3520 © *1993 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***66****, 3520—3521(1993)* [Vol. 66, No. 11

Enhancement of Catalytic Activity of $ZnCl_2$ in the Friedel–Crafts Benzylation of Benzenes Using Polar Solvents

Eiji HAYASHI, Yukio TAKAHASHI,† Hironori ITOH, and Norihiko YONEDA*
Faculty of Engineering, Department of Applied Chemistry, Hokkaido University, Sapporo 060
† Department of Industrial Chemisty, Kitami Institute of Technology, Kitami 090

(Received April 26, 1993)

Synopsis. Zinc chloride was successfully employed in the Friedel–Crafts benzylation of benzenes as a useful catalyst in the presence of polar solvents. Particularly, zinc chloride dissolved in primary alcohols, ketones, and water with a molar ratio of 1 was a highly effective catalytic system in the reaction.

Although zinc chloride has been used to catalyze a variety of organic reactions,[1)] it has a slight catalytic activity compared with other Lewis acids, such as $AlCl_3$ and $FeCl_3$, and has been reported to be inactive for the benzylation of benzenes with benzyl chlorides[2)] due to its poor solubility in inert solvents. Zinc chloride is soluble in donor solvents, but its activity in these solvents is limited because of the formation of complexes with the solvents. Recently, however, $Et_2O/ZnCl_2$ with a molar ratio of 1.1 or a higher system in CH_2Cl_2 was reported to promote the addition reaction of alkenes and alkyl halides[3)] and alkenes or dienes with allyl or propargyl halides,[4)] the acylation of silyl enol ethers with acid chlorides,[5)] and alkylation of silyl dienol ethers with orthoformicester.[6)] However, this catalyst is not effective in aromatic Friedel–Crafts benzylation. On the other hand, it has been reported that impregnating $ZnCl_2$ with K10 montmorillonite improves the catalytic activity under Friedel–Crafts benzylation.[7)] In the present paper we report that $ZnCl_2$ can be employed as a useful catalyst with a suitable amount of some polar solvents for the Friedel–Crafts benzylation of benzenes.

Experimental

To an equimolar solution of benzene (B), toluene (T), and *p*-xylene (X) (10 mmol each) benzyl chloride (3.7 mmol) was added in the presence of $ZnCl_2$ (1—2.4 mmol) with vigorous polar solvents under vigorous stirring at the desired temperatures (50—85 °C) for 1—6 h. After the resulting solution was treated in the usual manner the products were identified by ordinary spectroscopic methods.

Results and Discussion

Typical results are shown in Table 1. Free $ZnCl_2$ did not exhibit any catalytic behavior for the benzylation of BTX under the presenit reaction conditions. However, $ZnCl_2$ with primary alcohols or ketones showed a higher activity compared with free $ZnCl_2$. Moreover, $ZnCl_2$ in these alcohols or ketones having a carbon number of 4—6 afforded remarkable activities in the reaction. Although the isomer distribution of phenyltolylmeth-

Table 1. Competitive Benzylation of Benzene, Toluene, and *p*-Xylene Using $ZnCl_2$–Polar Solvents

Solvent	Solv./$ZnCl_2$	Temp	Time	Conversion[a)]
	mol/mol	°C	h	%
None		50	2	NR[b)]
CH_3OH	1	50	1	16
CH_3CH_2OH	1	50	1	58
1-Propanol	1	50	1	73
1-Butanol	1	50	1	84
1-Pentanol	1	50	1	98
1-Hexanol	1	50	1	97
1-Heptanol	1	50	1	86
1-Octanol	1	50	1	81
1-Decanol	1	50	1	70
Acetone	1	50	1	23
2-Butanone	1	50	1	24
2-Pentanone	1	50	1	47
2-Heptanone	1	50	1	67
2-Octanone	1	50	1	78
2-Decanone	1	50	1	27
H_2O	2	85	6	85
H_2O	4	85	6	85
H_2O	6	85	4	85
$H_2O+Fe_2O_3^{c)}$	1	50	2	85
Et_2O	1–2	50	6	NR
Dibutyl ether	1–2	50	6	NR
$Et_2O–CH_2Cl_2$[d)]	1.5	50	2	47
THF	2	50	2	43
Sulfolane	1	50	6	20
DMSO	1	50	6	6
DMF	0.5	50	6	24
Pyridine	1	50	4	NR
CH_3CN	4	50	4	NR
CH_3NO_2	1	50	2	NR
CH_3NO_2	20	50	2	55
Nitrobenzene	40	50	2	32
Tributyl phosphate	0.5	50	2	54
CH_3CO_2H	1	50	2	23
CH_3CO_2H	4	50	2	34
CF3CO_2H	4	50	4	34
85%H_3PO_4	2	85	15	44

a) Conversion of benzyl chloride. b) No reaction. c) $H_2O/Fe_2O_3/ZnCl_2=1/0.1/1$ (mol ratio). d) Commercial available reagent. $Et_2O/ZnCl_2/CH_2Cl_2=1.5/5/1.5$ (mol ratio).

ane produced from toluene was almost similar regardless of the nature of the solvents (*o*-/*m*-/*p*-isomer ratio $\approx$36/4—5/60), the observed relative reactivites (k_T/k_B and k_X/k_B) were somewhat increased with an increase in the carbon number of the alcohols and ketones. Secondary and tertiary alcohol did not show any increase in activity because of the conversion of these alcohol into olefins in the presence of $ZnCl_2$.

Zinc chloride with water also has a higher activity, and the addition of Fe^{3+} ion into this system accelerated the reaction even more. In the other solvents used, some enhancement of activity was recognized in systems of $ZnCl_2$ with sulfolane, DMSO, DMF, CCl_3CH_2OH, and THF but the other solvents, such as triethylamine, pyridine, CH_3CN and CH_3NO_2, did not enhance the activity. However, $ZnCl_2$ with a larger amount of CH_3NO_2 (molar ratio of $CH_3NO_2/ZnCl_2>20$) showed an increase in activity. The activity of $ZnCl_2$ increased in the presence of acetic acid, CF_3CO_2H or tributyl phosphate.

These results are very intriguing since Lewis acids, such as $AlCl_3$ and BF_3, usually lose their catalytic activity in the presence of donor solvents, such as primary alcohols or ketones. Although no quantitative analysis can presently be offered for the increasing catalytic activity of $ZnCl_2$ in the presence of some polar solvents, the addition of these solvents increased the solubility of $ZnCl_2$ and, thus, may enhance the catalytic activity of the Lewis acid in the reaction.

References

1) For example: M. Fieser and J. G. Smith, "Reagents for Organic Synthesis," Wiley-Interscience Pub., John Wiley & Sons, N. Y. (1988), Vol. 13, p. 108.

2) G. A. Olah, K. Kobayashi, and M. Tashiro, *J. Am. Chem. Soc.*, **94**, 7448 (1972).

3) H. Mayr and S. Wilhelm, *J. Org. Chem.*, **50**, 2995 (1985).

4) H. Mayr and H. Klein, *J. Org. Chem.*, **56**, 4097 (1991).

5) R. E. Tripak and M. W. Rathke, *J. Org. Chem.*, **47**, 5099 (1982).

6) E. Akgun and U. Pindur, *Synthesis*, **1984**, 227.

7) A. Cornelis, C. Dony, and P. Laszlo, *Tetrahedron Lett.*, **32**, 1423 (1991).