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## A facile synthesis of 5-arylidene barbituric/thiobarbituric acid derivatives catalyzed by NaOH/fly ash

Lakshman S.Gadekar<sup>1\*</sup>, Machhindra K.Lande<sup>2</sup><sup>1</sup>Department of Chemistry, Padmabhushan Vasantdada Patil College Patoda, Dist. Beed (MS) - 431004, (INDIA)<sup>2</sup>Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (MS) - 431004, (INDIA)

E-mail: lsgadekar@rediffmail.com

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### ABSTRACT

A new route to obtain 5-arylidene barbituric/thiobarbituric acid derivatives is reported using a fly ash. It was modified by fusion with NaOH and characterized by XRD, FT-IR spectroscopy. It has been found that modified fly ash shows efficient catalytic property in the synthesis of 5-arylidene barbituric/thiobarbituric acid derivatives by Knoevenagel condensation of aromatic aldehydes with barbituric/thiobarbituric acid in aqueous medium. The method is simple, high yielding and cost efficient.

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### KEYWORDS

Fly ash;

Fusion;

XRD;

FT-IR;

Knoevenagel condensation.

### INTRODUCTION

Barbituric acid and its derivatives are associated with a number of biological activities such as antibacterial, hypotensive and sedatives<sup>[1]</sup>. Also it acts as hypnotic and anaesthetic agents<sup>[2]</sup>. Benzylidene barbituric acids are useful as potential organic oxidizer for the asymmetrical synthesis of disulfides<sup>[3]</sup>. Some of them have been recently studied as nonlinear optical materials<sup>[4]</sup>.

As a result of their importance from a pharmacological, industrial and synthetic point of view, there has been increasing interest in the development of efficient methodologies for the synthesis of 5-arylidene barbituric/thiobarbituric acid *via* Knoevenagel condensation reaction. Generally they are synthesized by condensing barbituric acid with aldehydes under conventional reflux conditions in aqueous medium<sup>[5]</sup>. In past decades many synthetic methods<sup>[6-8]</sup> for the preparation of these

compounds have been reported and uses variety of catalysts such as aminosulfonic acid<sup>[9]</sup>, NH<sub>4</sub>OH/AcOH, K-10 clay, silica gel, basic alumina, NaCl, KSF clay, KSF NaCl<sup>[6]</sup>. Many of these methods involve expensive reagents, higher temperature and lower yields. However, the research continues for the mild, efficient and versatile method for the synthesis of 5-arylidene barbituric/thiobarbituric acid.

The Knoevenagel condensation of aldehydes with active methylene compounds is an important and widely employed carbon-carbon bond formation in organic synthesis<sup>[10]</sup> with numerous applications in the synthesis of the fine chemicals and in synthesis of carbocyclic as well as heterocyclic<sup>[11]</sup> compounds of biological significance. The reactions are usually catalyzed by bases such as amines, ammonia or sodium ethoxide in organic solvents. Lewis acids<sup>[12]</sup>, surfactants<sup>[13]</sup>, zeolites<sup>[14]</sup> and heterogeneous catalysts<sup>[15]</sup> have also been employed to catalyze the reactions.

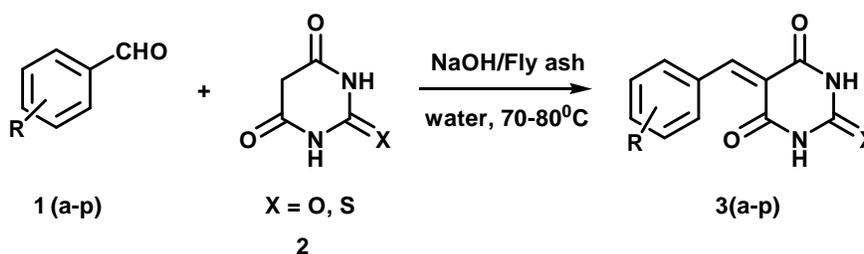
The development in catalysts during last few decades have been mandated mainly by considerations related to the abatement and prevention of pollution conservation of raw materials and eco-friendly production of fine chemicals. With growing ecological concern chemical procedures have been subjected to increasing pressure to minimize the dispersion of waste chemical.

In recent years, fly ash attracts attention of chemist due to its abundant availability through thermal power plant. Fly ash is the solid waste residue produced from coal, oil, and biomass combustion. Large quantities of fly ash are produced in electric power plants throughout the world every year. Efficient disposal of coal fly ash is a worldwide issue. The fly ash produced from the burning of pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected from flue gas by means of electrostatic precipitators, baghouses, or mechanical collection devices such as cyclones. Because of variations in coals from different sources, as well as differences in the design of fired boilers, not all fly ash is the same.

In past two decades, a great deal of effort has been conducted for the application of fly ash as value-added

products, these major applications include building and construction materials such as cement<sup>[16]</sup>, geopolymer<sup>[17]</sup>, ceramic material<sup>[18]</sup>, zeolite synthesis<sup>[19]</sup>, nuclear waste stabilization<sup>[20]</sup>. Except the utilization in construction material, no other applications have put into practice thus more efforts are required to explore new applications of fly ash. In recent years, more and more research has been carried out to explore the applications of fly ash in heterogeneous catalysis in Knoevenagel condensation, Biginelli, Hantzsch reaction, Beckmann rearrangement, formation of Schiff bases<sup>[21]</sup> and 1,2,4,5-Tetrazines<sup>[22]</sup>. It also used as solid support<sup>[23]</sup> in H<sub>2</sub> production.

In continuation of our work on synthesis of organic compounds using solid catalyst<sup>[24-26]</sup>, herein, we wish to report synthesis of 5-arylidene barbituric/thiobarbituric acid by condensation of aromatic aldehydes with barbituric acid using modified fly ash. The purpose of present investigation is to activate the as received fly ash by chemical method followed by thermal method and to study the influence of activated fly ash to catalyze condensation reaction. Activated fly ash was shown to be one of the most efficient for this reaction.



Scheme 1

## EXPERIMENTAL

All chemicals are commercially available from Aldrich and Rankem. The <sup>1</sup>H NMR spectra were recorded on 400 MHz instrument in DMSO as a solvent and the chemical shifts were reported with TMS as an internal standard. Melting points were measured in open capillaries in paraffin bath and are uncorrected.

### General procedure

A mixture of aromatic aldehydes (5 mmol), barbituric acid (5 mmol) and the catalyst, NaOH/fly ash (4%

weight with respect to the reactants) in water (20mL) was refluxed at 70-80°C for the time mentioned in TABLE 2. The reaction was monitored by TLC. After completion of reaction, the catalyst was filtered under hot conditions and washed with acetone several times. The filtrate poured on ice in beaker. The product solidifies; it was filtered, washed with water and recrystallized in ethanol to afford the product in excellent purity. All synthesized compounds were characterized with <sup>1</sup>H NMR and Mass spectroscopy. Also the melting points recorded were consistent with literature value.

### Spectral data of selected compound

3b) <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 7.54 (d, 2H),

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8.08 (d, 2H), 8.25 (s, 1H), 11.27 (s, 1H), 11.41 (s, 1H).

MS(ESI):  $m/z = 251(M+1)$

3c)  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 7.64-8.32 (m, 4H), 8.90 (s, 1H), 11.36 (s, 1H), 11.51 (s, 1H).

MS(ESI):  $m/z = 262(M+1)$

3i)  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 3.12 (s, 6H), 6.80 (d, 2H), 8.15 (s, 1H), 8.42 (d, 2H), 10.90 (s, 1H), 11.03 (s, 1H).

MS(ESI):  $m/z = 260(M+1)$

3k)  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ , 400 MHz)  $\delta$ : 7.78 (s, 1H), 7.89 (t, 2H), 7.97 (d, 1H), 9.32 (d, 1H), 10.13 (s, 1H), 11.71 (s, 1H).

MS(ESI):  $m/z = 278(M+1)$

### Details of fly ash

The fly ash powder with an average diameter of 20-30  $\mu\text{m}$  used in this study was collected from Thermal Power Station, Parli, Beed District, Maharashtra, India. TABLE 1 shows the chemical composition of the fly ash (on dry basis) used.

TABLE 1 : Composition of fly ash used in this study.

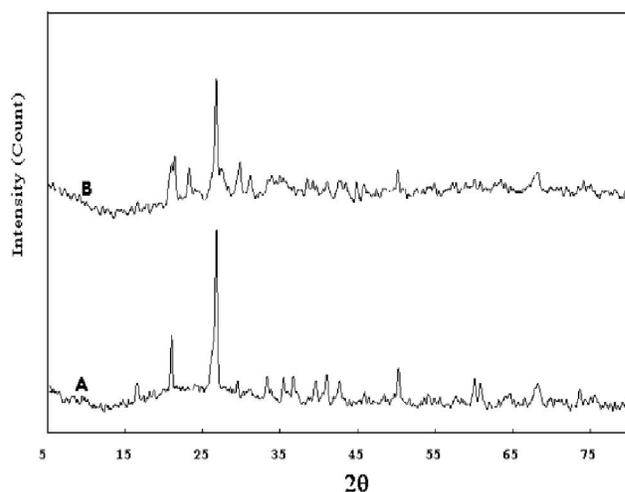
Constituents	Fly ash (%)
$\text{SiO}_2$	70.14
$\text{Fe}_2\text{O}_3$	7.01
$\text{Al}_2\text{O}_3$	20.31
$\text{Na}_2\text{O}$	0.22
$\text{CaO}$	1.64
$\text{MgO}$	0.27
$\text{K}_2\text{O}$	0.38

### Catalyst preparation

Fly ash (20gm) was mixed with 4gm of NaOH. This mixture fused in air, dried in electric oven at 70°C for 1.5 hr, the fused product was calcined at 600°C for 2 hr in high temperature muffle furnace in presence of air. This catalyst is used for condensation reaction.

### X-ray diffraction

The X-ray diffraction (XRD) patterns were recorded on Bruker 8D X-ray diffractometer using monochromator  $\text{CuK}\alpha_1$  radiation (40 Kv and 30 mV) of wavelength ( $\lambda$ )=1.54056 Å fly ash analyzed in the range 5-80° (2 $\theta$ , where  $\theta$  is angle of diffraction).

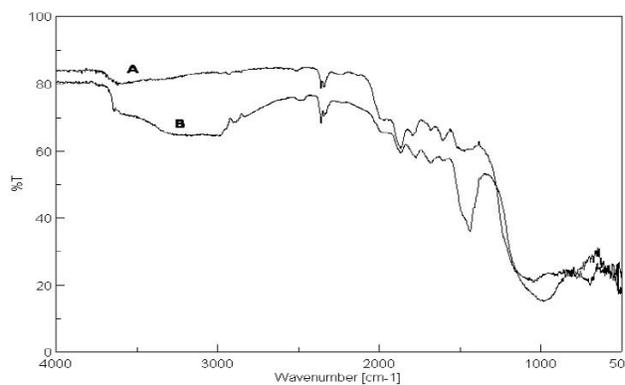


(A) XRD spectra of Fly ash before fusion; (B) XRD spectra of Fly ash after fusion with NaOH

X-ray diffraction pattern shows fly ash is crystalline in nature. 'A' shows the XRD pattern of fly ash and 'B' shows the XRD pattern of NaOH/fly ash. Some new high intense peaks at 23.21°, 29.7° and 31.2° observed in the XRD spectrum after fusion treatment to fly ash due to surface modification of fly ash by fusion with NaOH.

### FT-IR spectroscopy

The IR spectra were recorded on FT-IR spectrophotometer (Jasco FTIR/4100 Japan) using dry KBr as standard reference in the range of 4000-500  $\text{cm}^{-1}$



(A) FT-IR spectra of fly ash before fusion; (B) FT-IR spectra of fly ash after fusion with NaOH.

From IR data it was observed that the band at 1047 and 525  $\text{cm}^{-1}$  are characteristic peak of stretching and bending of Si-O-T (T=Al or Fe) respectively. After chemical and thermal treatment stretching and bending modes of Si-O-T shifts towards lower wavelength i.e. 986 and 697  $\text{cm}^{-1}$  and new intense peak appeared at 1441  $\text{cm}^{-1}$ . The broad peak around 3500-3000  $\text{cm}^{-1}$

was due to O-H stretching of water and the peak at around  $1682\text{ cm}^{-1}$  corresponding to bending modes of O-H of water.

**TABLE 2 : Condensation reaction of aromatic aldehydes and barbituric acid or 2-thiobarbituric acid.**

Entry	R	X	Time (min)	Yield <sup>a,b</sup> (%)	M.P. in °C	
					Found	Lit.
3a	H	O	30	92	255-256	256-258 <sup>[27]</sup>
3b	4-Cl	O	35	86	294-295	297-298 <sup>[28]</sup>
3c	3-NO <sub>2</sub>	O	40	78	245-246	245-245.5 <sup>[8]</sup>
3d	4-OH	O	35	91	>300	>300 <sup>[8]</sup>
3e	4-OCH <sub>3</sub>	O	30	89	298-299	296-298 <sup>[28]</sup>
3f	4-F	O	25	94	295-296	295-297 <sup>[28]</sup>
3g	4-CH <sub>3</sub>	O	30	94	276-277	276-277 <sup>[28]</sup>
3h	2-OCH <sub>3</sub>	O	35	87	263-264	267.5-268 <sup>[8]</sup>
3i	4-(CH <sub>3</sub> ) <sub>2</sub> N	O	30	95	276-277	274-276 <sup>[8]</sup>
3j	4-Cl	S	35	91	293-294	291-292 <sup>[28]</sup>
3k	3-NO <sub>2</sub>	S	45	89	263-265	261.5-264 <sup>[29]</sup>
3l	4-F	S	35	96	217-219	217-218 <sup>[28]</sup>
3m	4-CH <sub>3</sub>	S	40	92	>300	>300 <sup>[28]</sup>
3n	4-OCH <sub>3</sub>	S	40	94	>300	>300 <sup>[28]</sup>
3o	4-(CH <sub>3</sub> ) <sub>2</sub> N	S	35	87	256-258	257-258.3 <sup>[29]</sup>
3p	2-OCH <sub>3</sub>	S	35	85	288-289	288.5-289.5 <sup>[29]</sup>

<sup>a</sup>Yield refer to isolated products; <sup>b</sup> all compounds are known and their physical and spectroscopic data consistent with those of authentic samples.

**TABLE 3 : Study of catalyst in condensation of benzaldehyde and barbituric acid.**

Weight of Catalyst	Time (min)	Yield <sup>a</sup> (%)
No catalyst	30	57
2	30	78
4	30	92
6	30	92
8	30	91

<sup>a</sup>Yield refer to isolated products.

## RESULTS AND DISCUSSION

The optimum reaction conditions were initially investigated by considering condensation of benzaldehyde (5 mmol) and barbituric acid (5 mmol) in water. The quantity of the catalyst used was with respect to the total weight percentage of the initial components. After cooling the reaction mixture it was observed that the product (3a, TABLE 2) was precipitated, so it necessary to filter the

reaction mixture in hot condition repeatedly. The products of reaction were purified by recrystallization process in ethanol. With these optimized conditions in hand, several substituted aromatic aldehydes were treated with barbituric acid and the results are summarized in TABLE 2. The recovered catalyst was washed several times with acetone and dried at  $110^{\circ}\text{C}$ .

To study the influence of catalyst amount on the yield of reaction product the amount of catalyst was varied in case of 3a reaction that is the reaction between benzaldehyde and barbituric acid (TABLE 3) when the catalyst was 2% then the product obtained only 78% and when the catalyst was doubled i.e. 4% with respect to initial reactant, substantial increase in the yield (92%) of product was observed, further increase in the amount of catalyst no change occurred in the product yield. A test without catalyst was also carried out in order to check whether some reactions under same condition could takes place. It was found that reaction occurs at a very lower extent (57%) than the catalytic reactions. The separated catalyst was again reused for condensation reaction and this was repeated three times. In these cases, the yield of 3a was found to be 89, 84, and 81% in each successive times use. Thus, the activity of the catalyst was found to decreases after its recyclability. The presence of high concentration of strong Bronsted acid sites along with Lewis acid sites in the catalyst are primarily responsible for rapid reaction leading to high yields of the product.

## CONCLUSION

Fly ash derived silica-alumina catalyst for condensation reaction was synthesized easily and inexpensively by the fusion of fly ash with NaOH followed by activation. The catalytic activity performed in condensation reaction and it was concluded that NaOH/fly ash catalyst could be a good for catalytic use. Chemical and heat treatments of the fly ash support greatly and improved its catalytic activity.

We have successfully carried out condensation reaction using fly ash as a solid acid catalyst for the synthesis of 5-arylidenobarbituric acid and 5-arylidenebarbituric acid derivatives. The experimental procedure is simple. Furthermore this method is advantageous because of clean reaction conditions, high

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yields and minimum environmental effects.

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