Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH ALKYL CHLORIDES

STANISŁAW PASYNKIEWICZ AND WITOLD KURAN

Department of Organic Technology I, Institute of Technology (Politechnika), Warsaw (Poland)

(Received June 18th, 1968)

SUMMARY

Reactions of organoaluminium compounds of type $(CH_3)_nAlCl_{3-n}$ ($n = 1,2,3$) with various alkyl chlorides were investigated. The reactivity of the methylaluminium compounds and alkyl chlorides was studied in relation to their structure. Reaction products were identified. The reaction mechanism was discussed in terms of NMR spectra and the products obtained.

Our earlier investigations on the reactions of ethylaluminium dichloride, ethylaluminium sesquichloride, diethylaluminium chloride, and triethylaluminium with ethyl chloride[1] showed the dichloride and the sesquichloride to react readily at 80° to yield saturated and unsaturated hydrocarbons, chiefly ethane and ethylene, and aluminium chloride. On the basis of these data an ionic mechanism for the reaction was suggested.

An intermediate donor–acceptor complex of ethylaluminium dichloride with ethyl chloride is dissociated into ions (reaction 1)

$$C_2H_5AlCl_2 + C_2H_5Cl \rightleftharpoons [C_2H_5Cl_2Al:ClC_2H_5] \rightleftharpoons C_2H_5AlCl_3^- + C_2H_5^+ \quad (1)$$

The labile cation, $C_2H_5^+$, is stabilized by elimination of a proton and formation of ethylene (reaction 2)

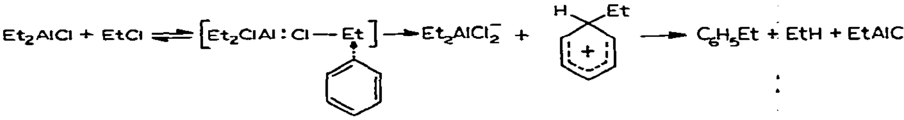
$$C_2H_5^+ \rightarrow C_2H_4 + H^+ \quad (2)$$

The proton reacts with the anion $C_2H_5AlCl_3^-$ to yield ethane and aluminium chloride (reaction 3)

$$C_2H_5AlCl_3^- + H^+ \rightarrow C_2H_6 + AlCl_3 \quad (3)$$

In contrast to the dichloride and the sesquichloride, diethylaluminium chloride and triethylaluminium do not react with ethyl chloride at temperatures up to 170°.

These differences in reactivity towards ethyl chloride may be explained in terms of the varying strengths of the compounds as Lewis' acids. Compared with ethylaluminium dichloride, diethylaluminium chloride is a weak acid and triethylaluminium even more so. It is, presumably, for this reason that polarization of the C–Cl bond in the diethylaluminium chloride–ethyl chloride intermediate complex is insufficient to cause elimination of a free $C_2H_5^+$ cation. The presence of benzene or other aromatic hydrocarbons as the reaction medium is favourable to the elimination of the $C_2H_5^+$ cation and thus also to reaction (4):



(4)

In the presence of benzene, diethylaluminium chloride reacts with ethyl chloride as low as 50°[3]. Again, ethylaluminium dichloride and ethylaluminium sesquichloride react with ethyl chloride much more readily in the presence of benzene than without a solvent[1]. To a rough approximation, the reaction of ethylaluminium sesquichloride may be assumed to start with an attack of ethyl chloride on ethylaluminium dichloride and to follow the sequence (1)–(3). The resulting aluminium chloride reacts immediately with diethylaluminium chloride (reaction 5) to yield ethylaluminium dichloride.

$$(AlCl_3)_2 + (Et_2AlCl)_2 \rightarrow 2\,(EtAlCl_2)_2 \qquad (5)$$

Experiments showed that a small addition of aluminium chloride (about 4%) to diethylaluminium chloride gives rise to decomposition[1]. As already mentioned, pure diethylaluminium chloride does not react with ethyl chloride below 170°.

Alkylaluminium compounds do not react with alkyl chlorides in the presence of diethyl ether[1] and anisole[4]. Also diethylaluminium chloride does not react in xylene solution provided the reaction medium contains triethylamine[3]. These data suggest that an intermediate complex is formed between an organoaluminium compound and ethyl chloride. The ethers and especially the amines are stronger bases than alkyl chlorides, and produce stable complexes with the organoaluminium compounds and thus render decomposition impossible at a specified temperature.

In addition to the decomposition of organoaluminium compounds on treatment with alkyl chlorides, replacement of iodine or bromine by chlorine was found to take place (reaction 6)[5].

$$R_2AlX + RCl \rightleftharpoons R_2AlCl + RX \qquad (6)$$

where $X = I$, Br.

If the resulting alkyl iodide or bromide is removed from the reaction mixture, the equilibrium moves completely to the right.

Pozamantir and Genusov[6] studied the reactions of other alkyl chlorides with ethylaluminium compounds. They found that higher alkyl chlorides are more reactive than ethyl chloride towards ethylaluminium dichloride: tert-amyl chloride reacts with triethylaluminium at a temperature as low as 0°. The reactivity of alkyl chlorides increases with increase in the positive induction effect of the alkyl group in the alkyl chloride molecule. These authors found in the reaction products, hydrocarbons formed by disproportionation and dimerization of the alkyl groups originating from the organoaluminium compound and alkyl chloride. Other hydrocarbons also were found to form as a result of isomerization and destruction of primary products by the resulting aluminium chloride.

Kaar and Schwindlerman[7] investigated the reactions of triisobutylaluminium with alkyl chlorides. On the basis of the products obtained and EPR spectra they suggested an ionic mechanism for the reactions examined.

So far no extensive data have been reported on the reactions of methylaluminium compounds with alkyl chlorides.

The present paper reports on the investigation of the reactions of methylaluminium dichloride with methyl chloride, ethyl chloride, isopropyl chloride, and tert-butyl chloride, and reactions of dimethylaluminium chloride and trimethylaluminium with isopropyl chloride (Table 1).

TABLE 1

REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH ALKYL CHLORIDES

Compound	Alkyl chloride	Solvent	Temp. (°C)	Reaction	Products[a]							
					CH_4		C_2	C_3	iso-C_4H_{10}	n-C_4H_{10}	neo-C_5H_{12}	liquid
$Me_{1.5}AlCl_{1.5}$	MeCl	–	> 180	slow	–	l	l	–	–	–	–	–
$MeAlCl_2$	MeCl	toluene	20	rapid	100[b]	vm	–	–	–	–	–	vm
$MeAlCl_2$	EtCl	–	50	rapid	80	vm	vm	l	vl	vl	–	–
$MeAlCl_2$	iso-PrCl	–	−75	violent	28	m	–	m	m	vl	m	vl
Me_2AlCl	iso-PrCl	cyclohexane	35	rapid	30	m	–	m	m	vl	m	vl
Me_3Al	iso-PrCl	cyclohexane	35	none	–	–	–	–	–	–	–	–
$MeAlCl_2$	tert-BuCl	–	−75	violent	17	l	–	–	m	l	vm	l

[a] vm – very much, m – much, l – little, vl – very little. [b] Yield based on the methyl groups in the organoaluminium compound (%).

Methylaluminium dichloride reacts violently with tert-butyl chloride and isopropyl chloride, at as low a temperature as −75°. The hydrolyzate of the reaction products contained no methane, which proves that the methyl groups of the dichloride react completely. Ethyl chloride is much less reactive: it reacts with methylaluminium dichloride only at 50°. Methyl chloride, still less reactive, reacts with the dichloride only above 180°. In addition to ethane and aluminium chloride, methane is formed indicating thermolysis of the organoaluminium compound. However, in toluene solution methyl chloride reacts easily with methylaluminium dichloride at room temperature to give methane, methylbenzenes and aluminium chloride.

The other methylaluminium compounds are much less reactive than methylaluminium dichloride towards alkyl chlorides. Dimethylaluminium chloride reacts with isopropyl chloride only at 35° to give the same products as formed in the reaction of methylaluminium dichloride with this chloride. Trimethylaluminium is the least reactive compound and fails to react with isopropyl chloride at 35°.

NMR spectra of the methylaluminium compounds with alkyl chlorides in hydrocarbon solutions were studied at temperatures lower than the reaction temperatures. Chemical shifts of the protons in the aluminium-bound methyl groups and in the alkyl chlorides were measured. The spectra of mixtures of methylaluminium dichloride with ethyl chloride and of dimethylaluminium chloride and trimethylaluminium with ethyl chloride and isopropyl chloride were recorded at room temperature in cyclohexane as solvent. A mixture of methylaluminium dichloride and methyl chloride was studied at −60° in toluene solution. NMR spectra of pure methylaluminium compounds and alkyl chlorides were recorded for comparison.

The chemical shifts for methylaluminium dichloride, dimethylaluminium chloride and trimethylaluminium at room temperature are 88, 104 and 102 cps, respectively, towards higher fields relative to cyclohexane; for methylaluminium dichloride at $-60°$, the shift is 157 cps towards higher fields relative to the toluene methyl group.

The above mixtures produced a single signal attributable to the protons of the methyl group combined with the aluminium atom. The chemical shift relative to the pure methylaluminium compound varied by no more than 1.5 cps towards higher fields.

The chemical shifts of protons in the alkyl chlorides in the mixtures do not exceed 2.5 cps towards lower fields relative to the pure alkyl chlorides.

DISCUSSION

The NMR spectra of the mixtures show that methylaluminium compounds produce no stable donor–acceptor complexes with alkyl chlorides. If such complexes were formed, the chemical shifts of the protons of the Al–CH_3 group in the complex would differ considerably from those of the same group in the uncomplexed organoaluminium compound. The pertinent observations were made by Zambelli *et al.*[8] and Mole[9]. However, these investigations do not rule out the possibility of a labile intermediate complex forming, which is subsequently decomposed into the starting materials or, in favourable conditions, dissociated into ions. This is represented by eqn. (7):

$$RCl + CH_3AlCl_2 \rightleftharpoons [RCl:AlCH_3Cl_2] \rightleftharpoons R^+ + CH_3AlCl_3^- \qquad (7)$$

If at low temperatures the collision of an alkyl chloride molecule with an organoaluminium dimer results in formation of a complex, this will be labile enough to decompose immediately into the starting materials.

Under suitable conditions (elevated temperature, concentration, etc.) the resulting transient complex may decompose into free ions. The C–Cl bond in the alkyl chloride molecule, partly polarized owing to the positive induction effect of the alkyl group, becomes in the complex much more polarized and thus weakened. This leads to dissociation of the complex into free ions. The stronger the organoaluminium compound as a Lewis acid and the higher the polarization of the C–Cl bond in the given alkyl chloride, the easier the dissociation. The reactivity of methylaluminium compounds increases in the order: $Me_3Al < Me_2AlCl < MeAlCl_2$, consistent with their rise in Lewis acid strength. As evident from Table 1, isopropyl chloride reacts with methylaluminium dichloride violently at $-75°$; with dimethylaluminium chloride rapidly at 35°, but fails to react with trimethylaluminium at 35°. The reactivity of alkyl chlorides increases in the following sequence: $MeCl < EtCl <$ iso-$PrCl <$ tert-BuCl consistent with the rise in the positive induction effect of the alkyl group and thus also with the polarization of the C–Cl bond.

The type of products obtained (Table 1) is related to the nature of the cation, R^+, forming in reaction (7).

The cation R^+ may become stabilized by elimination of a proton followed by formation of a corresponding olefin (which in the given reaction medium may undergo a partial or complete polymerization) (reaction 8)

$$R^+ \rightarrow R_{(-H)} + H^+ \tag{8}$$

where $R_{(-H)}$ denotes ethylene, propylene and isobutylene for ethyl chloride, isopropyl chloride and tert-butyl chloride, respectively. The released proton reacts with the $CH_3AlCl_3^-$ anion to give methane and aluminium chloride (reaction 9a) as well as hydrogen chloride and methylaluminium dichloride which further react to yield methane and aluminium chloride (reaction 9b)

$$H^+ + CH_3AlCl_3^- \begin{array}{ll} \nearrow CH_4 + AlCl_3 & \qquad (9a) \\ \searrow HCl + CH_3AlCl_2 & \qquad (9b) \end{array}$$

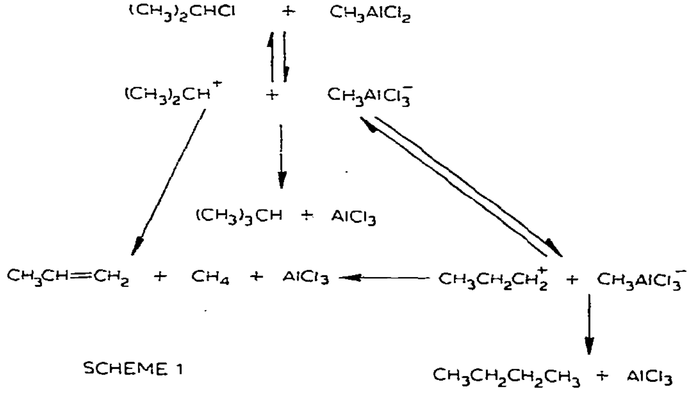
The cation R^+ also can react directly with the $CH_3AlCl_3^-$ anion to yield a corresponding alkane, and aluminium chloride (reaction 10a) or to revert to alkyl chloride and methylaluminium dichloride (reaction 10b)

$$R^+ + CH_3AlCl_3^- \begin{array}{ll} \nearrow RCH_3 + AlCl_3 & \qquad (10a) \\ \searrow RCl + CH_3AlCl_2 & \qquad (10b) \end{array}$$

Again, the cation R^+ can undergo some isomerization affording an isomer R'^+ which will further react similarly as cation R^+. For example, the isopropyl cation yields the n-propyl cation (reaction 11), and the isobutyl cation is obtained from the tert-butyl. However, only few isomers are formed because the equilibrium of the cation isomerization is shifted towards the most stable isomer.

$$(CH_3)_2CH^+ \rightleftharpoons CH_3CH_2CH_2^+ \tag{11}$$

The direction of the reaction of cation R^+ (stabilization through proton elimination (8); reaction with anion $CH_3AlCl_3^-$ (10); isomerization to cation R'^+ (11)) depends on its stability, or on the nature of alkyl chloride. The less stable the cation R^+, the more ready and efficient is its stabilization through proton elimination (8). The more stable the cation, the lower the yield of reaction (8) and the greater the yields of reaction (10) with anion $CH_3AlCl_3^-$ and isomerization (11) to cation R'^+. The volume of methane evolved is a measure of the stabilization of cation R^+. With cation R^+, stabilization increasing in the order: $C_2H_5^+ < \text{iso-}C_3H_7^+ < \text{tert-}C_4H_9^+$; the amount of methane evolved diminishes from 80 to 17% (Table 1). On the other



SCHEME 1

hand, ethyl chloride yields slight amounts of propylene as the result of the reaction of cation $C_2H_5^+$ with anion $CH_3AlCl_3^-$; the iso-$C_3H_7^+$ cation produces considerable amounts of isobutane, and the tert-$C_4H_9^+$ cation yields mainly neopentane. The above reactions are represented in Scheme 1 with isopropyl chloride as example. In addition to the hydrocarbons formed in the above-mentioned conversions of cation R^+ or its isomer R'^+ (*e.g.*, for isopropyl chloride: methane, propylene, isobutane and n-butane (Scheme 1)), the reaction products contain also other hydrocarbons (Table 1). For isopropyl chloride these are: propane and neopentane; for ethyl chloride; ethane, isobutane and n-butane; and for tert-butyl chloride: isobutane, n-butane and isohexane. The occurrence of these hydrocarbons may be explained in terms of reactions of cation R^+ or its isomer R'^+ with the alkane RCH_3 or its isomer $R'CH_3$ afforded by reactions (10a) and (11), respectively. These reactions may be represented as

$$R^+ + RCH_3 \rightleftharpoons RH + R_{(-H)}CH_3^+ \tag{12a}$$

$$R'^+ + RCH_3 \rightleftharpoons R'H + R_{(-H)}CH_3^+ \tag{12b}$$

The resulting cation, $R_{(-H)}CH_3^+$, may react with anion $CH_3AlCl_3^-$, similarly as cation R^+, to give a saturated hydrocarbon and aluminium chloride (reaction 13)

$$R_{(-H)}CH_3^+ + CH_3AlCl_3^- \rightarrow R_{(-H)}(CH_3)_2 + AlCl_3 \tag{13}$$

For isopropyl chloride, the reactions are represented by eqns. (14a, b) and (15):

$$(CH_3)_2CH^+ + (CH_3)_3CH \rightleftharpoons (CH_3)_2CH_2 + (CH_3)_3C^+ \tag{14a}$$

$$CH_3CH_2CH_2^+ + (CH_3)_3CH \rightleftharpoons (CH_3)_2CH_2 + (CH_3)_3C^+ \tag{14b}$$

$$(CH_3)_3C^+ + CH_3AlCl_3^- \rightarrow (CH_3)_4C + AlCl_3 \tag{15}$$

The reaction of cation R^+ with the hydrocarbon RCH_3 involves transfer of the hydride anion from the hydrocarbon to the cation, and production of new, more stable cation. Reactions of such a type proceed under the action of aluminium chloride; they are generally known although their mechanism has not yet been unequivocally elucidated.

The hydride anion can be most readily abstracted by cation R^+ from the tertiary carbon atom in the isobutane molecule. The resulting cation, $(CH_3)_3C^+$, is more stable than its precursor, $(CH_3)_2CH^+$ (14a). Therefore, in the reaction with isopropyl chloride, propane and neopentane are formed in large amounts in addition to the main product, isobutane. Abstraction of the hydride anion from the secondary carbon atom in propane is much more difficult. As a result, ethyl chloride yields, in addition to the main products (methane, ethylene, and propane), only a little ethane and isobutane. Abstraction of the hydride anion from the primary carbon atom in neopentane appears to proceed with difficulty, if at all. The products formed in the reaction of tert-butyl chloride are, presumably, generated as the result of abstraction of the hydride anion from the isopentane molecule.

In addition to the above reactions, analogous reactions of cation R'^+ and hydrocarbon $R'CH_3$ can also proceed.

Compared with other alkyl chlorides, methyl chloride reacts with methylaluminium compounds at much higher temperatures. As already established[1], it does not decompose methylaluminium sesquichloride at temperatures below 120°.

This was explained in terms of the impossibility of the methyl cation being stabilized *via* proton elimination (8). With benzene present in the reaction medium, the Friedel-Crafts reaction proceeds already at 50°, and toluene, methane and aluminium chloride are formed. Toluene as solvent depresses the reaction temperature to 20° (Table 1). The present studies showed that at temperatures above 180°, methylaluminium sesquichloride is violently decomposed (the reaction rate increases with temperature) in the reaction with methyl chloride and partially on account of thermolysis. Ethane and methane are the gaseous products. Ethane is formed as follows (reaction 16):

$$CH_3Cl+CH_3AlCl_2 \rightarrow C_2H_6+AlCl_3 \qquad (16)$$

Methane is presumably a product of thermolysis. The literature describes the thermal decomposition of trimethylaluminium at 200° and above[10,11]. Methane is the only product (reaction 17):

$$4\,(CH_3)_3Al \rightarrow Al_4C_3+9\,CH_4 \qquad (17)$$

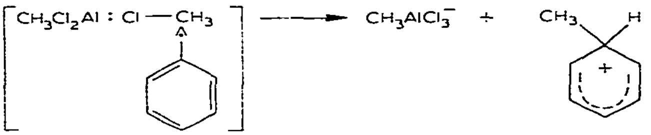
For explanation of the present data the following two possibilities must be taken into account:

(a) The intermediate complex $[CH_3Cl_2Al:ClCH_3]$ decomposes into free ions at temperatures below 180°. Since the cation CH_3^+ cannot be stabilized by elimination of a proton, the reaction is completely reversible. At 180° or above, the methyl cation reacts with the methyl group of the anion to yield ethane and aluminium chloride (reaction 18):

$$CH_3^+ + CH_3AlCl_3^- \rightarrow CH_3CH_3+AlCl_3 \qquad (18)$$

In the presence of benzene or toluene, a Friedel-Crafts type of reaction occurs.

(b) The intermediate complex is not decomposed into free ions at temperatures below 180°. Only at temperatures close to 180° are free ions formed and reaction (18) commences. The presence of benzene or toluene in the reaction medium gives rise to a reduction in the temperature of dissociation of the complex into free ions and renders the Friedel-Crafts reaction possible.



The available data indicate that the latter possibility is the more likely.

EXPERIMENTAL

1. *Reactants*

The methylaluminium compounds used were prepared by the conventional methods described in the literature. Methylaluminium dichloride was purified by crystallization from n-heptane. Dimethylaluminium chloride and trimethylaluminium were distilled before use.

Commercial methyl chloride and ethyl chloride, oxygen-free, were dried by passage through a type-4A molecular sieve column. Commercial, pure isopropyl chloride and tert-butyl chloride were dried over anhydrous calcium chloride, distilled in a nitrogen atmosphere and stored over type-4A molecular sieves.

Commercial, pure hydrocarbons were distilled from sodium in a nitrogen atmosphere and stored over type-4A molecular sieves.

2. *Method*

Reactions were carried out in a 30-ml reactor equipped with a stirrer and a cold trap connected to a gas burette; a nitrogen atmosphere was maintained. To the reactor containing an organoaluminium compound (in solution or with no solvent) cooled to −75°, alkyl chloride was added (methyl chloride and ethyl chloride in the gaseous state), by means of a hypodermic syringe, through a serum cap in the reactor wall. With ethyl chloride, the reactor was placed in a thermostat the temperature of which was progressively increased until the reaction commenced. The gaseous products (CH_4, C_2) not condensed in the cold trap were collected in the gas burette. After completion of the reaction, the condensed products were transferred to another gas burette. The reactor was then flushed with nitrogen and the reaction mixture was hydrolyzed with a 10% hydrochloric acid solution.

The reactions of methylaluminium sesquichloride with methyl chloride were carried out in the gas phase in a flow reactor. The products were analyzed by the use of a Chrom II gas chromatograph.

3. *NMR studies*

All spectra were recorded on a JEOL JNM-C-60H spectrometer, cyclohexane or the toluene methyl group being used as internal standards.

REFERENCES

1 S. Pasynkiewicz, W. Dahlig and M. Cieślak, *Roczniki Chem.*, 35 (1961) 1283.
2 S. Pasynkiewicz, *Vysomolekul. Soedin.*, 5 (1963) 1585.
3 E. B. Milovska, B. A. Dolgoplosk and P. J. Dolgopolska, *Vysokomolekul. Soedin.*, 4 (1962) 1503.
4 S. Pasynkiewicz, W. Dahlig and K. Starowieyski, *Roczniki Chem.*, 36 (1962) 1583.
5 S. Pasynkiewicz, W. Dahlig and L. Meszorer, *Roczniki Chem.*, 35 (1961) 1301.
6 A. G. Pozamantir and M. L. Genusov, *Zh. Obshch. Khim.*, 32 (1962) 1175.
7 H. Kaar and G. Schwindlerman, *Eesti NSV Teaduste Akad. Toimetised Tehniliste, Füüsikalis Mat. Teaduste Seeria*, 13 (1964) 148.
8 A. Zambelli, A. L. Segre, A. Marinangeli and G. Gatti, *Chim. Ind. (Milan)*, 48 (1966) 1.
9 T. Mole, *Australian J. Chem.*, 16 (1963) 801.
10 L. M. Yeddanpalli and C. C. Schubert, *J. Chem. Phys.*, 14 (1946) 1.
11 K. Ziegler, K. Nagel and W. Pfohl, *Ann. Chem.*, 629 (1960) 210.