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Comparison of Lewis Acids as Catalyst for the Alkylation of Benzene with *s*-Butyl Chloride

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Synopsis. The Friedel-Crafts alkylation of benzene with *s*-butyl chloride has been carried out in the presence of various Lewis acid catalysts. The relative order of catalyst activity is: $AlBr_3$, $AlCl_3$, $MoCl_5$, $SbCl_5 > TaCl_5 > NbCl_5 > FeCl_3 > ZrCl_4 > TiCl_4 \gg WCl_6$. The effect of addition of nitromethane on alkylation has been investigated.

Recently a report was given on the stereospecific Friedel-Crafts alkylation with optically active secondary alkyl chloride derivatives.[1] The reactions were so sensitive to moisture and the activity of aluminium chloride that it was difficult to control stereospecificity with sufficient reproducibility. The stereospecificity changed a great deal when iron (III) chloride was used as a catalyst instead of aluminium chlroide.[2] The results prompted us to compare Lewis acids as catalyst for the alkylation of benzene with *s*-butyl chloride.

The order of Lewis acid catalyst activity changes with reaction and/or reactant.[3] Comparison of Lewis acids in the Friedel-Crafts reaction has been reported with ethylene and hydrogen chloride,[4] benzyl chloride,[5] and acetyl chloride.[6] However, no report seems to have appeared on the reactions using secondary alkyl chloride as a reactant. The order of catalyst activity did not differ as compared with the case of primary alkyl chloride. Alkylation with $AlCl_3$–CH_3NO_2 catalyst proceeds through a homogeneous system, the catalytic activity of $AlCl_3$ decreasing moderately with the addition of nitromethane.[7] Nucleophiles which possess lone pair electrons, *e.g.* ethers and halides, are available as additives to $AlCl_3$ catalyst, but react with benzene as reactants. We have studied the effects of the addition of nitromethane to some active Lewis acids.

Results and Discussion

s-Butyl chloride and benzene were condensed at various temperatures by means of various Lewis acid catalysts for 10 min. The ratio *s*-butyl chloride : Lewis acid : benzene was kept 1 : 0.15 : 25 in each case. Below 5 °C, dichloromethane (4 ml) was added in order to prevent coagulation of benzene. 2-Phenylbutane produced was determined by GLC.

The Lewis acid catalysts were classified into four groups according to their activities in the alkylation with *s*-butyl chloride: (1) very active catalysts; (2) moderately active catalysts; (3) weak catalysts; (4) inactive catalysts (Table 1). In the case of (1), alkylation gave 2-phenylbutane with 100% conversion at −30 °C for 10 min. Figure 1 shows a comparison of the reaction rates of alkylation in the case of (2) and (3). The relative order of catalyst activity is: $NbCl_5 > FeCl_3 > FeCl_3$–CH_3NO_2 (10 times mol) $\simeq AlCl_3$–CH_3NO_2 (1.3 times mol) $> ZrCl_4 > AlCl_3$–CH_3NO_2 (10 times mol) $> AlCl_3$–$C_6H_5NO_2$ (10 times mol) $> TiCl_4 \gg WCl_6$. It seems that there is no relationship between the order and the configuration of electrons in the metal atom of catalysts. The difference in catalyst activity in the Friedel-Crafts alkylation has been elucidated mainly by means of the electrophilicity of catalyst-reactant complex formed.[8]

Table 1. Classification of Friedel-Crafts catalysts based on their activities in the alkylation with *s*-butyl chloride

(1) Very active catalysts
$AlBr_3$ (IIIa), $AlCl_3$ (IIIa), $MoCl_5$ (VIb), $SbCl_5$ (Va), $TaCl_5$ (Vb)
(2) Moderately active catalysts
$NbCl_5$ (Vb), $FeCl_3$ (VIII), $FeCl_3$-CH_3NO_2 (10 times mol), $AlCl_3$-CH_3NO_2 (1.3 times mol)
(3) Weak catalysts
$ZrCl_4$ (IVb), $AlCl_3$-CH_3NO_2 (10 times mol), $AlCl_3$-$C_6H_5NO_2$ (10 times mol), $TiCl_4$ (IVb), WCl_6 (VIb)
(4) Inactive catalysts
Cu_2Cl_2 (Ib), $ZnCl_2$ (IIb), $CdCl_2$ (IIb), $HgCl_2$ (IIb), $SnCl_4$ (IVa), $BiCl_3$ (Va), VCl_3 (Vb), $NiCl_2$ (VIII), $CoCl_2$ (VIII), $PdCl_2$ (VIII)

( ) is the group of periodic table.

In the presence of the aluminium chloride catalyst the reaction mixture is not homogeneous, due to the limited solubility of the catalyst. It becomes completely homogeneous by the addition of nitromethane, the catalytic activity becoming milder as compared with the case of aluminium chloride only. When $SbCl_5$, $FeCl_3$, $AlCl_3$, $AlBr_3$, $MoCl_5$, $TaCl_5$, or $NbCl_5$ in nitromethane solvent (10 times mol) was used as catalyst at 20 °C for 10 min, the conversion was 100, 100, 17.1, 7.9, 2.5, 2.3, 0%, respectively. It seems that the addition of nitromethane would form a Lewis acid–nitromethane (1:1) complex similar to the case of aluminium chloride,[9] tending to decrease the catalytic activity for alkylation.

Experimental

IR spectra were determined on a JASCO DS-301 spectrometer. GLC analysis was carried out on a 2 m column of 10% Carbowax 20 M on Diasolid L for 2-phenylbutane.

Aluminium chloride of commercial grade was purified by sublimation under nitrogen. Lewis acids of commercial grade were used without further purification. Benzene was washed with concentrated sulfuric acid and water, and distilled after being dried on sodium ribbon. Other solvents were dried[10] and distilled before use.

Reaction Procedures. To a stirred mixture of dry benzene (10 ml) and Lewis acid (0.81 mmol) was added a solution of *s*-butyl chloride (5.4 mmol) in benzene (2 ml) at the

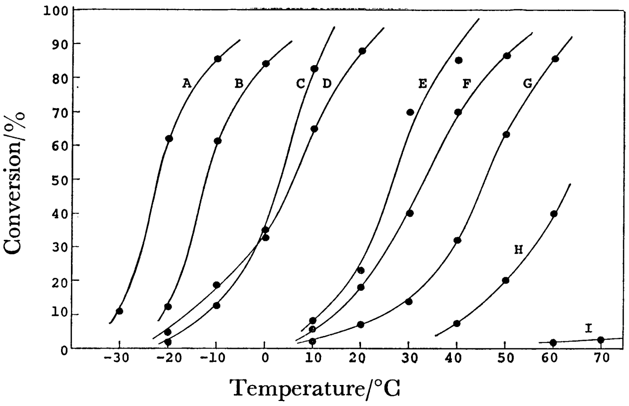

Fig. 1. Conversion percent in the alkylation of benzene with *s*-butyl chloride in the presence of catalysts in Groups 2 and 3 at −30 °C—70 °C for 10 min; A: $NbCl_5$, B: $FeCl_3$, C: $FeCl_3$-CH_3NO_2 (10 times mol), D: $AlCl_3$-CH_3NO_2 (1.3 times mol), E: $ZrCl_4$, F: $AlCl_3$-CH_3NO_2 (10 times mol), G: $AlCl_3$-$C_6H_5NO_2$ (10 times mol), H: $TiCl_4$, I: WCl_6.

rate required to maintain the desired temperature (Fig. 1). The reaction mixture was stirred at this temperature for 10 min, and then poured onto a mixture of crushed ice, concentrated hydrochloric acid (5 ml), and *p*-methylanisole (9.0 mmol) (internal standard). The benzene layer was separated and the aqueous layer extracted twice with 10 ml benzene. The combined organic layers were washed with water (15 ml) and dried over anhydrous sodium sulfate. The product was then determined by GLC by internal standardization technique.

References

1) T. Nakajima, S. Masuda, S. Nakashima, T. Kondo, Y. Nakamoto, and S. Suga, *Bull. Chem. Soc. Jpn.*, **52**, 2377 (1979).

2) S. Masuda, T. Nakajima, and S. Suga, *J. Chem. Soc., Chem. Commun.*, **1974**, 954.

3) G. A. Olah, "Friedel-Crafts and Related Reactions," Wiley-Interscience, New York (1963), Vol I, Chap. XI, p. 853.

4) A. V. Gross and V. N. Ipatiff, *J. Org. Chem.*, **1**, 599 (1936).

5) O. Tsuge and M. Tashiro, *Bull. Chem. Soc. Jpn.*, **40**, 119 (1967); G. A. Olah, S. Kobayashi, and M. Tashiro, *J. Am. Chem. Soc.*, **94**, 7448 (1972).

6) O. C. Dermer, D. M. Wilson, F. M. Johnson, and V. H. Dermer, *J. Am. Chem. Soc.*, **63**, 2881 (1941).

7) G. A. Olah, "Friedel-Crafts and Related Reactions," Wiley-Interscience, New York (1963), Vol I, Chap. IV, p. 246.

8) R. Nakane, *Yuki Gosei Kagaku Kyokai Shi*, **36**, 440 (1978).

9) L. Schmering, *Ind. Eng. Chem.*, **40**, 2072 (1948).

10) J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd ed, Interscience Publishers, Inc., New York (1955).