

CATALYTIC ACTIVITY OF TRIVALENT LANTHANIDE SALTS IN THE  
 ALKYLATION REACTIONS OF AROMATIC HYDROCARBONS BY THE  
 ACTION OF A MIXTURE OF AN ACYL HALIDE AND BENZALDEHYDE

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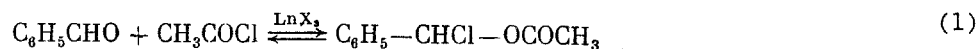
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*A study was carried out on the electrophilic substitution reactions of benzene and toluene by the action of a mixture of an acyl halide and benzaldehyde in the presence of trivalent lanthanide salts  $\text{LnCl}_3$ , where  $\text{Ln} = \text{Ce}, \text{Dy}, \text{Er}, \text{Sm}, \text{Yb}$ , and  $\text{Yb}(\text{O}_3\text{SCF}_3)_3$ , as catalysts at  $40^\circ\text{C}$  over 24 h. The reaction stops at the formation of the corresponding triarylmethane compounds. A mechanism was proposed for this reaction. Lanthanide salts were found not to catalyze the usual Friedel-Crafts acylation of arenes.*

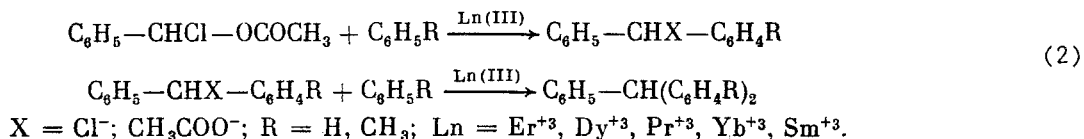
According to theoretical calculations, rare earth chlorides are hard but weak Lewis acids [1, 2]. Their catalytic activity in Friedel-Crafts alkylation reactions proved negligible even in the benzylation of donor arenes [3, 4].

According to our data, rare earth chlorides and triflates are also not capable of catalyzing the acylation of benzene and toluene by the action of a broad range of acylating agents such as acyl halides and carboxylic acid anhydrides under the standard heterogeneous conditions upon heating a mixture of the reagent and catalyst in an excess of the aromatic substrate over 24 h. The yields of the corresponding ketones do not exceed 1-2% even upon ultrasonic activation.

We used the properties found for the lanthanide salts for studying the alkylation of benzene and toluene by the action of a mixture of an acyl halide and benzaldehyde. Acetyl chloride reversibly adds to the carbonyl group of benzaldehyde in the presence of  $\text{ZnCl}_2$  [5]. Thus, the reaction in the presence of  $\text{LnX}_3$  should proceed analogously.



According to the gas-liquid chromatographic analysis and chromato-mass spectrometric data, the aromatic substrates used undergo alkylation by the action of  $\text{CH}_3\text{COCl}-\text{C}_6\text{H}_5\text{CHO}$  upon heating of the reaction mixture in the presence of  $\text{LnX}_3$  and the reaction is terminated by the formation of the corresponding triarylmethanes. The greatest yield of the final products, which is a mixture of isomeric phenylditolylmethanes, was obtained using  $\text{Yb}(\text{O}_3\text{SCF}_3)_3$  as the catalyst (50%). The following reaction scheme was proposed.



We note that the formation of both the corresponding benzhydryl chlorides and the corresponding benzhydryl acetates is possible in the first step in reaction (2). As shown in the case of  $(\text{C}_6\text{H}_5)_2\text{CHCl}$  and  $(\text{C}_6\text{H}_5)_2\text{CHOCOCH}_3$ , both types of products are excellent alkylating

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agents under the reaction conditions [the greatest yields of  $(C_6H_5)_2CHC_6H_4R$  upon the benzhydrylation of toluene were 75 and 67%, respectively, upon catalysis by  $Yb(O_3SCF_3)_3$ ]. The formation of  $\alpha$ -acetoxyphenyltolylmethane during the reaction was confirmed by chromatomass spectrometry, while  $\alpha$ -chlorophenyltolylmethane could not be detected.\*

As indicated from the reaction scheme, the nature of the acyl halide should not affect the structure of the major products. Indeed, we showed that a mixture of phenylditolylmethanes is formed with maximum yield of 40-50 using  $C_6H_5COCl$  and  $Yb(O_3SCF_3)_3$  as the catalyst.

In the presence of  $ZnCl_2$ , significant amounts of methylacetophenone (up to 10%) and tarry products are formed along with phenylditolylmethanes in the reaction with toluene.

Thus, lanthanide salts may be used as selective catalysts for the preparation of triarylmethanes under the proposed conditions.

#### EXPERIMENTAL

**General Procedure for the Alkylation of Aromatic Substrates.** A sample of 10 ml aromatic substrate, 0.002 mole catalyst, 0.001 mole  $RCOCl$ , and 0.001 mole  $C_6H_5CHO$  were added to a 25-ml flask equipped with a magnetic stirrer and the mixture was heated for 24 h at  $40^\circ C$ . A weighed amount of a standard was added to the reaction mixture, filtered through a layer of silica gel (L40  $\times$  100), eluted by ether, and evaporated on a rotary evaporator. The products were analyzed by gas-liquid chromatography on a LKhM-8MD chromatograph with a flame ionization detector using a 3 m  $\times$  3 mm column packed with 5% SE-30 on Chromaton N-AW. The nitrogen gas carrier flow rate was 40 ml/min. The chromatomass spectral analysis was carried out on a Finnigan MAT-113 instrument on a 3 m  $\times$  3 mm column packed with 5% SE-54 on Chromaton N-AW. Samples of  $LnCl_3$  [6],  $Ln(O_3SCF_3)_3$  [7], benzhydryl chloride (bp  $158-159^\circ C$  (10 mm)) [8], and benzhydryl acetate (mp  $40-42^\circ C$ ) [9] were obtained according to standard procedures.

#### LITERATURE CITED

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\*We also observed  $C_6H_5CH(OCOCH_3)_2$ , whose formation is probably a consequence of  $S_N$  substitution of  $Cl^-$  by  $CH_3CO_2^-$  in the product of the acetylation of toluene.