

The role of $\text{AlPO}_4\text{-11}$ in the synthesis of bisphenol-A and cinnamic acid

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$\text{AlPO}_4\text{-11}$ was used as catalyst for the synthesis of bisphenol-A by Friedel-Crafts condensation of acetone with phenol in presence of carbon tetrachloride and synthesis of cinnamic acid by Knoevenagel condensation of aromatic aldehydes with malonic acid in presence of ethyl alcohol.

Zeolites have been extensively used in the acid catalysis of a wide range of organic reactions in which the zeolite catalysts act as a solid Lewis or Brønsted acid. Zeolites are inexpensive, stable and offer several advantages over strong acidity, non-corrosives, mild reaction conditions, higher yield and/or selectivity, ease of experimental set-up. The framework microporous crystalline $\text{AlPO}_4\text{-11}$ are, in principle, neutral and as a result, these materials do not have ion-exchange capacity and are not able to bear Brønsted acidity. The temperature program desorption (TDP) of NH_3 profile for $\text{AlPO}_4\text{-11}$ exhibit only one desorption peak at around 150°C , attributed to Lewis acid sites.

Generally bisphenol-A is prepared by the condensation of acetone with phenol in the presence of an ion exchanger resin¹, hydrochloric acid², sulphonic acid resins³, 2-rolusulphoric acid and alkyl mercaptans⁴ and other catalysts. Naito *et al.*⁵, synthesized bisphenol-A by treating acetone with 2-20 mol% mercaptoamine. However, all these catalysts have to be used in very high concentration that could lead to the problems related to the moisture and effluent pollution. In this paper, the authors report the synthesis of bisphenol-A by Friedel-Crafts condensation of acetone with phenol under catalysis of $\text{AlPO}_4\text{-11}$ at 60°C

in the presence of carbon tetrachloride as a solvent.

$\text{AlPO}_4\text{-11}$ was also used as a catalyst for the synthesis of cinnamic acid via Knoevenagel condensation of the aromatic aldehydes with malonic acid in the presence of ethyl alcohol. Usually, Knoevenagel condensation involves base catalyzed reaction of malonic acid and aromatic aldehydes with the elimination of water molecule⁶. Herein the synthesis of cinnamic acid using $\text{AlPO}_4\text{-11}$, as acid catalyst for the condensation of aromatic aldehydes is reported.

Experimental Procedure

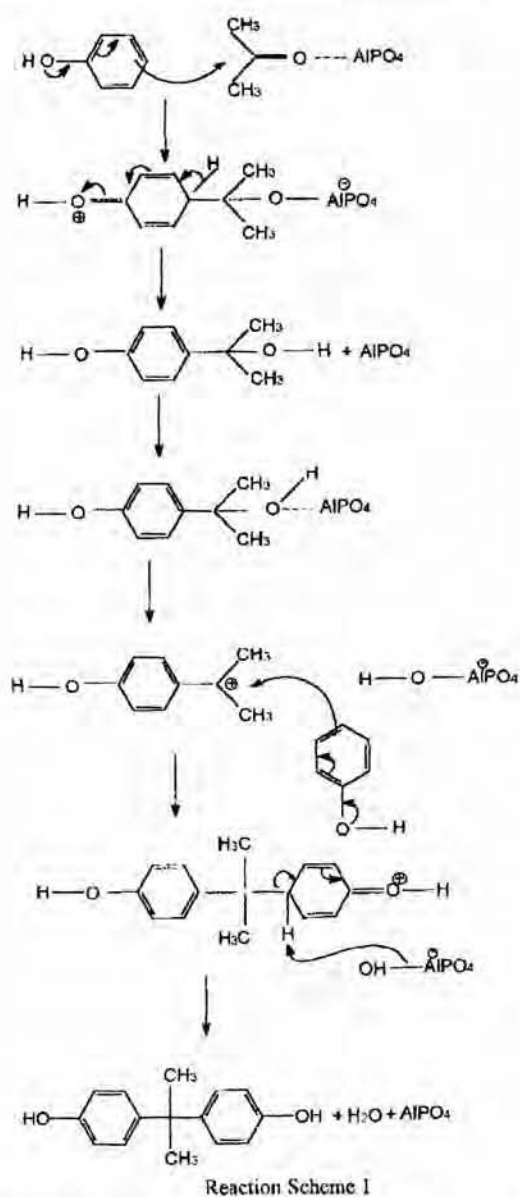
Preparation of bisphenol-A

In a typical experiment, a mixture of acetone (0.818 g), phenol (1.5 g) and $\text{AlPO}_4\text{-11}$ (30 wt% to acetone) in CCl_4 (40 mL) was refluxed for 4 h (Friedel-Crafts condensation). The progress of reaction was monitored by thin layer chromatography using chloroform as eluent. The mixture was cooled to room temperature and treated with acetone (5 mL). $\text{AlPO}_4\text{-11}$ was recovered by filtration and washed twice with 5 mL of acetone. The solvent was removed under reduced pressure to afford the crude material containing essential product along with little phenol, which was then purified by column chromatography. The evaporation of the solvent from the eluent afforded crystalline bisphenol-A. The identity of bisphenol-A was confirmed through its melting point and NMR (¹H NMR (CDCl_3): 1.40-1.52 (s, 6H, CH_3), 4.00-5.00 (bs, 2H, OH), 7.08-7.12 (bd, 4H, ArH), 7.48-7.54 (bd, 4H, ArH).

Preparation of cinnamic acid

In a typical experiment, a mixture of benzaldehyde (1.044 g), malonic acid (1.02 g) and $\text{AlPO}_4\text{-11}$ (30 wt% of malonic acid) in alcohol (50 mL) was refluxed for 2 h, while monitoring the reaction by thin layer chromatography using chloroform as eluent. The mixture was cooled to room temperature and treated with ether (5 mL). $\text{AlPO}_4\text{-11}$ was recovered by filtration and washed with ether. The solvent was removed under reduced pressure to afford the crude material containing cinnamic acid, which was then purified by column chromatography. The evaporation of the solvent from the eluent yielded cinnamic acid. The

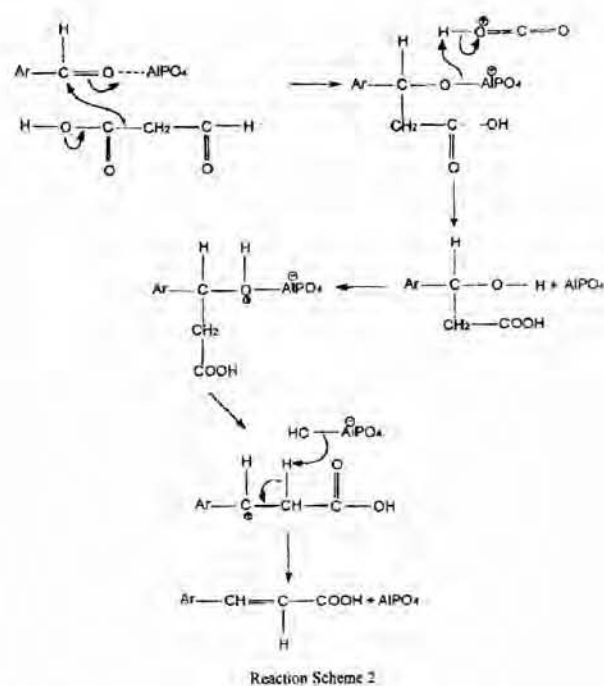
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melting point of the synthesized compound was found to be identical with that of authentic sample. Further, it was confirmed through thin layer chromatography, and spectral studies. Similarly, the cinnamic acid derivatives were prepared from anisaldehyde, 3,4-dimethoxy benzaldehyde, 3,4,5-trimethoxy benzaldehyde, pipernal and parachlorobenzaldehyde.

Results and Discussion

In the preparation of bisphenol-A, the Lewis acid site could be responsible for generating the partial positive charge on the carbonyl carbon by coordinating with its oxygen, and thereby facilitating C-C bond formation via electrophilic substitution reaction with



phenol. Subsequent transfer of a proton led to the formation of transient *t*-alcohol, which later coordinates with Lewis acid site to form the carbocation. The resultant carbocation further adds electrophilically to another molecule of phenol leading to the formation of bisphenol-A [Reaction Scheme 1].

The mechanism for the formation of cinnamic acid involves the complexation of aromatic aldehydes with AlPO_4 -11, forming a positive charge of carbonyl carbon and thereby facilitating C-C bond formation via the path shown in the reaction Scheme 2. Resultant adduct loses catalyst AlPO_4 -11, forming hydroxy phenyl propanic acid. This acid later coordinates with Lewis acid site to form the carbocation. Resultant carbocation, loses proton by forming cinnamic acid.

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