



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

Cs_{2.5}H_{0.5}PW₁₂O₄₀-catalyzed conjugate addition of indole to α , β -unsaturated ketones

Hojatollah Khabazzadeh *, Esmat Tavakolinejad Kermany *, Morteza Eghbali

Department of Chemistry, Shahid Bahonar University of Kerman, 76169 Kerman, Iran

Received 7 April 2011; accepted 11 July 2011

KEYWORDS

Indole;
Conjugate addition;
 α , β -Unsaturated ketones;
Heterogeneous;
Heteropoly acid;
Cesium salt;
Tungstophosphoric

Abstract Conjugate addition of indole to a variety of α , β -unsaturated ketones was catalyzed by the cesium salt of tungstophosphoric acid as a heterogeneous catalyst. The reaction was performed in molten tetrabutyl ammonium bromide.

© 2011 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

Catalysis by heteropoly acids (HPAs) is a well established area (Hirano et al., 1996). Arguably, it is one of the most successful areas in contemporary catalysis, where systematic studies of HPA catalysts at the molecular level have led to a string of large-scale industrial applications. HPAs possess unique physicochemical properties, with their structural mobility and multifunctionality being the most important for catalysis (Kozhevnikov, 1998).

* Corresponding authors. Tel./fax: +98 341 322 2033.
E-mail addresses: hkhazzadeh@mail.uk.ac.ir (H. Khabazzadeh),
etavakoly@yahoo.com (E.T. Kermany).

1878-5352 © 2011 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2011.07.012

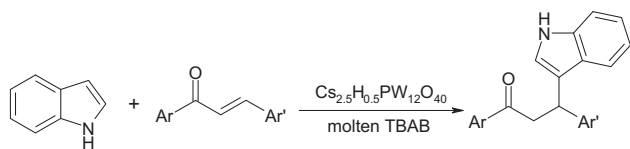


Production and hosting by Elsevier

A major drawback to the HPAs is their high solubility in water and polar solvents, which impedes recovery and reuse of the catalyst. To conquer this shortcoming, several studies have put efforts into the immobilization of the HPAs on high-surface-area solid supports, such as zeolite, SiO₂, and TiO₂ (Friesen et al., 2000; Ozer and Ferry, 2002). Another way to overcome this problem is by changing these HPAs into their corresponding salts, which are generally insoluble in polar solvents.

The salts of heteropoly acids have many applications, such as catalysts in oxidation, alkylation, or hydrosulfurization reactions, resulting in many cases in higher specific conversion rates than those obtained with their parent acids (Misono and Nojiri, 1990; Nomiya et al., 1980; Izumi et al., 1983) and in higher thermal stability (Kobayashi and Iwamoto, 1998; Matsuo et al., 2000).

Ionic liquids (ILs) are very attractive and environmentally acceptable solvents because they have very low vapor pressure and are stable in a wide temperature range (Wasserscheid et al., 2000a,b). Therefore, they can be used as environmentally benign solvents for a number of chemical processes, such as separations (Huddleston et al., 1998), reactions (Sheldon, 2001), homogeneous two-phase catalysis (Holbrey and Seddon, 1999) and extractions (Eber et al., 2004).



Scheme 1 $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalyzed conjugate addition of indole with α , β -unsaturated ketones.

The current emphasis on novel reaction media is motivated by the need for efficient methods for replacing of toxic or hazardous solvents and catalysts. The use of ionic liquids as novel reaction media may offer a convenient solution to both the solvent emission and the catalyst recycling problem (Gmouh et al., 2003). Another promising class of new media is molten salts which can be used instead of ionic liquids. Molten salts are generally thermally stable and chemically resistant.

Addition reactions of indoles to α , β -unsaturated compounds have received much interest because their derivatives occur in nature and possess a variety of biological activities (Sundberg, 1996). Since 3-position of indole is the preferred site for electrophilic substitution reaction, 3-alkyl or acyl indoles are versatile intermediates for the synthesis of a wide range of indole derivatives (Moore et al., 1984). The simple and direct method for the synthesis of 3-alkylated indoles involve the conjugate addition of indoles to α , β -unsaturated compounds in the presence of either protic (Szmuszkovicz, 1957) or Lewis acids (Bandini et al., 2002).

However, the acid-catalyzed conjugate addition of indoles requires careful control of acidity to prevent side reactions such as dimerisation or polymerization. Further, many of these procedures involve strongly acidic conditions, expensive reagents, longer reaction time, low yields of products due to the dimerisation of indoles or polymerization of vinyl ketones and cumbersome products isolation. Thus, a number of milder reagents and Lewis acids catalysts such as Al_2O_3 (Ranu et al., 1991) rhodium complex (Paganelli et al., 1991) $\text{Bi}(\text{NO}_3)_3$ (Khadai et al., 2008), $\text{HClO}_4/\text{SiO}_2$ (Khan et al., 2006), have been developed over the past few years.

As a part of our ongoing research program to develop new synthetic methodologies (Khabazzadeh et al., 2009; Seyedi et al., 2009; Mozaffari Majd et al., 2010) we performed $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalyzed conjugate addition of indole with α , β -unsaturated ketones in molten salt media (Scheme 1). Previously, molten tetrabutylammonium bromide (TBAB) was used as cost-effective ionic liquid in a number of useful synthetic transformations so we used it as the reaction media.

2. Materials and methods

All commercially available chemicals were obtained from Merck and Fluka companies, and used without further purifications. All products are known and were identified by the comparison of their spectral data and physical properties with those of the authentic samples. ^1H and ^{13}C NMR spectra were determined on a Bruker 500-DRX Avance instrument at 500 and 125 MHz.

2.1. General procedure for the conjugate addition of indole to chalcones

A mixture of indole (1 mmol), chalcone (1 mmol), tetrabutyl ammonium bromide (1 mmol) and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$

Table 1 $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ -catalyzed conjugate addition of indole to chalcones.

Entry	Product	Time (min)	Yield (%)
2a		45	70
2b		40	67
2c		40	85
2d		40	73
2e		45	80
2f		45	75
2g		50	72
2h		50	80

(0.05 mmol) was stirred for appropriate time at 110°C (checked by TLC). When the reaction was completed, 2 mL of ethanol was added and after the filtration of catalyst the

Download English Version:

<https://daneshyari.com/en/article/5142546>

Download Persian Version:

<https://daneshyari.com/article/5142546>

[Daneshyari.com](https://daneshyari.com)