Microwave Assisted Synthesis of 2,4-Diphenyl-4*H*-chromen-5-one Using ZnCl₂/Montmorillonite K-10

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Abstract: α , β -Unsaturated carbonyl compounds and 1, 3-cyclohexanedione under microwave irradiation in the presence ZnCl₂/montmorillonite K-10 offers the corresponding 2,4-diphenyl-4*H*-chromen-5-one in excellent yield. Catalyst is recycled and reused for several times.

Keyword: α - β -Unsaturated carbonyl compounds, 1,3-Cyclohexanedione, 2,4-Diphenyl-4*H*-chromen-5-one, Microwave irradiation, ZnCl₂/ K-10.

Introduction

2,4-Diphenyl-4*H*-chromen-5-one is an important class of organic compounds, which received a considerable attention due to their wide range of biological activities. They possess antijuvenile hormone activity¹, antianaphylactic activity in trachea² as antiallergic, anti-inflammatory, anticancer agents and used in diabetic complications.

Methods used for the synthesis of title compounds were reported³ in acetic acid and phosphorous pentaoxide at 120⁰C, in methanol triethylamine at reflux temperature, in toluene *n*-heptane using⁴ anhydrous ZnCl₂, in benzene *n*-heptane and anhydrous ZnCl₂ at reflux temperature⁵ for 28-30 h, BF₃ etherate⁶ *etc*. All the above-mentioned methods have several limitations such as pro longer reaction time, strong acidic conditions and low yield. Consequently there is a scope for further work on this reaction towards mild reaction conditions, simple workup procedure, and better yield.

In the continuation of our work⁷ for synthesis of tetrahydro chromen-5-one using STO-DMF, the title compound synthesis was achieved by microwave irradiations in the presence of ZnCl₂/montmorillonite K-10. The corresponding 2,4-diphenyl-4*H*-chromen-5-one forms in excellent yield.

Chemical and pharmaceutical industries are always under pressure to develop more environmentally friendly organic reaction methodologies using heterogeneous catalysis. Microwave irradiation is used for a variety of organic reactions due to decrease in reaction time, cleaner reactions, easier work-up and better yield. Thus the microwave oven procedure is now well established in MORE chemistry⁸. Faster rate of organic reactions under microwave irradiation has been also reported in our earlier work⁹. Solvent free microwave assisted chemical reactions in combination of solid supported reagents was used to carry out a wide range of reaction in shorter times as compare to other conventional reaction methods.

Industrial interest has been focused on the use of montmorillonite K10-supported zinc chloride (zinc montmorillonite) heterogeneous catalyst. The use of such remarkable material has been firstly reported in 1989. It is used in several reactions^{10,11}, such as dehydration reaction, Beckmann rearrangement, synthesis of flavones, thiazoles, quinolones, nitriles, *etc.* Considerable attention has been focused on the use of montmorillonite K10-supported zinc chloride for the synthesis of 5-nitrofurfurylidine, fisher synthesis, in synthesis of alkyl halide from alkyl alcohol or alkyl ether and hydrogen halide, in a chloroformyl reaction of hydrogen chloride and formaldehyde, benzodiazepine¹², in an olefin polymerization, alkylation, preparation of 1,1-diacetates from aldehydes¹³, hydroamination, 3-aza-cope rearrangement *etc.*¹⁴.

Scheme 1

Experimental

ZnCl₂/montmorillonite K-10 catalysts was prepared according to the literature procedure^{13,14}. All reagents were obtained from commercial sources and used without further purification. Melting points were determined in open glass capillaries using electro thermal melting point apparatus and are uncorrected. The reactions were monitored by TLC using pre coated silica plates (Merck, silica gel 60F-254 on glass). Column chromatography was performed using Acme silica gel (100–200 mesh). A Samsung domestic microwave oven was used at 800-watt power for all the experiments.

Catalyst preparation

A requisite amount of Zinc chloride is dissolved in water at room temperature. Impregnate the solid support as montmorillonite K-10 so that the aqueous solution of zinc chloride is adsorbed on the surface of or in porous portion of the solid montmorillonite K-10. Excess of water was evaporated by heating, to load zinc chloride on montmorillonite K-10. Since zinc chloride has a high deliquescence, it deteriorates during storage before or after the preparation of catalyst. Therefore the prepared catalyst should be stored in sealed bottle or in dry room.

Synthesis of 7,8-dihydro-7,7-dimethyl-4-phenyl-2-p-tolyl-4H-chromen-5(6H)-one

A mixture of 3-phenyl-1-p-tolylprop-2-en-1-one (2.222 g, 10 mmol) (**1a**), 5, 5-dimethylcyclohexane-1,3-dione (1.402 g, 10 mmol) (**2a**) and ZnCl₂/montmorillonite K-10 (10 mmol%) in a 100 mL beaker was irradiated in a domestic microwave oven for a specified time period. The progress of reaction is monitored on TLC. After completion of

reaction, the reaction mixture was cooled and diluted with ethyl acetate (5 mL). The catalyst was filtered off and washed with ethyl acetate (2×5 mL). The catalyst is activated at 120°C for one hour and reused for other reactions with slight decrease in catalyst efficiency (Table 3). Combined filtrates were concentrated under reduced pressure to afford the crude 7,8-dihydro-7,7-dimethyl-4-phenyl-2-*p*-tolyl-4H-chromen-5(6H)-one (**3a**). The obtained crude product was further purified by column chromatography using chloroform: ethyl acetate (3:1) as an eluent.

Similarly the other 2,4-diphenyl-4H-chromen-5-one (**3b-3i**) were also prepared using the same method. The obtained products were identified by comparison with authentic samples and their melting points (Table 1).

Table 1. Synthesis of 2,4-diphenyl-4H-chromen-5-one catalyzed by ZnCl₂ and montmorillonite K-10.

Entry	α - β -unsaturated ketone (1)	1,3-Diketones (2)	Products (3)	Time, min.	M.P. °C (Reported)	Yield, % ^b
a				9	157 (162-163) ⁴	85
b				8.5	193 (188-190) ⁴	88
c				8	209 (213-214) ⁶	84
d				8,5	178 (175-176) ⁴	88
e				8	134 (131-132) ⁴	85
f				8.5	246 (248-249) ⁶	85

g				8.5	195 (192-193) ⁶	80
h				8	150 (153-154) ⁶	83
i				9	184 (186-187) ⁶	88

^bIsolated and unoptimized yield.

Results and Discussion

In a model (Scheme 1) reaction α - β -unsaturated carbonyl compounds (**1**) and 1, 3-cyclohexanedione (**2**) with ZnCl₂/montmorillonite K-10 catalysts was irradiated in microwave oven for a specific time. After usual work up it offered the pure compound (**3**). The catalyst is recycled for several times in subsequent reactions without change in its efficiency.

Synthesis of title compound using ZnCl₂/montmorillonite K-10 catalysts under microwave irradiations is rapid & ecofriendly process. The reaction takes place in two steps. In first step Michael addition of cyclic 1, 3 diketone to chalcone followed by cyclization of resultant diketo intermediate and formation of the product. Most of the reaction was completed within 8-9 minutes giving 90-95% yield of products. However the earlier reported method required strong acidic conditions³ and longer reaction time⁵. The suggested method is more suitable due to the shorter reaction time and easy workup. Use of ZnCl₂ catalyst alone in organic solvent required longer reaction time (Table 2). The best result was obtained with 10 mol% of ZnCl₂/montmorillonite K-10 catalysts. High amount of the catalyst does not improve the yield of products. Recovery of catalyst was very easy so that it can be reused for consecutive reactions without any significant loss of efficiency (Table 3). ZnCl₂/montmorillonite K-10 exhibited superior catalytic activity as compare to the unsupported salts such as ZnBr₂, ZnCl₂ in terms of regeneration and easy disposal. Furthermore, the homogeneous ZnCl₂ catalyst is least preferred by the industry because environmental pollution, safety and corrosion problems.

Table 2. Synthesis of 7,8-dihydro-7,7-dimethyl-4-phenyl-2-*p*-tolyl-4H-chromen-5(6H)-one (**3a**) catalyzed by ZnCl₂ under various conditions.

Entry	Solvent	condition	Time	Yield ^b , %
1	ZnCl ₂ -Toluene/ <i>n</i> -heptane	Reflux ⁴	28 h.	70
2	ZnCl ₂	MW	16 min.	80
3	ZnCl ₂ and montmorillonitK10	MW	8 min	92

^aReaction conditions:- 5,5-dimethyl-cyclohexane-1,3,dione (10 m mol), 3-phenyl-1-*p*-tolylprop-2-en-1-one (10 m mol), ZnCl₂(10 mol%) ^bIsolated and unoptimized yield.

Table 3. Recovery of ZnCl₂ loaded on montmorillonite K-10 catalyst in the synthesis of 2,4-diphenyl-4*H*-chromen-5-one

Entry	α - β -unsaturated ketone (1)	1,3-Diketone (2)	Products (3)	Yield, %		
				Recycle1	Recycle 2	Recycle3
1	1a	2a	3a	92	90	84
2	1b	2b	3b	93	91	85

Conclusion

In summary, we have been demonstrated an efficient and mild protocol for the synthesis of 2,4-diphenyl-4*H*-chromen-5-one using ZnCl₂ loaded on montmorillonite K-10 as a recyclable heterogeneous catalyst. Excellent yield of products were obtained and the catalyst is recycled and reused for several times. The procedure is simple, ecofriendly, solvent free and can be used as an alternative to the existing procedure.

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