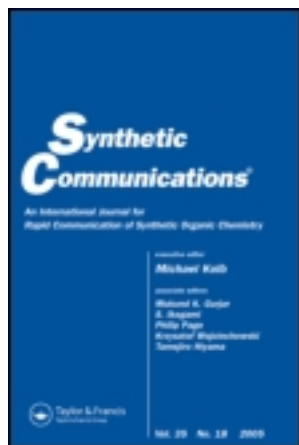


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## FRIEDEL-CRAFTS BENZYLATION OF ARENES USING FeCl<sub>3</sub> IMPREGNATED MONTMORILLONITE K10.

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**Abstract :** FeCl<sub>3</sub> impregnated Montmorillonite K10 was found to catalyze the Friedel-Crafts benzylation of arenes. Monobenylation, with the *para* isomer predominating, was achieved with trace amounts of dibenzylated product.

Since Laszlo's pioneering work on the catalysis of Friedel-Crafts alkylation<sup>1</sup> and acylation<sup>2</sup> by cation exchanged Montmorillonite K10, the catalysis of Friedel-Crafts reaction using modified clays has remained a thrust area in catalysis<sup>3</sup>. Out of the different Lewis acids used for the cation exchange, Fe<sup>3+</sup> has been found to be most interesting due to its Lewis acidity and reducible nature<sup>4,5</sup>. The recent two reports attracted our attention in this context. Clark noted that the catalyst prepared

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by impregnating Montmorillonite K10 with  $\text{FeCl}_3$  from its methanolic solution was a poor catalyst for the benzylation of benzene (<6% conversion in 1 h), as compared to “clayzic” i.e.  $\text{ZnCl}_2$  impregnated on Montmorillonite K10, which under similar conditions gave 100% conversion at 40°C in 15 minutes<sup>6</sup>. Moreover, Montmorillonite K10 impregnated with  $\text{ZnCl}_2$  from its methanolic solution or an acetonitrile solution was a better catalyst than  $\text{Zn}^{2+}$  exchanged Montmorillonite K10. This could be due to faster diffusion of the reactants to the catalytic sites, which leads to a much improved catalytic activity<sup>7</sup>. This highlighted the importance of impregnation of the clay and specifically the importance of organic solvents in the same. Cseri et al have highlighted the importance of  $\text{Fe}^{3+}$  in heterogeneous catalysis and demonstrated that the  $\text{Fe}^{3+}$  content of the clay controls the activity of  $\text{Fe}^{3+}$  containing clays, inspite of their low acidity<sup>4</sup>. They have also proposed a radical mechanism for the Friedel-Crafts alkylation using benzyl chloride<sup>5</sup>. Recently, we have shown that Montmorillonite K10 impregnated with  $\text{FeCl}_3$  from an acetonitrile solution has remarkable catalytic activity in the Beckmann rearrangement of substituted diaryl ketoximes<sup>8</sup>. Acetonitrile was chosen because of its low basicity and also due to the fact that  $\text{FeCl}_3$  is reasonably soluble in it. It is expected that in an organic solvent the Lewis acid would not undergo hydrolysis and remain either free or in the form of a complex. On this background, we attempted the benzylation of arenes using Montmorillonite K10 impregnated with  $\text{FeCl}_3$  from its acetonitrile solution (K10-FeOO).  $\text{FeCl}_3$  was dissolved in acetonitrile and Montmorillonite K10 was equilibrated with the solution. DSC (Differential Scanning Calorimetry) analysis of the resulting catalyst showed that there is one exotherm between 80°C and 130°C (due to liberation of HCl), an endotherm between 130°C and 290°C and a sharp endotherm at 550°C. Hence, the catalyst was activated at 120°C, 280°C and 550°C. (Henceforth will be referred to as K10-FeOO120, K10-FeOO280 and K10-FeOO550 respectively). As the Friedel-Crafts reaction is

mainly a kinetically controlled reaction, the benzylation of arenes was carried out at 40°C and 80°C; only the latter temperature has been selected by the previous workers<sup>1,3</sup>.

The benzylation of benzenes was carried out with benzyl chloride, in the presence of the three catalysts at 40°C. For the sake of comparison, the reaction was also carried out in the presence of other well known Montmorillonite based acidic catalysts. We observed that the catalyst we had prepared had a tremendous potential in the reaction and the catalyst prepared by activation at 120°C was the most active amongst all, where complete conversion of benzyl chloride was obtained in 60 min (Table 1). Hence, for studying the reaction at 40°C, the conversion was monitored at 60 minutes. For further studies, K10-FeOO120 was selected.

Using K10-FeOO120 as a catalyst, benzylation of different arenes was carried out at 40°C and the product mixture analyzed for monobenzylation and dibenzylation products (Table 2). From the results, it appears that conversion in the case of benzenes with a substituent having a lone pair was low possibly due to complexation of such groups with the catalyst, deactivating the active sites. Maximum conversion was obtained in the case of Benzene and Toluene. In all cases, the selectivity for monobenzylation was very high.

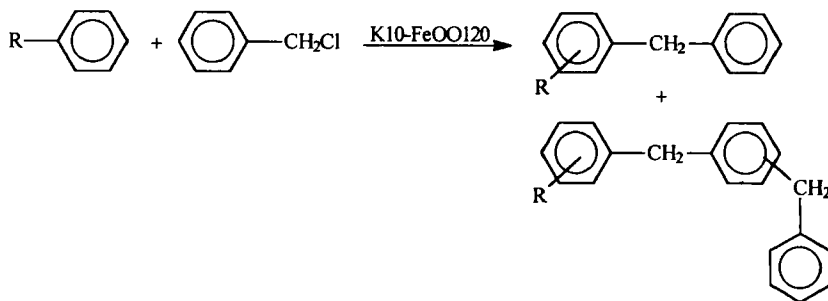
It was observed that the reaction was very fast at 80°C, hence the reaction was studied with respect to more substrates at 80°C (Table 3). At 80°C, the reaction gave quantitative yields for almost all the substrates within 15 minutes. The significant point was even at this temperature, dibenzylation was low.

Comparing the results of monobenzylation at the two temperatures, we found that at 40°C, no *meta* or negligible *meta* isomer is formed in any of the substrates and there was very high selectivity for the *para* isomer. At 80°C, however, the selectivity decreased. The *p*- isomer was found in a major amount in the case of benzenes with a bulky substituent.

**Table 1** : Comparison of the activity of different commercially available clays in the Friedel-Crafts reaction of Benzene with benzyl chloride at 40°C<sup>a</sup>.

Entry	Clay	% conversion of benzyl chloride
1	Na <sup>+</sup> -Bentonite <sup>b</sup>	no reaction
2	Montmorillonite KSF	no reaction
3	Montmorillonite K10	2
4	Montmorillonite KO	3
5	Filtrol-24	6
6	Al-PILC <sup>c</sup>	negligible
7	Fe <sup>3+</sup> -K10 <sup>d</sup>	14
8	K10-FeOO120 <sup>e</sup>	100
9	K10-FeOO280	12
10	K10-FeOO550	- <sup>f</sup>

a : All yields are based on GC analyses (error of  $\pm 4\%$ ) after 1 h at the specified temperature. All the clays specified were dried at 120°C overnight prior to use. Benzylchloride (2mmol), excess arene (10ml) and 0.1g catalyst (as specified) was stirred at the specified temperature in all cases. b: Na<sup>+</sup>- Montmorillonite (pH = 7) procured from Sud-Chemie AG, Munich, Germany. c: Gift sample Al-PILC procured from Sud-Chemie AG, Munich, Germany. d : Catalyst preparation described in Ref. 5. e: Catalyst preparation described in the Experimental section below. f : 8% conversion after 8 h.



**Scheme 1**

**Table 2 :** Benzylation of arenes with benzyl chloride using K10-FeOO120<sup>a</sup> as catalyst after 1 h at 40°C<sup>b</sup>.

Entry	Substrate	% conversion	Monobenylation			Dibenylation
			<i>o</i> -	<i>m</i> -	<i>p</i> -	
1	Benzene	100	97	-	-	3
2	Toluene	100	44.5	6.1	48.3	1.1
3	Anisole	49	48.5	-	51.5	-
4	Ethylbenzene	69	47.5	-	52.5	-
5	Cumene	64	35	-	65	-

a : K10-FeOO activated at 120°C.

b : The products were identified on the basis of GC-MS and the % of the monobenzylated to dibenzylated product have been calculated assuming that the mass spectrograph detector gives equal response to both the products and are uncorrected.

**Table 3 :** Benzylation of arenes with benzyl chloride using K10-FeOO120 as catalyst after 15 min at 80°C.

Entry	Substrate	% conversion	Monobenylation			Dibenylation
			<i>o</i> -	<i>m</i> -	<i>p</i> -	
1	Benzene <sup>a</sup>	100	93.6	-	-	6.4
2	Toluene <sup>a</sup>	100	45.2	8.1	45.3	1.4
3	Ethylbenzene	100	49	-	51	-
4	Cumene	100	30.5	13.8	55.7	-
5	Propylbenzene	94	49	-	51	-
6	Anisole	100	49	-	51	-
7	Phenetole	100	45.6	-	50.5	3.9
8	Chlorobenzene	100	41.5	1.7	56.8	-

<sup>a</sup>: Complete conversion of benzyl chloride obtained in 5 minutes.

Thus, it is observed that the catalyst K10-FeOO120 prepared by impregnation of  $\text{FeCl}_3$  on Montmorillonite K10 was a superior catalyst compared to the catalyst  $\text{Fe}^{3+}$ -K10 prepared by ion-exchange.

**Experimental:**

$^1\text{H-NMR}$  were recorded on a 300 MHz (Varian VXR 300S) in  $\text{CDCl}_3$ . GC-MS are recorded on a Hewlett Packard GCD Series Gas Chromatograph G1800A equipped with an ECD. G.C. analyses were carried out on a Chemito 2865 using a 5% SE-30 column. The relative proportion of monobenzylated and dibenzylated products are calculated assuming that the detector gave equal response for each compound.

**Catalyst Preparation :**

$\text{FeCl}_3$  (15g) was dissolved in dry acetonitrile (60 ml) and Montmorillonite K10 (10g) added over a period of 10 minutes. The resulting slurry was stirred at room temperature for 5 h. The clay was then filtered, washed with acetonitrile (10 ml), and then with benzene (60 ml). The yellowish powder obtained was thermally activated overnight at  $120^\circ\text{C}$ , when a reddish powder was obtained. It is designated as K10-FeOO and the clay activated at  $120^\circ$  is designated as K10-FeOO120. Similarly K10-FeOO280 and K10-FeOO550 were prepared by activation at  $280^\circ\text{C}$  and  $550^\circ\text{C}$  respectively.

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