



Na₂CaP₂O₇, a new catalyst for the synthesis of unsaturated arylsulfones

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Abstract—The synthetic diphosphate Na₂CaP₂O₇ is a new basic catalyst for the synthesis of unsaturated arylsulfones. The condensation was carried out under mild conditions at room temperature in methanol or ethanol. The optimum of the catalyst's activity is reached when water is added, leading to good yields. © 2003 Elsevier Science Ltd. All rights reserved.

The Knoevenagel condensation¹ of arylsulfones and aldehydes is one of the most popular methods for the synthesis of unsaturated arylsulfones. The deprotonation of phenylsulfonylalkanes generally involves strong bases such as sodium hydride,² butyl lithium³ or lithium diisopropylamide (LDA).⁴ However, the deprotonation strongly depends on the presence of adjacent electron-withdrawing groups such as ester,⁵ nitrile or ketone.⁶

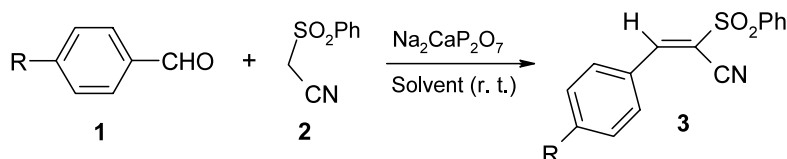
The sulfones are of interest as intermediates in organic synthesis.⁷ This interest comes from the fact that arylsulfonyl groups can stabilize adjacent carbanions⁵ and may easily be removed by hydrolysis, reduction or elimination⁸ and used to introduce carbon–carbon double bonds into organic molecule.⁹ Thus, they are useful temporary activating groups for alkylation,¹⁰ acylation¹¹ and addition¹² reactions.

We report here the use of the synthetic diphosphate¹³ Na₂CaP₂O₇ as a new heterogeneous catalyst in the Knoevenagel condensation between phenylsulfonyl-

tonitrile **2** and benzaldehyde or 4-substituted benzaldehydes **1**, at room temperature (Scheme 1).

The diphosphate Na₂CaP₂O₇ was prepared as a powder by a solid–solid method using the starting materials Na₂CO₃, CaCO₃ and NH₄H₂PO₄ in high purity grade and in the proportions 1:1:2. These materials were ground together and heated in a porcelain crucible progressively to 700°C. The final product was identified by X-ray powder diffraction using a Siemens D-500 diffractometer (CuK α radiation 1.5406 Å; space group: triclinic *P*1 bar; *a*=5.361, *b*=7.029 and *c*=8.743 Å) and infrared spectroscopy IR. The surface area of Na₂CaP₂O₇ was determined by the BET method from the adsorption–desorption isotherm of nitrogen at its liquid temperature, using a conventional volumetric apparatus and was equal to 2.4 m² g^{−1}.

The structure¹⁴ is characterized by the presence of tunnels built up from P₂O₇ entities and CaO₆ polyhedra where Na⁺ cations are located at two crystallographic



Scheme 1.

Keywords: diphosphate; Knoevenagel; heterogeneous catalysis; arylsulfones; recyclable catalyst.

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sites. The distribution of the powder's particle size was determined. The result shows that all the sizes were statistically distributed below 50 μm .

The results for a variety of α,β -unsaturated arylsulfones prepared by Knoevenagel condensation catalyzed by $\text{Na}_2\text{CaP}_2\text{O}_7$ are summarized in Table 1.¹⁵ In general the use of $\text{Na}_2\text{CaP}_2\text{O}_7$ as heterogeneous catalyst in the Knoevenagel condensation has allowed the isolation of α -phenyl sulfonyl cinnamonnitrile with modest yields (Table 1).

Under the same conditions, the addition of water remarkably increases the reaction yields in the Knoevenagel synthesis of α,β -unsaturated arylsulfones (Table 1). For example, for the alkene **3a**, the yield of reaction goes from 62 to 68% in methanol and from 58 to 74% in ethanol. In this, 10% of water is the optimum condition for the synthesis of alkene **3b** (Fig. 1). This activation is probably due to the interaction between water and the solid surface. If a large amount of water is used a thin film of water will be formed between the organic reagents and catalyst which explain the decreasing of the yields (Fig. 1). The $\text{Na}_2\text{CaP}_2\text{O}_7$ was regenerated by calcination at 500°C during 15 min, and after

five successive recoveries, product **3b** was obtained with the same yield.

To evaluate the effect of the presence of electron acceptor or donor on the aromatic ring of benzaldehyde, the Knoevenagel condensation was carried out between phenylsulfonylacetonitrile **2** and substituted benzaldehyde derivatives (**1a–d**) using $\text{Na}_2\text{CaP}_2\text{O}_7$ as catalyst. Results from Table 1 show that the presence of electron acceptor groups on the aromatic ring increases the reaction rate. The presence of electron donor groups decreases the reaction rate, demonstrating the participation of the aldehyde in the controlling step of the reaction.

Thus, we estimate that the surface of catalyst $\text{Na}_2\text{CaP}_2\text{O}_7$ presents certainly multicatalytic active sites. The basic sites (oxygen of the P_2O_7 group and CaO_6 octahedra) polarize the C–H bond of the active methylene compound. The acidic sites (phosphorus of P_2O_7 group, Na^+ and Ca^{2+} cations) probably coordinate with the oxygen of the carbonyl carbon on which a partial positive charge appears. Consequently, the C–C bond formation is facilitated and the final alkene is obtained by transfer of a proton followed by dehydration.

In summary, we have reported an efficient and convenient route to α,β -unsaturated arylsulfones by the Knoevenagel reaction. The $\text{Na}_2\text{CaP}_2\text{O}_7$ catalyst shows high catalytic activity under very mild liquid-phase conditions. The advantages of this method are an easy separation of the catalyst by filtration, possible recycling of the catalyst, elimination of salts and by-product pollutants. This solid base catalyst is certainly a practical alternative to soluble bases.

Table 1.

Arylsulfones	R	Solvent	Yield/% (1 h) ^a
3a	H	MeOH	62
3a	H	EtOH	58
3a	H	MeOH	68 ^b
3a	H	EtOH	74 ^b
3b	<i>p</i> -NO ₂	EtOH	80
3b	<i>p</i> -NO ₂	EtOH	94 ^b
3c	<i>p</i> -Cl	EtOH	69
3c	<i>p</i> -Cl	EtOH	81 ^b
3d	<i>p</i> -OMe	EtOH	50
3d	<i>p</i> -OMe	EtOH	68 ^b

^a Yields in pure products isolated by chromatography (AcOEt/hexane) or distillation under vacuum and identified by mass spectra, ¹H, ¹³C NMR and IR spectroscopy.

^b Solvent/water ratio: 90/10.

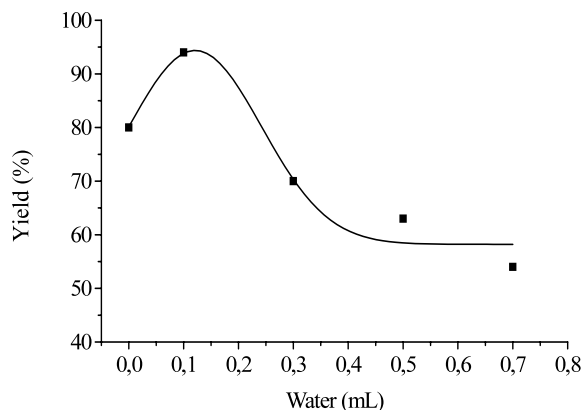


Figure 1. Influence of water in the synthesis of unsaturated arylsulfone **3b** (with 1 mL of ethanol).

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15. The general procedure is as follows: In a typical procedure,

the substituted benzaldehyde **1** (1.2 mmol) and phenylsulfonylacetonitrile **2** in solvent (methanol or ethanol: 1 mL), were stirred with diphosphate $\text{Na}_2\text{CaP}_2\text{O}_7$ (0.1 g) at room temperature for 1 h. Workup included extraction with dichloromethane, filtration and evaporation. The crude product was purified by chromatography (AcOEt/hexane) or distillation under vacuum and identified by mass spectral, IR spectrometry and ^1H , ^{13}C NMR. The same procedure was used for the reactions carried out in the presence of $\text{Na}_2\text{CaP}_2\text{O}_7$ activated with water (0.1 mL). Water was always added in the last place.