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Synthesis of Arylidene (thio)barbituric Acid Derivatives using Bentonite as a Natural and Reusable Catalyst in Green Media

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Abstract

Known as a Lewis acid which acts as a natural catalyst, bentonite can be used to produce several arylidene (thio) barbituric acid derivatives through conducting a Knoevenagel reaction between aromatic aldehydes and (thio) barbituric acid. Water is considered as the medium for this reaction and the results are at arange of good to excellent over a reasonable reaction time. This method is natural and economic as well as convenient to work with, while the reaction time is also short. In addition to excellent results, this method is also environment-friendly due to the use of water as solvent that broadens the domain of organic synthesis in aqueous medium.

***Keywords*:** Natural catalyst, Bentonite ($Al_2O_3.4SiO.H_2$), Arylidene (thio) barbituric acids, Water media, Knoevenagel condensation.

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Introduction

A Knoevenagel condensation is a particular type of aldol condensation reaction in which active hydrogen compounds such as Meldrum's acid, dimedone, barbituric acid, malononitrile, cyanoacetamide, acetylacetone, ethyl acetoacetate, ethyl cyanoacetate, and cyanoacetic acid undergo nucleophilic addition reaction with a carbonyl group. This classic method is used to establish carbon-carbon bond but it also has the potential and functional characteristics required in organic synthesis and medicinal chemistry [1,2].

The value of green chemistry in the realization of sustainable development goals was introduced to the world in early 21st century. Selection of appropriate solvent is significant and crucial aspect of green chemistry [3]. Although some conventional methods applied in the synthesis of various organic materials contribute significantly in industries, they lead to massive chemical waste including carcinogen and pollutant solvents, on the one hand and corrosive as well as dangerous catalysts on the other. Accordingly, researchers in academic and industrial fields are currently concentrating on the development of some strategies under the principles of green chemistry [4].

Water is usually considered the most suitable solvent for organic transformation [5, 6] because it is both accessible and incurs lower costs while show in genvironmentally-friendly features as well. The rate of some organic reactions in organic chemistry can be significantly increased due to hydrophobic characteristics, while high polarity makes water unmixable with many organic compounds, making it convenient to work with. Furthermore, almost all living organisms and enzymes contain water as their natural solvent in which catalysis of biological reactions yields much better results than organic reactions [7]. Thus, scientists are currently interested in the use of catalysts derived from natural substances for organic synthesis.

Pyrimidine-2,4,6(1H,3H,5H)-trione or barbituric acid was synthesized and introduced for the first time in 1863 by Adolf von Baeyer through reduction of dibromo alloxan (5,5-dibromo barbituric acid) by hydrocyanic acid. Despite having no pharmacological activity of its own, substituted barbituric acid derivatives show good bioactivity [8, 9].

Barbituric acids have wide range of applications in the establishment of coordination and supramolecular compounds [10]. Different derivatives of 5-arylidene barbituric acid [11-13] have attracted great attention as starting materials, in synthesize of heterocyclic compounds such as oxadiazafavines, asymmetric disulphides, and also the derivatives of benzyl barbituric acid, dyes and nonlinear optical materials [14, 15].

5-Arylidene barbituric and thiobarbituric acids are active precursors which can be used to in given the fact that 5-arylmethylenepyrimidine-2,4,6-triones have a considerable range of biological and pharmacological activities, synthesis of derivatives of 5-arylidene (thio) barbituric acids in some

cases is reported as catalyst-free but researchers have sought to synthesize them using several catalysts such as PVP-Ni nanoparticles [16], sodium *p*-toluene sulfonate (NaPTSA) [16], BF_3/nano-γ-Al_2O_3 [17], $Ce_1Mg_xZr_{1-x}O_2$(CMZO) [18], ethylammoniumnitrate (EAN) [19], aminosulfonic acid [20], [bmim]BF_4 [21], NaOH/fly ash [22], taurine [23], cetyltrimethyl ammonium bromide [24], [DABCO]$(SO_3H)_2(HSO_4)_2$ [25], [DABCO]$(SO_3H)_2Cl_2$ [26], sulfonic acid functionalizednanoporoussilica (SBA-Pr-SO_3H) [27], copper oxide nanoparticles (CuO-NPs) [28], 2-amino-3-(4-hydroxyphenyl) propanoic acid (*L*-tyrosine) [29], $CoFe_2O_4$ nanoparticles [30], cetyltrimethylammonium bromide (CTMAB) [24], sodium acetate **(**CH_3COONa) [31], ZrO_2/SO_4^{-2} [32], $CoFe_2O_4$-NPs [33], sodium *p*-toluene sulfonate (NaPTSA) [16], silicotungstic acid [34], aminosulfonic acid [35], ethylammonium nitrate [19], *p*-dodecylbenzenesulfonic acid (DBSA) [36], $FeCl_3.6H_2O$ [37], nanoporous MMT-$HClO_4$, basic alumina [38] verjuice [4], succinimidiniumN-sulfonic acid hydrogen sulfate ([SuSA-H]HSO_4) [12],basic alumina/MW [39],non-catalyst/infrared irradiation [40], and chlorosulfonic acid, CdI_2 [41], Ni-SiO_2 [42], KF–Al_2O_3 [43]. Although the proposed protocols improved the synthesis of these heterocyclic compounds and displayed some advantages, some of them suffered considerable restrictions: for instance, besides resulting in low production, the catalyst is too expensive and its preparation requires harsh reaction conditions, while a large number of catalysts or reagents cannot be used again. Other limitations include the requirement to deal with the application of corrosive inorganic acids and/or polluting organic solvents, expensive catalysts and reagents, tedious work-up, necessity of excessive amounts of catalysts or reagents, long reaction times, low yields and non-reusability of the catalyst. Thus, a sustainable, suitable, effective, green and natural catalyst is recommended to perform the reactions according to green chemistry principles.

Bentonite is absorbent aluminum phyllosilicate clay which mainly consists of montmorillonite. A number of clays including montmorillonite-based minerals are famous for their structure and bentonite content and they include various cations such as crystalline hydrous alumino-silicates. Bentonite is formed by nanoparticles in a stratified configuration. Cations such as Na^+,K^+, Ca^{+2} and so on neutralize the net negative charged layers after which these cations arelocated in interlamellar space. These interlamellar cations can be conveniently replaced by other molecules and cations, making them suitable for adjustment applications. Stratified atoms are held through covalent bonds between molecules.

Replacement of liquid acids with solid acids is desirable in the chemical industries due to the simplicity of separation and recycling of solid acids which makes them eco-friendly and cost-effective. As nanostructured materials, bentonite is one of the best candidate substances to be used as support in design of catalysts because of their availability and low cost [44]. The use of water as

solvent system makes the protocol environmentally benign and expands the scope of aqueous-media organic synthesis. We decided to introduce an eco-friendly, simple, efficient, green and natural catalyst for the promotion of the proposed reaction.

Experimental

General

The required materials and solvents were provided by Merck company and no further refinement was needed. Thin layer chromatography (TLC) was applied in order to determine the purity of the materials and specify the reaction development. The output was totally associated with the isolated products. An Electrothermal 9100 was used to determine the melting points, while records of infrared spectra were prepared on a Perkin-Elmer 240-C Fourier-transform Infrared (FT-IR), after which measurements were performed as KBr discs. Records of ^{1}H NMR spectra were provided on a Bruker Avance spectrometer at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR in $CDCl_3$, while tetramethylsilane was considered as internal standard.

The general process of preparing derivatives of benzylidene (thio)barbituric acid

In a 50 mL round-bottomed flask a mixture of aldehyde (1 mmol), (thio)barbituric acid (1 mmol) and bentonite (%25 mol, 0.112 g) was stirred and heated at 90 ℃ in water.The reaction was completed under TLC control, using n-hexane/EtOAc (3:2). Subsequently, filtration of the mixture was performed. Ethanol and water were used to purify the product, eliminate the excess Meldrum's acid and benzaldehyde and then the solution of the precipitates in DMSO was used to separate catalyst and product. Finally, the unrefined product was available after the materials were dried at room temperature.

1,2-Bis(2 - (2 - ((tetrahydro - 2,4,6 - trioxopyrimidin - 5(6H) - ylidene)methyl)phenoxy)ethoxy)ethane **(3t):**

Yield: 90 %. M.P. 220–225 °C. IR (KBr) (ν_{max},,cm^{-1}):3.217, 3.074, 1.751, 1.708,1.679, 1.561.^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.64 (4 H, *s*, 2 CH_2–O), 3.76-3.79 (4H,m, *J* = 4.8 Hz, 2 CH_2–O), 4.19-4.22 (4H, m, 2 CH_2–O), 6.96 (2H, t, *J* = 7.4 Hz, H-Ar), 7.10 (2H, d, *J*= 8.4 Hz, H-Ar), 7.45-7.50 (2H, m, H-Ar), 7.98 (2H, *dd*, *J* = 7.8, 1.2 Hz, H-Ar), 8.52 (2H, *s*, 2 = CH), 11.15 (2H, *s*, 2 NH), 11.32 (2H, *s*, 2 NH) ppm.^{13}C NMR (100 MHz, DMSO-d_6) δ = 68.1, 68.8, 70.0, 112.1, 118.6, 119.5, 121.9, 130.1, 132.5, 134, 150.0, 150.2, 158.3, 161.4, 163.4 ppm.

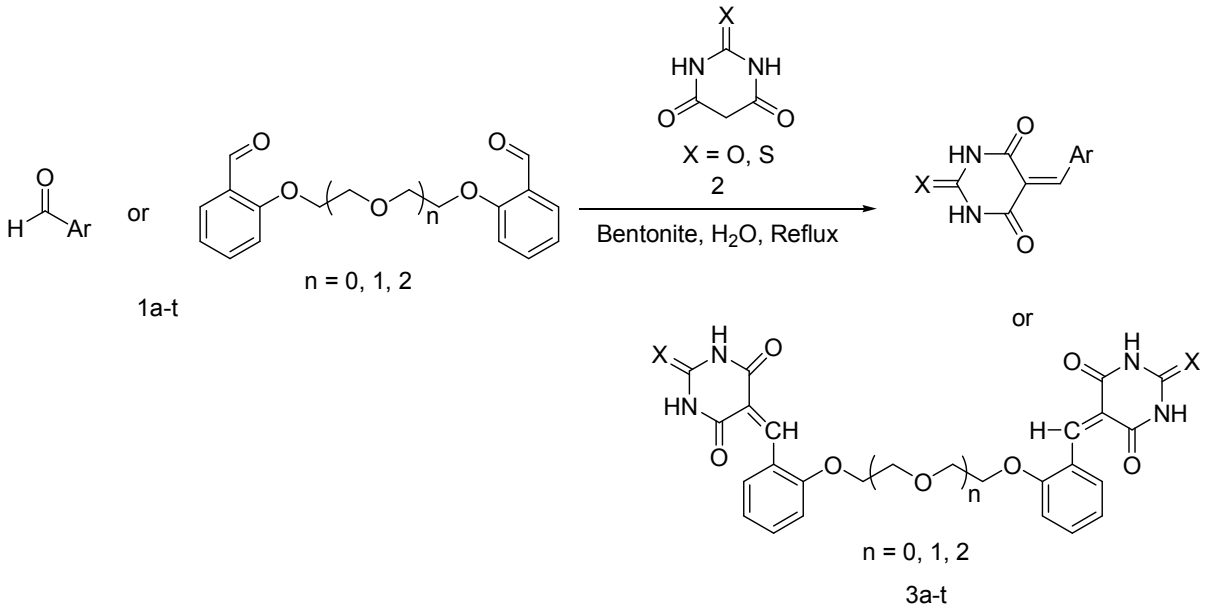
5-(4-Methoxybenzylidene)pyrimidine-2,4,6(1H,3H,5H)-trione(**3d**):

Yield: 96%. M.P.298-299 ℃. IR (KBr) (cm^{-1}): 3209, 1728, 1673. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.65 (3H, s, OCH_3), 7.07 (2H, d, J = 9.2 Hz, H-Ar), 8.26 (1H, s, = CH), 8.37 (2H, d, J= 7.6 Hz, H-Ar), 11.17 (1H, s, NH), 11.29 ((1H, s, NH) ppm.

Results and discussion

The present paper aimed at investigating the effect of $Al_2O_3.4SiO.H_2$ which is a natural, green, reusable and inexpensive catalyst, considerably capable of catalyzing the solution of (thio) barbituric acids bioactive derivatives in water as the medium (scheme 1).

Following the previous study [36, 45] and according to the Lewis acidity power of bentonite, the effects of $Al_2O_3.4SiO.H_2$ on the synthesis of the specific derivatives of pyrimidine were examined in this study.



Scheme 1. Synthesis of arylidene (thio)barbituric acidderivatives.

Table 1. Optimization of reaction conditions for preparation of 5-arylidene (thio) barbituric acid derivatives, in the presence of bentonite in aqueous media.[a]

Entry	Catalyst	Solvent	Tem(^{0}C)	Time(min)	Yield(%)
1	------	CH_3OH	r.t.	30	60
2	Bentonite %20	CH_3OH	r.t	25	60
3	Bentonite 20%	C_2H_5OH	r.t	25	55
4	Bentonite 20%	H_2O	r.t	20	92
5	Bentonite 5%	H_2O	90	7	45
6	Bentonite 10%	H_2O	90	7	63
7	Bentonite 15%	H_2O	90	7	74
8	Bentonite 20%	H_2O	90	7	85
9	Bentonite 25%	H_2O	90	5	97
10	Bentonite 30%	H_2O	90	5	98
11	Bentonite 25%	CH_3OH	90	120	72
12	Bentonite 25%	C_2H_5OH	90	100	67
13	Bentonite 25%	H_2O: CH_3OH	90	45	80
14	Bentonite 25%	H_2O: C_2H_5OH	90	15	73
15	Bentonite 25%	DMSO	90	110	78
16	Bentonite 25%	CH_2Cl_2	90	N.R	N.R
17	Bentonite 25%	$CHCl_3$	90	N.R	N.R
18	Bentonite 25%	CH_3CN	90	Incomplete	Trace

[a] *Reaction conditions: 4-dimethylaminobenzaldehyde (1.0 mmol), barbituric acid (1.0mmol), solvent (8 mL) and required amount of the catalyst(25% mmol).*[b]*The yields are related to the isolated products.*

Initially, 4-aminobenzaldehyde and (thio) barbituric acid were selected to synthesize 5-benzylidene barbituric acid derivatives in order to optimize the method. In the first step, the reaction was studied in CH_3OH in the absence of catalyst (table1, entry1) and the results indicated a slow process according to expectations. Short time and yield improvement were observed after introducing bentonite as Lewis acid to the reaction mixture. The most desirable results were obtained after optimizing the reaction conditions such as the amount of solvent and catalyst, along with the required time, while water temperature was set at 90℃ and a 25% catalyst was used (table1).

It is worth noting that water and ethanol mixture was examined, and the findings showed a significant decrease in the reaction time, which could be possibly due to solubility of (thio) barbituric acid. Using ethanol can lead to the removal of (thio) barbituric acid from the homogeneous phase of the reaction because of its solubility in water.

After improvement of the reaction conditions(Table2), a variety of aldehydes (such as those donating or withdrawing electrons) were used along with diethylene and triethylene ether-based aromatic and also (thio) barbituric acid as a homologue of a barbituric acid which contains sulfur

for the synthesis ofother derivatives. A review of the related literature indicates that the presence of thiobarbituric structure and ethylene ether groups in benzylidene barbituric acids could promote biological activity [46]. Generally, all reactions resulted in high to excellent range of products in a desirable time period and no high costs were incurred for chromatographic methods. Overall, introduction of thiobarbituric acid would lead to shorter reaction time; however, aldehydes did not show any significant alternative effects in these types of reaction (Table2).

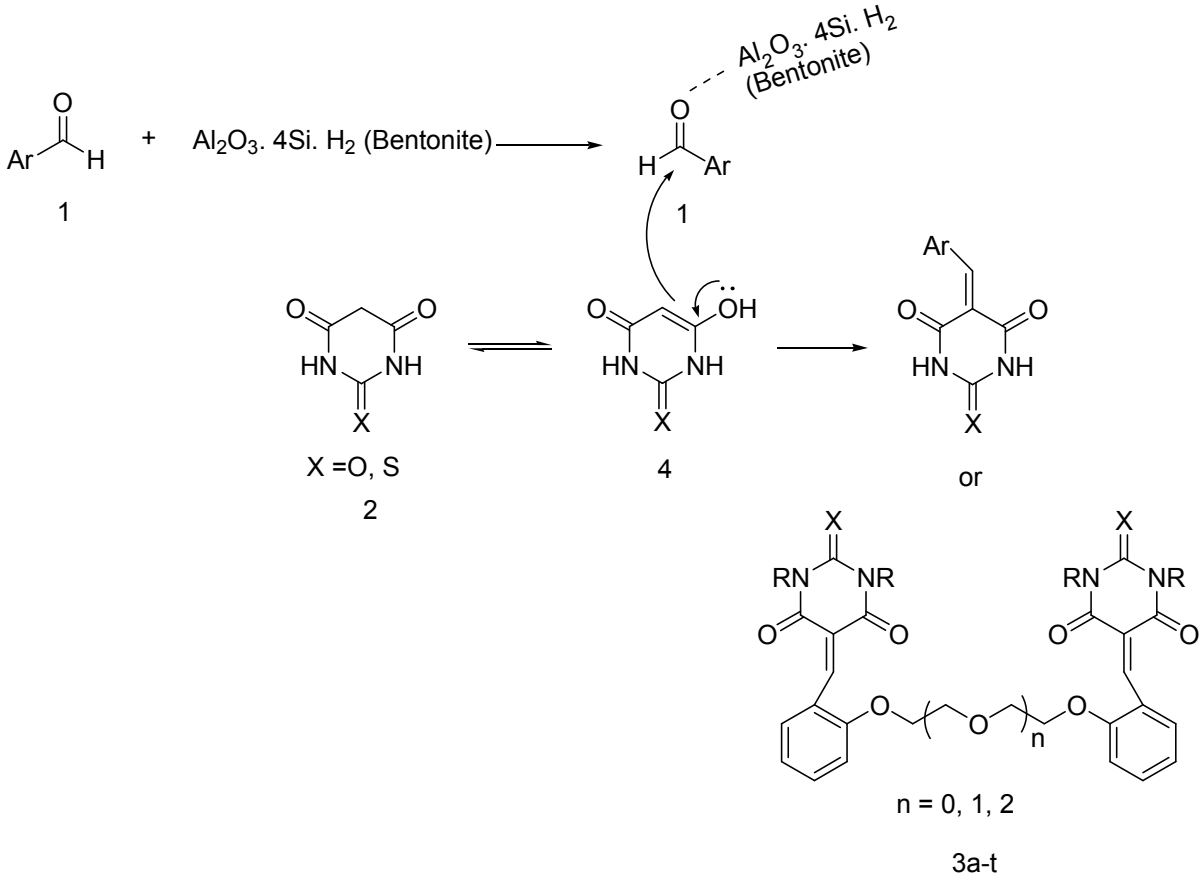
Table 2. Synthesized benzylidene (thio) barbituric acid derivatives via Knoevenagel condensation. [a]

Entry	R(aldehyde)	X	Product	Time(min)	Yield(%)	$m.p.$ (℃)	
						Observed	***Reported*** [$ref.$]
1	2-$NO_2C_6H_4$-	O	3a	10	96	272-276	274-276[47]
2	4-$(CH_3)_2NC_6H_4$-	O	3b	5	98	280-282	281-282 [47]
3	3-$NO_2C_6H_4$-	O	3c	20	92	228-231	231-233 [47]
4	4-$CH_3OC_6H_4$-	O	3d	5	92	300-302	306-308 [47]
5	4-OHC_6H_4-	O	3e	5	90	>300	>300 [47]
6	4-ClC_6H_4-	O	3f	10	90	296	298 [47]
7	2-ClC_6H_4-	O	3g	10	91	261	268 [47]
8	2-$OCH_3C_6H_4$-	O	3h	5	93	263-266	268-269[47]
9	4-$NO_2C_6H_4$-	O	3i	25	94	271-273	272-274[48]
10	3-$NO_2C_6H_4$-	S	3j	17	95	258-260	261-263 [4]
11	2-$NO_2C_6H_4$-	S	3k	17	96	246-247	247-248 [25]
12	4-ClC_6H_4-	S	3l	3	96	289-290	291-292 [25]
13	4-$OCH_3C_6H_4$-	S	3m	5	95	>300	>300 [25]
14	2-$(OH)C_6H_4$-	O	3n	15	93	247-249	249-250 [25]
15	C_6H_5CH=CH-	O	3o	1	98	267-270	268 [25]
16	4-$(CH_3)_2NC_6H_4$-	S	3p	10	95	>300	>300 [25]
17	C_6H_5-	O	3q	5	97	252-255	255-256 [47]
18	C_6H_5-	S	3r	10	95	270-273	271-272 [25]
19	$C_{16}H_{14}O_4$	O	3s	7	97	293-295	295[45]
20	$C_{20}H_{22}O_6$	O	3t	8	98	220-224	220-225 [46]

[a]Reaction conditions: bentonite (25 mol%, 0.112 g), solvent: H_2O (90℃).

In the present study, the melting points were compared against the reports in the relevant literature and in two cases ^{1}H NMR and ^{13}C NMR spectrum of the product 3t were used to extract the structures of compounds 3a-t. The ^{1}H NMR spectrum of the product 3t indicated a significant peak in δ= 3.65 ppm for methoxy group and one singlet in δ = 8.26 for the = CH olefin proton, while two singlets were also evident, pertaining to NH protons at δ: 11.17, 11.29ppm.The phenyl protons lead to prominent characteristic signals within the spectrum's aromatic area (δ = 7.07 and δ =8.37 ppm) in two doublets arising para substitution. These resonances are presented in experimental section.

The mechanism proposed for the aforementioned reactions is illustrated in scheme 2, according to which enolized (thio) barbituric acid (4) rushes toward aldehyde (1) when bentonite is present. It should be mentioned that aldehyde is also activated by Lewis acid catalyst. Arylidene (thio) barbituric acid derivative (3a-t) can be obtained after removal of water molecule.



Scheme 2. Plausible mechanism for the arylidene (thio) barbituric acid derivatives using bentonite as a natural and reusable catalyst.

Comparison of the catalytic ability

A comparison of the results obtained from the proposed methods with those reported in the literature can be observed in table3. Utilization of bentonite has made the catalyst relatively green in comparison to some others, and bentonite as catalyst has some advantages including high and excellent reusability. Furthermore, the presented catalyst does not show the disadvantages associated with using expensive starting materials, harsh reaction conditions, chromatographic purification, and the use of inorganic acids and organic solvents.

Table 3. Comparation of our result with some of these reported in literature for the synthesis of arylidene barbituric acid.

Entry	Catalyst	Conditions	Time (min)	Yield (%)[a]	Ref
1	PVP-Ni-NPs	Ethylene glycol /50℃	10-15	93	[15]
2	BF_3/nano-γ-Al_2O_3	Ethanol/r.t.	30	84	[17]
3	NH_2SO_3H	Grinding-laying	180	93	[20]
4	CH_3COONa	Grinding	10	91	[48]
5	CMZO	Ethanol /60-70℃	60	85	[18]
6	NaOH	Fly ash /water 70-80℃	35	86	[22]
7	Verjuice	60℃	7	96	[4]
8	[H_2-pip][H_2PO_4]	H_2O/ethanol (1:1) 80℃	20	96	[49]
9	Fe_3O_4@SiO_2-Propy-Pip-SO_3H.HSO_4	H_2O/80°C	15-90	90-98	[47]
10	Nanoporous MMT-$HClO_4$	H_2O/70℃	4	94	[38]
11	*P*-Dodecylbenzene sulfonic acid (DBSA)	H_2O/Reflux	67	62	[36]
12	Taurine	Water/90 ℃	9	96	[23]
13	Nanoporous MMT-$HClO_4$	H_2O/70 °C	4	94	[38]
14	[DABCO]$(HSO_3)_2(HSO_4)_2$	Water, r.t.	5	94	[25]
15	[DABCO]$(SO_3H)_2Cl_2$	80 ℃	6	90	[26]
16	Bentonite (Al_2O_3.4SiO.H_2)	90℃/H_2O	5-25	90-98	This work

[a] Isolated yields.

Reusability of the catalyst

The same conventional reaction (table2, entry1) was replicated in improved reaction conditions as model reactions in order to find out whether the catalysts could be reused. The reaction mixture filtration was performed after one model reaction was run in optimal conditions. Subsequently, the precipitate obtained was dissolved in DMSO so that the catalyst could be separated. According to table4, no considerable changes were reported in terms of yield and time even after four successive runs. Bentonite could be efficiently reused and was highly stable in water as the medium.

Table 4. Reusability of the catalyst in the preparation of 5-arylidene barbituric acid derivative of 4-aminobenzaldehyde.

Run	Yield of 3n (%)
First of renewed catalyst	98
Second of renewed catalyst	92
Third of renewed catalyst	92
Fourth of renewed catalyst	90

Conclusion

In conclusion, bentonite was proposed as a novel and effective natural catalyst in the synthesis of derivatives of benzylidene (thio) barbituric acid. Synthesis of the desired products was performed in

a reasonable reaction time with excellent results. The method proposed here does not have disadvantages such as costly starting materials, considerably difficult conditions to work with, requirement of chromatographic refinement, and application of inorganic acids along with organic solvents, while it has also the advantage of being recoverable.

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