

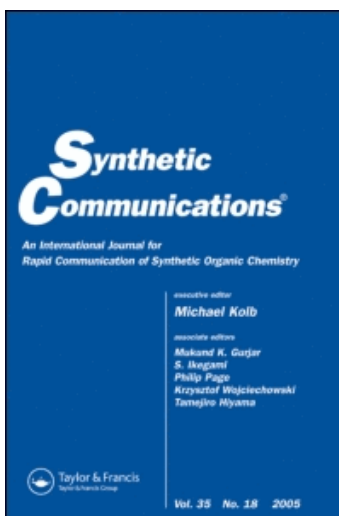
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Synthesis of Isobenzofuran-1(3*H*)-ones with the Aid of Silica-Supported Preyssler Nanoparticles

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Abstract: Silica-supported Preyssler nanoparticles appear to be a new and efficient solid acid catalyst for an economical, and environmentally benign one-pot synthesis of 3-substituted phthalides.

Keywords: Isobenzofuran-1(3*H*)-ones, one-pot synthesis, phthalaldehydic acid, silica-supported Preyssler nanoparticles, solvent-free condition

INTRODUCTION

Isobenzofuran and phthalides [isobenzofuran-1(3*H*)-ones] are integral parts of many naturally occurring substances. Isobenzofuran-1(3*H*)-ones possess a wide range of medicinal properties.^[1] In particular, 3-substituted phthalides are vital heterocyclic motifs in many bioactive compounds such as isocoumarins, anthraquinones, anthracyclines, and several alkaloids.^[2]

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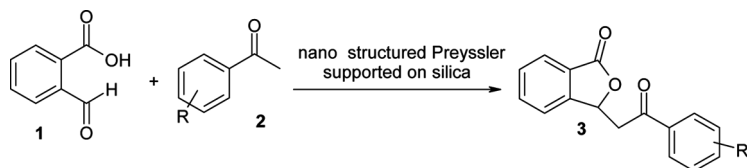
In view of their importance, various methods have been developed for the synthesis of phthalides [isobenzofuran-1(3*H*)-ones].^[1]

These methods include cyclization reactions catalyzed by strong acids such as trifluoroacetic acid^[3] and trifluoromethanesulfonic acid.^[4] Strong bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),^[5,6] sodium hydroxide (NaOH),^[7] and potassium hydroxide (KOH)^[8] are also used in the synthesis of 3-phenacylphthalides. However, these methods involve strong, corrosive, and harmful acids and bases, and high temperatures for the reactions are required. Thus, the development of a simple and efficient method under green reaction conditions for constructing of these heterocycles is still in demand.

Polyoxometalates (POMs) are metal-oxo anionic clusters whose chemical properties can be controlled by transition-metal substitution and the counteranion used. POMs have wide applications in many fields such as catalysis, medicine, magnetic properties, materials, surface chemistry, photochromism, and electrochromism, owing to their so-called "value-adding properties." These properties, combined with their ability to donate and accept electrons and their stability over a wide range of conditions, make them attractive candidates for catalysis. On the other hand, they are economically and environmentally attractive in both academic and industrial settings as useful acids and/or oxidation catalysts in various organic reactions because their catalytic features can be controlled at a molecular level.^[9]

In continuation of our efforts to explore the catalytic utility of heteropolyacid supported on silica gel,^[10–12] herein we report for the first time a direct and efficient method for the preparation of substituted isobenzofuran-1(3*H*)-ones from the reaction of phthalaldehydic acid, substituted acetophenones, and cyclic ketones using silica-supported Preyssler nanoparticles as a novel and efficient catalytic system (Scheme 1).

To determine the most appropriate reaction conditions and evaluate the catalytic efficiency of silica-supported Preyssler nanoparticles, the synthesis of **3a** (as model reaction) was carried out in various conditions. First, we tried the reaction without catalyst. When a mixture of



Scheme 1.

Table 1. Reaction of phthalaldehydic acid with acetophenone in the presence of a catalytic amount of silica-supported Preyssler nanoparticles in different solvents

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%) ^a
1	Ethanol	78	10	68
2	Acetonitrile	82	10	75
3	CHCl ₃	61	10	58
4	THF	88	10	67
5	Water	100	8	79
6	—	110	6	96

^aYields were analyzed by GC.

phthalaldehydic acid and acetophenone was stirred (oil bath, temperature 110°C) for 18 h in the absence of silica-supported Preyssler nanoparticles, no conversion was detected. This observation indicated that a catalyst is necessary for this transformation.

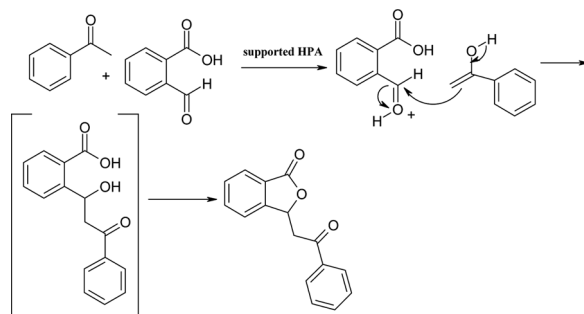
To study the effect of solvent on the yield of this reaction, the model reaction was carried out in various solvents and a solvent-free system using 0.03 mmol of silica-supported Preyssler nanoparticles as the catalyst. As shown in Table 1, the best results in terms of yield and time were achieved in solvent-free conditions.

To investigate the effect of silica-supported Preyssler nanoparticles, we carried out comparative experiments with some silica-gel-supported heteropolyacids, and the comparative results are summarized in Table 2.

Comparison of silica-supported Preyssler nanoparticles, H₃[PMo₁₂O₄₀]/SiO₂, H₄[PMo₁₁VO₄₀]/SiO₂, and H₃[PW₁₂O₄₀]/SiO₂ shows that silica-supported Preyssler nanoparticles led to greater yields. This observation can be explained by considering the reaction mechanism. As shown in Scheme 2, the first stage of the reaction is the activation

Table 2. Comparative study of various supported heteropolyacid catalysts for the preparation of **3a** at 110°C

Entry	Catalyst	Amount of catalyst (mmol)	Time (h)	Yield (%)
1	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ nanoparticles	0.03	6	96
2	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂	0.05	8	89
3	H ₃ [PMo ₁₂ O ₄₀]/SiO ₂	0.05	9	79
4	H ₄ [PMo ₁₁ VO ₄₀]/SiO ₂	0.05	9	73
5	H ₃ [PW ₁₂ O ₄₀]/SiO ₂	0.05	8	84



Scheme 2.

of the carbonyl group by an acidic catalyst. According to previous reports, the acidic property of the Preyssler type of heteropolyacids is greater than the Keggin.^[13]

The efficiency of $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ as catalyst was also studied for this reaction, but the model reaction (reaction of phthalaldehydic acid and acetophenone) did not go to completion in the presence of these catalysts even after long reaction times (8 h) and more amounts of catalyst (Table 2).

In $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ nanoparticles, the catalyst is supported into silica nano-particles. As the particle size decreases, the relative number of surface atoms increases, and thus activity increases. Moreover, because of quantum size effects, nanometer-sized particles can exhibit unique properties.

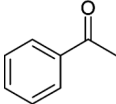
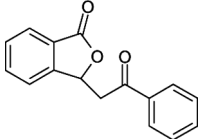
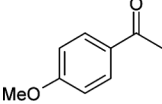
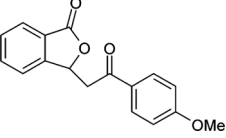
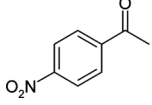
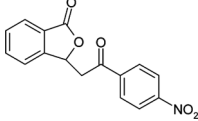
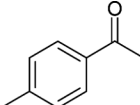
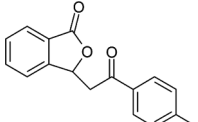
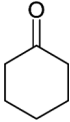
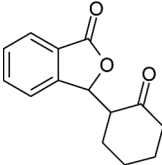
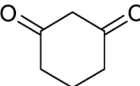
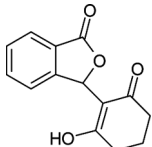
The scope and generality of this process were illustrated with respect to various substituted acetophenones and cyclic ketones, and the results are presented in Table 3.

For optimization of reaction time, the yield of reactions were compared at various times (1, 2, 4, and 6 h). The results indicate that in each reaction, increasing the reaction time from 4 h to 6 h increases the yield, but longer reaction times had no effect on the yields of reactions. Thus the reaction time was fixed at 6 h.

The insolubility of the catalyst in different organic solvents provided an easy method for its separation from the product. The catalyst was easily separated by filtration and reused with only a gradual decrease in its activity. For example, the reaction of phthalaldehydic acid and acetophenone afforded corresponding isobenzofuran-1(3H)-one derivative in 96, 94, and 89% yields over three successive runs.

In conclusion, we report a new and efficient method for the synthesis of functionalized isobenzofuran-1(3H)-ones by the one-pot cascade reaction of phthalaldehydic acid with substituted acetophenones and cyclic

Table 3. Synthesis of substituted isobenzofuran-1(3*H*)-ones by nano-structured Preyssler supported on silica-catalyzed cyclization of phthalaldehydic acid with ketones^a

Entry	Ketone	Product	Yield ^b (%)	Mp (°C)	Ref. mp (°C)
a			96	144–145	145 ^[3]
b			98	120 ^[3]	119–120
c			93	210 ^[3]	218–219
d			95	149 ^[3]	148
e			98	Oil	Oil ^[16]
f			96	219–220 ^[6]	219

^aReaction conditions: phthalaldehydic acid (0.8 mmol), ketone (1 mmol), nano-structured Preyssler supported on silica (0.03 mmol), 110°C, 6h.

^bGC yields, based on phthalaldehydic acid.

ketones. There are several advantages for the use of nano-structured Preyssler supported on silica as catalyst for this transformation, which include high conversions, lowcost, and reusability of the catalyst. In

addition, the use of supported catalyst under heterogeneous conditions facilitates ease of separation and recovery of the catalyst.

EXPERIMENTAL

Catalyst Preparation

Supported heteropolyacid catalyst was synthesized according to our previous report^[14] using a support in powder form (SiO_2) with an aqueous solution of the heteropolyacids. After stirring the mixture, the solvent was evaporated, dried at 120°C and calcined at 250°C in a furnace prior to use.

Silica-supported Preyssler nano-structures were obtained through the microemulsion method.^[15]

Synthesis of Isobenzofuran-1(3H)-ones: General Procedure

A mixture of phthalaldehydic acid **1** (0.8 mmol) and an appropriate ketone **2** (1 mmol) was heated under reflux (oil bath, temperature 110°C) with magnetic stirring until the mixture melted. Silica-supported Preyssler nanoparticles (0.03 mmol) were added to this mixture and stirred at 110°C for 6 h. The progress of the reaction was monitored by thin-layer chromatography (TLC). At the end of the reaction, the mixture was cooled, diluted with dichloromethane, and separated from the catalyst by filtration. Pure products were obtained after the addition of water to the organic layer. Two phases of solution were extracted and then the solvent was evaporated to afford isobenzofuran-1(3H)-ones **3**.

All compounds were known, and their physical and spectroscopic data were compared with those of authentic samples and found to be identical.^[3,6,16]

Reusing the Catalyst

The reusability of the catalyst was also investigated. The synthesis of **3a** was selected as the model reaction (Scheme 1). After completion, the catalyst was filtered off and washed three times with 10 ml of dichloromethane, dried at 80°C under reduced pressure (2 h), and subjected to the second run of the model reaction.

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