REDUCTIVE AMINATION OF CARBONYL COMPOUNDS USING LIGNIN SULFONIC ACID AS CATALYST AND BOROHYDRIDE EXCHANGE RESIN

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Abstract : An efficient and mild method for reductive amination of a variety of aldehydes with amines in presence of lignin sulphonic acid as catalyst and borohydride exchange resin at room temperature was explored. Borohydride exchange resin was utilized successfully for the reductive amination of saturated as well as unsaturated aldehydes.

Key words: amination, lignin sulphonic acid, Borohydride exchange resin

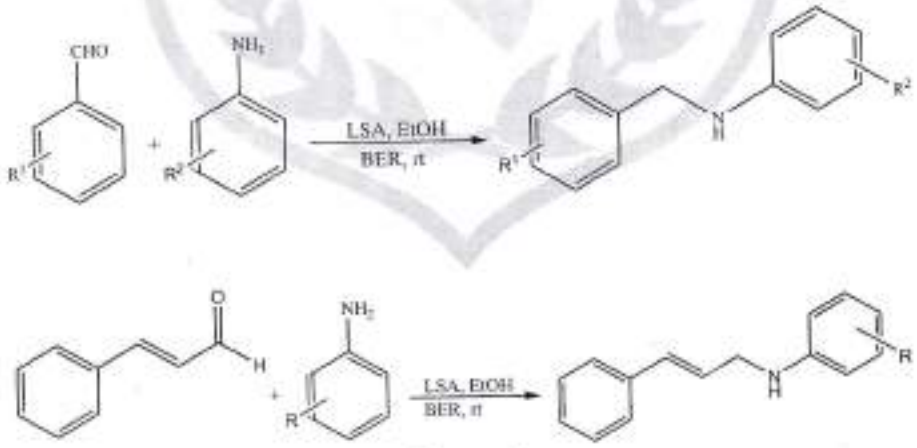
I. INTRODUCTION

The selective reduction of functional groups is a common need in organic synthesis. Polymer supported borohydride exchange resin (BER) was first synthesized by Gibson and Baily.[1] They reported BER as a reducing agent for the reduction of benzaldehyde to benzyl alcohol. BER has several advantages over other polymer supported reagents.[2] As compared to sodium borohydride, BER is highly stable and easy to handle.[3]

A number of reagents[4] were developed for the selective reduction of carbonyl compounds to the corresponding products. These reagents used have some disadvantages like complex reaction work up, low yields, etc. BER was extensively used in the reduction of carbonyl compounds in alcohol solvents.[5] Aromatic as well as aliphatic aldehydes and ketones reduced using BER as a reducing agent. Selective reduction of α,β- unsaturated aldehydes and ketones was done using BER.[5b]

Several reducing systems were developed using BER in combination with catalysts such as phenyl disulfide,[6] 2,4 Ionene,[7] Et_3NHCl,[8] $NiCl_2$-$6H_2O$.[8] BER reduces conjugated ethylenic linkage selectively.[9] It was used as reducing agent for the reduction of conjugated acid chlorides,[10] aryl and sulfonyl,[5c] benzonitriles,[11] oximes,[12] alkynes,[13] nitroso amines,[14] selenium.[15] BER as a mild, efficient and selective reducing agent than $NaBH_4$ for the reduction of carbonyl compounds without being reduction of α, β-unsturation was reported.

In the present work, we herein report the application of BER as a mild and selective reducing agent for the reductive amination of aldehydes I with amines II using lignin sulphonic acid in ethanol at room temperature. (Scheme 1)



Scheme 1

II. EXPERIMENTAL PROCEDURE

1. Preparation of Borohydride exchange resin (BER)

To 5 g of resin (Amberlyte IRA-400) 100 mL of 10% HCl was added and the contents were kept overnight. The resin was transferred to 500 mL beaker and washed with distilled water 4-5 times, filtered and wet resin was obtained (the nitrate was

II. General procedure

Aromatic aldehyde (1 mmol), aniline (1 mmol) and catalyst lignin sulphonic acid in solvent ethanol (5 mL) were stirred at room temperature for about 10 minutes. Sodium borohydride exchange resin (2 mmol) was then added to the reaction mixture and stirring was continued. After completion of the reaction as judged by TLC, the contents of flask were filtered, washed with dichloromethane (2 x 15 mL), evaporated and concentrated. The solid obtained was then purified by column chromatography (petroleum ether : ethylacetate = 9:1 V/V).

III. RESULTS AND DISCUSSION

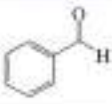
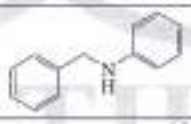
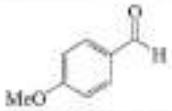
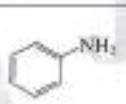
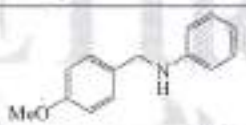
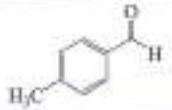
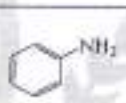
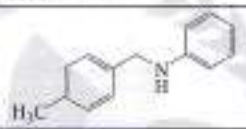
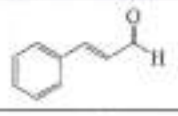
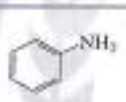
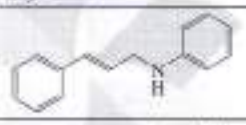
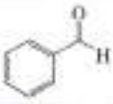
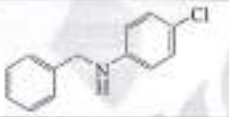
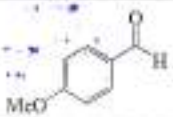
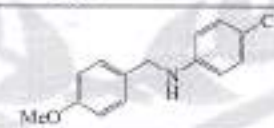
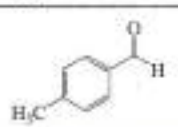
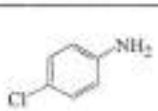
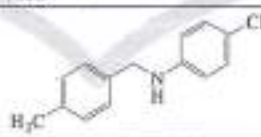
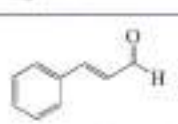
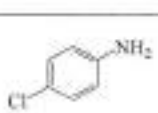
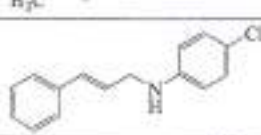
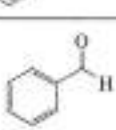
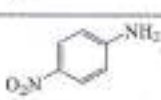
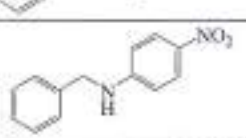
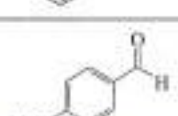
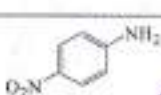
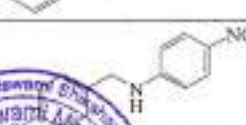
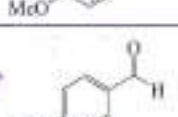
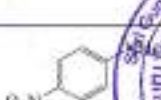
The reductive amination of a variety of aldehydes by lignin sulphonic acid as catalyst with a mild reducing agent BER was studied. The results are summarized in Table 1. It was observed that the aromatic aldehydes having different substituents underwent the reduction in 2-2.5 h. affording the corresponding amines in good yields.

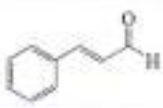
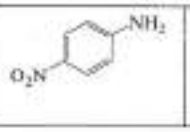
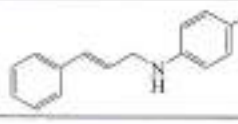
Entries (4, 8, 12) clearly demonstrate that the olefinic functionality is stable to the present experimental conditions. Thus as compared to $NaBH_4$, BER was found to be specific reagent for the α, β- unsaturated aldehyde.

IV. CONCLUSION

An efficient method for the reductive amination of carbonyl compounds using lignin sulfonic acid as a catalyst and BER as mild reducing agent with different amines has been reported. BER was found to be an interesting chemoselective reducing agent for carbonyl compounds especially for α, β- unsaturated aldehyde which was sensitive to $NaBH_4$.

Table 1 : Reductive amination of carbonyl compounds using LSA and BER

Entry	Aldehyde	Amine	Product	Time (h)	Isolated yield (%)
1				2	90
2				2.5	89
3				2.5	88
4				2.5	90
5				2	91
6				2.5	88
7				2	91
8				2	90
9				2	92
10				2.5	89
11				2	91

12				2	92

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Synthesis of Phenoxy Acetic Acid Esters of Phenols Using Phosphonitrilic Chloride as an Activator

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ABSTRACT

A simple procedure is described for the synthesis of phenoxy acetic acid esters by activation of carboxylic acid group of phenoxyacetic acid using Phosphonitrilic Chloride and N-methyl morpholine.

Keywords: Phenoxyacetic acid, Phenols, Phosphonitrilic chloride, N-methyl morpholine.

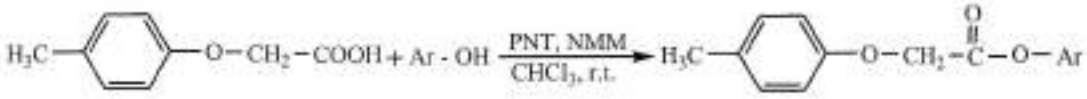
INTRODUCTION

Esterification is one of the most important and commonly used reactions in organic chemistry. In organic synthesis, the conversion of carboxylic acids to corresponding esters is an important and well known organic transformation [1-3]. Esterification reactions have great importance [4,5] in the synthesis of natural products containing two or more carboxylic groups.

In food chemistry, phenolic esters of organic acids, particularly those of cresols and phenols which are excellent flavor compounds as they possess a combination of sweet, floral and fruity odours were studied [6]. The corresponding esters having different functionalities have been used in the manufacture of insecticides, anti-oxidants and photosensitizers [7,8]. Several methods were developed for esterification using catalysts. The various catalysts/reagents used for the esterification are Me_2NSO_2Cl [9], Trifluoroacetic anhydride (TFAA) [10], Diisopropylazodicarboxylate (DIAD)/Ph_3P [11], CCl_4/PPh_3 [12], Anhydrous $ZnCl_2/AlCl_3$ [13], 2-Chloro-1-methylpyridinium iodide [14], N,N-Bis (2-oxo-3-oxazololidinyl) phosphordiamidic chloride [15], Paratoluene sulfonyl chloride (p-TSC) [16], Mn $(OAC)_3$ [17], TiO $(acac)_2$ [18], Montmorillonite-Ti^{4+} [19], Benzotriazol-1-yloxytris (dimethylaminophosphonium-hexafluorophosphate) [BOP] [20], Dicyclohexylcarbodiamide (DCC) [21], Diaryl ammonium arsen sulfonate [22-26].

Phosphonitrilic chloride (PNT) is a white crystalline compound which is thermally stable and soluble in variety of organic solvents. It is less moisture sensitive, non-irritating compound and easy to handle. PNT has been used as an activator in various organic transformations [27-33]. Therefore we report herein the PNT as an activator for the activation of phenoxy acetic acid.

In the present work, phenoxy acetic acid (I) was activated by using PNT and NMM in chloroform and coupled with variety of phenols (II) to get the corresponding phenoxy acetic acid esters (III) at room temperature (Scheme 1).



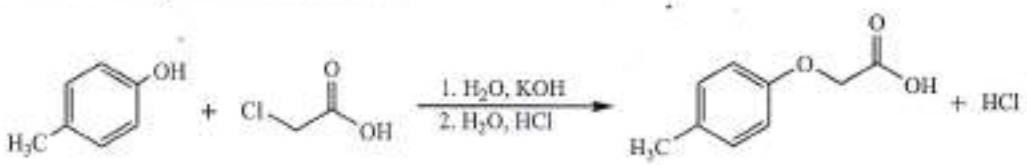
I **II** **III**

Scheme 1: Phenoxy acetic acid esters formation

EXPERIMENTAL PROCEDURE

Preparation of p-Methyl Phenoxy Acetic Acid

In a round bottom flask *p*-cresol (1 g) and NaOH (9 mol%) were taken. Chloro acetic acid (2.5 mL) was added drop-wise and little water was added in a round bottom flask. The contents of the flask were heated on water bath for 1 h, cooled and water (10 mL) was added. The contents were acidified with dilute HCl to congo-red and extracted with diethyl ether. The ethereal extract was then washed with water (10 mL). The aryloxy acetic acid obtained was then extracted by shaking with 5% Na_2CO_3 (25 mL) solution and acidified with dilute HCl. The *p*-methyl phenoxy acetic acid obtained was recrystallized from ethanol.

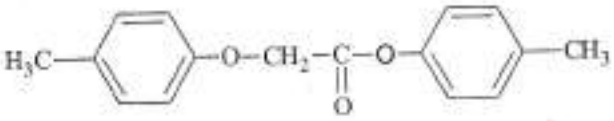


p-Cresol Chloroacetic acid *p*-Methylphenoxyacetic acid

Preparation of Phenoxy Esters of Phenols

Typical procedure: PNT (0.025 mmol), NMM (1.5 mmol) and chloroform were stirred at room temperature for about 5 minutes. *p*-Methyl phenoxy acetic acid (1.5 mmol) was added and stirred at room temperature for 30 minutes. Then *p*-cresol (1.5 mmol) was added to the reaction mixture and stirring was continued at room temperature. The progress of reaction was monitored by TLC and after completion of the reaction, the contents of the flask were transferred to separating funnel, washed 3-4 times by 10% NaOH, water, dried over Na_2SO_4 and filtered. The organic layer obtained was evaporated in vaccum and purified by flash column chromatography. A similar procedure was used for the synthesis of other esters.

Spectral analysis: The products were confirmed by their physical constants and characterized by spectral analysis IR, ^{1}HNMR and mass spectroscopy. The spectral analysis of the representative compound is given as:



P-(tolylphenoxy)-4-methylphenoxyacetate

IR (cm^{-1}): 1755 -C(=O)-O ester

1220 Ar-O-C

^{1}HNMR (δ ppm): 2.3, S, 3H, Ar-CH_3; 2.3, S, 3H, Ar-CH_3;

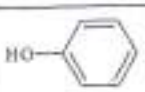
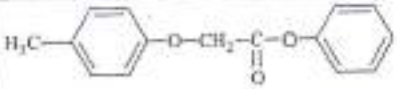
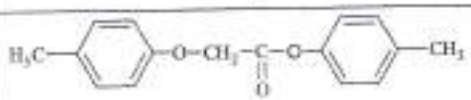
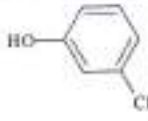
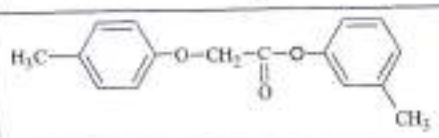
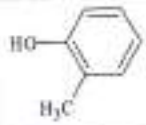
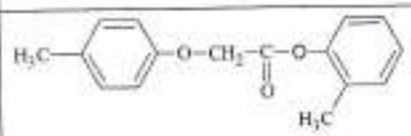
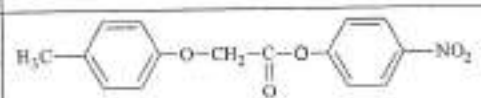
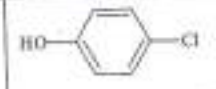
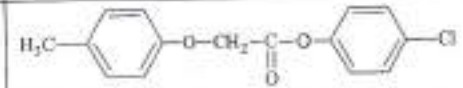
4.5, S, 2H, -CH_2-; 6.8-7.3, M, 8H, Ar-H

Mass: (M+) 256

RESULTS AND DISCUSSION

Condensation of *p*-methyl phenoxy acetic acid with a variety of phenols was carried out by using PNT together with NMM as activator in chloroform at room temperature. The results are summarized in Table 1. In this method, PNT was activated with NMM in chloroform at room temperature which then activates phenoxy acetic acid. The activated *p*-methyl phenoxy acetic acid then reacted with various phenols to afford the corresponding phenoxy esters in good yields.

Table 1. Synthesis of phenoxy acetic acid esters of phenols using PNT/NMM

Entry	Phenol	Phenoxy acetic acid ester	Yield (%)
1			92
2			91
3			89
4			92
5			93
6			92

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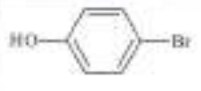
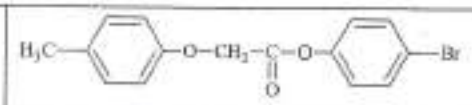
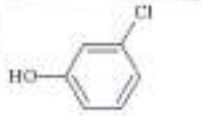
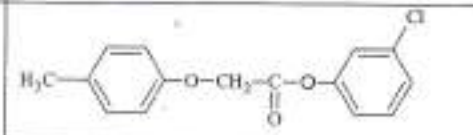
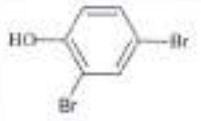
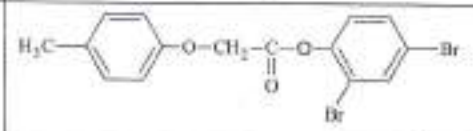
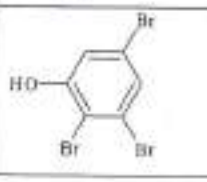
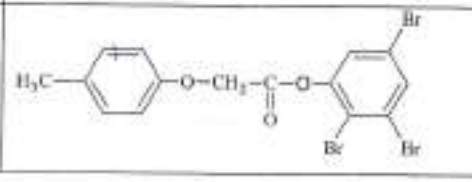
7			91
8			89
9			92
10			91

CONCLUSION

PNT in combination with NMM was proven to be an effective activator of phenoxy acetic acid to couple with phenols for the preparation of biologically important phenoxy acetic acid esters under mild conditions in good yields.

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MICROWAVE ASSISTED SYNTHESIS OF 1, 8-DIOXOOCTAHYDROXANTHENES USING PHOSPHONITRILIC CHLORIDE AS CATALYST

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ABSTRACT

Microwave assisted effective procedure for the synthesis of 1,8-dioxooctahydroxanthenes through one-pot condensation of aldehydes and dimedone using Phosphonitrilic Chloride as catalyst and tetra butyl ammonium bromide as phase transfer catalyst was described. Aromatic aldehydes having electron withdrawing or electron donating groups reacted with dimedone to give corresponding 1,8-dioxooctahydroxanthenes derivatives in moderate to good yields.

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INTRODUCTION

The use of microwave irradiation in organic synthesis has become increasingly popular within the pharmaceutical and academic areas, because it is a new enabling technology for drug discovery and development [1-13]. New synthetic applications show a variety of new chemistries performed with microwave irradiation. Leadbeater and co-workers [14] have shown that reacting an activated aryl bromide with an arylboronic acid in water, using tetra-butyl ammonium bromide (TBAB) as a phase-transfer catalyst (PTC), results in a successfully coupled biaryl Suzuki product without the aid of a palladium catalyst. In addition, a transition-metal-free Sonogashira reaction between an aryl bromide or iodide and phenylacetylene results in respectable yields [15]. In this case, polyethylene glycol was used as the phase-transfer agent. One interesting example is the palladium-catalyzed amination of (azahetero) aryl chlorides. Aryl chlorides are known to be quite unreactive due to the C–Cl bond strength, but with microwave heating for 10 minutes, these aminations were reactive [16]. Microwave-assisted, improved intramolecular amination of aryl bromides to benzimidazoles [17] is another example.

Microwave irradiation is fast becoming a source of energy for biochemical applications. Many of the biochemical molecules are temperature-sensitive. At present, there have been studies published on carbohydrates [18-24], nucleosides [25-30], peptides [31-39], proteins [14, 40,41], peptoids [42] the polymerase chain reaction (PCR), and trypsin digestion. Keeping in view the applications of microwave chemistry, we herein report our studies of microwave assisted synthesis of 1,8-dioxooctahydroxanthenes using PNT as catalyst and TBAB as PTC.

Xanthene derivatives has attracted the considerable interest of the chemists because of their wide range of biological and pharmaceutical properties like antiviral, [43-44] antibacterial [45], anti-inflamatory [46-47], anticancer [48], anti-nociceptive [49] and anti-plasmodial [50] etc activities. These are also used as sensitizers in photodynamic therapy [51, 52], as antigonists of paralyzing action of zoxazolamine [53], leuco-dyes [54], laser technology [55], as versatile synthons because of the inherent reactivity of the inbuilt pyran ring [56]. 1,8-dioxooctahydroxanthenes are very important derivative of xanthenes in which a phenyl substituted pyran ring is fused on either side with two cyclohexenone rings. 1,8-dioxooctahydroxanthenes have wide range of applications in the field of medicinal chemistry. It shows biological activities such as antiviral, antibacterial and anti-inflammatory activities [57]. Several methods were developed and adopted to synthesize 1,8-dioxooctahydroxanthenes including cyclo dehydration, trapping of benzynes by phenol [58], the cyclocondensation of 2-hydroxy aromatic aldehydes and 2-tetralone [59-60]. These procedures involve acid or base-catalysed condensation of active methylene carbonyl compounds with aldehydes. However, these methods have limitations of prolonged reaction times, poor yields and side reactions of aldehydes.

Synthetic methods reported using variety of catalysts/reagents such as Silica sulphuric acid [61], Dowex-50 W [62], $HClO_4.SiO_2$ and $PPA.SiO_2$ [63], Fe^{3+}-Montmorillonite [64], Diammonium hydrogen phosphate [65], TMSCl [66], Tetrabutyl ammonium hydrogen sulphate [67], Hydrochloric acid [68], $SbCl_3.SiO_2$ [69], Cyanuric chloride [70], $BiCl_3$ [71], Selectfluor™ [72], $NaHSO_4.SiO_2$ and Silica chloride [73], $InCl_3.4H_2O$ in ionic liquid [74], *p*-Dodecylbenzenesulfonicacid (DBSA) [59, 60], *p*-TSA [75], Amberlyst-15 [76], ZnO-nano particle, [77] Fe- Cu/ZSM-5 [78]Ce-ZSM-11 Zeolite [79], FeNP@SBA-15 [80].

Present work

In the present work, we herein report the microwave assisted synthesis of 1,8-dioxooctahydroxanthene derivatives III by the condensation of a variety of aldehydes I, with dimedone II in water using phosphonitrilic chloride as catalyst and TBAB as PTC (Scheme 1).

Scheme 1.

Experimental procedure

A mixture of aromatic aldehyde (1 mmol), dimedone (2 mmol), and phosphonitrilic chloride (0.1 mmol) as catalyst were taken in a 50 mL beaker containing TBAB (50 mg) dissolved in water (10 mL). The contents of the beaker were irradiated under microwave (450 W) for appropriate time as shown in Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature, water was added and solid product obtained. It was filtered off and was purified by recrystallization from ethanol.

Spectral analysis

Essentially pure products were obtained which were confirmed by comparison with authentic samples by their physical constants and characterized by spectral analysis IR, ^1H NMR and mass spectroscopy.

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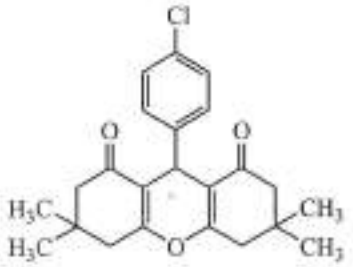
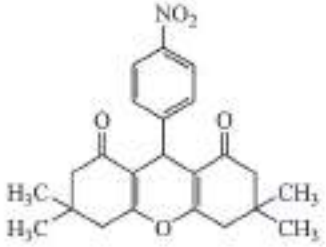


3,3,6,6-tetramethyl-9-chlorophenyl-2,4,5,7-tetrahydro(2H)-9-hydro(1H)xanthene-1,8-dione
IR (cm^{-1}) : 3100, 2962, 2875, 1678, 1624, 1550, 1361
^{1}HNMR (δ ppm) : 1.00 (6H, s, C Me_2); 1.12 (6H, s, C Me_2);
2.10 - 2.23 (4H, 2×CH_2); 2.41 (4H, s, 2× CH_2);
4.63 (1H, s, CH); 7.12 (2H, Ar-H); 7.29 (2H, Ar-H)
Mass : 385 (+M)



3,3,6,6-tetramethyl-9-(4-nitrophenyl)-2,4,5,7-tetrahydro(2H)-
9-hydro(1H)-xanthene-1,8-dione
IR (cm^{-1}) : 3070, 2958, 2870, 1654, 1616, 1514, 1361
^{1}HNMR (δ ppm) : 1.00 (6H, s, C Me_2); 1.12 (6H, s, C Me_2);
2.10 - 2.3 (4H, 2× CH_2); 2.45 (4H, s, 2×CH_2);
4.80 (1H, s, CH); 7.25 (2H, Ar-H); 7.4 (2H, Ar=H)
Mass : 395 (+M)

RESULTS AND DISCUSSION

The condensation of dimedone and aromatic aldehydes with TBAB in presence of the catalyst PNT afforded the corresponding 1,8-dioxooctahydroxanthene derivatives under the microwave conditions.

Several functionalities present in aryl aldehydes such as chloro, nitro, methoxy, methyl and hydroxyl groups tolerated the reaction conditions in 2-3 minutes of short time. Aromatic aldehydes having both electron donating or withdrawing groups reacted readily with dimedone to products in 87-96 % yields (Table 1). As can be seen from the table, it was possible to carry out the reaction within shorter times in moderate to good yields.

Initially the reactions were carried out without addition of TBAB, but with the addition of TBAB as phase transfer agent, the reactions proceeded cleanly. Thus, PNT together with TBAB under microwave irradiation was found to be a suitable method for the condensation of various aromatic aldehydes with dimedone in water to afford the corresponding products.

CONCLUSIONS

In conclusion, a series of 1,8-dioxooctahydroxanthenes were synthesized using PNT as an efficient catalyst by the condensation of aldehydes and dimedone in good yields. All the reactions were conducted in water as a green solvent under microwave irradiation.

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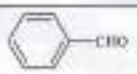
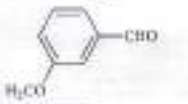
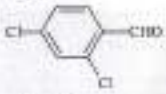
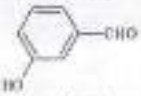
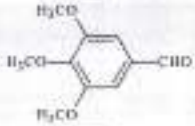
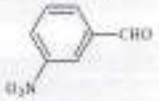
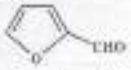
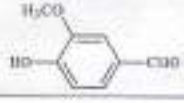
Table 1 : Phosphonitrilic chloride catalysed synthesis of various 1,8–dioxooctahydroxanthene derivatives.

Entry	Aldehyde	Time (Min.)	Yield (%)	M.P.(°C) Observed	M.P.(°C) Literature
1		2	96	202-203	205 [81]
2		2.5	94	231-232	228-230 [59]
3		3	87	243-244	241-243 [59]
4		3	89	163-165	164-165 [59]
5		2.5	90	247-250	248-250 [59]
6		3	92	226-228	226 [82]
7		3	91	248-251	246 [81]
8		3	86	187-188	187-189 [81]
9		2.5	96	224-225	221-223 [59]
10		3	92	169-171	168-170 [59]
11		2.5	90	61-63	62-64 [59]
12		2	88	215-217	217-218 [59]
13		3	90	228-230	226-228 [59]

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