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REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH PROPYLENE OXIDE

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Summary

Reactions of $(CH_3)_nAlCl_{3-n}$ ($n = 1, 2, 3$) with propylene oxide have been studied. At room temperature, donor-acceptor complexes are formed; at elevated temperatures, they enter into further reactions. With trimethylaluminium, addition occurs exclusively, resulting in opening of the epoxide ring chiefly at the more-substituted carbon atom and, after hydrolysis, 2-methylpropanol is the major product. With methylaluminium dichloride, which is a more powerful Lewis acid than trimethylaluminium and gives rise to enhanced mobility of hydrogen atoms attached to the epoxide ring carbon atoms in the complex molecule, elimination of methane occurs. The ring becomes opened primarily at the more-substituted carbon atom. With dimethylaluminium chloride, both reactions take place. Mechanisms for methane elimination and consecutive reactions which yield C_4 hydrocarbons and other products are discussed.

Introduction

The only reactions of organoaluminium compounds with epoxides investigated so far have been those involving aluminium trialkyls, which react with epoxides to yield products of addition and reduction [1, 2]. With propylene oxide the reaction leads, after hydrolysis, to the formation of two isomeric alcohols depending on the direction of ring opening. When the trialkylaluminium/propylene oxide mole ratio is higher than unity, the ring becomes opened primarily at the more-substituted carbon atom. As the reactant mole ratio is decreased to unity and below, addition to the less-substituted carbon atom increases [1]. For non-symmetrically substituted epoxides, rearrangement of initially formed trialkylaluminium—epoxide complex can occur and the addition involves displacement of the alkyl group to the carbonyl carbon atom [1]. If the reaction is carried out in diethyl ether, addition via intermediate formation of an aldehyde is the only feasible route [3].

TABLE 1

REACTIONS OF METHYLALUMINIUM COMPOUNDS WITH PROPYLENE OXIDE

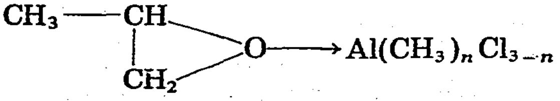
Me_nAlCl_{3-n}/epoxide mole ratio		Reaction			Products (%) [a]							
		medium	temp. (°C)	time (h)	CH_4	2-butene		isobutene	n-C_4H_{10}	i-C_4H_{10}	2-methyl-1-propanol	2-butanol
						cis	*trans*					
Me_3Al	1/1	C_6H_{14}	70	48							45	5
Me_3Al	1/1		130	48							90	6
Me_3Al	1/1	Bu_2O	130	24								
Me_2AlCl	1/1	$C_{10}H_{22}$	130	35	13	3		1			24	
Me_2AlCl	1/1		140	9	21	1	2	1				2
Me_2AlCl	2/1		140	9	38	7	10	4				
$MeAlCl_2$	1/1	$C_{10}H_{22}$	140	1	57	8	12	5	2	1		
$MeAlCl_2$	1/1	C_6H_{12}	80	8	40	1	2	1	2	<1		
$MeAlCl_2$	2/1	C_6H_{12}	70	6	40	<1	<.1	<1	4	<1		
$MeAlCl_2$	2/1	C_6H_{12}	80	10	86 [b]							
$MeAlCl_2$	1/1		120	0.5	38	2		<1				
$MeAlCl_2$	2/1		60	1	45	<1		<1				
$MeAlCl_2$	1/1 [c]	C_6H_6	20									
$MeAlCl_2$	1/1	Bu_2O	130	24								

[a] Yields based on epoxide. [b] Methane and C_4-fraction. [c] Vigorous evolution of CH_4 on mixing of reactants.

The purpose of the present work is to study the reactions of propylene oxide with $MeAlCl_2$ and Me_2AlCl which are more powerful Lewis acids than aluminium trialkyls. For comparison, the reaction of propylene oxide with Me_3Al was also studied.

Results and discussion

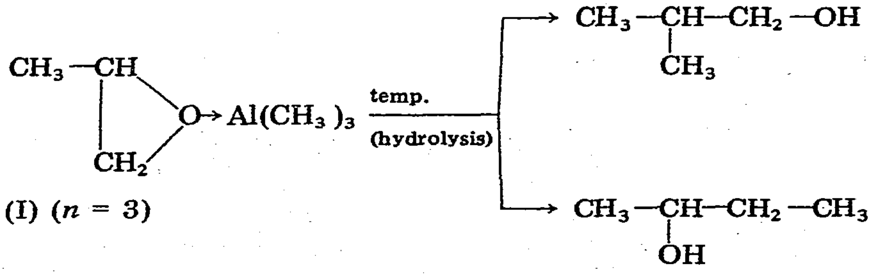
The first stage of the reactions of the methylaluminium compounds with propylene oxide was found to involve formation of equimolecular complexes I with the dative bond from the oxygen to the aluminium atom.



(I) (n = 1, 2, 3)

NMR spectra of these complexes showed that most affected by complexation are the signals of protons attached in propylene oxide to the methylidyne and methylene carbon atoms. Chemical shift differences, $\Delta\tau$, for the methylidyne and methylene protons between the propylene oxide complexed with Me_3Al, Me_2AlCl and $MeAlCl_2$ and the uncomplexed oxide, are about —1.0, —1.1 and —1.25 ppm, respectively. Therefore, the more pronounced the electron-acceptor character of the propylene oxide-complexing compound, the greater the downfield shift it causes. There is an upfield shift of the aluminium methyl proton signals on complexation, which diminishes ($\Delta\tau$ 0.38, 0.33 and 0.16 ppm) with the rising electron-accepting character of the compound.

At elevated temperatures, the complexes I enter into various reactions, depending on the methylaluminium used (Table 1). Trimethylaluminium reacts with propylene oxide in hexane by addition of a methyl group to one of the two carbon atoms in the epoxide ring. Epoxide bond rupture occurs primarily at the more-substituted carbon atom and the methyl group adds to this atom (eqn. 1a). As the temperature is raised, the yield of this reaction increases. Bond rupture at the less-substituted carbon atom occurs less readily and addition to this carbon atom (eqn. 1b) proceeds to a minor extent. Increase of temperature enhances its yield only slightly.



(I) (n = 3)

(1a)

(1b)

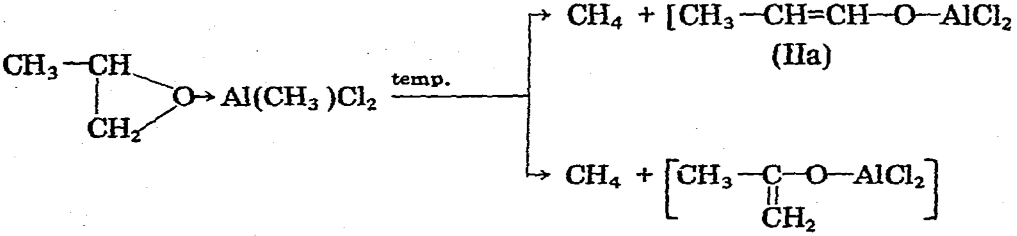
It appears that the mechanism of the above reactions should be analogous to that suggested earlier by Lundeen and Oehlschlager [1] for the reaction between Et_3Al and propylene oxide. This may involve electrophilic opening of the epoxide ring caused by attack of the alkyl group of trimethylaluminium complexed with another epoxide molecule, (1a), or with an addition product molecule, (1b).

Me_2AlCl reacts with propylene oxide much less readily than does Me_3Al. Addition occurs in two directions, primarily to the more-substituted carbon atom, similar to Me_3Al, but also elimination of methane occurs. Furthermore, other gaseous products like *cis*- and *trans*-2-butene and isobutene are formed (Table 1).

In the reaction of $MeAlCl_2$ with propylene oxide no addition products are obtained whatsoever. On the other hand, methane elimination proceeds more easily than with Me_2AlCl with subsequent reactions yielding *cis*- and *trans*-2-butene and isobutene as gaseous products. When the reaction is carried out in the presence of alkanes or cycloalkanes, n-butane and isobutane are also obtained in low yields.

The relative reactivities of the organoaluminium compounds towards addition (1) suggest that the reaction depends on the ease with which the methyl group with an electron pair can be cleaved from the aluminium atom. A nucleophilic attack by this group at the epoxide-ring carbon atom will occur most readily with Me_3Al. In complexes with propylene oxide, as in complexes with other Lewis bases [4], the partial negative charge on the aluminium atom decreases in the order $Me_3Al > Me_2AlCl > MeAlCl_2$.

In contrast to addition, elimination of methane is controlled by the mobility of hydrogen atoms in the organoaluminium—propylene oxide complex. Complexation gives rise to enhanced mobility of the hydrogen atoms at the epoxide ring carbon atoms. Mobility increases with rise in the electron-accepting properties of methylaluminium compounds in the following order: $Me_3Al < Me_2AlCl < MeAlCl_2$. This fact is evident both from the present NMR studies and from published [4] data on the reactions of methylaluminium compounds with organic electron donors endowed with mobile hydrogen atoms in the molecule. As in addition, elimination can proceed in either of two directions according to the mode of epoxide ring opening (eqns. 2a, b).



(2a)

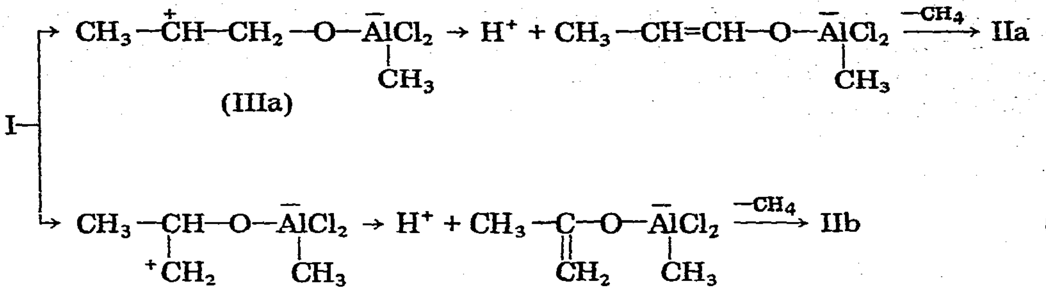
(IIa)

(2b)

(I) ($n = 1$)

(IIb)

It appears that methane elimination proceeds via an intermediate stage involving species IIIa and IIIb. These species can loose a proton which reacts subsequently with corresponding newly formed anions to eliminate methane from them (eqns. 3a, b).



$$\mathrm{I} \rightarrow \overset{+}{C}H(CH_3)\text{—}CH_2\text{—}O\text{—}\bar{A}lCl_2(CH_3) \rightarrow H^+ + CH_3\text{—}CH{=}CH\text{—}O\text{—}\bar{A}lCl_2(CH_3) \xrightarrow{-CH_4} \mathrm{IIa} \quad (3a)$$

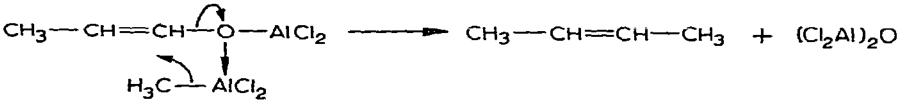
(IIIa)

$$\mathrm{I} \rightarrow CH_3\text{—}CH(\overset{+}{C}H_2)\text{—}O\text{—}\bar{A}lCl_2(CH_3) \rightarrow H^+ + CH_3\text{—}C({=}CH_2)\text{—}O\text{—}\bar{A}lCl_2(CH_3) \xrightarrow{-CH_4} \mathrm{IIb} \quad (3b)$$

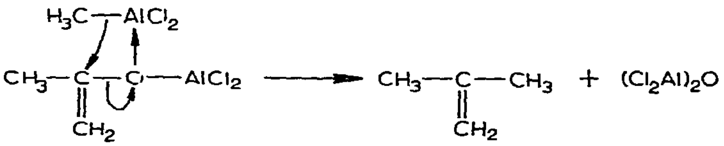
(IIIb)

The species IIIa formed by cleavage of the bond at the more-substituted carbon atom in the complex I, is the more stable intermediate, and the reaction takes place preferentially by this route (eqn. 3a).

Hydrolytic work-up of the reaction mixture gave neither propionaldehyde nor acetone. This fact is presumably due to the high reactivity of elimination products IIa and IIb which enter into further reactions. The reaction mixture (after hydrolysis) was found to contain higher hydrocarbons (heart-cut 80°—200°) and oxygen-containing derivatives. IIa and IIb also react with $MeAlCl_2$ present in the reaction medium to afford C_4 alkenes. In all likelihood, these reactions proceed via formation of suitable donor-acceptor complexes which subsequently undergo intramolecular rearrangement and elimination reactions (eqns. 4a, b).

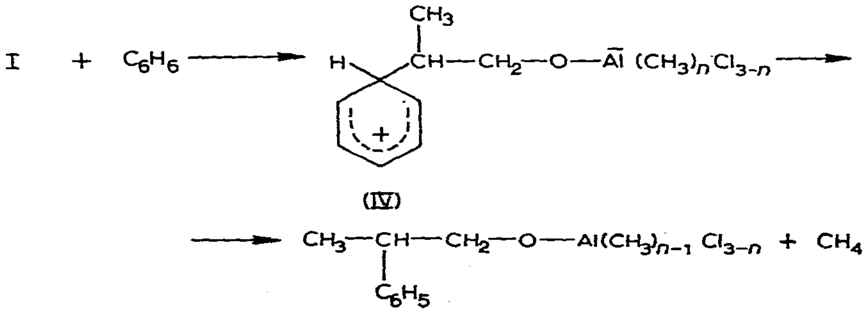


$$CH_3\text{—}CH{=}CH\text{—}O(\leftarrow H_3C\text{—}AlCl_2)\text{—}AlCl_2 \longrightarrow CH_3\text{—}CH{=}CH\text{—}CH_3 + (Cl_2Al)_2O \quad (4a)$$



$$CH_3\text{—}C({=}CH_2)\text{—}O(\leftarrow H_3C\text{—}AlCl_2)\text{—}AlCl_2 \longrightarrow CH_3\text{—}C({=}CH_2)\text{—}CH_3 + (Cl_2Al)_2O \quad (4b)$$

Introduction of benzene to the reaction medium renders elimination of methane much more facile, and the aromatic ring is alkylated (eqn. 5) in a similar manner to the reaction between triethylaluminium and propylene oxide described earlier [5]:



$$\mathrm{I} + C_6H_6 \longrightarrow \mathrm{IV}\; [H(C_6H_5^{+})\text{—}CH(CH_3)\text{—}CH_2\text{—}O\text{—}\bar{A}l(CH_3)_nCl_{3-n}] \longrightarrow CH_3\text{—}CH(C_6H_5)\text{—}CH_2\text{—}O\text{—}Al(CH_3)_{n-1}Cl_{3-n} + CH_4 \quad (5)$$

(IV)

The intermediate IV is in this case more stable than the corresponding species IIIa formed in the absence of benzene. In the presence of benzene, elimination of methane can proceed in the reaction of propylene oxide with Me_3Al, although the latter is much less of an electrophile than is $MeAlCl_2$.

Experimental

Chemicals

The methylaluminium compounds were prepared by conventional methods from methylaluminium sesquichloride (from aluminium metal and methyl chloride). Commercial pure-grade propylene oxide was distilled from calcium hydride prior to use. Solvents were purified conventionally.

Procedure

Each reaction was carried out under nitrogen. About 5 g of a methylaluminium compound and 10 ml of a solvent were used for the reaction. After the reactants had been mixed (exothermic reaction), the reaction vessel was placed in a thermostatted bath. Gaseous reaction products were collected in a gas burette and analyzed by GLC. The reaction mixture was hydrolyzed with aqueous 12% hydrochloric acid (if the reaction was carried out in non-solvent conditions, about 10 ml of the solvent was added before hydrolysis). The organic phase was separated from the aqueous phase, dried and analyzed by GLC. NMR spectra were recorded on a JEOL JNM C-60H spectrometer.

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