

The use of bentonite in heterogeneous medium as an efficient recyclable catalyst in the synthesis of iminoesters

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Abstract: A new solid catalyzed synthesis of α -iminoesters is described. Various α -aminoesters react readily with aryl aldehydes to produce the corresponding imines in heterogeneous medium in the presence of bentonite (montmorillonite from Oust region of Algeria). The products have been isolated in good to excellent yields.

This new environmentally friendly catalyst provides significantly higher yields than traditional methods during relatively short reaction times for the preparation of the target compounds.

Keywords: Iminoester, catalyst, heterogeneous medium, bentonite.

Introduction

Imines are important intermediate compounds in organic and pharmaceutical chemistry. Iminoester derivatives are particularly important as precursor products or as building blocks for the synthesis of biologically active molecules¹.

In response to the increasing industrial importance of imines, several research works are directed toward the development of catalytic methods for their preparation. Many useful methods have been developed for the synthesis of imines from the corresponding carbonyl compounds and amines using both traditional liquid and contemporary "green" solid acid catalysts². The preparation of imines can be carried out by condensation of aldehydes and amines in the presence of desiccant, Lewis or Brønsted acid catalysts such as APTS^{3,4}, TiCl₄⁵, silica gel or alumina⁶, MgSO₄⁷, Na/CH₃OH⁸, BF₃(C₂H₅)₂O⁹. However, some of these catalysts suffer from the drawback of prolonged reaction times, toxic reagents, and low yields. The recovery and reusability of the catalyst is also a problem. Therefore, the cleaning processes and the use of eco-friendly, heterogeneous, have been under permanent attention. In the conditions of the use of recyclable catalyst¹⁰ in heterogeneous medium, we develop here a safe alternate method for the synthesis of imines.

Natural bentonite as a recyclable solid catalyst was dehydrated for many hours at 100°C and stocked at this temperature. The montmorillonite catalyst has been used in some organic reactions, such as oxidation¹¹, addition reactions to alkenes¹², epoxides and ethers¹³, Diels

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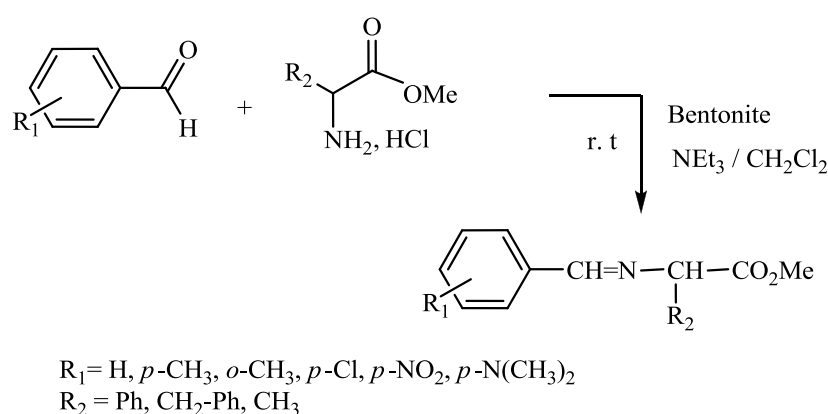
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Alder cycloaddition¹⁴, alkylation aromatic compounds¹⁵, synthesis of enaminic compounds¹⁶, thioacetals and thioenol ethers¹⁷, alkenes¹⁸, Friedel Crafts alkylation, dehydrogenation¹⁹.

With the aim to develop more efficient synthetic processes, we herein describe a practical and inexpensive method for the preparation of α -iminoester derivatives *via* the condensation reaction in the presence of this catalyst.

Results and discussion

In this program, we report a new simple and effective procedure for the synthesis of iminoester derivatives *via* the condensation reaction between aryl aldehydes and aminoesters at room temperature in the presence of bentonite as catalyst (Scheme 1).



Scheme 1

The bentonite coming from the west Algerian region is considered as a natural catalyst which can be easily prepared by dehydrating at 100°C for many hours and used for preparation of iminoesters. To prove the better catalytic activity of this clay, we have carried out a model study with benzaldehyde and methyl α -phenylglycinate using of catalytic process at room temperature (25°C) under aprotic solvent conditions (Table 1).

Table 1: Reaction of benzaldehyde and methyl α -phenylglycinate in CH_2Cl_2 in different catalytic conditions at room temperature.

Entry	Catalyst	Time	Yield ^a
1	none	48 h	00
2	Bentonite ^b	3 h	67
3	Dehydrated bentonite ^b	20 min	74

^a: isolated yield

^b: 28 mg of bentonite/mmol of benzaldehyde

Table 1 clearly demonstrates that the dehydrated bentonite is an effective catalyst in terms of reaction time and yield of obtained product. Then, we attempted the reaction of benzaldehyde derivatives with methyl phenylglycinate in the presence of this catalyst at room temperature.

To find out the optimum quantity of catalyst, the reaction of methyl phenylglycinate and benzaldehyde was carried out in CH_2Cl_2 using different quantities of bentonite (Table 2). Bentonite 15 mg/mmol of reagent gave an excellent yield in 20 min.

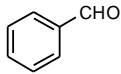
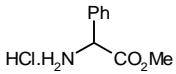
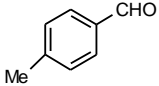
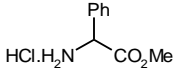
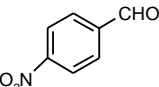
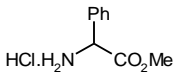
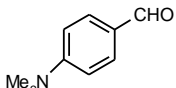
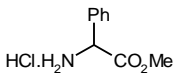
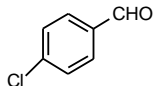
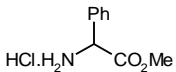
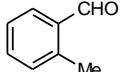
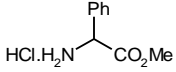
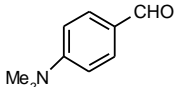
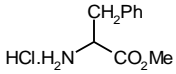
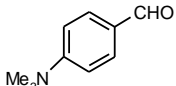
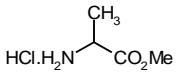
Table 2: Optimization amount of bentonite on the reaction of benzaldehyde and methyl phenylglycinate in CH_2Cl_2 at room temperature.

Entry	Catalyst (mg/mmol)	Time (min)	Yield ^a (%)
1	05	40	62
2	10	30	70
3	15	20	78
4	20	20	77
5	30	20	76

^a: Yields refer to the pure isolated products

Then, we attempted the reaction of benzaldehyde derivatives with α -aminoesters in the presence of this amount catalytic montmorillonite at room temperature. Thus, we prepared a range of iminoesters under the optimized reaction conditions: α -aminoester salt (1 mmol), triethylamine (1.1 mmol), and aryl aldehydes (1 mmol), in aprotic solvent CH_2Cl_2 (5 mL) in the presence of bentonite (15 mg). A serie of iminoesters were prepared in high to excellent yields (Table 3).

Table 3: Preparation of iminoesters

Entry	Aldehyde	Aminoester Hydrochloride	Time (min)	Yield (%)
1			20	78
2			45	70
3			20	89
4			60	68
5			30	79
6			45	68
7			60	75
8			60	87

In all cases, aromatic substituted aldehydes bearing either electron-donating or electron-withdrawing groups react successfully and gave the desired products in fair to good yields (68-89%) after 20-60 minutes. It was shown that the aromatic aldehydes bearing an electron withdrawing groups reacted faster than the other aromatic ones.

The mechanistic sequence of events can be explained by the suggested route: benzaldehyde reacts firstly with catalyst through interaction between oxygen and acidic sites of bentonite which activates the carbonyl group then its coupling with aminoester to produce an intermediate. After deshydration initiated by the catalyst, the desired iminoester is isolated as pure product.

We carried out a comparative study of our results with those reported by others authors. In the table 4, the results obtained by condensation of different aldehydes with different aminoesters are compared to some ones reported in the literature.

Table 4: Comparison result of bentonite with MgSO₄, MeOH/Na, APTS and BF₃Et₂O in the synthesis of some Schiff bases.

Entry	catalyst	Temperature (°C)	Time (h)	Yield(%)	Ref ^a
1	bentonite (CH ₂ Cl ₂)	25	0.3 – 1.0	68 – 89	-
2	MgSO ₄	25	24	75	[7]
3	MeOH/Na	25	12	72 – 85	[8]
4	CH ₂ Cl ₂ ^b	25	24	66 – 75	[20]
5	APTS (benzene)	80	06	60 – 85	[3,4]
6	BF ₃ Et ₂ O (Xylene)	110	06	87	[9]

^a: The references of known products in the literature.

^b: transimination reaction

To show the merit of the present work in comparison with reported results in the literature, we compared results of bentonite with those of MgSO₄, MeOH/Na, APTS, BF₃Et₂O and transimination reaction in the synthesis of iminoester derivatives. As shown in table 4, bentonite can act as effective catalyst with respect to reaction times and yields of the obtained products. Thus, the present protocol with bentonite catalyst is convincingly superior to the reported catalytic methods. Moreover, it's a simple, effective methodology and especially more practical than the other methods.

The reusability of the catalysts is an important benefit and makes them useful for commercial applications. Thus, the recovery and reusability of bentonite was investigated. The recyclability of the catalyst in the reaction of benzaldehyde and α -methyl phenylglycinate in the presence of bentonite (15 mg/mmol) was checked (Table 5). The separated catalyst can be reused after washing with CH₂Cl₂ and drying at 100°C. The catalyst was recovered with excellent yield and then can be used in the mentioned reaction for three times without any loss of its activity.

Table 5: Recyclability of the catalyst in the reaction of benzaldehyd and α -methyl phenylglycinate in the presence of bentonite:

Run	Yield (%)
1	78
2	76
3	77

Conclusion

In conclusion, we have demonstrated that bentonite is considered as a new efficient and green catalyst for synthesis of α -iminoesters derivatives. These latter, were prepared without loss of the ester function, *via* a condensation reaction of aryl aldehydes and α -aminoesters in the presence of catalytic bentonite in aprotic solvent at room temperature. This green procedure offers some advantages such as shorter reaction times, simple work-up, environmentally benign, excellent yield, cost effective recovery, and reusability of catalyst without appreciable loss of activity.

Experimental Section

General

All reagents were purchased from Merck and Aldrich and used without further purification. Montmorillonite of Maghnia was used without ulterior purification, excepted dehydration at 100°C.

All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopic data (IR, ^1H NMR, ^{13}C NMR spectra and UV). The NMR spectra were recorded on a Bruker AC 200 MHz instrument. The spectra were measured in CDCl_3 referred to TMS as internal standard. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Melting points were determined in open capillaries on a BUCHI 510 melting point apparatus. TLC was performed on silica gel polygram SIL G/UV 254 plates, with CH_2Cl_2 as eluent.

General procedure:

To a solution of aminoester salt (1 mmol) and triethylamine (1,1 mmol) in dichloromethane (5 mL), benzaldehyde derivatives (1 mmol) was mixed with bentonite (15 mg). The mixture was stirred at room temperature and the reaction progress was monitored by TLC. After completion, the reaction mixture was filtered and the heterogeneous catalyst was recovered. The filtrate was washed with water (3x10 mL), dried under MgSO_4 and concentrated to produce a solid which can be purified from precipitation in chloroforme- petroleum ether or by recrystallization in ethanol

The iminoesters **1**, **2**, **5** and **6** are known compounds, their spectral data and their melting points compare favourably with those cited in the literature^{3, 4, 7, 8, 9, 20,21}.

The other compounds **3**, **4**, **7** and **8** are not found in the literature. Their physical and spectral data are below:

Methyl N-*p* nitrobenzylideneiminophenylglycinate (3): Yield: 89%, mp:139°C

IR: (KBr) : 2936, 1722, 1629, 1602 cm⁻¹.

UV (CH₃CN):λ(nm) (ε): 217 (0.25), 223 (0.21), 283 (0.,62).

¹H NMR (CDCl₃) δ (ppm): 3.76 (s, 3H), 5.27 (s, 1H), 7.49 (m, 5H), 7.97 (d, J₂₋₃=6.52, 2H), 8.29 (d, J₅₋₆= 6.52, 2H), 8.41 (s, 1H).

¹³C NMR (CDCl₃) δ (ppm): 171.00, 161.45, 149.33, 140.99, 137.36, 129.40, 128.85, 128.45, 127.89, 123.81, 76.38, 52.65.

Méthyl N-*p*dimethylaminobenzylideneiminophenylglycinate (4): Yield: 68%, mp : 91°C

IR: (KBr): 3101, 2985, 1732.15, 1628.40, 1600.2 cm⁻¹.

UV (CH₃CN):λ(nm) (ε): 211 (0.08), 223 (0.12), 235 (0.09), 331 (0.26).

¹H NMR (CDCl₃) δ (ppm): 3.77 (s, 3H), 5.12 (s, 1H), 6.66 (d, J₂₋₃= 2.22, 2H), 7.68 (d, J₅₋₆=2,22, 2H), 7.53-7.26 (m, 5H), 8.20 (s, .H).

¹³C NMR (CDCl₃) δ (ppm): 171.69, 163.50, 152.41, 138.93, 130.24, 128.5, 127.80, 123.98, 111.46, 76.48, 52.43, 40.20.

Methyl *p*-N, N-dimethylaminobenzylideneiminophenylalaninate(7): Yield:75%, mp: 87°C

¹H NMR (CDCl₃) δ (ppm): 3.01 (s,6H), 3.16 (d,J₁₋₂=2.25 , 1H), 3.31 (d,J₁₋₂=1.95, 1H), 3.77 (s, 3H), 4.12 (s, 1H), 6.65 (d, J₂₋₃ =2.23, 2H), 7.57 (d, J₅₋₆ =2.23, 2H), 7.16-7.26 (m, 5H), 7.83 (s, 1H).

¹³C NMR (CDCl₃) δ (ppm): 171.72, 163.47, 130.06, 129.85, 128.27, 126.42, 123.98, 111.46, 75.25, 61.03, 40.25, 40.14, 14.26.

Methyl *p*-N, N-diméthylaminobenzylideneiminoalaninate (8): Yield: 87%, mp: 37°C

IR (KBr) : 2980, 2840, 1735, 1630, 1600 cm⁻¹.

¹H NMR (CDCl₃) δ (ppm): 8.16 (s, 1H), 7.70-6.63 (m, 4H), 4.13 (q, 1H), 3.73 (s, 3H), 3.02 (s, 6H), 1.51 (d, 3H).

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