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VARIOUS
TECHNOLOGIES

Solvent-free Synthesis of 4,4'-Diaminotriarylmethanes-Leuco Malachite Materials in the Presence of $FePO_4$*

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Abstract—A fast, efficient and versatile route for the synthesis of 4,4'-diaminotriarylmethanes is reported using *N,N*-dimethyl aniline and aryl aldehydes in presence of $FePO_4$ under solvent-free condition at 100°C.

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INTRODUCTION

Dyes may be classified according to chemical structure or by their usage or application method. According to the chemical structure classification, triarylmethane dyes are among the most important dyes. Triarylmethane dyes are monomethine synthetic dyes with three terminal aryl groups, of which at least one, but preferably two or three, are substituted by a donor group para to the methane carbon atom. Due to the importance of 4,4'-diaminotriarylmethanes (DTM) compounds, several reviews have disclosed on di- and triarylmethane derivatives [1–5]. These compounds have a broad range of applications in color-forming, manufacturing of novel types of various colorless copying papers, pressure-sensitive heat-sensitive materials, high-speed photo duplicating copying papers, light-sensitive papers, ultrasonic recording papers, electrothermic heat-sensitive recording papers, inks, crayons, typewritten ribbons, and photoimaging systems [6]. Accordingly, different methods for the preparation of the aforementioned compounds have been described such as those from arene nucleophiles and triethyl orthoformate, or benzhydrol in the presence of acid catalysts [7], from condensation of amines and anilines using acids [8] or zeolites [9] and also by reaction of anilines with metal catalysts such as $Pd(OAc)_2$ [10] or clay-mediated oxidative coupling of disubstituted anilines using microwave radiation, in which DTM derivatives were obtained in low to moderate yields [11]. One of the most useful methods for the synthesis of DTM is the reaction of arylaldehydes with *N*,*N*-dimethylaniline in the presence of an acid such as sulfuric acid, HCl, *p*-TSA, zeolites or montmorillonite K-10 [12]. Although different methods for the preparation of the aforementioned compounds have been described, most of them however, suffer from drawbacks such as the use of corrosive acids or toxic or hazardous chemicals, excess of solvents and harsh reaction conditions, which will result in generation of waste streams, complicated workup procedures, byproducts and isomeric mixtures and consequently low yields. Therefore, there is still a need to search for a better catalyst regarding to toxicity, selectivity, availability and operational simplicity for the synthesis of triarylmethanes. In addition to cases mentioned above, $FePO_4$ is cheap, safe and available reagent [13] that has also been employed for the selective oxidation of CH_4 to CH_3OH [14] and benzene to phenol [15], one-pot synthesis of dihydropyrimidinones and thiones [16], one-pot three component synthesis of 2,4,5-trisubstituted imidazoles [17], synthesis of 1,2,4,5-*tetra*-arylated imidazoles [18], acetylation of alcohols and phenols with acetic anhydride [19], synthesis of bis(indolyl)methanes [20] and synthesis of 1,2-disubstituted benzimidazoles [21].

In this communication, we wish to report a green synthesis method for the preparation of DTMs using arylamines and aldehyde derivatives in the presence of $FePO_4$ as catalyst (Scheme 1).

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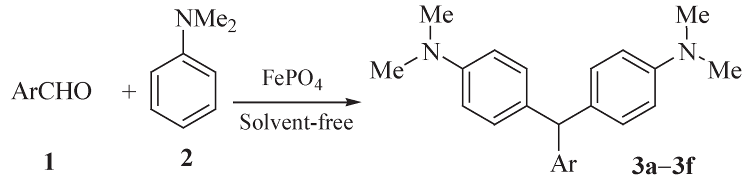
* The text was submitted by the authors in English.

Scheme 1. Synthesis of 4,4'-diaminotriarylmethanes using $FePO_4$ and solvent-free condition



EXPERIMENTAL

Mps were measured by using the capillary tube method with an electro thermal 9200 apparatus. IR spectra were recorded on Perkin Elmer FT-IR spectrometer did scanning between 4000–400 cm^{-1}. ^{1}H NMR spectra were obtained on Bruker DRX-300MHz NMR instrument in $CDC1_3$. Analytical TLC of all reactions was performed on Merck precoated plates (silica gel 60F-254 on aluminium). All compounds are known and spectra and physical data were compared with those of authentic samples [22–25].

Synthesis of 4,4'-diaminotriarylmethane using iron(III) phosphate procedure: A vial equipped with a stir bar was charged with aryl aldehyde (0.5 mmol), *N,N*-dimethyl aniline (1.5 mmol) and $FePO_4$ (0.05 mmol, 10 mol %) and the vial was capped. The resulting mixture was heated in an oil bath at 100°C for 5–6 h, and the course of the reaction was monitored using TLC on silica gel with ethyl acetate: *n*-hexane (1 : 4) as eluent.

Table 1. Optimizing of the catalytic amount of $FePO_4$ for the synthesis of 4-{[(4-(dimethylamino)phenyl](phenyl)methyl}-*N,N*-dimethylbenzenamine

Entry	$FePO_4$, mol %	Time, h	Yield, %
1	15	4	82
2	10	"	82
3	5	"	75
4	2	"	70
5	free	24	20

[a] Reaction Condition: Benzaldehyde (0.5 mmol), *N,N*-dimethyl aniline (1.5 mmol) at 100 °C.

Table 2. Use of the varying solvents for the synthesis of 4-{[4-(dimethylamino)phenyl](phenyl)methyl}-*N,N*-dimethylbenzenamine

Entry	Solvent	Temperature, °C	Yield%[a]
1	free	25	–
2	free	100	82
3	H_2O	reflux	–
4	EtOH	reflux	65

[a] Reaction condition: Benzaldehyde (0.5 mmol), *N,N*-dimethyl aniline (1.5 mmol) and $FePO_4$ (10 mol%) at 100°C.

After completion of the reaction, hot ethanol (10 mL) was added to the reaction mixture, the catalyst was immediately filtered off, and mother liquor was cooled to obtain crystals. The desired product was separated by filtration. For more purification the product was recrystallized from ethanol.

Recycling of the catalyst. The catalyst separated from the reaction mixture was washed with hot ethanol and air dried for the catalyst recovery study. Some reactions were carried out by recovered catalyst without observation of appreciable loss in catalyst activity.

RESULTS AND DISCUSSION

Our initial attempts to test the feasibility of the reaction employed benzaldehyde and *N,N*-dimethyl aniline under various reaction conditions. To optimize the reaction conditions, the influence of reaction time, temperature, solvent and the amount of catalyst was investigated.

To establish the optimum amount of the catalyst for this reaction, various ratios of $FePO_4$ were examined using benzaldehyde (0.5 mmol), *N,N*-dimethyl aniline (1.5 mmol) at 100°C as a model reaction (Table 1). Observed that 20% of the desired products were obtained in the absence of catalyst over 24 h. As shown in Table 1, the best results were obtained with 10 mol % of $FePO_4$. Thus the catalyst is essential component for the synthesis of 4,4'-diamino)triarylmethanes.

The reaction of *N,N*-dimethyl aniline with benzaldehyde in the presence of $FePO_4$ was carried out in various solvents such as water, ethanol and under solvent-free condition. Found solvent-free is the most effective condition (entry 2, Table 2).

The results revealed that a wide variety of substituents were tolerated on the arene, in different positions. The aryl aldehydes with electron-withdrawing groups such as halo-substituents at the *para*- and nitro-substituents at the *ortho*-, *meta-,* and *para* positions gave excellent yields. However with electron-donating groups such as

Table 3. Catalytic preparation of 4-((4-(dimethylamino)phenyl)(phenyl)methyl)-*N,N*-dimethylbenzenamine in presence of $FePO_4$

Entry	Ar	Product	Time, h	Yield, %	mp, °C	
					found	reported [ref.]
1	C_6H_5	**3a**	4	82	89–91	91–92 [22]
2	4-Me-C_6H_4	**3b**	5	75	95–97	97–98 [22]
3	4-Cl-C_6H_4	**3c**	3	92	88–90	88–89 [22]
4	3-NO_2-C_6H_4	**3d**	2	86	145–147	146–148 [22]
5	4-N$(Me)_2$-C_6H_4	**3e**	5	70	166–167	167–68 [23]
6	3,4-$(OMe)_2$-C_6H_4	**3f**	5	68	Oil	Oil [24]
7	2-NO_2-C_6H_4	**3g**	3	90	152–154	153–154 [22]
8	4-NO_2-C_6H_4	**3h**	2	94	170–172	170–171 [25]

methyl were obtained lower yields of the desired products in longer reaction times than those of with electron-withdrawing groups. These substituents decrease the electrophilicity of carbonyl group in the corresponding electrophilic aromatic substitution reactions (Scheme 1).

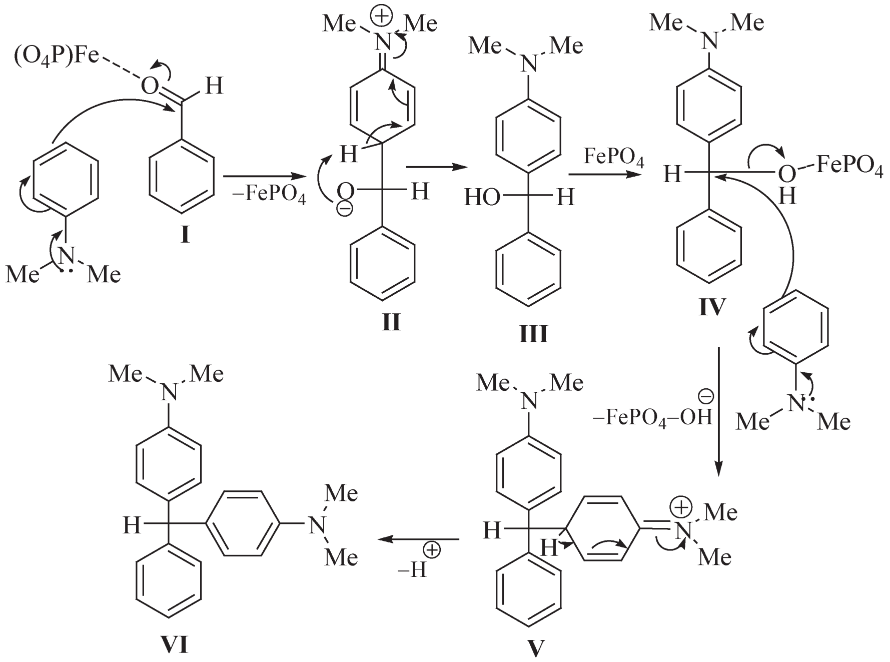
A reasonable pathway for the synthesis of 4,4'-diaminotriarylmethanes in the presence of $FePO_4$ is presented in Scheme 2.

This reaction probably proceeds through the activation of a carbonyl group by coordination $FePO_4$ as a Lewis acid to give intermediate **I** and is followed by *N,N*-dimethyl aniline attack to **I** to give **II**. After proton rearrangement to result **III**, the other *N,N*-dimethyl aniline is added to **IV**-$FePO_4$-activated complex. Loss of $FePO_4$–OH^- to afford **V**, and deprotonation of **V** to give the product **VI** (Scheme 2).

CONCLUSIONS

We have developed a simple, efficient and green methodology for the synthesis of diaminotriarylmethane leuco base materials using a catalytic amount of $FePO_4$.

Scheme 2. Proposed mechanism for the synthesis of 4,4'-diaminotriarylmethanes catalyzed by $FePO_4$



The simple experimental procedure and good yields are the advantages of the present method.

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