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Triethylammonium hydrogen sulfate ionic liquid accelerated one-pot synthesis of 1,8-dioxo-octahydroxanthenes

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Abstract : The one-pot reaction of aldehydes and dimedone afford 1,8-dioxo-octahydroxanthene derivatives in the presence of triethylammonium hydrogen sulfate ionic liquid $[Et_3NH][HSO_4]$. Simplicity of the reaction, high yields of the products, short reaction times, easy work-up, ease of the preparation of the catalyst and environmentally benign reaction conditions are the most significant advantages of this method which make this procedure a useful addition to the available methods

Keywords : 1,8-Dioxo-octahydroxanthenes; Ionic liquid; Aldehydes; Dimedone.

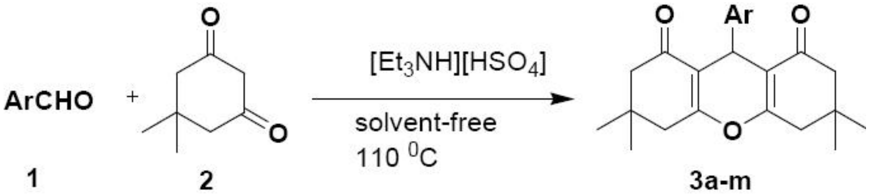
INTRODUCTION

Xanthenes and its derivatives are known as important class of organic heterocyclic compounds because of their wide range of biological and pharmaceutical properties active such as antiviral, antibacterial, anti-inflammatory and anticancer properties[1-4]. In addition these compounds are widely used in dyes, laser technologies and as PH-sensitive fluorescented materials for visualization of bio molecules[5-6]. Some Xanthene derivatives are presented in natural products with different biological activities[7].

As a consequence, several reports have been devoted for the synthesis of 1,8-dioxooctahy droxan thenederiv atives employing aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione (dimedone)[8-17]. However, the introduction of milder, fasterand more eco-friendly methods is still in great demand.

Ionic Liquids (ILs) have attracted much attention in the scientific community during the past two decades. The application of ILs is growing continuously due to their attractive properties. They have very low vapor pressure and are nonexplosive and thermally stable in a wide temperature range[18]. Now ionic liquids have been used as environmentally benign solvents or catalysts for a number of chemical processes[19-20].

Based on our interest in the developmen to fenviron mentally benign methodologies for the synthesisof benzoxanthenes,[21-23] herein, we report a simple and efficient method for the synthesis of 1,8-dioxo-octahydroxanthenes through the one-pot reaction of dimedone and aldehydes in the presence



Scheme 1 : Synthesis of 1,8-dioxo-octahydroxanthenes

TABLE 1 : Synthesis of 1,8-dioxo-octahydroxanthenes using[Et_3NH][HSO_4]

Entry	Ar	Product	Time (min)	Yield (%)	m.p. (°C)[ref.]
1	C_6H_5	3a	6	89	201-202[13]
2	3-ClC_6H_4	3b	7	86	183-185[10]
3	4-ClC_6H_4	3c	5	88	230-232[13]
4	2-$NO_2C_6H_4$	3d	5	90	246-248[17]
5	3-$NO_2C_6H_4$	3e	5	89	165-167[13]
6	4-$NO_2C_6H_4$	3f	5	92	222-224[13]
7	4-BrC_6H_4	3g	5	88	226-229[17]
8	4-CNC_6H_4	3h	5	90	217-218[16]
9	2,4-$Cl_2C_6H_3$	3i	5	85	251-253[10]
10	4-$CH_3C_6H_4$	3j	7	86	212-214[17]
11	4-$CH_3OC_6H_4$	3k	7	85	242-245[10]
12	4-HOC_6H_4	3l	8	85	244-246[10]
13	4-FC_6H_4	3m	5	93	225-227[13]

of [Et_3NH][HSO_4] ionic liquid catalyst. Our literature surveyrevealed that there are no reports available on the synthesisof the above-mentioned compounds using this catalyst.

RESULTS AND DISCUSSION

Triethylammonium hydrogen sulfate ([Et_3NH][HSO_4]) was easily prepared from trimethyl amine and sulfuric acid without using any solvent. This is a low cost due to using cheap amine and acid, mild, non-volatile and non-corrosive acidic ionic liquid[20].

To find out the suitable conditions for the reaction, a series of experiments were performed with the standard reaction of benzaldehyde and dimedone as a model reaction. The reactions were scrutinized using different conditions. The best results have been obtained at 110 °C with 1 mmol of benzaldehyde and 2 mmol of dimedone using 10 mol% of [Et_3NH][HSO_4].

Under the given reaction conditions several aromatic aldehydes containing electron donating aswell as electron withdrawing groups with diverse substitution pattern were effectively cyclized togive 1,8-dioxo-octahydroxanthenes3a-m. The results are summarized in TABLE 1.

The experimental method with this catalyst is very easyand the catalyst can be readily removed from the reaction mixture. The products are known and their structures werecharacterized by comparing their physical and spectral data withthose of authentic samples[9-17]. Note that all the products werepurified by a simple process of crystallization and filtration; nochromatography was involved.

CONCLUSION

An efficient method has been described for the synthesis of 1,8-dioxo-octahydroxanthenes through the one-pot reaction of dimedone and aldehydes in the presence of [Et_3NH][HSO_4] ionic liquid catalyst. This method offers some advantages in term of simplicity of performance, very low reaction times, easy work-up, and environmental friendliness reaction conditions. However, the ionic liquid catalyst is air and water stable, easy to prepare from amine and acid and easily separated from the reaction mixture.

EXPERIMENTAL

Triethylammonium hydrogen sulfate $[Et_3NH][HSO_4]$ has been easily prepared from the reaction of trimethyl amine and sulfuric acid according to reported method[20].

General procedure for the synthesis of 1,8-dioxo-octahydroxanthenes

A solution of aromatic aldehyde (1 mmol), dimedone (2 mmol), and $[Et_3NH][HSO_4]$ (10 mol%) was stirred at 110 °C for the appropriate times (Table 1).The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool to room temperature. The solid was purified by recrystalization from ethylacetate-hexane.

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