INTRODUCTION

In recent years the xanthene fascinated considerable interest to organic synthesis since it exhibits antibacterial, antiviral, anticoagulant, anticancer, diuretic, spasmolytic and anti-inflammatory properties [1,2]. Besides, these compounds have been explored for agricultural bactericidal activity and photodynamic therapy [3,4]. Xanthenediones are integral part of number of natural products [5]. The presence of pyran ring in xanthenediones makes it as versatile synthons [6]. Moreover, their applications are explored in cosmetics, pigments, laser technologies [7,8] and in fluorescent material for revelation of biomolecules [9,10].

In synthesis of xanthenediones, usually acid or base catalyzed condensation of suitable active methylene group containing carbonyl compounds with aldehydes is carried out [11]. In literature different methods have been reported for synthesis of xanthenediones such as condensation of active methylene compounds with aldehydes catalyzed by sulfuric acid or hydrochloric acid [12], TiO₂/SO₃²⁻ [13], polyaniline p-toluenesulfonate [14], PPA-SiO₂ [15], Amberlyst-15 [16], Fe₃⁺-montmorillonite [17], NaHSO₄·SiO₂ or silica chloride [18], cellulose-sulfuric acid [19], InCl₃/ionic liquid [20], Dowex-50W [21], ZrOCl₂·8H₂O₄, trimethylsilyl chloride (TMSCl) [22], ω-4°-ammoniumalkyl sulfonate [23], polytungstozincate acid [24] and cyanuric chloride [10]. However these methods require harsh reaction conditions, long reaction time, low yields, use toxic and expensive catalysts. So in preparation of xanthenediones, novel methods are desirable, which overcomes afore mentioned drawbacks.

Heterogeneous catalysis has more advantages than homogeneous catalysis because in industrial practice, the removal of the product and recovery of the catalysts are comparatively easier. The development of nonmetallic heterogeneous catalyst is essential due to their advantage of nominal product contamination from metal release during reaction. Recently, silica supported catalysts such as HClO₄/SiO₂ [25], H₃PO₄·SiO₂ [26] and ionic liquid prompted microwave irradiation [27] have been used by various research group for organic transformation. Herein, we report silica supported orthophosphoric acid as a novel heterogeneous, reusable catalyst for synthesis of xanthenediones. To the best of our knowledge, catalyst (H₃PO₄·SiO₂) has not been reported earlier for synthesis of xanthenediones (Scheme-I). This catalyst was found to be highly efficient, recyclable and environmentally benign for synthesis of xanthenediones.

EXPERIMENTAL

All commercially available reagents were used as received without further purification. ¹H NMR spectra were recorded...
Synthesis of silica supported orthophosphoric acid:
Silica supported orthophosphoric acid catalyst was prepared by reported method [26]. In typical procedure suspension of (5 g) SiO2 in 30 mL chloroform was obtained. Then 3.5 g of orthophosphoric acid was added to above suspension of SiO2 and stir at room temperature for 2 h. This reaction mass was concentrated by heating at 100 °C to get free-flowing powder. This powder was washed with water and finally with 50 mL of ethanol and dried at 110 °C to get a desired catalyst.

General procedure for the synthesis of xanthenediones:
Aldehyde, dimedone (1:2 mmol) and 30 mg catalyst was refluxed at 80 °C in ethanol. Completion of reaction was monitored on TLC. After completion of reaction, product was filtered to remove catalyst. Product was purified by column chromatography (ethyl acetate and petroleum ether). Product were characterized by melting points were compared with the literature and proved by spectroscopic data.

RESULTS AND DISCUSSION

Reaction between 4-methoxybenzaldehyde and dimedone was used as model reaction for optimization of reaction conditions (Table-1). As shown in Table-1, the reaction could proceed efficiently in presence of 30 mg silica supported orthophosphoric acid as heterogeneous catalyst (Table-1 entries 1-3). The reaction temperature effects on the yields of the products were studied by performing the condensation reaction at room temperature and reflux, respectively (Table-1 entries 4-6). The results shows that the higher reaction temperature, the more efficiently the reaction could proceed. The various solvents such as water, DMSO, DMF and ethanol have been tried for these reaction (Table-1 entries 7-9). The reaction gave high yield of corresponding product in presence of ethanol. The optimized reaction conditions are catalyst: 30 mg (H3PO4·SiO2), solvent: ethanol, time 30 min and temperature: reflux.

Then at above optimized conditions, various aldehydes were studied and the results are presented in Table-2. The catalyst (H3PO4·SiO2) was found to be worked effectively for substituted and unsubstituted benzaldehyde (Table-2 entries 1-13). Electron-withdrawing substituents bearing aromatic aldehydes reacted smoothly in short time as compared to electron donationg subtituents (Table-2 entries 3-13). We have also investigated activity of catalyst for cinnamaldehyde which
|   |      |      |      |   |      
|---|------|------|------|---|------|
| 4 | CH₃  | H    | H    | 60|      |
| 5 | CH(CH₃)₂ | H | H | 80|      |
| 6 | OCH₃ | H    | H    | 45|      |
| 7 | OCH₃ | OCH₃ | H    | 60|      |
| 8 | H    | H    | NO₂  | 30|      |
| 9 | H    | NO₂  | H    | 60|      |
|10 | NO₂  | H    | H    | 45|      |
|11 | H    | OH   | H    | 70|      |
|12 | OH   | H    | H    | 45|      |
|13 | N(CH₃)₂ | H | H | 55|      |

*Reaction conditions: Aromatic aldehyde (1 mmol), dixedone (2 mmol) H₃PO₄·SiO₂ (30 mg), ethanol (2 mL), reflux time: 30 min. *Isolated yield.
afforded 91% yield of the corresponding product (Table-2 entry 2). All the reactions were monitored by TLC. The synthesized compounds were characterized by ¹H NMR, ¹³C NMR and DEPT-135 spectral techniques. Further structures of compounds were confirmed by FTIR spectroscopy.

In order to check usefulness of the catalyst for commercial applications, reusability of the catalyst was also investigated for model reaction (Table-3). After completion of the reaction, the reaction mixture was isolated with CH₂Cl₂. The catalyst was easily recovered by filtration after washing with ethyl acetate and drying at 80 °C. The recycled catalyst was used for the next. The decrease in product yield after 4th cycle could be due to leaching of the catalyst. Thus catalyst, (H₃PO₄·SiO₂) could be reused four times without any loss of its activity.

The catalytic activity of our catalyst is compared with earlier reported catalyst for synthesis of xanthenedione (Table-4). The catalyst reported in this work is simple, more efficient and less time consuming compared with other reported catalysts.

**Conclusion**

In summary, the reported protocol is simple and effective for the synthesis of various substituted and unsubstituted xanthenediones. In addition to this, low-cost, easy availability, recyclability, low toxicity, stability of the catalyst, excellent yields of products and short reaction time make this protocol a viable contribution to the existing processes.

**ACKNOWLEDGEMENTS**

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**CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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**TABLE-3**

**TABLE-4**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(H₃PO₄·SiO₂)</td>
<td>Ethanol, reflux</td>
<td>30-80</td>
<td>85-94</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>InCl₃·4H₂O</td>
<td>Ionic liquid/80 °C</td>
<td>240-600</td>
<td>76-95</td>
<td>[28]</td>
</tr>
<tr>
<td>3</td>
<td>Fe³⁺-montmorillonite</td>
<td>EtOH (reflux)</td>
<td>360</td>
<td>84-96</td>
<td>[29]</td>
</tr>
<tr>
<td>4</td>
<td>NaHSO₄·SiO₂</td>
<td>CH₂CN (reflux)</td>
<td>360</td>
<td>90-98</td>
<td>[18]</td>
</tr>
<tr>
<td>5</td>
<td>Amberlyst-15</td>
<td>CH₂CN (reflux)</td>
<td>300</td>
<td>90-96</td>
<td>[16]</td>
</tr>
</tbody>
</table>

**REUSABILITY OF THE CATALYST**

<table>
<thead>
<tr>
<th>Run</th>
<th>1ˢᵗ</th>
<th>2ⁿᵈ</th>
<th>3ᵗʰ</th>
<th>4ᵗʰ</th>
<th>5ᵗʰ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>94</td>
<td>92</td>
<td>91</td>
<td>89</td>
<td>84</td>
</tr>
</tbody>
</table>

*Reaction conditions: Aromatic aldehyde (1 mmol), dimedone (2 mmol) H₃PO₄·SiO₂ (30 mg), ethanol (2 mL), reflux time: 30 min. *Isolated yield