



SYNTHESIS OF β -AMINO CARBONYL COMPOUNDS AND 5-UNSUBSTITUTED 3, 4-DIHYDROPYRIMIDINONES USING SOLID SUPPORTED $\text{Co}(\text{ClO}_4)_2$ UNDER SOLVENT FREE CONDITION

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ABSTRACT

Silica supported $\text{Co}(\text{ClO}_4)_2$ was prepared and found to be thermally stable over a long range of temperature. It was found to be an efficient, recyclable and heterogeneous catalyst for synthesis of both 5-unsubstituted 3, 4-dihydropyrimidinones and β -amino carbonyl compounds under solvent free condition. The simple procedure, high yield of desired products and solvent free reaction condition making it environment benign are important aspects of this protocol.

Key words: Silica supported $\text{Co}(\text{ClO}_4)_2$, Recyclable, High yields, Solvent free, Environment benign.

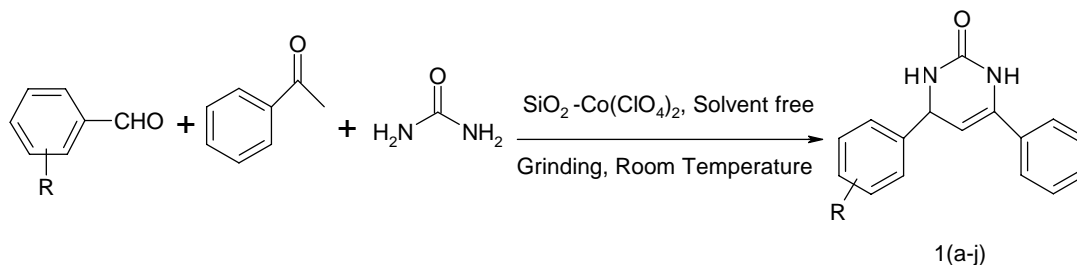
INTRODUCTION

Multi-component reactions have gained lot of importance in synthesis of organic compounds. By using these reactions, it is possible to produce desired complex organic molecule in a single step without involvement of intermediate reducing the reaction times and energy¹⁻³. Further, from economic and environmental points of views, uses of heterogeneous catalysts in various organic syntheses have gained lot of importance⁴. The heterogeneous catalysts are cost effective and easy to handle materials⁵⁻⁸. They exhibit high reactivity, greater selectivity, reduction in reaction times and easy recoverability from reaction medium⁹⁻¹². The solid-supported catalysts are the materials, which possess all the mentioned characteristics of heterogeneous catalysts due to which they find wide applications in organic synthesis¹³.

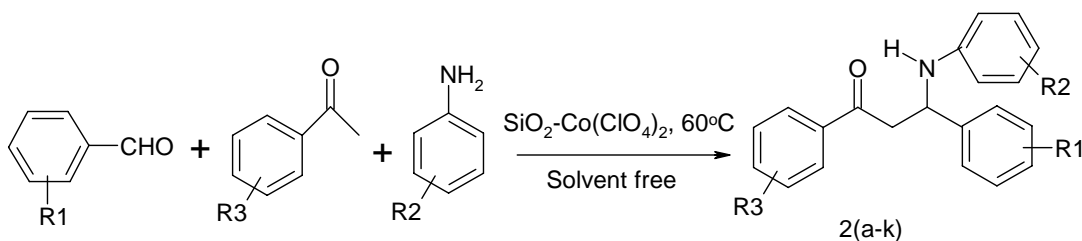
β -amino carbonyl compounds are basic structural units for the preparation of 1,3-amino alcohols,^{14,15} β -amino acids¹⁶. These compounds are used in the synthesis of various the antibiotics such as neopolyoxines and nikkomyocins^{17,18}. These biologically active organic compounds have been synthesized by using SmI_3 ,¹⁹ $\text{AuCl}_3\text{-PPh}_3$,²⁰ Amberlyst-15,²¹ bromo dimethylsulfonium bromide (BDMS),²² silica supported sulfuric acid²³ and p-TSA.²⁴ Similarly, 5-unsubstituted 3,4-dihydropyrimidinones show antiparasitic, antitumor, anti-inflammatory and antibacterial activities²⁵⁻²⁷. A number of Brønsted and Lewis acid catalysts such as trifluoroacetic acid,²⁸ cerium (III) chloride,²⁹ ytterbium chloride,³⁰ strontium (II) nitrate,³¹ L-proline,³² polyoxometalate³³ and hetero polyacids³⁴ are used to synthesize these compound.

Even if these protocols for the synthesis of β -amino carbonyl compounds and 5-unsubstituted 3, 4-dihydropyrimidinones possess their own merits, they suffer from one or other disadvantages such as use of costly chemicals, complex procedure, harsh reaction conditions, low yields etc. So there is still need to develop improved versions of methodologies in terms of procedure, nature of chemicals involved, yield and reaction time for synthesis of 5-unsubstituted 3, 4-dihydropyrimidinones and β -amino carbonyl compounds.

In this regard, we wish to report the synthesis of both 5-unsubstituted 3, 4-dihydropyrimidinones (**Scheme 1**) and β -amino carbonyl compounds (**Scheme 2**) using silica supported $\text{Co}(\text{ClO}_4)_2$ as catalyst under solvent free condition.



Scheme 1



Scheme 2

EXPERIMENTAL

Materials and methods

All chemicals and solvents were purchased from Sigma-Aldrich, Merck, and used without further purification. The reaction was monitored by TLC using 0.25 mm E-Merck Silica Gel 60F254 precoated plates. Melting points were taken in open capillaries and data was used without correction. All ^1H NMR spectra were recorded on 300 MHz Avance FT-NMR spectrometer. Tetramethyl Silane (TMS, $\delta = 0$) was used as an internal standard. All chemical shifts were given as δ values with reference to it and expressed as parts per million. IR spectra were recorded on Perkin-Elmer FTIR spectrometer with KBr pellets. Silica Gel (60-120 mesh) was used to prepare solid supported catalyst.

Preparation of silica supported $\text{Co}(\text{ClO}_4)_2$

Silica supported $\text{Co}(\text{ClO}_4)_2$ was prepared by using the prescribed method.³⁵ Its characterization involved Thermo gravimetric (TGA) analysis and surface area determination by standard BET technique.

General procedure for synthesis of 5-unsubstituted 3, 4-dihydropyrimidinones

A reaction mixture prepared by mixing an aromatic aldehyde (1 mmol), acetophenone (1 mmol, 0.112 mL) and urea (2 mmol, 2.130 g) with silica supported $\text{Co}(\text{ClO}_4)_2$ (0.06 g) was gently grinded in mortar with pestle of suitable size. The progress of reaction was studied by using TLC (System–A mixture of Pet ether and ethyl acetate in suitable proportions). The product was extracted in ethyl acetate (3 x 10 mL) and

catalyst was separated carefully. The extracts were dried over anhydrous Na_2SO_4 . The obtained crude product was purified by using Column Chromatography (Using Silica gel of 60-120 mesh size and mixture of Pet ether and Ethyl acetate in suitable proportions as system). All the 5-unsubstituted 3, 4-dihydropyrimidinones prepared using the same procedures were confirmed by comparing their melting point data with data available in literature. The separated catalyst was washed with ethyl acetate and used for three more cycles.

Spectral data of selected 5-unsubstituted 3, 4-dihydropyrimidinones

Entry-1 (1a) 3, 4-Dihydro-4, 6-diphenylpyrimidin-2(*IH*)-one

IR (KBr): 3228, 2926, 1694, 1605, 1456 cm^{-1} ; ^1H NMR (300MHz, CDCl_3): δ = 5.10 (d, 1H, CH), 5.50 (d, 1H, CH), 7.15–7.96 (m, 10H, ArH), 8.60 (s, 1H, NH), 9.07 (s, 1H, NH).

General procedure for synthesis of β -amino carbonyl compounds

A silica supported $\text{Co}(\text{ClO}_4)_2$ (0.08 g) was added in reaction mixture prepared by mixing an aromatic aldehyde (1 mmol), acetophenone/ketone (1 mmol) and aromatic amine (1 mmol). It was heated with stirring at 60°C for appropriate time. The progress of reaction was studied by using TLC. The reaction mixture was cooled to room temperature and diluted with ethyl acetate (3 x 10 mL) to extract product. The catalyst was separated carefully. The extracts were dried over anhydrous Na_2SO_4 followed by purification of product using Column Chromatography (Using Silica gel of 60-120 mesh size and mixture of Pet ether and Ethyl acetate in suitable proportions as system). The separated catalyst was washed with ethyl acetate and used for three more cycles. The prepared β -amino carbonyl compounds were confirmed by comparing melting point data with data available in literature.

Spectral data of selected β -amino carbonyl compounds

Entry-1 (2a) 1, 3-Diphenyl-3-phenylamino-propan-1-one

IR (KBr): 3378, 2920, 1669, 1288, 860, 750 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ = 3.47-3.32 (m, 2H), 4.98 (t, 1H), 6.51 (d, J 8.0 Hz, 2H, Ar-H), 6.63-6.69 (m, 1H, Ar-H), 7.04-7.00 (m, 2H, Ar-H), 7.20 (d, J 6.5 Hz, 2H, Ar-H), 7.26-7.23 (m, 1H, Ar-H), 7.41-7.38 (m, 2H, Ar-H), 7.51-7.45 (m, 1H, Ar-H), 7.57-7.53 (m, 2H, Ar-H), 7.84 (d, J 7.8 Hz, 2H, Ar-H).

RESULTS AND DISCUSSION

Characterization of catalyst [Silica supported $\text{Co}(\text{ClO}_4)_2$]

When catalyst and bare SiO_2 were analyzed by standard B.E.T. technique, a large decrease in surface area of SiO_2 was observed due to occupation of its active sites by $\text{Co}(\text{ClO}_4)_2$ species. As per the report of TGA analysis, the prepared catalyst was found to be thermally stable up to 350°C and could be used over a wide range of temperature. The prepared SiO_2 supported $\text{Co}(\text{ClO}_4)_2$ material was evaluated for its catalytic activity by using it in synthesis of 5-unsubstituted 3, 4-dihydropyrimidinones and β -amino carbonyl compounds.

Selection of catalyst for the synthesis of 5-unsubstituted 3, 4-dihydropyrimidinones and β -amino carbonyl compounds

No product formation was observed when model reaction for each Scheme was performed with bare SiO_2 . Even $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ failed to form any product when used as catalyst. So SiO_2 supported $\text{Co}(\text{ClO}_4)_2$ was tried as a catalyst.

The study of catalytic activity of SiO₂ supported Co(ClO₄)₂

The optimum conditions were established by selecting model reactions for each Scheme. Accordingly, a reaction between benzaldehyde (1 mmol, 0.101 mL), acetophenone (1 mmol, 0.112 mL) and urea (2 mmol, 2.130 g) to prepare 3, 4-Dihydro-4,6-diphenylpyrimidin-2(1H)-one was selected as model reaction for synthesis of 5-unsubstituted 3, 4-dihydropyrimidinones.

When model reaction was performed in a series of solvents, no satisfactory yield was obtained (Table 1, Entries 1 to 5). So reaction was tried under solvent free condition when excellent yield was obtained in short reaction time (Table 1, Entry 6). The amount of catalyst to be loaded to get satisfactory yield was found to be 0.06 g (Table 1, Entry 6).

Table 1: Optimization of reaction conditions for the synthesis of 3, 4-Dihydro-4,6-diphenylpyrimidin-2(1H)-one

Entry	Selection of solvent			Loading amount of catalyst (gm)		
	Solvent	Time (min)	Yield ^a (%)	Amount (g)	Time (min)	Yield ^a (%)
1	CH ₂ Cl ₂	> 180	N.R.	0.01	> 120	35
2	CHCl ₃	100	35	0.02	25	80
3	CH ₃ CN	120	45	0.04	20	85
4	C ₂ H ₅ OH	150	42	0.06	10	93
5	CH ₃ OH	> 180	40	0.08	10	93
6	Solvent free	10	93	0.06	10	93

^{aa} Isolated yields

By using optimum conditions thus established, the general applicability of the Scheme 1 was studied (Table 2).

Table 2: Synthesis of 5-unsubstituted 3, 4-dihydropyrimidinones using SiO₂ supported Co(ClO₄)₂ by grinding under solvent free condition at room temperature

Entry	R ^a	Product ^b 1(a-j)	Time (min)	Yield ^c (%)	Melting point (°C) (Literature value)
1	-H	1a	10	93	245-246 (244) ³⁷
2	4-OH	1b	20	89	255-257 (256) ³⁷
3	4-Cl	1c	22	90	266-267 (266) ³⁷
4	3-Cl	1d	22	89	211-212 (210-212) ³⁸
5	2-Cl	1e	25	88	260-263 (261-262) ³⁷
6	4-OCH ₃	1f	08	94	257-258 (258) ³⁷
7	3-OCH ₃	1g	10	93	255-257 (256) ³⁷
8	4-CH ₃	1h	10	95	248-249 (249) ³⁷
9	3-Br	1i	20	90	256-257 (257-258) ³⁷
10	4-F	1j	25	86	158-160 (159-161) ³⁸

^aAromatic aldehyde (1 mmol) was treated with acetophenone (1 mmol) and urea (2 mmol) in presence of SiO₂ supported Co(ClO₄)₂ as catalyst at room temperature; ^bAll products were confirmed by comparing melting point data with Literature values; ^cIsolated Yields

Different aromatic aldehydes reacted smoothly with acetophenone and urea in presence of SiO₂ supported Co(ClO₄)₂ as catalyst to form corresponding products in good to excellent yields in short reaction time (Table 2, Entries 1 to 10). Aromatic aldehydes bearing electron donating substituents gave maximum yield in short reaction time (Table 2, Entries 6, 7, 8). On the other hand, aromatic aldehydes with withdrawing substituents gave satisfactory yield in longer reaction time (Table 2, Entries 2, 3, 4, 9, 10). Ortho substituted aromatic aldehyde reacted sluggishly due to steric reason (Table 2, Entry 5). Thus, SiO₂ supported Co(ClO₄)₂ was proved to be an efficient catalyst for the synthesis of 5-unsubstituted 3, 4-dihydropyrimidinones.

The efficiency of SiO₂ supported Co(ClO₄)₂ was further proved when it was successfully used in synthesis of β -amino carbonyl compounds. By using a model reaction involving benzaldehyde (1 mmol, 0.101 mL), acetophenone (1 mmol, 0.112 mL) and aniline (1 mmol, 0.09 mL) to prepare 1, 3-Diphenyl-3-phenylamino-propan-1-one, optimum experimental conditions were established (Table 3) for **Scheme 2**.

Table 3: Optimization of reaction conditions for synthesis of 1, 3-diphenyl-3-phenylamino-propan-1-one

Entry	Catalyst	Amount (g)	Temperature (°C)	Solvent	Time (min/hrs)	Yield ^a (%)
1	SiO ₂ - Co(ClO ₄) ₂	0.02	30	Solvent free	1 Hr	45
2	SiO ₂ - Co(ClO ₄) ₂	0.04	40	Solvent free	45	60
3	SiO ₂ - Co(ClO ₄) ₂	0.06	50	Solvent free	40	65
4	SiO₂- Co(ClO₄)₂	0.08	60	Solvent free	15	92
5	SiO ₂ - Co(ClO ₄) ₂	0.1	70	Solvent free	15	92
6	SiO ₂ - Co(ClO ₄) ₂	0.08	60	Solvent free	15	92
7	SiO ₂ - Co(ClO ₄) ₂	0.08	60	C ₂ H ₅ OH	3.5 Hr	45
8	SiO ₂ - Co(ClO ₄) ₂	0.08	60	CH ₃ CN	3 Hr.	40
9	SiO ₂ - Co(ClO ₄) ₂	0.08	60	CH ₂ Cl ₂	1.2 Hr.	30
10	SiO ₂ - Co(ClO ₄) ₂	0.08	60	DMF	2 Hr.	NR
11	SiO ₂ - Co(ClO ₄) ₂	0.08	60	DMSO	2Hr.	NR

^aIsolated Yields

Thus, the most appropriate reaction conditions for the synthesis of β -amino carbonyl compounds was found to be the use of 0.08 gm of SiO₂ supported Co(ClO₄)₂ as catalyst under solvent free condition at 60°C. By using these experimental conditions, general applicability of Scheme 2 was checked (Table 4).

Thus, SiO₂ supported Co(ClO₄)₂ was found to be an effective catalyst for the synthesis of β -amino carbonyl compounds as a variety of reactants including cyclic ketones reacted smoothly and gave respective products in short reaction time with maximum yields (Table 4, Entries 1 to 11). The electron donating substituents were found to be activating aromatic aldehydes in terms of short reaction time and high yield (Table 4, Entries 4, 6, 8). The presence of electron withdrawing substituents in both aromatic aldehydes and amines found to be deactivating the reactants as reflected in longer reaction time and comparatively low yield (Table 4, Entries 5, 7, 9, 10).

Table 4: Synthesis of β -amino carbonyl compounds using SiO₂ supported Co(ClO₄)₂ under solvent free condition at 60°C

Entry	R1 ^a	R2 ^a	R3/Ketone ^a	Product ^b 2 (a-k)	Time (min)	Yield ^c (%)	Melting point (°C) (Literature value)
1	H-	H-	H-	2a	15	92	168-169 (168-170) ³⁹
2	H-	H-	4-CH ₃	2b	12	93	139-141 (139-140) ³⁹
3	H-	H-	Cyclohexanone	2c	18	90	136-137 (137-138) ³⁹
4	4-OCH ₃	H-	Cyclohexanone	2d	15	91	132-133 (133-134) ³⁹
5	H-	4-Cl	Cyclohexanone	2e	22	89	137-139 (137-138) ³⁹
6	4-CH ₃	H-	H-	2f	12	92	128-129 (129-130) ³⁹
7	H-	4-NO ₂	H-	2g	20	89	185-186 (184-185) ³⁹
8	4-OCH ₃	H-	H-	2h	10	93	135-136 (135-137) ³⁹
9	4-NO ₂	H-	H-	2i	20	88	102-103 (103-104) ³⁹
10	4-Cl	H-	H-	2j	25	89	119-120 (118-120) ³⁹
11	H-	4-Cl	H-	2k	20	89	168-169 (169-171) ⁴⁰

^aReactants (1mmol each) were reacted in presence of SiO₂ supported Co(ClO₄)₂ as catalyst under solvent free condition at 60°C; ^bAll products were confirmed by comparing melting point data with Literature values

^c Isolated yields

Study of recyclability of SiO₂ supported Co(ClO₄)₂

The prepared catalyst was found to be heterogeneous in reaction mixture. It was easily separated and used for three more turns for each Scheme. It was found to retain its catalytic activity for almost three more turns (Table 5).

Table 5: Study of recyclability of SiO₂ supported Co(ClO₄)₂

Entry	Run	Synthesis of 3, 4-dihydro-4,6-diphenylpyrimidin-2(1H)-one		Synthesis of 1, 3-diphenyl-3-phenylamino-propan-1-one	
		Time (min)	Yield ^b (%)	Time (min)	Yield ^b (%)
1	1	10	93	15	92
2	2	15	90	22	90
3	3	28	86	30	85
4	4	35	83	40	82

^{bb} Isolated yields

CONCLUSION

Thus, SiO₂ supported Co(ClO₄)₂ was successfully prepared using easily available chemicals and simple method. The obtained data for characterization confirmed the diffusion of Co(ClO₄)₂.6H₂O in SiO₂ followed by occupation of its active sites forming –Si-O-Co(ClO₄)₂ linkages. SiO₂ supported Co(ClO₄)₂ was easy to store and thermally stable up to 350°C. Moreover, due to its heterogeneous nature, its recyclization without loss of much catalytic activity was possible. This made overall procedure cost effective.

Further, the prepared material was found to be quite useful as catalyst in synthesis of both 5-unsubstituted 3, 4-dihydropyrimidinones and β -amino carbonyl compounds. In both Schemes, good to excellent yields were obtained in short reaction time.

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