

## Acylation of aromatic alcohols and phenols over $\text{InCl}_3$ /montmorillonite K-10 catalysts

VASANT R CHOUDHARY\*, KAILASH Y PATIL and SUMAN K JANA

Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune 411 008, India

e-mail: vrc@ems.ncl.res.in; vrc@che.ncl.res.in

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**Abstract.** Montmorillonite K-10 clay supported  $\text{InCl}_3$  is a highly active catalyst for the acylation of aromatic alcohols and phenols with different acyl chlorides. This catalyst can be reused in reactions a number of times without very significant loss of catalytic activity.

**Keywords.** Acylation of aromatic alcohols; acylation of phenols;  $\text{InCl}_3$ /montmorillonite K-10 catalyst; acyl chloride.

### 1. Introduction

Acylation of aromatic alcohols and phenols is an important reaction in organic synthesis for preparing aromatic esters and also for protecting OH groups, particularly during oxidation, peptide coupling and glycosidation reactions.<sup>1</sup> This reaction is generally carried out using homogeneous basic (e.g. amine,<sup>2</sup> DMAP<sup>3</sup> or tri-butyl phosphine<sup>4</sup>) or acidic [e.g. *p*-toluene sulphonic acid,<sup>5</sup>  $\text{ZnCl}_2$ ,<sup>6</sup>  $\text{COCl}_2$ ,<sup>7</sup>  $\text{Sc}(\text{OTf})_3$ <sup>8</sup> or  $\text{Bi}(\text{OTf})_3$ <sup>9</sup>] catalyst with acid chloride or anhydride as the acylating agent. However, the use of homogeneous catalysts poses several serious problems, such as difficulty in the separation and recovery of the catalyst, disposal of the spent catalyst, corrosion problems etc. Development of easily separable and reusable solid catalyst having high activity for the acylation reaction is, therefore, of great practical importance. Recently, a few studies<sup>10,11</sup> have been reported on the use of acidic solid catalysts viz. commercial HY zeolite<sup>10</sup> and montmorillonite K-10 or KSF clay,<sup>11</sup> for the acylation of alcohols and phenols by acetic anhydride.

In our earlier studies, we have reported  $\text{InCl}_3$  supported on montmorillonite K-10 clay or mesoporous Si-MCM-41 showed very high activity in the acylation of benzene and other aromatic compounds.<sup>12,13</sup> In this communication, we report the use of  $\text{InCl}_3$ /montmorillonite K-10 (Mont. K-10) catalyst for the

syntheses of different aromatic esters with high yields at low temperature (30–50°C) for short reaction periods (0.2–2 h), by the acylation (with acyl chloride) of different aromatic alcohols and phenols. The catalyst can be easily separated and reused several times in the reaction.

### 2. Experimental

#### 2.1 Catalyst preparation

$\text{InCl}_3$ /Mont. K-10 catalysts (loading of  $\text{InCl}_3 = 2$  to 20 wt%) were prepared by impregnating montmorillonite K-10 clay (obtained from Aldrich, USA) with indium chloride (purity 99.99%, Aldrich) from its acetonitrile solution by an incipient wetness technique, evaporating the solvent in a vacuum oven at 120°C for 8 h. Before use, the catalyst was pre-treated at 100°C in a flow of moisture-free nitrogen for 1 h to remove the adsorbed moisture.

#### 2.2 General procedure for the acylation reaction

The acylation reaction over the  $\text{InCl}_3$ /Mont. K-10 catalyst was carried out in a magnetically stirred glass reactor (capacity: 25 cm<sup>3</sup>) fitted with a reflux condenser, with low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free  $\text{N}_2$  (30 cm<sup>3</sup> min<sup>-1</sup>) through the liquid reaction mixture at the following reaction conditions by the procedure described earlier<sup>12</sup>: reaction mixture = 20.0 mmol of moisture-free liquid or solid

\*For correspondence

aromatic compound mixed with 11 ml of moisture-free dichloroethane + 8.6 mmol of acyl chloride, amount of catalyst = 0.1 g.

The reaction work-up involved filtration and removal of solvent from the reaction mixture by distillation. The acylated products were purified by column chromatography using silica gel (SRL 60-120 mesh) as the stationary phase and a mixture of petroleum ether and ethyl acetate as the eluent. The analyses of products was confirmed by their <sup>1</sup>H NMR spectroscopy.

### 3. Results and discussion

Results showing the effect of InCl<sub>3</sub> loading (on Mont. K-10) on the yield of benzyl benzoate in the benzylation of benzyl alcohol (by benzoyl chloride) at 50°C over the InCl<sub>3</sub>/Mont. K-10 catalyst

**Table 1.** Effect of InCl<sub>3</sub> loading on the acidity (ammonia chemisorbed at 200°C) and yield in the benzylation of benzyl alcohol (by benzoyl chloride) over InCl<sub>3</sub>/Mont. K-10 catalyst at 50°C.

| InCl <sub>3</sub> loading (wt %) | Ammonia chemisorbed at 200°C (mmol g <sup>-1</sup> ) | Isolated yield (%) of benzyl benzoate <sup>a</sup> |
|----------------------------------|--|--|
| 0                                | 0.3  | 7  |
| 2                                | –  | 30   |
| 5                                | –  | 63   |
| 10                               | 0.7  | 85   |
| 20                               | 0.9  | 96   |

<sup>a</sup>Based on acyl chloride for a reaction period of 1.0 h

are presented in table 1. The product yield increases from 7 to 96% on increasing the InCl<sub>3</sub> loading from zero to 20%. The results clearly show that InCl<sub>3</sub> (20%)/Mont. K-10 is a much superior catalyst than the Mont. K-10 without InCl<sub>3</sub>. It may be noted that use of InCl<sub>3</sub> as a catalyst has also been reported earlier in a number of other organic reactions.<sup>14-17</sup>

Results showing the product yields in the acylation of different aromatic alcohols and phenols with different acyl chlorides over InCl<sub>3</sub> (20%)/Mont. K-10 catalysts are presented in table 2. In all the cases, the yields are quite high, indicating high acylation activity of the catalyst, even under the mild reaction conditions (at 30 or 50°C). InCl<sub>3</sub>/Mont. K-10 catalyst also shows excellent reusability in the acylation of alcohols and phenols. After the fifth reuse, the product yield (benzyl benzoate) for the benzyl alcohol benzylation was 91% (table 2). It may be noted from the comparison of results (entry nos. 1 and 14 in table 2) that the equivalent amount of free (i.e. dissolved) InCl<sub>3</sub> showed very poor performance as compared to the InCl<sub>3</sub> impregnated on Mont-K-10 in the benzylation of benzyl alcohol. Thus, as compared to the homogeneous catalysts, the heterogeneous one showed much better performance. Further work is necessary to understand this. Nevertheless, InCl<sub>3</sub>/Mont K-10 catalyst appears very promising in the acylation of alcohols and phenols.

The high catalytic activity of the InCl<sub>3</sub>/Mont. K-10 is attributed both to its much higher acidity as

**Table 2.** Results on the acylation of different aromatic alcohols and phenols (by acyl chloride) over InCl<sub>3</sub>(20%)/Mont. K-10 catalyst.

| Entry           | Substrate      | Acyating agent                     | Reaction temp. (°C) | Reaction time (h) | Product                 | Product yield <sup>a</sup> (%) |
|-----------------|----------------|------------------------------------|---------------------|-------------------|-------------------------|--------------------------------|
| 1               | Benzyl alcohol | C <sub>6</sub> H <sub>5</sub> COCl | 50                  | 1.0               | Benzyl benzoate         | 96                             |
| 2 <sup>b</sup>  | Benzyl alcohol | C <sub>6</sub> H <sub>5</sub> COCl | 50                  | 1.0               | Benzyl benzoate         | 91                             |
| 3               | Benzyl alcohol | CH <sub>3</sub> COCl               | 30                  | 0.7               | Benzyl acetate          | 92                             |
| 4               | Benzyl alcohol | C <sub>2</sub> H <sub>5</sub> COCl | 50                  | 0.2               | Benzyl propionate       | 93                             |
| 5               | Benzyl alcohol | C <sub>3</sub> H <sub>7</sub> COCl | 50                  | 0.3               | Benzyl butyrate         | 91                             |
| 6               | Phenol         | C <sub>6</sub> H <sub>5</sub> COCl | 50                  | 0.3               | Phenyl benzoate         | 95                             |
| 7               | Phenol         | CH <sub>3</sub> COCl               | 30                  | 0.4               | Phenyl acetate          | 89                             |
| 8               | 4-Nitro phenol | C <sub>6</sub> H <sub>5</sub> COCl | 50                  | 0.4               | 4-Nitro phenyl benzoate | 98                             |
| 9               | 4-Nitro phenol | CH <sub>3</sub> COCl               | 30                  | 0.5               | 4-Nitro phenyl acetate  | 91                             |
| 10              | 1-Naphthol     | C <sub>6</sub> H <sub>5</sub> COCl | 50                  | 2.0               | 1-Naphthyl benzoate     | 82                             |
| 11              | 1-Naphthol     | C <sub>3</sub> H <sub>7</sub> COCl | 50                  | 1.5               | 1-Naphthyl butyrate     | 88                             |
| 12              | 2-Naphthol     | C <sub>6</sub> H <sub>5</sub> COCl | 50                  | 0.5               | 2-Naphthyl benzoate     | 87                             |
| 13              | 2-Naphthol     | C <sub>3</sub> H <sub>7</sub> COCl | 50                  | 0.3               | 2-Naphthyl butyrate     | 90                             |
| 14 <sup>c</sup> | Benzyl alcohol | C <sub>6</sub> H <sub>5</sub> COCl | 50                  | 1.0               | Benzyl benzoate         | 11                             |

<sup>a</sup>Product yield is based on the acyl chloride; <sup>b</sup>Data for the fifth reuse of the catalyst; <sup>c</sup>when 0.02 g anhydrous InCl<sub>3</sub> dissolved in the reaction mixture was used as a catalyst instead of the InCl<sub>3</sub>/Mont.K-10 catalyst

compared to that of Mont. K-10 (table 1) and also to its redox properties<sup>12</sup>.

In summary, the InCl<sub>3</sub>/Mont. K-10 is a highly active catalyst for the acylation of aromatic alcohols and phenols by acyl chloride. All the aromatic esters are obtained in high yields under quite mild and simple experimental conditions. The catalyst can be reused in the reaction number of times with only small loss of its initial activity.

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