

## Synthesis of 4,4'-Diaminotriphenylmethane Derivatives Using $H_3PW_{12}O_{40}$ and HZSM5 Zeolite under Solvent-Free Conditions

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An efficient and very simple method for synthesis of 4,4'-diaminotriphenylmethane and its derivatives has been achieved *via* reaction of various substituted aromatic aldehydes containing both electron-donating and electron-withdrawing groups with various anilines having electron-withdrawing and electron-donating groups in the presence of catalytic amounts of HZSM5 zeolite and  $H_3PW_{12}O_{40}$  under solvent-free conditions. The reaction proceeded with shorter reaction time and higher yield compared to the results obtained in different solvents. Anilines having electron-donating groups in comparison with those having electron-donating group performed this transformation in better yields. Also the results show that the steric hindrance plays an important role in this transformation. Reusability is an advantage of the HZSM5 zeolite, while it showed lesser activity than  $H_3PW_{12}O_{40}$ . The one-pot reaction, simple work up, high yields, use of efficient catalytic amount and eco-friendly reagents are the advantages of the proposed method. All products were characterized using  $^1H$  NMR,  $^{13}C$  NMR and IR.

**Keywords:** Zeolite,  $H_3PW_{12}O_{40}$ , Diaminotriphenylmethane, Solvent-free

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### INTRODUCTION

Heteropoly acids (HPAs) and zeolites have been extensively studied as acid catalysts for many reactions and have found industrial applications in several processes [1,2]. These catalysts are very important for industries associated with fine chemicals, flavours, pharmaceuticals and foods [3,4] and are also used as industrial catalysts for several liquid-phase reactions [5,6] such as alkylation [7,8], esterification [9,10] and reductive amination [11]. From among heteropoly acids and H-type zeolites, polytungstic acids and HZSM5 have been widely used in various organic reactions because they are strong Bronsted and Lewis acids [12,13].

An extensive application of heterogeneous catalysts in synthetic organic chemistry can help to render more attractive

the processes from environmental as well as economic point of view [14,15].

The *para*-substituted triphenylmethane dyes represent a class of synthetic dyes of commercial and analytical importance. These dyes are renowned for their outstanding intensity of color, their brilliant shades of red, blue and green, and low light fastness on many substrates. In fact, it is due to these features that triphenylmethane dyes are divided into two categories, namely, situations where, (1) low light fastness is not a problem and intensity of color is advantageous, and (2), where low light fastness is of interest [16]. Numerous applications capitalize on the intensity, range, and light fastness of color exhibited by these dyes. For example, triphenylmethane dyes are used extensively in the textile industries for dyeing cotton, wool, silk, nylon. They are generally considered as the xenobiotic compounds, which are very recalcitrant to biodegradation [17]. Triphenylmethane

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dyes also function as colorants in food, cosmetic, and ink industries, as saturable absorbers in laser mode locking, as reagents in protein assays, as histological stains [16], and as indicators in spectrophotometric determinations of surfactants [18,19], metal ions [20], and fungicide [21,22].

Now, we report here an efficient and convenient procedure for the synthesis of diaminotriphenylmethane and its derivatives in the presence of HZSM5 zeolite and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  as catalysts under solvent-free conditions.

## EXPERIMENTAL

### Materials and Apparatus

Zeolite characterized by X-ray diffraction (XRD), measured on a Philips analytical PC-APD X-ray diffractometer using monochromator CV  $K\alpha$  radiation (30-40 KV and 40-50 mA), was used. The signals in the XRD pattern of ZSM5 powder can be indexed from the ASTM data. The XRD pattern shows signals at ranges of  $2\theta = 7-9^\circ$  and  $23-25^\circ$ , which correspond to the specific peaks of ZSM5 zeolite. This indicates that the used zeolite powder is ZSM5 zeolite crystal.

Materials were purchased from Fluka and Merck companies. IR spectra were recorded on Bruker VECTOR 22 spectrometer.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra were recorded with Bruker DRX500 AVANCE (300 MHz) spectrometers, using  $\text{CDCl}_3$  as solvent. Reaction monitoring and purity determination of the products were accomplished by TLC.

### Typical Procedure for Synthesis of 4,4'-Diamino-4''-hydroxytriphenylmethane Using $\text{H}_3\text{PW}_{12}\text{O}_{40}$ under Solvent-Free Conditions

4-Hydroxybenzaldehyde (0.122 g, 1 mmol), aniline (0.282 g, 3 mmol) in the presence of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (0.07 g) was ground under solvent-free conditions. The mixture was heated at  $120^\circ\text{C}$  for 0.5 h under inert atmosphere ( $\text{Ar}$  or  $\text{N}_2$ ). The reaction mixture was then cooled to room temperature, and the excess of aniline was distilled in vacuum. The mixture was dissolved in acetonitrile and the product was purified by column chromatography (eluent: *n*-hexane:*EtOAc* 1:1). The 4,4'-diamino-4''-hydroxytriphenylmethane was obtained (0.202 g, 70%) m.p.:  $200-202^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.9 (s,  $\text{NH}_2$ , 4H), 5.1 (s, CH, 1H), 6.4-6.9 (m, Ph, 12H), 9.2 (s, OH, 1H).

### Typical Procedure for Synthesis of 4,4'-Diaminotriphenylmethane Using HZSM5 under Solvent-Free Conditions

Benzaldehyde (0.106 g, 1 mmol), aniline (0.282 g, 3 mmol) in the presence of HZSM5 (0.1 g) was ground under solvent free condition. The mixture was heated at  $120^\circ\text{C}$  for 8 h under inert atmosphere ( $\text{Ar}$  or  $\text{N}_2$ ). The reaction mixture was then cooled to room temperature, and the excess of aniline was distilled in vacuum. The mixture was dissolved in acetonitrile and the product was purified by column chromatography (eluent: *n*-hexane:*EtOAc* 3:2). The 4,4'-diaminotriphenylmethane was obtained (0.232 g, 85%) m.p.:  $138-139^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.6 (s,  $\text{NH}_2$ , 4H), 5.4 (s, CH, 1H), 6.6-7.3 (m, Ph, 13H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ); 55.6, 115.5, 126.4, 128.6, 129.8, 130.6, 135.2, 144.9, 145.6.

## RESULTS AND DISCUSSION

At first, the reaction conditions were optimized by investigating the reaction of aniline with benzaldehyde using 2:1 and 3:1 mole ratios, respectively, in the presence of catalyst (0.1 g) under solvent-free conditions at  $120^\circ\text{C}$ . Higher yields were observed in the case of using 3:1 mole ratio (Table 1).

As shown in Table 1, the reaction proceeded efficiently under inert atmosphere ( $\text{Ar}$  or  $\text{N}_2$ ) and in the presence of catalytic amounts of HZSM5 zeolite (0.1 g) and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (0.07 g) at 8 and 0.5 h, respectively, with 3:1 mole ratio of aniline and benzaldehyde at  $120^\circ\text{C}$ .

Then, the obtained results under solvent-free conditions were compared with those obtained in different solvents such as DMSO, *p*-xylene and tetrahydronaphthalene (5 ml) using 0.1 g of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  or HZSM5 (Table 2). As shown in Table 2, the reaction proceeded under solvent-free conditions with shorter reaction time and higher yield compared to the results obtained in different solvents.

The method was then applied for the efficient and chemoselective synthesis of diaminotriphenylmethane derivatives from aromatic aldehydes and different anilines containing either electron-donating or electron-withdrawing groups in the presence of HZSM5 zeolite and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  as catalysts under solvent-free conditions. All reactions were

## Synthesis of 4,4'-Diaminotriphenylmethane Derivatives

**Table 1.** Synthesis of Diaminotriphenylmethane Using H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and HZSM5 under Solvent-Free Conditions and Inert Atmosphere (Ar or N<sub>2</sub>) at 120 °C<sup>a</sup>

Entry	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> (g)	HZSM5 (g)	Isolated yields (%)	
			H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	HZSM5
1	0.05	0.05	55	50
2	0.07	0.07	80	65
3	0.10	0.10	80	85
4 <sup>b</sup>	0.10	0.10	75	70
5 <sup>c</sup>	0.10	0.10	80	85
6	0.15	0.15	80	85

<sup>a</sup>Molar ratio of aldehyde:amine was 1:3. <sup>b</sup>The reaction was carried out at 100 °C. <sup>c</sup>The reaction was carried out at 140 °C.

**Table 2.** Synthesis of Diaminotriphenylmethane Using H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and HZSM5 under Inert Atmosphere (Ar or N<sub>2</sub>) at 120 °C<sup>a</sup>

Entry	Solvent	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>		HZSM5	
		Yields (%)	Time (h)	Yields (%)	Time (h)
1	DMSO	35	24	35	24
2	<i>p</i> -Xylene	20	24	20	24
3	Tetrahydronaphthalene	10	24	10	24
4	Solvent-free	80	0.5	85	8

<sup>a</sup>Reactions were occurred in different solvents and under solvent free condition using catalytic amount of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> or HZSM5 (0.1 g) and molar ratio of benzaldehyde:aniline was 1:3.

completed in good yields. The results are summarized in Table 3.

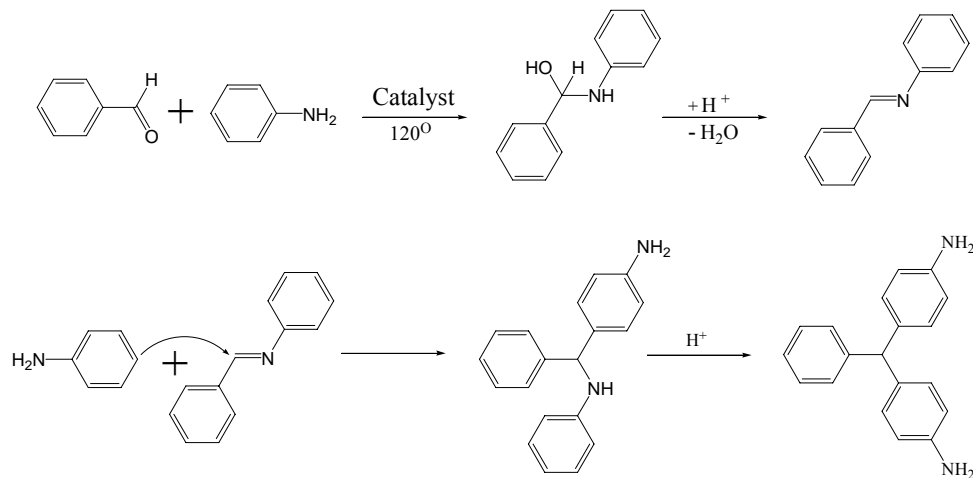
The reaction involves the initial formation of an amine which is converted to the product in the presence of excess of aniline (Scheme 1).

As shown in Table 3, various substituted aromatic aldehydes containing both electron-donating and electron-withdrawing groups (entries 6-9) were converted to diaminotriphenylmethane derivatives in good yields. Aromatic aldehydes having electron-withdrawing groups in *ortho* or *para* positions such as NO<sub>2</sub> and Cl performed this transformation in higher yields compared to aldehydes carrying electron-donating groups such as OH. Aromatic aldehydes with electron-withdrawing groups such as Cl in

*meta* position show less reactivity (Table 3, entry 10). The effect of electron-withdrawing groups such as NO<sub>2</sub> and Cl on aniline was studied wherein the corresponding diaminotriphenylmethane in slightly lower yields in comparison with compounds having electron-donating groups was obtained (Table 3, entries 2,4,11).

Anilines having electron-donating groups such as CH<sub>3</sub>, in comparison with those having the NO<sub>2</sub> group, performed this transformation in better yields (entries 2-3). Entry 4, Table 3, shows that the steric hindrance plays an important role in this transformation.

In order to show the advantages and drawbacks of our method, we have compared some of our results with those reported in the literature in Table 4. This shows that our



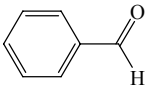
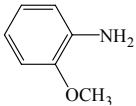
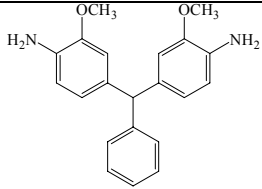
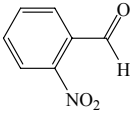
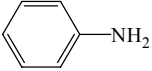
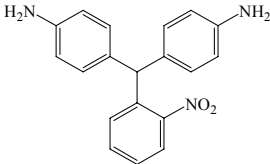
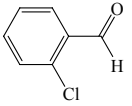
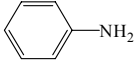
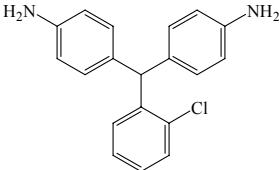
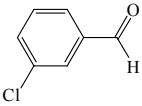
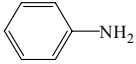
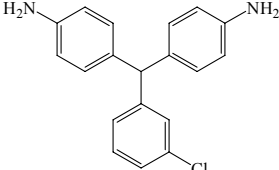
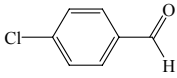
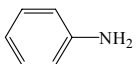
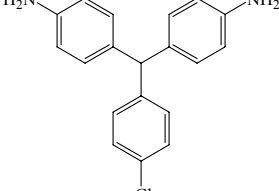
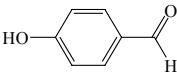
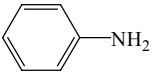
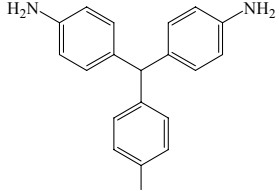
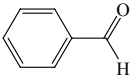
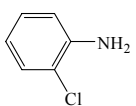
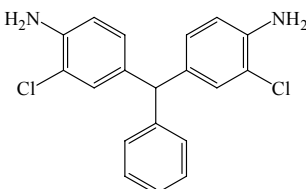
Scheme 1

**Table 3.** Synthesis of Diaminotriphenylmethane Derivatives Using H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub><sup>a</sup> and HZSM5<sup>b</sup>

Entry	Aldehyde	Amine	Product	Isolated yield <sup>c</sup>	
				H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	HZSM5
1				80	85
2				85	90
3				45	50
4				77	80

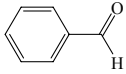
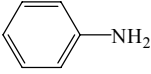
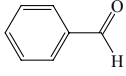
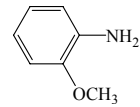
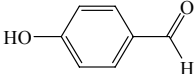
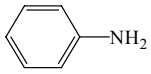
## Synthesis of 4,4'-Diaminotriphenylmethane Derivatives

Table 3. Continued

5				70	75
6				78	84
7				76	80
8				40	45
9				77	80
10				70	80
11				50	55

<sup>a</sup>Reactions were occurred in 0.5 h under solvent-free condition at 120 °C using catalytic amount of  $H_3PW_{12}O_{40}$  (0.07 g, 2.5 mol%) and molar ratio of aldehyde:amine was 1:3. <sup>b</sup>Reactions were occurred in 8 h under solvent free condition at 120 °C using catalytic amount of HZSM5 (0.1 g) and molar ratio of aldehyde:amine was 1:3. <sup>c</sup>All products were characterized spectroscopically ( $^1H$  NMR,  $^{13}C$  NMR and IR) and showed physical spectral data in accordance with their expected structure and by comparison with authentic samples.

**Table 4.** Comparison of the Results Obtained by  $H_3PW_{12}O_{40}$  and HZSM5 with Other Reagents for Synthesis of Diaminotriphenylmethane Derivatives

Entry	Aldehyde	Amine	$H_3PW_{12}O_{40}$ Yield (%)	HZSM5 Yield (%)	Other methods [23] Yield (%)	
					I	II
1			80	85	91	75
2			70	75	81	65
3			70	80	90	65(40) [24]

I) Aniline hydrochloride/MW at power 100 W and 90 °C. II) Aniline hydrochloride using heating method (150 °C).

method gives higher yields of the corresponding amines compared with similar conditions (method II).

## CONCLUSIONS

In this study, we have described an effective and very simple method for preparation of diaminotriphenylmethane and its derivatives using catalytic amounts of HZSM5 zeolite and  $H_3PW_{12}O_{40}$  under solvent-free conditions.

Good catalytic properties of  $H_3PW_{12}O_{40}$  and HZSM5 zeolite are responsible for easy synthesizing of the industrially important diaminotriphenylmethane.  $H_3PW_{12}O_{40}$  showed better activity than the HZSM5 zeolite according to the reaction time (0.5 h compared to 8 h). Reusability of the HZSM5 zeolite is its advantage.

The one-pot reaction, simple work up, high yields, use of efficient catalytic amount and eco-friendly reagents with no special handling techniques are the notable advantages of the presented method.

## ACKNOWLEDGEMENTS

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