

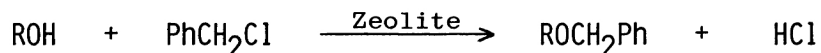
BENZYLATION OF ALCOHOLS TO BENZYL ETHERS WITH
ALKALI CATION EXCHANGED Y TYPE ZEOLITE

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Benylation of alcohols with benzyl chloride is found to proceed efficiently in the presence of alkali cation exchanged Y type zeolite in a non-polar solvent under neutral conditions. The effects of solvent and alkali cation of zeolite are studied.

Recently there have been reported a lot of studies on alumina-induced selective organic syntheses.¹⁾ These heterogeneous organic reactions are thought to be promoted by the acid or base sites on the porous alumina surface, and the surface nature of alumina is often greatly influenced by the preparative conditions of alumina, e.g., calcination temperature, and included impurities.^{2,3)} In general, it is difficult to modify the acid-base nature of alumina arbitrarily. Compared with alumina, zeolites have several specific features: their properties can be easily altered by cation exchange to exhibit both acidic and basic characters, and therefore under definite circumstances zeolites can act as bifunctional catalysts.

We have been applying a variety of zeolites to useful synthetic organic reactions in the liquid phase, and reported that potassium cation exchanged X and Y type zeolites facilitate selective N-monoalkylation of aniline with an alkylating agent in benzene.⁴⁾ We wish to report here that, in the presence of potassium cation exchanged Y type zeolite (abbreviated as KY), benzylation of alcohols with benzyl chloride readily takes place to afford the corresponding benzyl ethers in non-polar organic solvents under neutral conditions.



KY was prepared from commercially available sodium cation exchanged Y type zeolite (NaY) by means of ion exchange.⁴⁾ Caesium cation exchanged Y type zeolite (CsY) was also prepared on treatment of KY with a CsCl aqueous solution. A typical procedure of the reaction is as follows. A mixture of alcohol (1 mmol), benzyl chloride (1 mmol) and powdered zeolite⁵⁾ (0.8 g) in 5 ml of an organic solvent was vigorously stirred under reflux for 5 h in an argon atmosphere. Then 3 ml of water was added and the reaction mixture was again refluxed for 0.5 h. The zeolite was filtered and washed with ethyl acetate. The organic layer was separated and

Table 1. Benzylation of 1-decanol with benzyl chloride ^{a)}

Additive	Solvent	Mol% ^{b)} of benzyl ether	Mol% ^{b)} of unreacted alcohol
None	Hexane	0	100
KY ^{c)} (0.8 g)	Pentane	24	70
	Hexane	73	23
	Heptane	32	54
	C ₆ H ₆	42	57
	C ₆ H ₅ Cl ^{d)}	77	21
	CHCl ₃	4	95
	CCl ₄	77	23
	THF	0	100
NaY (0.8 g)	Hexane	15	47
CsY ^{e)} (0.8 g)	Hexane	62	37
KX ^{f)} (0.8 g)	Hexane	8	92
KL ^{g)} (0.8 g)	Hexane	10	88
Alumina, basic ^{h)} (1.2 g)	Hexane	48	52
Alumina, neutral ⁱ⁾ (1.2 g)	Hexane	41	58
K ₂ CO ₃ (0.5 g)	THF	0	100
Et ₃ N (1 mmol)	THF	0	100

^{a)} Reaction conditions: 1-decanol (1 mmol), benzyl chloride (1 mmol), under reflux for 5 h.

^{b)} Determined by GLC using an internal standard.

^{c)} Potassium content (99.3%), sodium content (0.7%).

^{d)} Carried out at 80°C.

^{e)} Caesium content (68%), potassium content (32%).

^{f)} Potassium content (93%), sodium content (7%).

^{g)} Commercially available L type zeolite.

^{h)} Woelm aluminium oxide W-200-basic, activity grade super I.

ⁱ⁾ Woelm aluminium oxide W-200-neutral, activity grade super I.

analyzed by gas chromatography.

In order to survey the benzylation of alcohols with benzyl chloride,⁶⁾ we investigated the effects of solvent, alkali cation of zeolite, and type of zeolite using 1-decanol as an alcohol component. The results are summarized in Table 1. Among the aliphatic hydrocarbon solvents, hexane was the best solvent under reflux conditions. In the case of benzene, diphenylmethane was produced as a by-product in a 28% yield owing to the Friedel-Crafts benzylation of benzene. The use of chlorobenzene depressed the unfavorable Friedel-Crafts reaction and increased the yield of benzyl decyl ether. Carbon tetrachloride was also a suitable solvent. In contrast, more polar solvents such as chloroform and tetrahydrofuran retarded the benzylation. The degree of interaction between zeolite and solvent appeared to give crucial effects on the efficiency of benzylation of alcohols.

Table 2. Benzylation of various alcohols with benzyl chloride ^{a)}

Alcohol	Mol% ^{b)} of benzyl ether	Mol% ^{b)} of unreacted alcohol
Benzyl alcohol	57	33
1-Decanol	73 (84) ^{c)}	23 (15) ^{c)}
1-Octanol	69	24
2-Octanol	51 (61) ^{d)}	25 (15) ^{d)}
4-Octanol	40	22
Phenol	12	43

a) Reaction conditions: alcohol (1 mmol), benzyl chloride (1 mmol), KY (0.8 g), in hexane under reflux for 5 h.

b) Determined by GLC using an internal standard.

c) The results obtained by use of 1.5 mmol of benzyl chloride.

d) The results obtained by use of 2 mmol of benzyl chloride.

The order of the effectiveness of alkali cation of Y zeolite was $K > Cs > Na$, which differed from that of the basic strength of the cation exchanged zeolite: $CsY > KY > NaY$.⁷⁾ This fact suggests that the acidic sites as well as the basic sites of the zeolite might participate in the present benzylation, because KY possesses not only basic sites but also acidic sites that can cause the Friedel-Crafts reaction described above. The titration by use of the Hammett indicators³⁾ showed that KY had the base sites of $H_0S+2.0$ and the acid sites of $H_0Z+3.3$ in hexane.

Among a variety of zeolites, KY revealed the highest activity. The use of KY exhibited a much better yield than that of neutral or basic alumina.⁵⁾ Over alumina, dibenzyl ether was produced in a 5% yield as a by-product.⁸⁾ The benzylation could not be accelerated by usual bases such as potassium carbonate and triethylamine.

The recovered zeolite, which had been washed with water and dried after the reaction, could be again applied to the benzylation to give benzyl ether in a 70% yield.

In addition, the reactions of various alcohols with benzyl chloride were investigated. The results are given in Table 2. The yield of benzyl ether of secondary alcohol was lower than that of primary alcohol, since dehydration of secondary alcohol to olefin occurred. In the case of phenol, a mixture of o- and p-benzylphenols was also obtained in a 32% yield.

Benzylation is one of the most important protecting methods of the hydroxyl groups in organic syntheses.⁹⁾ It should be, therefore, noted that the present paper offers a facile procedure to convert primary alcohols into the corresponding benzyl ethers even in non-polar solvents under neutral conditions.¹⁰⁾

The study of the correlation between the benzylation activity and the acid-base properties of zeolite is now under way.

References

- 1) G. H. Posner, *Angew. Chem. Int. Ed. Engl.* **17**, 487(1978), G. H. Posner and M. Oda, *Tetrahedron Lett.*, **22**, 5003(1981), S. S. Rana, J. J. Barlow, and K. L. Matta, *ibid.*, **22**, 5007(1981).
- 2) C. N. Satterfield, "Heterogeneous Catalysis in Practice," McGraw-Hill, New York(1980), p. 87.
- 3) K. Tanabe, "Solid Acids and Bases, their catalytic properties," Kodansha, Tokyo(1970).
- 4) M. Onaka, K. Ishikawa, and Y. Izumi, *Chem. Lett.*, **1982**, 1783.
- 5) All zeolites and aluminas were calcinated at 500°C for 5 h in air and stored in a desiccator prior to use.
- 6) The use of benzyl chloride showed a better yield than that of benzyl bromide.
- 7) The lower the electron negativity of the alkali cation, the higher the basic strength of the alkali cation exchanged Y type zeolite: T. Yashima, H. Suzuki, and N. Hara, *J. Catal.*, **33**, 486(1974).
- 8) We assumed that benzyl chloride was hydrolyzed by adsorbed water in alumina to give benzyl alcohol, which was subsequently benzylated to afford dibenzyl ether.
- 9) T. W. Greene, "Protective Groups in Organic Synthesis," John Wiley & Sons, New York(1981).
- 10) The direct alkylation of alcohol by use of KF on alumina has recently been reported: T. Ando, J. Yamawaki, T. Kawate, S. Sumi, and T. Hanafusa, *Bull. Chem. Soc. Jpn.*, **55**, 2504(1982).

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