# AN OVERVIEW ON SYNTHETIC METHODS OF ALKYL CINNAMATES

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Some industrial synthetic methods for an analogous series of $C_{1-5}$ alkyl cinnamates using different catalysts such as sulfonic acids (p-toluene-sulfonic acid), inorganic salts ($NH_4Fe(SO_4)_2 \cdot 12H_2O$) and solid superacids ($SO_4^{2-}/La_2O_3$-$ZrO_2$-HZSM-5) are reviewed. Yields of an analogous series of $C_{1-5}$ alkyl cinnamates are improved by the addition of the above mentioned catalysts. The main advantages of these methods are the simple process operation and low investment costs.

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## Introduction

Alkyl cinnamates are important organic intermediates and are widely used in perfume, soap and flavouring essences due to pronounced fruit or flower aromas.[1] Cinnamic acid in presence of a catalyst reacts with alcohol to produce alkyl cinnamates. An analogous series of alkyl cinnamates consists of methyl, , ethyl, *n*-propyl , *n*-butyl , isobutyl , *n*-pentyl and isopentyl cinnamate etc.[2] Two methods (the classical method and the microwave heating method) are used to synthesize alkyl cinnamates in the industry. In the classical method cinnamic acid in presence of a catalyst reacts with methanol or ethanol to produce corresponding cinnamate. The disadvantage of this method is that it takes a long time to finish the reaction, benzene or toluene has to be used as dehydrating agent, requires a large amount of catalyst and gives low yield of alkyl cinnamates. The microwave heating method, though decreases the reaction time and increases the yield of alkyl cinnamates, the unit is very complicated and it is difficult to increase output of alkyl cinnamates.[3]

The present paper discusses new catalysts such as p-toluene-sulfonic acid, $NH_4Fe(SO_4)_2 \cdot 12H_2O$ and solid superacids ($SO_4^{2-}/La_2O_3$-$ZrO_2$-HZSM-5).

## Results and Discussion

### *p*-Toulene sulphonic acid as a catalyst

Xu Tongtao[2] discussed different reaction conditions on yields of alkyl cinnamates such as methyl, ethyl, *n*-propyl, *n*-butyl, isobutyl, *n*-pentyl and isopentyl cinnamate. Using *p*-toluene-sulfonic acid as a catalyst and cinnamic acid and alcohols (methanol, ethanol, *n*-propyl, *n*-butanol, isobutanol, *n*-amyl and isoamyl alcohol) produced an analogous series of alkyl cinnamates.

Table 1 shows optimal reaction conditions for the synthesis of $C_{1-5}$ alkyl cinnamates. The experimental results showed that different yields of alkyl cinnamates were obtained. Methyl cinnamate had the highest yields and that of isobutyl cinnamate was the lowest. This may be related to their molecular structure. On the other hand, although *n*-butyl and isobutyl cinnamate or *n*-pentyl and isopentyl cinnamate have similar molecular weights, the yields of *n*-butyl and *n*-pentyl cinnamate were more than that of isobutyl and isopentyl cinnamate respectively. This may be related with steric hindrance of larger alkyl groups.

### $NH_4Fe(SO_4)_2 \cdot 12H_2O$ as a catalyst

Wen Ruiming[4] described the use of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ as a catalyst for the synthesis of alkyl cinnamates. The effect of different reaction conditions such as the reaction time, the molar ratio of cinnamic acid to alcohol, the amount of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ on yields of alkyl cinnamates were discussed. Table 2 presents the relationship between different reaction conditions and yields of alkyl cinnamates. The experimental results show that the yield of ethyl cinnamate was the highest and that of isobutyl cinnamate was the lowest.

### $SO_4^{2-}/La_2O_3$-$ZrO_2$-HZSM-5 as a catalyst

Chen Shufen[5] described the use of $SO_4^{2-}/La_2O_3$-$ZrO_2$-HZSM-5 as the catalyst and discussed the effect of different reaction conditions such as the amount of $SO_4^{2-}/La_2O_3$-$ZrO_2$-HZSM-5 and the molar ratio of cinnamic acid to *n*-butyl alcohol on yields of alkyl cinnamates. Table 3 shows the effect of different reaction conditions on yields of alkyl cinnamates. It is noted that the yield of *n*-pentyl cinnamate was the highest and that of ethyl cinnamate was the lowest.

**Table 1.** Optimal reaction conditions for the synthesis of $C_{1-5}$ alkyl cinnamates

| Alkyl cinnamates | Amount of catalyst, g | Amount of alcohol, mol | Molar ratio of cinnamic acid to alcohol | Reaction time, h | Yield, % |
|---|---|---|---|---|---|
| methyl cinnamate | 6.41% of total reactant weight | 0.15 | 0.02:0.15 | 5.0 | 90.2 |
| ethyl cinnamate | 5.32% of total reactant weight | 0.18 | 0.02:0.18 | 5.0 | 80.4 |
| n-propyl cinnamate | 4.00% of total reactant weight | 0.20 | 0.02:0.20 | 5.0 | 81.6 |
| n-butyl cinnamate | 3.97% of total reactant weight | 0.30 | 0.02:0.30 | 3.5 | 80.0 |
| isobutyl cinnamate | 3.97% of total reactant weight | 0.30 | 0.02:0.30 | 3.5 | 75.0 |
| n-pentyl cinnamate | 4.85% of total reactant weight | 0.20 | 0.02:0.20 | 3.5 | 80.3 |
| isopentyl cinnamate | 4.85% of total reactant weight | 0.20 | 0.02:0.20 | 3.5 | 78.0 |

**Table 2.** The relationships between different reaction conditions and yields of $C_{1-5}$ alkyl cinnamates

| Alkyl cinnamates | Amount of a catalyst, g | Amount of alcohol, mol | Molar ratio of cinnamic acid to alcohol | Reaction time, h | Yield, % |
|---|---|---|---|---|---|
| methyl cinnamate | 53.19% of total reactant weight | 0.20 | 1.0:10.0 | 7.0 | 87.5 |
| ethyl cinnamate | 40.98% of total reactant weight | 0.20 | 1.0:10.0 | 7.0 | 94.3 |
| n-propyl cinnamate | 33.33% of total reactant weight | 0.20 | 1.0:10.0 | 7.0 | 89.5 |
| n-butyl cinnamate | 15.34% of total reactant weight | 0.40 | 1.0:20.0 | 2.0 | 80.0 |
| isobutyl cinnamate | 15.34% of total reactant weight | 0.40 | 1.0:20.0 | 2.0 | 75.0 |
| n-pentyl cinnamate | 24.27% of total reactant weight | 0.20 | 1.0:10.0 | 2.0 | 84.9 |
| isopentyl cinnamate | 24.27% of total reactant weight | 0.20 | 1.0:10.0 | 2.0 | 75.7 |

**Table 3.** The effect of different reaction conditions on yields of an analogous series of $C_{1-5}$ alkyl cinnamates

| Alkyl cinnamates | Amount of a catalyst, g | Molar ratio of cinnamic acid to alcohol | Reaction time, h | Yield, % |
|---|---|---|---|---|
| methyl cinnamate | 1.8% of total reactant weight | 1.0:5.0 | 2.0 | 92.7 |
| ethyl cinnamate | 1.8% of total reactant weight | 1.0:6.0 | 2.5 | 86.5 |
| n-propyl cinnamate | 1.8% of total reactant weight | 1.0:6.0 | 2.5 | 89.8 |
| n-butyl cinnamate | 1.8% of total reactant weight | 1.0:5.0 | 2.0 | 92.7 |
| isobutyl cinnamate | 1.8% of total reactant weight | 1.0:5.0 | 2.0 | 91.3 |
| n-pentyl cinnamate | 1.8% of total reactant weight | 1.0:5.0 | 2.0 | 93.6 |

## Conclusion

Based on the above results it is noted that the yield of ethyl cinnamate in the presence of *p*-toluene sulfonic acid was the highest and that of isobutyl cinnamate was the lowest. On the other hand, although *n*-butyl and isobutyl cinnamate or *n*-pentyl and isopentyl cinnamate have similar molecular weights, yet the yields of *n*-butyl- and *n*-pentyl cinnamate were more than that of isobutyl and isopentyl cinnamate respectively.

The yield of ethyl cinnamate was the highest using $NH_4Fe(SO_4)_2{\cdot}12H_2O$ as the catalyst whereas the yield of isobutyl cinnamate was the lowest.

Using $SO_4^{2-}/La_2O_3$-$ZrO_2$-HZSM-5 as the catalyst, the yield of *n*-pentyl cinnamate was the highest and that of ethyl cinnamate was the lowest.

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