CATALYTIC ACTIVITY OF TRIVALENT LANTHANIDE SALTS IN THE

CHLOROMETHYLATION OF AROMATIC HYDROCARBONS

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A study was carried out on the electrophilic substitution reactions in benzene and toluene by the action of $ClCH_2OCH_3$ in the presence of trivalent lanthanide salts, $LnCl_3$, where Ln = Ce, Dy, Er, and $Sm(O_3SCF_3)_3$ as the catalysts, at room temperature over 24 h. These lanthanide salts display the properties of weak but hard Lewis acids. The reaction proceeds exclusively by chloromethylation with the subsequent formation of diarylmethanes.

According to Olah [1] and Mine [2], rare earth chlorides display weak catalytic activity in electrophilic aromatic substitution reactions. On the basis of theoretical data, $LnCl_3$ should also be considered as a weak but hard Lewis acid [3, 4]. Hence, rare earth chlorides are promising catalysts for carrying out selective organic reactions with a suitable reagent-substrate pair. In contrast to ordinary Lewis acids, lanthanide salts are readily regenerated after the reaction, which serves as an additional argument for their use in organic synthesis [2].

Chloromethyl ether, which has two independent donor sites, namely, the hard oxygen site and soft chlorine site, is a convenient model for studying the catalytic activity of Lewis acids in electrophilic aromatic substitution reactions. In light of the possible coordination of the catalyst at the different sites of the electrophilic reagent, the reaction may proceed along two pathways [5].

$$ArH + ClCH_2OCH_3 \xrightarrow{Cat} ArCH_2Cl + ArCH_2OCH_3$$
(1)

Hard, strong Lewis acids such as $AlCl_3$ display low selectivity in coordination with $ClCH_2OCH_3$ such that products of both chloromethylation and methoxymethylation are formed. Hard but weak Lewis acids such as $SnCl_4$ selectively coordinate at the oxygen site of the alkylating reagent such that benzyl chlorides are formed exclusively [6]. We studied the alkylation of benzene and toluene by the action of $ClCH_2OCH_3$ in the presence of a series of lanthanide chlorides and triflates at room temperature.

Gas-liquid chromatographic and chromato-mass spectrometric data indicate that the reaction proceeds exclusively through chloromethylation for both substrates and all the catalysts. As in the case of other Lewis acids [6], the reaction does not stop at the chloromethylation step but rather is terminated by the formation of diarylmethanes [2].

| $C_6H_5R +$ | CICH ₂ OCH ₃ $\frac{\text{Cat}}{24}$ | RC ₆ H ₄ CH ₂ Cl | $\stackrel{Cat}{\longrightarrow} \mathrm{RC}_{\mathfrak{g}}\mathrm{H}_{4}\mathrm{CH}_{2}\mathrm{C}_{\mathfrak{g}}\mathrm{H}_{4}\mathrm{R}$ | ł | (2) |
|-----------------|--|--|--|---|-----|
| | 24 | ⁿ Yield of | Yield of | | |
| R | Cat | RC ₆ H ₄ CH ₂ Cl, % | RC ₆ H ₄ CH ₂ C ₆ H ₄ R, % | | |
| н | CeCl ₃ | 6,0 | Traces | | |
| н | DyCl ₃ | 10,5 | 6,0 | | |
| H | ErCl ₃ | 9.6 | 5,2 | | |
| н | $Sm(O_3SCF_3)_3$ | 5,0 | 50,1 | | |
| CH_3 | CeCl ₃ | 21.0 | 4,3 | | |
| CH_3 | DyCl ₃ | 24,0 | 15,0 | | |
| CH ₃ | ErCl ₃ | 27,0 | 29,0 | | |
| CH₃ | Sm (O ₃ SCF ₃) ₃ | 8,0 | 62,0 | | |

We should note that the reaction rate is low for all the catalysts used, especially in the case of $CeCl_3$. $Sm(O_3SCF_3)_3$ proved the most efficient catalyst for the reactions studied.

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An alternative pathway for the reaction lies in the formation of the corresponding methyl benzyl ether with subsequent benzylation of the aromatic substrate with the participation of this ether. We demonstrated the possibility of such a reaction in the case of the reaction of both substrates upon catalysis with $CeCl_3$, $ErCl_3$, $DyCl_3$, and $Sm(O_3SCF_3)_3$. The corresponding diarylmethanes were obtained under the same conditions with 3Q-40% yields.

$$RC_{6}H_{5} + RC_{6}H_{4}CH_{2}OCH_{3} \xrightarrow{Cat}_{24}RC_{6}H_{4}CH_{2}C_{6}H_{4}R$$

$$R = CH_{3}, H; Cat = LnX_{3}; Ln = Er^{+3}, Dy^{+3}, Sm^{+3}; X = Cl^{-}, O_{3}SCF_{3}^{-}.$$
(3)

However, only the corresponding $RC_6H_4CH_2Cl$ derivatives could be detected as an intermediate during the course of the reaction with $ClCH_2OCH_3$ upon catalysis with LnX_3 . Chromatomass spectrometric experiments showed that methyl benzyl ether could be detected even upon the background of an enormous excess of benzyl chloride. We also note that both types of products are readily detected in the reaction catalyzed by $AlCl_3$ [6]. Thus, we may assume that $RC_6H_4CH_2OCH_3$ is not formed and does not participate in further reactions with the aromatic substrate in electrophilic aromatic substitution by the action of $ClCH_2OCH_3$ using lanthanide salts as the catalyst.

EXPERIMENTAL

General Procedure for the Alkylation of Aromatic Substrates. A sample of 10 ml aromatic substrate, 0.002 mole catalyst, and 0.001 mole $ClCH_2OCH_3$ was added to a 25-ml flask equipped with a magnetic stirrer and stirred for 24 h at room temperature. A weighed amount of a standard was added and the mixture was filtered through a layer of silica gel (L40 \times 100), eluted with ether, and evaporated in a rotary evaporator. The products were analyzed by gas-liquid chromatography on an LKhM-8MD chromatograph with a flame ionization detector on 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 chromato-mass spectral analysis was carried out on a Finnigan MAT-113 instrument using a 3 m \times 3 mm column packed with 5% SE-54 on Chromaton N-AW.

4-Methylbenzyl chloride [7], the methyl esters of benzyl and 4-methylbenzyl alcohols [8], $LnCl_3$ [9], and $Ln(0_3SCF_3)_3$ [10] were obtained by standard procedures.

LITERATURE CITED

- 1. G. A. Olah, S. Kobayashy, and M. Tashiro, J. Am. Chem. Soc., 92, 7448 (1972).
- 2. N. Mine, J. Fujiwara, and H. Taniguchi, Chem. Lett., 357 (1986).
- 3. G. Klopman, J. Am. Chem. Soc., 90, 223 (1968).
- 4. R. G. Parr and R. G. Pearson, J. Am. Chem. Soc., 105, 7512 (1983).
- 5. L. Summers, Chem. Rev., 55, 301 (1955).
- 6. M. Sommelet, Compt. Rend., 157, 1443 (1913).
- 7. Y. Kamitory, M. Hojo, R. Masuda, et al., Synthesis, 387 (1983).
- 8. N. J. Fafadia, D. M. Wakankar, and M. E. N. Nambudiry, Chem. Ind. (London), 203 (1988).
- 9. J. Kutscher and A. Schneider, Inorg. Nucl. Chem. Lett., 7, 81 (1971).
- 10. J. H. Forsberg, V. T. Spaziano, T. M. Balasubramanian, et al., J. Org. Chem., 52, 1017 (1987).