a diisooctyl isosebacate column**, and a fraction b.p. 76–77° (0.1 mm). (Found: C, 85.5; H, 14.4; mol. wt., 231. $C_{16}H_{32}$ calcd.: C, 85.7; H, 14.3 %; mol. wt., 224.)

Higher boiling material was not identified. Refluxing a solution of triethylaluminum in the absence of cobalt chloride produced no gas.

h) *In ether containing benzyl chloride.* Triethylaluminum (0.1 mole), cobalt chloride (0.010 mole), and benzyl chloride (0.27 mole) in 200 ml of refluxing ether gave 0.04 mole of gas overnight. Distillation of the ether solution after hydrolysis gave 1 g of benzene, 3.75 g of toluene, and 19.2 g of unchanged benzyl chloride, all identified by gas chromatography. The last fraction, 2.9 g, b.p. 105° (0.1 mm), solidified and proved to be bibenzyl by its infrared spectrum. (Found: C, 91.9; H, 7.9. $C_{14}H_{14}$ calcd.: C, 92.25; H, 7.7 %.)

i) *In chlorobenzene.* In the reaction of cobalt chloride (0.010 mole), triethylaluminum (0.10 mole), and chlorobenzene (0.27 mole) at 130°, 95 % of the ethyl groups were accounted for by the gas liberated during reaction (0.099 mole) and on hydrolysis (0.185 mole). Chlorobenzene (0.19 mole) was recovered by distillation, and the residue was shown to contain mainly biphenyl.

---

* The diisopropylbenzenes were obtained from K & K Laboratories, Inc., Jamaica, N.Y.

** Authentic samples of hexenes and octenes were obtained from the Phillips Petroleum Co., Bartlesville, Okla.

Reaction of diethylaluminum ethoxide with cobalt chloride

Triethylaluminum (10 mmoles) in 5 ml of methylcyclohexane was reacted at room temperature with a solution of absolute ethanol (10 mmoles) in the same quantity of solvent. The required volume of gas (10 mmoles) was rapidly evolved. The resulting solution was reacted with 10 mmoles of cobalt chloride as usual.

The same procedure was followed with diethylaluminum diethylamide, which was prepared from diethylaluminum hydride and diethylamine. The etherate and triethylaminate of triethylaluminum were obtained by adding the donors to the alkyl, and removing the excess of the former by pumping under high vacuum.

Reaction of lithium butyltriethylboron with cobalt chloride

The addition of triethylboron* (3.3 mmole) to butyllithium (3.3 mmole) in pentane–heptane solution** produced a colorless solid in an exothermic reaction. This was dissolved in 10 ml of ether, and the solution was added to cobalt chloride (5.0 mmoles) in 10 ml of ether. On refluxing for 12 h, 2.0 mmoles of gas was evolved.

The triethylboron-pyridine complex was prepared and reacted in a similar manner.

ACKNOWLEDGEMENTS

This work was supported by the Aeronautical Research Laboratory, Wright-Patterson Air Force Base, Ohio, under contract AF 33(616)-5610. We wish to thank Professor CHARLES J. MARSEL for his continued interest and encouragement. We are also grateful to Mr. SEYMOUR ZOLTY for the mass spectrometric analyses.

SUMMARY

The oxidation of aluminum alkyls by various metal halides has been investigated. Alkenes and alkanes derived from the alkyl groups are the gaseous products, the composition of which varies with the metal halide, the solvent, and the number of aluminum-bound alkyl groups. Abstraction of hydrogen from the solvent occurs in most cases. Complex changes take place with unsaturated solvents, which result in isomerization and polymer formation. In the presence of organic halogen compounds the metal halide is regenerated, or another oxidizing species is produced. The results are discussed in terms of a modified version of Eden and Feilchenfeld's mechanism, in which radical attack on adjacent metal-bound alkyl groups plays an important role.

REFERENCES

1 C. EDEN AND H. FEILCHENFELD, *Tetrahedron*, 18 (1962) 233.
2 F. PATAT AND H. SINN, *Angew. Chem.*, 70 (1958) 496; G. NATTA, *Angew. Chem.*, 68 (1956) 393; G. NATTA, I. PASQUON AND E. GIACHETTI, *Angew. Chem.*, 69 (1957) 213.
3 N. G. GAYLORD AND H. F. MARK, *Linear and Stereoregular Addition Polymers*, Interscience Publishers, New York, 1959, Chapter 7.
4 G. N. PETROV AND A. KOROTKOV, *Dokl. Akad. Nauk SSSR*, 141 (1961) 632.
5 K. ZIEGLER, in H. ZEISS, *Organometallic Chemistry*, Reinhold, New York, 1960, pp. 250–1.
6 W. SCHLENK AND T. WEICHSELFELDER, *Ber.*, 56 (1923) 2230.
7 M. S. KHARASCH AND O. REINMUTH, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, Chapters 5 and 16.

---

* Callery Chemical Co., Pittsburgh, Pa.

** Foote Mineral Co., Philadelphia, Pa.

8 K. Ziegler, H. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll and W. Kroll, *Ann. Chem.*, 629 (1960) 121.
9 K. Ziegler, W. Kroll, W. Larbig and O. Steudel, *Ann. Chem.*, 629 (1960) 53.
10 E. Perry and H. O. Ory, *J. Org. Chem.*, 25 (1960) 1685.
11 K. Ziegler, H. Martin and F. Krupp, *Ann. Chem.* 629 (1960) 14.
12 G. Natta P. Pino, G. Mazzanti, P. Longi and F. Bernardini, *J. Am. Chem. Soc.*, 81 (1959) 2561.
13 W. Pfohl, *Ann. Chem.*, 629 (1960) 207.
14 E. Bergmann, H. Taubadel and H. Weiss, *Chem. Ber.*, 64 (1931) 1493.
15 C. C. Price, in R. Adams *et al.*, *Organic Reactions*, Vol. 3, Wiley, New York, 1946, p. 9.
16 M. S. Kharash, R. Lewis and W. Reynold, *J. Am. Chem. Soc.*, 65 (1943) 493.
17 E. G. Hoffmann, *Trans. Faraday Soc.*, 58 (1962) 642, which also cites other literature.
18 J. Smidt, M. P. Groenewege and H. de Vries, *Rec. Trav. Chim.*, 81 (1962) 729.
19 E. G. Hoffmann, *Ann. Chem.*, 629 (1960) 104.
20 M. I. Prince and K. Weiss, *J. Organometal. Chem.*, 2 (1964) in press.
21 H. C. Brown, C. Verbrugge and C. N. Snyder, *J. Am. Chem. Soc.*, 83 (1961) 1001; H. C. Brown, N. C. Hébert and C. N. Snyder, *J. Am. Chem. Soc.*, 83 (1961) 1001; H. C. Brown and C. N. Snyder, *J. Am. Chem. Soc.*, 83 (1961) 1002.
22 H. Gilman, R. G. Jones and L. A. Woods, *J. Am. Chem. Soc.*, 76 (1954) 3615, and earlier papers cited therein.
23 H. Gilman and R. G. Jones, *J. Org. Chem.*, 10 (1945) 505.
24 J. A. Kerr and A. F. Trotman-Dickinson, in G. Porter, *Progress in Reaction Kinetics*, Vol. 1, Pergamon Press, New York, 1961, p. 111.
25 C. D. Wagner, *J. Phys. Chem.*, 64 (1960) 231.
26 K. Ziegler, R. Köster, H. Lehmkuhl and K. Reinert, *Ann. Chem.*, 629 (1960) 33.
27 H. Gilman and J. M. Straley, *Rec. Trav. Chim.*, 55 (1936) 821; G. Costa and A. Camus, *Gazz. Chim. Ital.*, 86 (1956) 77; C. E. H. Bawn and R. Johnson, *J. Chem. Soc.*, (1960) 4162.
28 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1961) 285.
29 E. Collinson and F. S. Dainton, *Nature*, 177 (1956) 1224; R. M. Haines and W. A. Waters, *J. Chem. Soc.*, (1955) 4256.
30 E. J. Arlman and J. R. de Jong, *Rec. Trav. Chim.*, 79 (1960) 910, 1319.
31 F. W. Frey, *J. Org. Chem.*, 26 (1961) 5187.
32 A. P. Batalov and I. A. Korshunov, *Zh. Obshch. Khim.*, 31 (1961) 1649; *Dokl. Akad. Nauk SSSR*, 136 (1961) 93; *Tr. po Khim. i Khim. Tekhnol.*, 3 (1960) 365; *Chem. Abstr.*, 56 (1962) 50*a*; I. A. Korshunov and A. P. Batalov, *Zh. Obshch. Khim.*, 31 (1961) 892; *Tr. po Khim. i Khim. Tekhnol.*, 3 (1960) 495; *Chem. Abstr.*, 55 (1961) 27024*i*.
33 M. S. Kharasch and W. H. Urry, *J. Org. Chem.*, 13 (1948) 101; D. Bryce-Smith, *J. Chem. Soc.*, (1955) 1712; (1956) 1603.
34 R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 3405 (1953).
35 G. Wilke and H. Müller, *Ann. Chem.*, 629 (1960) 222.
36 M. S. Kharasch and R. L. Huang, *J. Org. Chem.*, 17 (1952) 669.
37 A. R. Pray, *Inorg. Syn.*, 5 (1957) 153.
38 W. C. Fernelius, *Inorg. Syn.*, 2 (1946) 1.
39 I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, 50 (1928) 1900.
40 R. A. Morton and A. J. de Gouveia, *J. Chem. Soc.*, (1934) 911.
41 P. E. Spoerri and M. J. Rosen, *J. Am. Chem. Soc.*, 72 (1950) 4918.