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Preliminary communication

REACTIONS OF METHYL BENZOATE WITH METHYLALUMINIUM COMPOUNDS

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Summary

Methyl benzoate reacts with methylaluminium compounds to give alkylation products. Only the dimethylaluminium chloride alkoxyaluminium compound, formed after double alkylation, readily undergoes further reactions, e.g. the formation of olefins or exhaustive methylation.

Introduction

Complexes of esters with organoaluminium compounds undergo rearrangement reactions under suitable conditions [1]. Compared with ketones, they are much less reactive because of a small positive charge on the carbonyl carbon [2]. Reactions of esters are more complex: the consecutive reactions involving alkylation, reduction and elimination can lead to various products. Up to now, few papers have dealt with the reactions of esters with trialkylaluminiums [3], and there is no information on reactions with chloroaluminium compounds. The present communication reports the products of the reaction of methyl benzoate with methylaluminium compounds.

Results and discussion

The products of the reaction between methyl benzoate and methylaluminium compounds are given in Table 1 and the most probable reaction course is shown in Scheme 1.

In both investigated systems the alkoxyaluminium compound IV is formed as a result of alkylation. In the reaction of methyl benzoate with trimethylaluminium the main product is dimethylphenylcarbinol (I), formed from IV after hydrolysis. The formation of different products, observed in the reaction with dimethylaluminium chloride, is presumably due to the lower stability of IV. It undergoes further reactions; formation of olefin II or exhaustive methylation to give III. It

TABLE 1

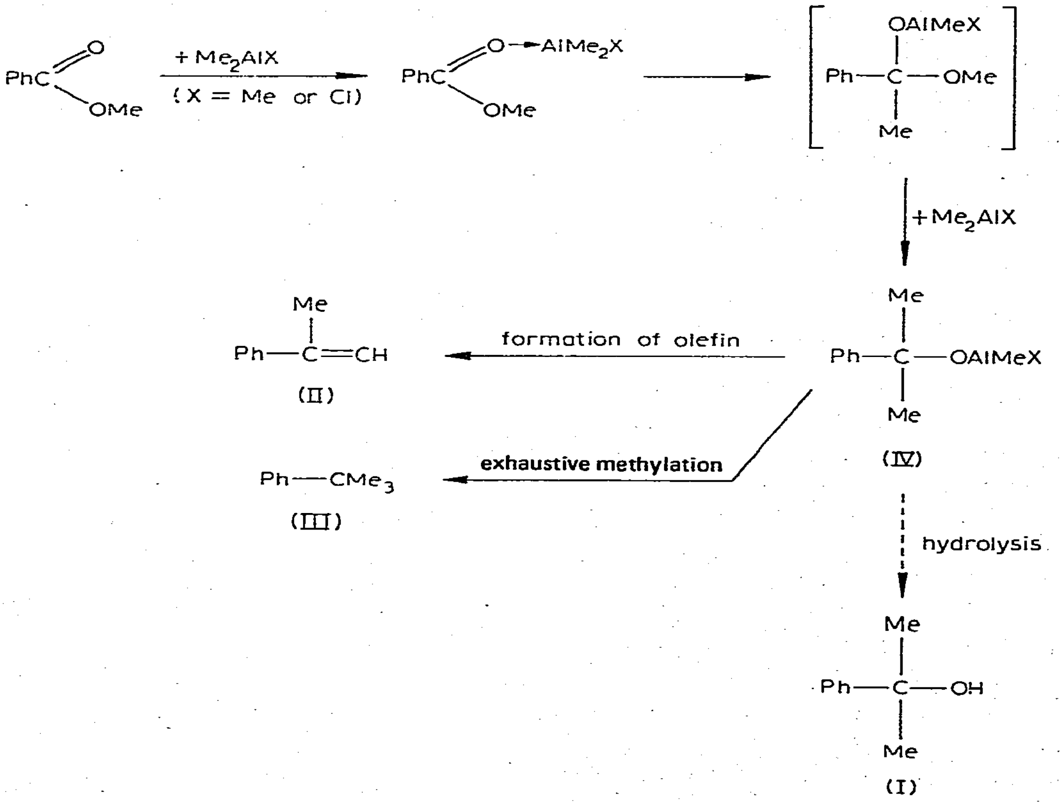
APPROXIMATE YIELDS OF THE PRODUCTS OF THE REACTION BETWEEN METHYL BENZOATE AND METHYLALUMINIUM COMPOUNDS IN HEPTANE (conc. ca 30%, temp. 98°C, reaction time 10 h)

Organo-aluminium compound	C=O/Al molar ratio	Product and yield (moles per 1 mol of initial PhCOOMe) $PhC(Me_2)OH^a$ (I)	$Ph(Me)C{=}CH_2$ (II)	$PhCMe_3$ (III)	CH_4	MeCl
Me_3Al	1/1	0.4	traces	—	traces	—
	1/2	0.7	traces	—	traces	—
Me_2AlCl	1/1	traces	0.05	0.05	0.20	traces
	1/2	traces	0.1	0.03	0.35	traces

[a] Obtained after hydrolysis.

SCHEME 1

Proposed pathways of reactions leading to the formation of products indicated in Table 1.

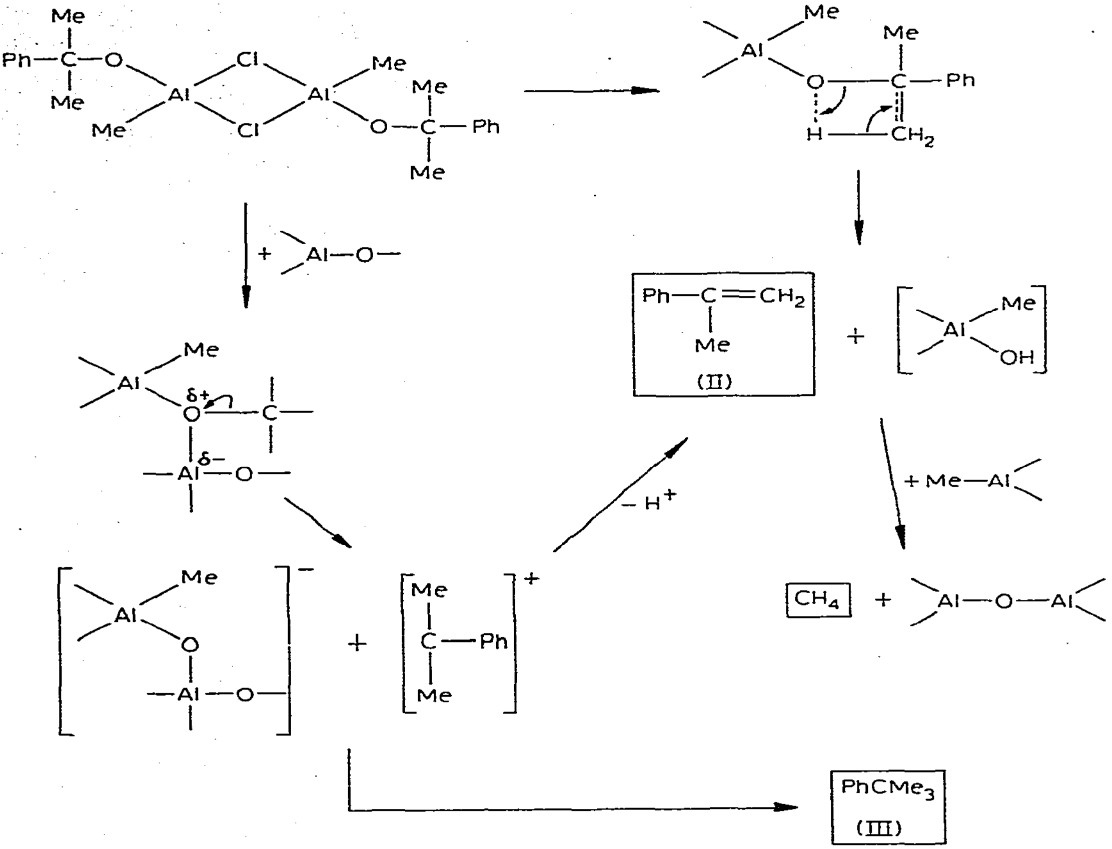


is likely that compound IV is associated. $Me_2AlOC(Me_2)Ph$ only forms oxygen bridged dimers whereas $Me(Cl)AlOC(Me_2)Ph$ also forms chlorine bridged dimers [4]. The terminal alkoxy group is less hindered than the bridging one and the oxygen atom is strongly basic, so further reactions are able to proceed. Scheme 2 shows the possible reaction pathways.

The evolution of a greater amount of methane than expected from methyl-

SCHEME 2

The explanation of the easier formation of products of exhaustive methylation and elimination reactions from alkoxyaluminium compound IV, when X = Cl. (Exhaustive methylation is autocatalysed by the products, e.g. by aluminoxanes [5].)



styrene, in the reaction with Me_2AlCl, is probably caused by consecutive reactions of aluminoxanes with organoaluminium chlorides at elevated temperatures [6].

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