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ORIGINAL PAPER

One-pot synthesis of 2-amino-3-cyano-4-arylsubstituted tetrahydrobenzo[*b*]pyrans catalysed by silica gel-supported polyphosphoric acid (PPA–SiO_2) as an efficient and reusable catalyst

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A convenient method for the synthesis of tetrahydrobenzo[*b*]pyrans by a one-pot three-component cyclocondensation of dimedone, aryl aldehydes, and malononitrile in water using silica gel-supported polyphosphoric acid (PPA–SiO_2) as an efficient and reusable catalyst is described. The present methodology offers several advantages, such as a simple procedure with ease of handling, short reaction time, high yields, and the absence of any volatile and hazardous organic solvents.

Keywords: tetrahydrobenzo[*b*]pyrans, PPA-SiO_2, heterogeneous catalysis, aqueous media

Introduction

4*H*-pyrans and 4*H*-benzo[*b*]pyrans are very important organic compounds with a wide range of biological activities. These compounds are reported to possess significant anti-coagulant, spasmolytic, diuretic, anti-cancer, and anti-anaphylactic activities (Foye, 1991; Singh et al., 1996; Bonsignore et al., 1993; Green et al., 1995). Also, a number of 2-amino-tetrahydropyrans are useful as photoactive materials (Armetso et al., 1989). Tetrahydrobenzo[*b*]pyrans are generally synthesised via a one-pot three-component reaction of aryl aldehyde, malononitrile, and dimedone in the presence of several catalysts such as hexadecyltrimethyl ammonium bromide (HTMAB) (Jin et al., 2004), rare earth perfluorooctanoate [RE(PFO)$_3$] (Wang et al., 2006), NaBr (Devi & Bhuyan, 2004), (*S*)-proline (Balalaie et al., 2006), KF-basic alumina under ultrasound irradiation (Li et al., 2004), and Na_2SeO_4 (Hekmatshoar et al., 2008). However, many of these methods are associated with expensive and highly acidic catalysts, lengthy reaction times, unsatisfactory yields, and difficult product isolation. Hence, the development of simple, efficient, clean, high-yielding, and environmentally friendly approaches using new catalysts for the synthesis of these compounds is an important task for organic chemists.

Solid-supported reagents, such as silica gel-supported acids, are catalysts that have become popular in organic synthesis because of their interesting properties such as high efficiency due to greater surface area, higher stability and reusability, low price, and ease of handling (Corma & Garcia, 2006; Hajipour & Ruoho, 2005; Kantevari et al., 2007; Shaterian et al., 2009a; Tavakoli-Hoseini & Davoodnia, 2010; Maghsoodlou et al., 2010; Zeinali-Dastmalbaf et al., 2011). Although the catalytic applications of silica-supported reagents for organic synthesis are well established, to the best of our knowledge there is no report in the literature on the use of PPA–SiO_2 as a catalyst for the synthesis of tetrahydrobenzo[*b*]pyrans.

The replacement of hazardous solvents with those that are environmentally benign is an active area of current research. Recently, several organic reactions have been performed using water as the reaction medium (Shen et al., 2008; DeBlase & Leadbeater,

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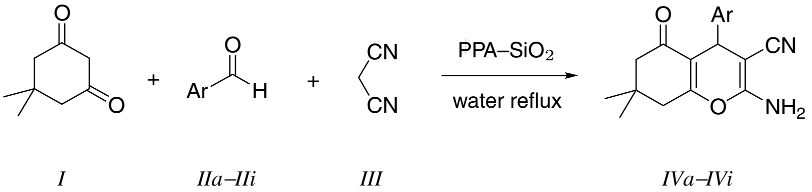


Fig. 1. Synthesis of tetrahydrobenzo[b]pyrans catalysed by PPA–SiO_2.

2010; Kumar et al., 2011). Water is clean, non-toxic, hazard-free in handling, non-flammable, cheap, and a readily available solvent. Therefore, it is important to carry out organic reactions in water instead of other solvents for environmental and economic reasons. Furthermore, because of its high polarity, high surface tension, high specific heat capacity and network of hydrogen bonds, water plays a significant role in some reactions (Narayan et al., 2005; Jung & Marcus, 2007).

Due to our interest in the synthesis of heterocyclic compounds (Davoodnia et al., 2006, 2007a, 2007b, 2007c, 2007d, 2008a), and in continuation of our previous works on the applications of reusable catalysts in organic reactions (Davoodnia et al., 2007a, 2008b, 2009, 2010a, 2010b, 2010c, 2010d, 2010e; Davoodnia, 2010), we wish here to report a simple and highly efficient method for the synthesis of tetrahydrobenzo[*b*]pyrans via a three-component cyclocondensation of dimedone, aryl aldehydes, and malononitrile in water using PPA–SiO_2 as heterogeneous catalyst (Fig. 1).

Experimental

All chemicals were purchased from Merck and Aldrich (Germany) and used without additional purification. Melting points were recorded on an electrothermal type 9100 melting point apparatus (HiTech Trader company, USA). The IR spectra using KBr disks were obtained on a 4300 Shimadzu spectrophotometer (Japan). The ^{1}H NMR (400 and 500 MHz) spectra were recorded with Bruker 400 and Bruker 500 (Germany) spectrometers.

Preparation of PPA–SiO_2

The PPA–SiO_2 was prepared following the procedure reported by Aoyama and co-workers (Aoyama et al., 2004). PPA (2.1 g) was transferred into a round-bottom flask and $CHCl_3$ (100 mL) was added. After the mixture was stirred at 50 ℃ for 1 h, SiO_2 (200–400 mesh, 4.9 g) was added to the solution, and the mixture was stirred for a further 1 h. The $CHCl_3$ was removed using a rotary evaporator and the resulting solid was dried in vacuum at laboratory temperature for 3 h. The amount of H^+ in the PPA–SiO_2 determined by acid–base titration was 0.5 mmol g^{-1}. For this purpose, a mixture of PPA–SiO_2 and a large volume of water was heated under reflux for 2 h, and then filtered. We believe that PPA–SiO_2 can be hydrolysed to free H_3PO_4 only after prolonged heating in water. The amount of free H_3PO_4 in the filtrate was measured by the method detailed by Shaterian et al. (2009b).

General procedure for the synthesis of tetrahydrobenzo[b]pyrans (IVa–IVi) using PPA–SiO_2

A mixture of dimedone *I* (1 mmol), an aromatic aldehyde *IIa–IIi* (1 mmol), malononitrile *III* (1 mmol), and PPA–SiO_2 (0.1 g, 0.05 mmol of H^+) in water (5 mL) was heated under reflux for an appropriate length of time. During the procedure, the reaction was monitored by TLC. Upon completion, the catalyst was removed by filtration under hot conditions. After cooling the filtrate, the precipitated solid was filtered and re-crystallised from ethanol to give compounds *IVa–IVi* in high yields. All the known products have already been reported in the literature (Devi & Bhuyan, 2004; Hekmatshoar et al., 2008) and were characterised by a comparison of melting points, IR, and ^{1}H NMR (of some products) spectra with authenticated samples.

Specific procedure for the synthesis of 2-amino-4-(4-chlorophenyl)-3-cyanotetrahydrobenzo[b]pyran (IVc) using PPA–SiO_2

A mixture of dimedone *I* (1 mmol), 4-chlorobenzaldehyde *IIc* (1 mmol), malononitrile *III* (1 mmol), and PPA–SiO_2 (0.1 g, 0.05 mmol of H^+) in water (5 mL) was heated under reflux for 10 min. During the procedure, the reaction was monitored by TLC. Upon completion, the reaction mixture was filtered whilst still hot to remove the catalyst. The catalyst was washed with a small portion of cold water (5 mL), and hot absolute ethanol (10 mL), respectively. The combined filtrate was reduced by half and allowed to stand at laboratory temperature for 0.5 h. The precipitated solid was collected by filtration and dried overnight to provide 0.313 g of a colourless amorphous product. The product was dissolved in hot absolute EtOH (10 mL), which, upon cooling to laboratory temperature, gave 0.306 g (93 %) of *IVc* as colourless needles (m.p. 206–207 ℃).

Table 1. Synthesis of compound *IVc* in the presence of PPA–SiO_2 (0.1 g) in different solvents[a]

Entry	Solvent	Temperature/ °C	Time/min	Yield/%[b]
1	EtOH	reflux	20	77
2	CH_3CN	reflux	20	50
3	$CHCl_3$	reflux	20	31
4	CH_2Cl_2	reflux	20	40
5	H_2O	reflux	10	93
6	Solvent-free	110	20	45

a) Dimedone *I* (1 mmol), 4-cholorobenzaldehyde *IIc* (1 mmol), malononitrile *III* (1 mmol); *b*) isolated yield.

Recycling and reuse of the catalyst

We believe that PPA is bonded to SiO_2 in a similar manner to the compound reported in the literature (Mahdavinia et al., 2009). Therefore, PPA–SiO_2 can remain intact in a small portion of hot water for a short period of time. Thus, the recyclability of the catalyst in the reaction of dimedone, aromatic aldehydes, and malononitrile in the presence of PPA–SiO_2 was checked. After completion of the reaction, the reaction mixture was filtered whilst still hot to separate the catalyst. The separated catalyst was washed with a small portion of cold water (5 mL), and hot absolute ethanol (10 mL), respectively, and dried at 100 °C under vacuum for 2 h. The catalyst could be used three times in the reactions with only a slight reduction in the catalytic activity. In addition, for the model reaction, the pH of the solvent after separation of the catalyst was checked and found to be 6.4.

Results and discussion

Initially, the synthesis of compound *IVc* was selected as a model reaction to optimise the reaction conditions. The reaction was carried out by heating a mixture of dimedone (1 mmol), 4-chlorobenzaldehyde (1 mmol), and malononitrile (1 mmol) in the presence of PPA–SiO_2 (0.1 g) as the catalyst in different solvents, and also under solvent-free conditions. The results are given in Table 1. As shown in Table 1, the reaction in water (entry 5) gave the best yield. It has been reported that water has a significant role in acceleration of the reaction rate (Ribe & Wipf, 2001). However, in this reaction, the high polarity of water enhances the reaction rate, probably by facilitating formation of the ionic intermediates.

In addition, the same model reaction was carried out in water at different temperatures to assess the effect of temperature on the reaction yield. It was observed that yield was a function of temperature, since the yield increased as the reaction temperature rose (Table 2), and at 100 °C, the product *IVc* was obtained in an excellent yield.

Further, to determine the optimum amount of PPA–SiO_2, the same model reaction was carried out again under the conditions previously detailed using different amounts of catalyst. The use of 0.1 g of catalyst resulted in the highest yield within appropriate time (Table 3). Consequently, all subsequent reactions were carried out in water at 100 °C in the presence of 0.1 g of PPA–SiO_2.

Table 2. Synthesis of compound *IVc* in the presence of PPA–SiO_2 (0.1 g) at different temperatures in water[a]

Entry	Temperature/ °C	Time/min	Yield/%[b]
1	25	120	56
2	50	40	62
3	75	30	75
4	100	10	93

a) Dimedone *I* (1 mmol), 4-cholorobenzaldehyde *IIc* (1 mmol), malononitrile *III* (1 mmol); *b*) isolated yield.

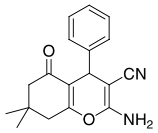
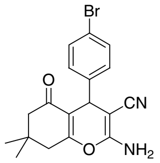
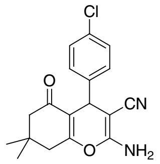
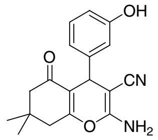
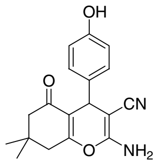
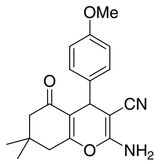
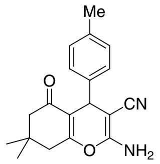
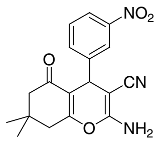
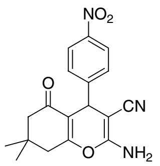
Table 3. Effect of amounts of PPA–SiO_2 on the model reaction[a]

Entry	Catalyst/g	Time/min	Yield/%[b]
1	None	180	Traces
2	0.02	90	35
3	0.05	60	65
4	0.1	10	93
5	0.15	10	93
6	0.2	20	94

a) Dimedone *I* (1 mmol), 4-cholorobenzaldehyde *IIc* (1 mmol), malononitrile *III* (1 mmol) in water at reflux temperature; *b*) isolated yield.

In order to evaluate the general character of this model reaction, we included a range of other aromatic aldehydes in the reaction of dimedone and malononitrile under the optimised reaction conditions. In all cases, the expected products were obtained in high yields in short reaction times. The results are given in Table 4. As shown, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the products in high yields. A plausible mechanism for this reaction, although using another catalyst, was shown by Jin et al. (2006). For comparison and to show the effect of PPA–SiO_2 as a solid acid catalyst, synthesis of the model compound, *IVc*, was also investigated using PPA, NaH_2PO_4, and SiO_2 in water separately.

Table 4. Synthesis of tetrahydrobenzo[*b*]pyrans *IVa*–*IVi* using PPA–SiO_2 (0.1 g) as catalyst^a

Product^b	Ar	Structure	Time/min	Yield/%^{c}	M.p./°C		Reference
					Found	Reported	
IVa	C_6H_5		13	80	231–232	230	Hekmatshoar et al. (2008)
IVb	4-BrC_6H_4		10	90	215–217	215	Hekmatshoar et al. (2008)
IVc	4-ClC_6H_4		10	93	206–207	206	Hekmatshoar et al. (2008)
IVd	3-HOC_6H_4		15	77	238–240	225	Hekmatshoar et al. (2008)
IVe	4-HOC_6H_4		10	78	209–211	210	Hekmatshoar et al. (2008)
IVf	4-$MeOC_6H_4$		14	84	202–203	203	Hekmatshoar et al. (2008)
IVg	4-MeC_6H_4		12	80	223–225	218	Hekmatshoar et al. (2008)
IVh	3-$O_2NC_6H_4$		8	80	214–216	212	Hekmatshoar et al. (2008)
IVi	4-$O_2NC_6H_4$		8	85	182–184	177–178	Devi and Bhuyan (2004)

a) Dimedone *I* (1 mmol), aryl aldehyde *IIa*–*IIi* (1 mmol), malononitrile *III* (1 mmol), and PPA–SiO_2 (0.1 g) in water under reflux; *b*) all the products were characterised by IR spectral data and by comparison of their melting points with those of authenticated samples. The structures of some products were also confirmed by ^{1}H NMR spectral data; *c*) isolated yield.

The results are given in Table 5. As shown in this Table, PPA–SiO_2 gave the best result. Using aqueous PPA as the catalyst gave the product *IVc* in relatively good yield (65 %) but it was not recyclable. Therefore,

Table 5. Comparison of various conditions in the synthesis of compound *IVc*[a]

Entry	Catalyst (mass/g)	Time/min	Yield/%[b]
1	PPA–SiO_2 (0.1)	10	93
2	PPA (0.5)	60	65
3	NaH_2PO_4 (0.2)	75	60
4	SiO_2 (0.1)	60	21

a) Dimedone *I* (1 mmol), 4-cholorobenzaldehyde *IIc* (1 mmol), malononitrile *III* (1 mmol) in water at reflux temperature; *b*) isolated yield.

Table 6. Comparison of efficiency of PPA–SiO_2 in the synthesis of tetrahydrobenzo[*b*]pyrans after being used three times

Entry	Ar	Yield/%[a] per run		
		First	Second	Third
IVc	4-ClC_6H_4	93	93	92
IVf	4-$MeOC_6H_4$	84	82	81
IVg	4-MeC_6H_4	80	79	78

a) Isolated yield.

PPA–SiO_2 can act as a solid acid catalyst in the synthesis of tetrahydrobenzo[*b*]pyrans.

The reusability of the catalyst was also investigated. After completion of the reaction, the reaction mixture was filtered whilst still hot to separate the catalyst. The separated catalyst was washed with a small volume of cold water (5 mL), and hot absolute ethanol (10 mL), respectively, dried at 100 ℃ under vacuum for 2 h, and reused in the subsequent reactions. The results obtained are given in Table 6. As shown in this Table, the catalyst could be used at least three times with only a slight reduction in the catalytic activity.

Conclusions

In conclusion, we report a simple new catalytic method for the synthesis of tetrahydrobenzo[*b*]pyrans by a one-vessel cyclocondensation reaction of dimedone, aryl aldehydes, and malononitrile in water using PPA–SiO_2 as an efficient, reusable and environmentally acceptable heterogeneous catalyst. The catalyst can be recycled after simple handling, and used at least three times without any substantial reduction in its catalytic activity. High yields, short reaction times, ease of handling, low cost of the catalyst, environmentally non-harmful media and the absence of any hazardous organic solvents are just a few of the advantages of this procedure. Although Sun et al. (2010) reported the synthesis of these compounds using LiBr as a catalyst within a shorter time and higher yields, the catalyst contains the halogen atom, which, may under certain conditions, cause serious concerns. For example, the presence of bromide anions in water resources generates bromate anions during water treatment with oxidant agents (von Gunten, 2003) which are highly toxic to humans. At the same time, PPA–SiO_2 with recyclability presents no environmental problems. Therefore, this efficient synthesis can offer an environmentally friendly synthetic strategy for the synthesis of heterocyclic compounds. Furthermore, we try to prepare the model compound, *IVc*, on a larger scale in the presence of PPA–SiO_2 as the catalyst and water as the medium. The reaction was carried out by heating a mixture of dimedone (20 mmol), 4-chlorobenzaldehyde (20 mmol), and malononitrile (20 mmol) in the presence of PPA–SiO_2 (2.0 g) as the catalyst in water (50 mL). The result shows that the catalyst performs very well and the product *IVc* is obtained in 91 % yield. Hence, we believe that this catalyst for the synthesis of tetrahydrobenzo[*b*]pyrans can also be used in large-scale industrial applications and that it is better than any other catalyst (Jin et al., 2004; Mahdavinia et al., 2009).

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