CHEMISTRY LETTERS, pp. 357-360, 1986.

TRICHLOROLANTHANOID($LnCl_3$)-CATALYZED FRIEDEL-CRAFTS ALKYLATION REACTIONS

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The usual Friedel-Crafts catalysts cannot be re-used after aqueous work-up. An alternative catalyst, based on rare earths has been found, which serves as an efficient Friedel-Crafts catalyst for alkylation of arenes by alkyl halides, and can be re-used after the reaction. Typical examples are shown in the reaction of benzene with benzyl halides using all of the rare earth trichlorides as catalyst, except $PmCl_3$.

Numerous Lewis acids, such as $AlCl_3$ etc., have been used to mediate the alkylation and acylation of arenes in Friedel-Crafts reaction.1) A common problem, particularly in industrial processes, is that catalysts cannot be re-used after the usual aqueous work-up.1)

We wish to report alternative catalysts based on the rare earths, which serve as Friedel-Crafts alkylation catalysts of arenes by alkyl halides, and can be re-used after the reaction. We have recently reported some reactions of organolanthanoids, RLnI with various substrates and have shown their unique reactivities.2)

Olah et al. reported that trichlorolanthanoids, $LnCl_3$ are very weak catalysts of the Friedel-Crafts reaction.3) In connection of our studies on the utilization of lanthanoids in organic reactions, we investigated catalytic activity of $LnCl_3$, and found that they efficiently catalyze the Friedel-Crafts alkylation of arenes by various alkyl halides. In this paper we wish to describe $LnCl_3$-catalyzed Friedel-Crafts alkylation reactions, with a wide variety of rare earth halides:

$$\mathrm{ArH} \quad + \quad \mathrm{RX} \xrightarrow{\mathrm{LnCl_3}} \mathrm{Ar\text{-}R}$$

(Ln=Sc,Y,La,Ce,Pr,Nd,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb,Lu)

$LnCl_3$-catalyzed alkylation of arenes was carried out using arene itself as solvent, alkyl halide (RX) and $LnCl_3 \cdot xH_2O$ as a catalyst in ca. 0.3 mol equiv. in relation to RX at 75 °C. The reaction is heterogeneous[4] and proceeds with evolution of HCl gas, but addition of solvents such as THF and nitromethane to give homogeneous solutions resulted in lower yields of alkylation. As alkyl halides, the usual organic halides such as butyl, propyl, and benzyl chlorides and bromides are available. Table 1 summarizes the $LnCl_3$-catalyzed alkylation of benzene with benzyl halides. The data in the table deserve some comments. First, all rare earth trichlorides, except $ScCl_3$ and $LaCl_3$, are good catalysts and the late lanthanoids, especially $DyCl_3$, $TmCl_3$, and $LuCl_3$ have particularly high activity. For example, the reaction with $TmCl_3$ as catalyst, is completed within 30 min yielding diphenylmethane in 70% yield with small amounts of dibenzylbenzenes (o-, m-, and p-isomers mixture) (run 19). If trichlorolanthanoid hydrates are used without prior dehydration by heating, the reaction is greatly retarded, indicating that the presence of water decreases the yield (run 14). In the $LnCl_3$-catalyzed alkylation the reactivity of chlorides is higher than that of bromides, just as in the case of $AlCl_3$.[1]

These $LnCl_3$ catalysts have an advantage over the usual Lewis acid catalysts such as $AlCl_3$ in that they can be recovered and re-used. $LnCl_3$ catalysts are recovered after the reaction by the following procedure.[5] After quenching of the reaction by aqueous acid, the organic products are separated by ether extraction and the aqueous layer which contains $LnCl_3$, is evaporated to dryness to which several drops of conc. HCl are added.[6] Some examples of the recycling of the catalyst are shown in Table 2. The recovered $LnCl_3$ are efficiently active for further reaction and $DyCl_3$ can maintain its activity even after 3-cycles (run 5).

Reaction of toluene at 75 °C for 1 h with benzyl chloride, with $DyCl_3$[7] as catalyst gave tolylphenylmethanes in 64% (635% on $DyCl_3$) yield and the o-, m-, and p-isomer ratio was found to be 31.2: 6.4: 62.4. Reaction of benzene at 65 °C with n-propyl bromide, with $LuCl_3$ gave cumene (24%) and n-propylbenzene (8%).

A typical experimental procedure is as follows. Hydrous trichlorolanthanoid ($LnCl_3 \cdot xH_2O$, x=6 or 7) (0.5 mmol) and a magnetic stirring bar were placed in a 50 ml centrifuge tube and dried by heating at 150 °C in vacuo for 2 h.[8] Then the tube was sealed with a cerum cap and the system was filled with nitrogen and dry benzene (2 ml) and benzyl chloride (1.34 mmol) were added by a syringe. The mixture was stirred at 75 °C untill HCl evolution ceased. The resulting mixture was then quenched by 2N-HCl and the products extracted by ether.[6] From the ethereal layer

Table 1. $LnCl_3$-Catalyzed Alkylation of Benzene with Benzyl Halides (RX) to Give Diphenylmethane[a)]

Run	$LnCl_3$	X in RX	Reaction time h	Yield of diphenylmethane %[b)]
1	$ScCl_3$	Cl	18	8(20)
2	YCl_3	Cl	18	52(137)
3	$LaCl_3$	Cl	18	3(7)
4	$CeCl_3$	Cl	18	56(149)
5	$PrCl_3$	Cl	18	64(172)
6	$NdCl_3$	Cl	18	63(170)
7	$SmCl_3$	Cl	18	60(161)
8	$EuCl_3$	Cl	18	45(118)
9	$GdCl_3$	Cl	18	65(173)
10	$GdCl_3$	Br	18	61(163)
11	$TbCl_3$	Cl	18	25(67)
12	$DyCl_3$	Cl	1	74(196)
13	$DyCl_3$	Br	2	57(154)
14	$DyCl_3 \cdot 6H_2O$	Cl	18	tr.
15	$HoCl_3$	Cl	18	72(192)
16	$HoCl_3$	Br	18	49(135)
17	$ErCl_3$	Cl	18	63(171)
18	$ErCl_3$	Br	18	61(163)
19	$TmCl_3$	Cl	0.5	70(188)
20	$TmCl_3$	Br	18	57(159)
21	$YbCl_3$	Cl	3	62(166)
22	$YbCl_3$	Br	18	55(148)
23	$LuCl_3$	Cl	3	69(186)

a)Reactions were carried out by using $LnCl_3$(0.5 mmol), RX(1.34 mmol), and benzene (2 ml) with stirring at 75 °C. In addition to diphenylmethane, dibenzylbenzenes were also formed in several percent yields. b)GC yields based on RX, the numbers in parenthesis are those based on $LnCl_3$.

Table 2. Reaction of Benzene with Benzyl Chloride with Recovered $LnCl_3$ to Give Diphenylmethane[a)]

Run	$LnCl_3$	Number of use	Reaction time/h	Yield/%[b)]
1	$YbCl_3$	1	18	64
2	$YbCl_3$[c]	2	18	33
3	$DyCl_3$	1	1	74
4	$DyCl_3$	2	2	40
5	$DyCl_3$	3	3	68

a)$PhCH_2Cl$(1.34 mmol), PhH(2 ml), $LnCl_3$(0.5 mmol), 75 °C. b)GC yields based on $PhCH_2Cl$. Small amounts of dibenzylbenzenes were also formed. c)Recovered $YbCl_3$ was not treated with conc. HCl.

diphenylmethane was obtained together with a small amount of disubstituted compounds, and from the aqueous layer the catalyst was recovered.

The data presented here indicate that trichlorolanthanoids, $LnCl_3$ serve as new and efficient catalysts for Friedel-Crafts alkylations. Furhtermore, the catalysts may be recovered and re-used. Further investigations of these novel reactions are in progress, and will be the subjects of future reports.

This work has been supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

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4) The fact that the filtrate of the suspension of $YbCl_3$ in toluene after stirring at 75 °C for 1 h cannot cause the reaction, supports that the reaction is heterogeneous.

5) Recovered catalysts were identified to be $LnCl_3 \cdot xH_2O$ by ion chromatography, fluorescent X-ray and X-ray diffraction analyses

6) The catalysts used can also be recovered by simple filtration of the reaction mixture without acid quenching, but the catalyst recovered by this method, has lower activity than that recovered by acid quenching because of some contamination of moisture and organic materials.

7) This anhydrous catalyst was prepared from Dy_2O_3 in Professors J. Shiokawa and G. Adachi's laboratory and generously gifted to us, for which we greatly thank them.

8) Drying of catalysts is essential in this reaction and an alternative method for dehydration of $LnCl_3 \cdot xH_2O$ is heating at 400 °C for 30 min under a stream of nitrogen.

(Received December 19, 1985)