Original Article

Microwave assisted synthesis of 4’, 4”-Dihydroxytriphenylmethane derivatives using Montmorillonite K10 clay

Kalyani Sambaru* and Ramchander Merugu
University College of Science and Informatics, Mahatma Gandhi University, Nalgonda, AP, India
*Corresponding author email: ksambaru@gmail.com

Received 25 January 2014; accepted 13 February 2014

Abstract
An efficient and very simple method for microwave assisted synthesis of 4’, 4”-dihydroxytriphenylmethane and its derivatives was carried out by condensation reaction of various substituted aromatic aldehydes with phenol in the presence of montmorillonite K10 clay. Compared to the other conventional acid catalysts, the reaction proceeds at a faster rate and gives higher yield. The one pot reaction, simple workup, high yields, use of efficient, ecofriendly, inexpensive stable catalyst are the advantages of the proposed method. The triphenylmethane products synthesized were characterized by their IR spectra, NMR and Mass spectra.

Key words: Microwave, Montmorillonite, Condensation, Dihydroxytriphenyl methane.

INTRODUCTION
In recent years, the use of microwave irradiation for organic synthesis has been well-established. Microwave (MW) activation as non-conventional energy source has become a very popular, useful and gained wide popularity due to short reaction times, high yields and environment-friendly reaction conditions. The application of the solvent-free technology coupled with the solid support provides an efficient method to prepare organic compounds very fast with high purity. Moreover, microwave irradiation is a very clean and modern technique widely used for green chemistry synthesis. Dihydroxytriphenylmethane derivatives are known for their biological activities such as antifungal, antitumor, antitubercular, antioxidant activity, anticancer activity, antiviral, inhibition activity for histidine protein kinases and as anti-inflammatory agents. They are also widely used in the chemical industry (Figure 1) as leuco dyes, phytochromatic agents, for generation of dendrimers, and substrates for theoretical and biological studies.

There are many methods for the construction of triphenylmethanes most of which are either multistep or requires harsh reaction conditions. Due to the above disadvantages there exists a need for the development of newer methods for the triphenylmethane derivative synthesis. Most methods known are protic acid catalysed where the catalysts are used in higher concentration. The catalysts used cause corrosion and environmental pollution. Herein is reported a practical and efficient method for the synthesis of some 4’, 4”-dihydroxytriphenylmethane derivatives using montmorillonite K10 clay under microwave irradiation which offers several advantages over classical acids. All the new compounds were characterized by their elemental analyses and their spectral data.

EXPERIMENTAL
All chemicals were purchased from Sigma-Aldrich and employed without further purification. The 1H NMR spectra were recorded on Varian Mercury 300 MHz using DMSO-d6 and tetramethylsilane (TMS) as solvent and internal standard, respectively. FTIR were recorded in KBr disc on Schimadzu 8300 spectrophotometer. All melting points were recorded using open capillary tube and uncorrected. TLC was performed on silica gel as a stationary phase, hexane and ethyl acetate as eluent. Chemicals and solvents were reagent grade and used without further purification. Melting points were determined on a Cintex melting point apparatus and are uncorrected.

Typical Procedure for Synthesis of 4’, 4”-Dihydroxydiphenyl (2-pyridyl) methane (1a):
To a solution of pyridine-2-carbalddehyde (1 g, 9.3 mmol) and phenol (1.75 g, 18.69 mmol) in CH2Cl2 (10 mL) was added clay (0.1 g) and subjected to microwave irradiation at 600W for 2 min. After completion of the reaction, the reaction mixture was filtered. It was then washed with water and concentrated to yield syrup. The crude syrup was chromatographed [SiO2 60-120 mesh, hexane: ethylacetate (3:7)] to obtain 4’, 4”-dihydroxydiphenyl (2-pyridyl) methane 1a in 65.4% yield and 2’, 4”-dihydroxydiphenyl (2-pyridyl) methane 1b as...
Scheme 1:

\[
\begin{align*}
&\text{1a) } R_1 = H, R_2 = H \\
&\text{2) } R_1 = \text{COCH}_3, R_2 = \text{COCH}_3 (\text{Bisacodyl})
\end{align*}
\]

Scheme 2:

\[
\begin{align*}
&\text{2a-8a} \\
&\text{2b-8b}
\end{align*}
\]

2 = X, Y = H, Z = F
3 = X, Y = H, Z = Me
4 = X = Cl, Y, Z = H
5 = X = H, Y = Cl, Z = H
6 = X, Y = H, Z = OCH\(_3\)
7 = X = Cl, Y = H, Z = Cl
8 = X, Y = H, Z = NO\(_2\)
In the present study, the generality of the condensation reaction of pyridine-2-aldehyde with phenol by use of Montmorillonite K10 clay as a catalyst to prepare bisacodyl has been explored (Scheme 1). The reactions were carried out by carrying condensation on various aromatic aldehydes substituted at ortho, meta and para positions to give the corresponding triphenyl methanes. The compound 1a was characterized from the 1H NMR by the appearance of two AB type doublets at δ 6.60 and 6.92. The methine hydrogen was seen as a singlet at δ 5.28. Appearance of m/z at 295 in the mass spectrum was in agreement with the structure. The IR spectrum showed absorption at 835 cm⁻¹ and 3092 cm⁻¹ indicating presence of para substituted benzene and the hydroxyl group respectively.

The compound 1b displayed complex aromatic signals, the methine hydrogen appeared at δ 5.40 (1H). The studies were continued on several other aromatic aldehydes bearing halogen substituents at ortho and para position eg. 2-chlorobenzaldehyde 4, 4-nitrobenzaldehyde 8, 3-chloro benzaldehyde 5, 2, 4-dichloro benzaldehyde 7, and aldehydes bearing electron donating substituents eg. 4-methylbenzaldehyde 3 and 4-methoxy benzaldehyde 6. These reactions led to the formation of the 4', 4''-linked product as a major product and the 2', 4''-linked product as a minor product. Only in the case of 2', 4''-dichloro benzaldehyde the 4', 4''-linked product was obtained.

Characterization of 4', 4'' and 2', 4''-products:
The 1H NMR spectrum of the 4', 4''-substituted product showed two AB type doublets. The 2', 4''-substituted product showed a complex aromatic pattern where the methine hydrogen appeared down field for the 2', 4''-product. IR spectrum showed absorption at 815 cm⁻¹ indicating a para substitution in case of 4', 4''-linked product while in the case of 2', 4''-linked product an absorption peak at 765 cm⁻¹ was seen.

RESULTS AND DISCUSSION

In the search of an effective green method for the synthesis of stated compounds, we carried out condensation on various aromatic aldehydes substituted at various positions on the aromatic ring with phenol using Montmorillonite K10 clay as a catalyst to prepare bisacodyl which is a one step preparation of bisacodyl syrup. These reactions led to the formation of the 4', 4''-linked product as a major product and the 2', 4''-linked product as a minor product. Only in the case of 2', 4''-dichloro benzaldehyde the 4', 4''-linked product was obtained.

CONCLUSIONS

In the search of an effective green method for the synthesis of stated compounds, we took the solid support montmorillonite K10 which is a one-pot reaction with simple work up giving higher yields under microwave irradiation.

REFERENCES

Source of support: Nil; Conflict of interest: None declared