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NOTE

REACTIONS OF ORGANOALUMINIUM COMPOUNDS WITH ETHERS

K. STAROWIEYSKI AND S. PASYNKIEWICZ
Department of Organic Technology I, Institute of Technology (Politechnika), Warsaw (Poland)

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In our earlier investigations[1], a complex of propylaluminium sesquichloride with anisole was found to react at 130–140° to yield methyl chloride and phenoxyaluminium compounds. Mardykin *et al.*[2] also noticed that ethylaluminium compounds react with phenetole to give diethylphenoxyaluminium, ethyl chloride, and butane.

These investigations were intended for exploring the reactions of methylaluminium compounds (Me_3Al, Me_2AlCl, $MeAlCl_2$) and aluminium chloride with anisole. The trimethylaluminium–anisole complex was found to react slowly at 135° to yield methane. The dimethylaluminium chloride–anisole complex reacted much more rapidly to yield methyl chloride, hydrogen chloride, methane, and ethane in small amounts. The methylaluminium dichloride–anisole complex reacted likewise, but faster, to yield gaseous products containing still higher proportions of methyl chloride and hydrogen chloride and lower proportions of methane and ethane. Aluminium chloride reacted with anisole to give methyl chloride and hydrogen chloride. Upon hydrolysis, the liquid products were found to contain phenol and anisole. With the organoaluminium compounds under investigation, the overall amount of the gaseous products did not exceed 0.5 mole per mole of anisole added.

The data obtained indicate that the mechanism of the reactions studied is rather complicated.

Similar investigations on the reactions of phenetole with ethylaluminium compounds demonstrated that alkyl chloride is formed from the alkyl group of the ether and the chlorine of the organoaluminium compound (1):

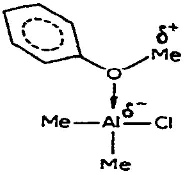
$$C_6H_5OR\cdot AlRCl_2 \longrightarrow C_6H_5OAlRCl + RCl \qquad (1)$$

The hydrocarbon, methane or ethane, is formed from the aluminium-bound alkyl group and the hydrogen of the phenyl group or the alkyl group of the ether.

The reactivity of the methylaluminium compounds towards anisole increases in the following sequence: $Me_3Al < Me_2AlCl < MeAlCl_2$.

It is well known that the reactivities of the aluminium compounds towards nitriles[3], ketones[4], and esters[5] follow the reverse sequence. In each of the above reactions, the alkyl group, activated owing to the complex formed, is rearranged from the aluminium atom to the positively charged site in the reacting molecule.

Owing to the donor–acceptor bond, $Al \leftarrow O$ formed, the O–C bond becomes, in the anisole complexes, increasingly polarized, which renders the splitting off of the cation, CH_3^+, or proton, H^+, easier.



The reactivity series established for the organoaluminium compounds is consistent with the above suggestions. With increase in the acidity of the organoaluminium compound, the O–C bond of anisole increases in polarity and the splitting off of the cation, CH_3^+, or proton, H^+, becomes easier.

On this basis it may be assumed that the reaction begins by allowing the cation to attack the organoaluminium compound in the complex. Should the reaction begin by the attack of a CH_3^- anion split off from the aluminium atom, then trimethylaluminium would be the most reactive compound and ethane or methane would be the major product.

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