

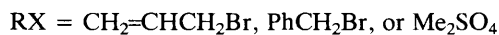
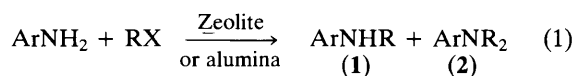
## ***N*-Alkylation of Aniline Derivatives by Use of Potassium Cation-exchanged Y-Type Zeolite**

**Makoto Onaka,\* Akihiro Umezono, Motomitsu Kawai, and Yusuke Izumi**

*Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan*

Zeolite K-Y is effective as a promoter in the *N*-alkylation of aniline derivatives in comparison with  $\gamma$ -alumina.

Various types of organic reactions have been promoted on  $\gamma$ -alumina under very mild conditions.<sup>1</sup> Both acidic and basic sites on the surface of the alumina are considered to work synergistically on substrates to promote the reactions. In contrast to alumina, the acid and base properties of zeolite can be easily modified by exchanging the cations involved in the zeolite.<sup>2</sup> Thus we have applied various cation-exchanged zeolites to liquid-phase organic reactions and have shown the effectiveness of the zeolite as acid and base.<sup>3-5</sup> *N*-Monoalkylation of aniline with an alkylating agent proceeded in the presence of a zeolite<sup>3</sup> or alumina.<sup>6</sup> We now present a comparison of zeolite and alumina as promoters in the *N*-alkylation of aniline derivatives, especially deactivated derivatives which have strongly electron-withdrawing groups [reaction (1)].



Alkali cation-exchanged X- and Y-type zeolites were prepared by the method described in ref. 3. A mixture of the aniline derivative (0.5 mmol), zeolite or alumina (Woelm-200 neutral) (1 g), and solvent (15 ml) was stirred for 30 min. The

alkylating agent (1 equiv.) was then added, and the suspension was warmed with stirring under the conditions shown in Tables 1 and 2. After the addition of water (5 ml), the mixture was stirred for 30 min. The zeolite or alumina was filtered off, the filtrate was made alkaline, and the organic products were extracted and separated by t.l.c.

Table 1 shows the result for the reaction of *p*-nitrobenzene and allyl bromide in the presence of five zeolites. Potassium cation-exchanged Y-type zeolite (K-Y) was the most effective. Under the same reaction conditions powdered KOH did not induce the reaction. A comparison of zeolite K-Y and alumina in

**Table 1.** *N*-Alkylation of *p*-nitroaniline with allyl bromide over zeolite.<sup>a</sup>

Zeolite <sup>b</sup>	Yield/% <sup>c</sup>	(1)/(2)
Na-Y	15	24
K-Y	79	19
Cs-Y	3.6	Only (1)
Na-X	25	4.9
K-X	14	5.2

<sup>a</sup> The reactions were carried out in benzene at 50 °C for 5 h. <sup>b</sup> Cation content in the zeolites: Na-Y (Na<sup>+</sup>, 100%), K-Y (K<sup>+</sup>, 98%; Na<sup>+</sup>, 2%), Cs-Y (Cs<sup>+</sup>, 68%; K<sup>+</sup>, 32%), Na-X (Na<sup>+</sup>, 100%), K-X (K<sup>+</sup>, 93%; Na<sup>+</sup>, 7%). <sup>c</sup> Isolated yields of (1) + (2).

**Table 2.** *N*-Alkylation with RX of aniline derivatives *p*-ZC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> over zeolite K-Y and alumina.

Z	Additive	Conditions <sup>a</sup>	Yield/% <sup>b</sup>	(1)/(2)
RX = CH <sub>2</sub> =CHCH <sub>2</sub> Br				
NO <sub>2</sub>	{K-Y	A	79	19
	{Al <sub>2</sub> O <sub>3</sub>	A	31	66
CN	{K-Y	A	87	25
	{Al <sub>2</sub> O <sub>3</sub>	A	40	19
CO <sub>2</sub> Et	{K-Y	A	74	7.1
	{Al <sub>2</sub> O <sub>3</sub>	A	35	13
H	{K-Y	A	89	9.2
	{Al <sub>2</sub> O <sub>3</sub>	A	50	1.8
RX = PhCH <sub>2</sub> Br				
NO <sub>2</sub>	{K-Y	B	76	9.0
	{Al <sub>2</sub> O <sub>3</sub>	B	71	9.1
CN	{K-Y	B	70	14
	{Al <sub>2</sub> O <sub>3</sub>	B	69	5.0
CO <sub>2</sub> Et	{K-Y	B	72	50
	{Al <sub>2</sub> O <sub>3</sub>	B	47	6.4
H	{K-Y	C	90	14
	{Al <sub>2</sub> O <sub>3</sub>	C	60	1.4
RX = Me <sub>2</sub> SO <sub>4</sub>				
NO <sub>2</sub>	{K-Y	D	55	4.6
	{Al <sub>2</sub> O <sub>3</sub>	D	38	7.3
CN	{K-Y	D	55	3.9
	{Al <sub>2</sub> O <sub>3</sub>	D	39	4.2
CO <sub>2</sub> Et	{K-Y	D	59	6.4
	{Al <sub>2</sub> O <sub>3</sub>	D	32	2.4
Cl	K-Y	E	74	11
H	{K-Y	F	58 <sup>c</sup>	21 <sup>c</sup>
	{Al <sub>2</sub> O <sub>3</sub>	F	67 <sup>c</sup>	1.2 <sup>c</sup>
Me	K-Y	G	68 <sup>c</sup>	5.9 <sup>c</sup>

<sup>a</sup> Conditions: A, benzene, 50 °C, 5 h; B, benzene, reflux, 5 h; C, benzene, 50 °C, 5 h; D, toluene, reflux, 15 h; E, toluene, reflux, 12 h; F, benzene, reflux, 9 h; G, toluene, reflux, 9 h. <sup>b</sup> Isolated yields of (1) + (2). <sup>c</sup> Determined by g.l.c.

the *N*-allylation, *N*-benzylation, and *N*-methylation of aniline derivatives is shown in Table 2. The study revealed that: (i) zeolite K-Y and alumina accelerated the *N*-alkylation of aniline derivatives which have low nucleophilicity, and better yields were obtained with zeolite K-Y than with alumina; (ii) although the Hammett substituent constants ( $\sigma$ ) of the electron-withdrawing groups are in the order NO<sub>2</sub> > CN > CO<sub>2</sub>Et,<sup>7</sup> the reactivities of *p*-nitroaniline, *p*-cyanoaniline, and ethyl 4-aminobenzoate were almost the same in the presence of zeolite K-Y or alumina; (iii) zeolite K-Y induced *N*-monoalkylation with high selectivity except for *N*-methylation. The external surface area of the Y-type zeolite is less than 2% of the total surface area,<sup>8</sup> and polar molecules like aniline can be easily adsorbed inside the zeolite. Thus, for the most part, the *N*-alkylation of aniline derivatives occurs within the intracrystalline pores.

We previously reported<sup>3</sup> that a zeolite acted simply as a base in the *N*-alkylation of aniline. In Table 1, zeolite Cs-Y, which is more basic than K-Y, leads to much inferior yields. Thus we assume that in the *N*-alkylation of aniline derivatives, the acid sites on the zeolite activate the alkylating agent and the base sites activate the amino group simultaneously in order to promote the reaction efficiently.

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