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$Na_2CaP_2O_7$, a new catalyst for Michael addition

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Abstract—The synthetic diphosphate $Na_2CaP_2O_7$ is a new basic catalyst for Michael addition of mercaptans to chalcone derivatives with high yields in a few minutes and mild reaction conditions. Products of undesirable side reactions resulting from 1,2-addition, polymerisation and bis-addition are not observed. © 2002 Elsevier Science Ltd. All rights reserved.

The Michael addition has attracted enormous attention as one of the most important carbon–carbon or sulfur–carbon bond-forming reactions in organic synthesis.[1] This reaction may be carried out in homogeneous or heterogeneous conditions.

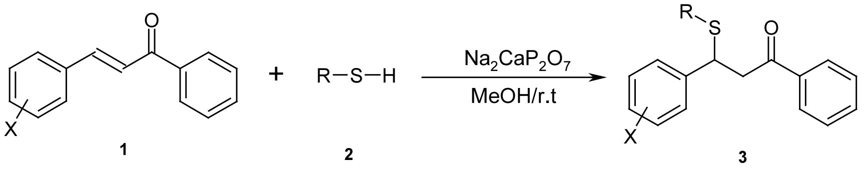
Various solid catalysts have been found useful in heterogeneous media, including aluminium oxide,[2] montmorillonite/$NiBr_2$,[3] Mg–Al hydrotalcite,[4] zeolite,[5] natural phosphate doped by potassium fluoride[6] and other catalysts with more or less success.[7]

We report here the use of a synthetic diphosphate $Na_2CaP_2O_7$[8] as a new solid state heterogeneous catalyst in the Michael addition between chalcone derivatives **1** and mercaptans **2**, at room temperature, with a solvent (Scheme 1).

The synthesis of the diphosphate $Na_2CaP_2O_7$ (Scheme 2) in powder state has been carried out from Na_2CO_3, $CaCO_3$ and $NH_4H_2PO_4$ in proportions 1:1:2, respectively (purity of starting materials higher than 99%). These materials were ground together in an agate mortar and heated in a platinum crucible progressively from 373 to 973 K. The final product is identified by X-ray powder diffraction using a Siemens D-500 diffractometer (CuKα radiation 1.5406 Å; space group: triclinic $P\bar{1}$; $a=5.361$ Å, $b=7.029$ Å and $c=8.743$ Å) and infrared spectroscopy IR.[8]

The use of $Na_2CaP_2O_7$ as heterogeneous catalyst in the Michael addition has allowed the isolation of products **3** rapidly (5–40 min)[9] and with good yields (58 to 96%; Table 1). Products of undesirable side reactions resulting from 1,2-addition, polymerisation and bis-addition are not observed.

The $Na_2CaP_2O_7$ was regenerated by calcination at 500°C during 15 min, and after seven successive recoveries, product **3a** was obtained with the same yield. We



Scheme 1.

$$Na_2CO_3 + CaCO_3 + 2NH_4H_2PO_4 \longrightarrow Na_2CaP_2O_7 + 3H_2O\uparrow + 2NH_3\uparrow + 2CO_2\uparrow$$

Scheme 2.

Keywords: Michael addition; diphosphate; heterogeneous catalysis; recyclable catalyst.

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Table 1. Synthesis of products **3** by Michael addition using $Na_2CaP_2O_7$

Products	X	R	Yield/% (time/min)[a]
3a	H	-Ph	94 (20)
3b	H	-2-NH_2Ph	96 (05)
3c	H	-CH_2-CO_2Et	58 (40)
3d	*m*-NO_2	-Ph	96 (10)
3e	*m*-NO_2	-2-NH_2Ph	91 (02)
3f	*m*-NO_2	-CH_2-CO_2Et	82 (40)
3g	*p*-Cl	-Ph	95 (30)
3h	*p*-Cl	-2-NH_2Ph	93 (05)
3i	*p*-Cl	-CH_2-CO_2Et	63 (40)

[a] Yields in pure products isolated by recrystallization with AcOEt/CH_2Cl_2 and identified by ^1H, ^{13}C NMR and IR spectroscopy.

speculate, in our case, that the reaction occurs on the surface of the catalyst and not inside tunnels. The dimensions of the tunnels in our catalyst are smaller[8] than of fluoroapatites[10] but not as large as those of zeolites.[11]

Thus, we estimate that the surface of $Na_2CaP_2O_7$ presents certainly multicatalytic active sites. The basic sites (oxygens of P_2O_7 group and CaO_6 octahedra) abstract the proton from the thiols. The acidic sites (phosphorus of P_2O_7 group, Na^+ and Ca^{2+} cations) probably induced the polarisation of the C=O bond for the Michael addition. Consequently, the S–C bond formation is facilitated and the final product is obtained by the transfer of a proton.

In summary, we have reported a selective 1,4-addition without any side reaction, condensation, dimerisation, or rearrangements in Michael. Two is made possible with $Na_2CaP_2O_7$. This catalyst brings advantages such as high catalytic activity and selectivity under very mild liquid phase conditions and easy separation of the catalyst by simple filtration. Other applications will be reported elsewhere.

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9. The general procedure is as follows: To a flask containing an equimolar mixture (1 mmol) of thiol **2** and chalcone derivative **1** in methanol (1.5 ml), $Na_2CaP_2O_7$ (0.1 g) was added and the mixture was stirred at room temperature until completion of the reaction, as monitored by thin layer chromatography (TLC). The catalyst was filtered, washed with dichloromethane and the filtrate was concentrated under reduced pressure. The crude product was purified by recrystallization. The product was analysed by ^1H, ^{13}C NMR and IR spectrometry.
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