



SHORT COMMUNICATION

An efficient synthesis and spectroscopic characterization of Schiff bases containing the 9,10-anthracenedione moiety

GHULAM FAREED^{1,2*}, MUHAMMAD ALI VERSIANI², NIGHAT AFZA¹,
NAZIA FAREED², MUHAMMAD IRFAN ALI¹ and MAHBOOB ALI KALHORO¹

¹Pharmaceutical Research Center, PCSIR Laboratories Complex Karachi, Shahrah-e-Dr. Salim-uz-Zaman Siddiqui, Karachi-75280, Sindh, Pakistan and ²Department of Chemistry, Federal Urdu University of Arts, Science and Technology, Ghulshan-e-Iqbal, Karachi-75300, Sindh, Pakistan

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Abstract: A new method was developed for the synthesis of novel Schiff bases containing the anthraquinone moiety using dodecatungstosilicic acid/P₂O₅ under solvent-free conditions at room temperature. The reaction was completed in 1–3 minutes with excellent yields. This method was found to be very efficient, easy and hazardous-free for the synthesis of azomethines. The development of these types of methodologies in synthetic chemistry may contribute to green chemistry. The structures of synthesized novel Schiff bases were elucidated using ¹H-NMR, ¹³C-NMR, LC–MS, FTIR and CHN analysis.

Keywords: azomethine; dodecatungstosilicic acid; P₂O₅; anthraquinone.

INTRODUCTION

Schiff bases, a versatile class of organic compounds synthesized by the condensation of primary amines with aromatic carbonyl compounds, bear many pharmaceutical properties, including anticancer, antitumor, antibacterial, antifungal, antioxidant, herbicidal, antiproliferative, antimalarial and anticovulsant activities.^{1–16} Schiff bases act as ligands in coordination chemistry¹⁷ and are considered a subject of interest due to their industrial and biological applications.¹⁸

Similarly 9,10-anthracenediones are a very important class of compounds having some remarkable *in vivo* biological activities, such as antibacterial, antifungal, antimalarial, antioxidant, antileukemic, hypotensive, mutagenic functions, and analgesic activity.^{19–27}

Moreover, in the recent era, the use environmentally benign, facile and low costing method for the synthesis of biologically active compounds has received

* Corresponding author. E-mail: fareedchm@yahoo.com
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great attention of synthetic chemists. Based on green chemistry and facile methodologies, numerous methods have been used for the synthesis of Schiff bases, *e.g.*, catalyzed by TiCl_2 ,²⁸ ZnCl_2 ,²⁹ $\text{Mg}(\text{ClO}_4)_2$,³⁰ $\text{P}_2\text{O}_5/\text{SiO}_2$,³¹ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$,³² montmorillonite K-10³³ and MgSO_4 -pyridinium *p*-toluenesulfonate (PPTL).³⁴

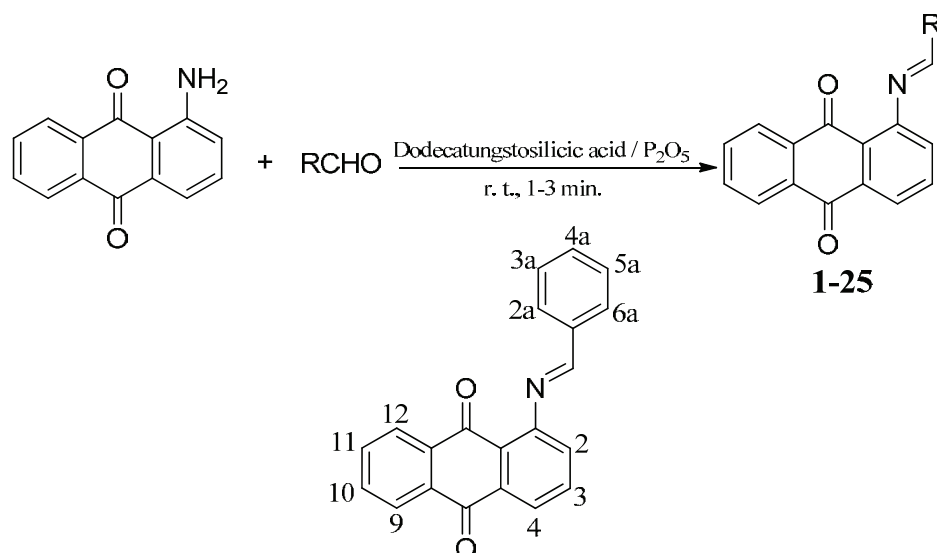
In view of the above facts, results concerning the syntheses of novel Schiff bases using dodecatungstosilicic acid/ P_2O_5 as a catalyst are reported herein. The employed method was found to be very efficient and environmentally friendly.

EXPERIMENTAL

Melting points were measured in open glass capillaries using a Gallenkamp MF-370 melting point apparatus. The IR spectra were recorded on a Nicolet Avatar 300 DTGS instrument. The ^1H - and ^{13}C -NMR were recorded on Bruker A V-300 instrument operating at 300 and 75 MHz, respectively, using deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) as the solvent and trimethylsilane (TMS) as an internal standard. The mass spectra were recorded on a Finnigan LCQ Advantage Max instrument. The CHN analyses were realized on a Carlo Erba instrument – Mod-1106. The purity of the products were determined by TLC using silica gel 60F₂₅₄ precoated cards (0.2 mm thickness) and visualized under UV light (254 and 366 nm) and by iodine vapors. All chemicals were of AR grade. Analytical and spectral data for the synthesized compounds are given in the Supplementary material.

General method for the synthesis of Schiff bases 1–25

A mixture of 1-aminoanthraquinone (1 mmol), a substituted aromatic aldehyde or ketone (1 mmol) and dodecatungstosilicic acid/ P_2O_5 (0.2 g, 1 mol % of 1-aminoanthraquinone/ P_2O_5) as a catalyst was ground in a mortar with a pestle under solvent-free conditions at room temperature for 1–3 min, Scheme 1. The reaction mixture turned to a pasty material that



Scheme 1. Preparation of Schiff bases.

indicated the completion of the reaction. Crushed ice was added to afford precipitates of the Schiff bases. In order to remove the catalyst, the product was washed several times with ice-cold water. The solid products were obtained in excellent yield.

RESULTS AND DISCUSSION

The aim of this work was to develop a new facile method for the preparation of Schiff bases. To the best of our knowledge and a literature search, the synthesis of novel Schiff bases using dodecatungstosilicic acid/P₂O₅ has not been previously reported.

An efficient methodology was established using an acidic catalyst for the synthesis of novel Schiff bases by the condensation of 1-aminoanthraquinone with aromatic carbonyl compounds under solvent free conditions at room temperature. The reactions were completed in 1–3 minutes and the products were obtained in high yield after simple work-up (Table I). In order to develop optimum conditions for this synthesis, varying amounts of dodecatungstosilicic acid/P₂O₅ were used using 4-hydroxybenzaldehyde and 1-aminoanthraquinone under solvent-free conditions at room temperature as a model reaction (Table II). The method is very simple and contributes to the hazardous-free synthesis. The catalyst dodecatungstosilicic acid/P₂O₅ was found to be very efficient compared to other catalysts used for the synthesis of imines (Table III).

TABLE I. Synthesis of Schiff bases using *dodeca*-tungstosilicic acid/P₂O₅ as a catalyst

Entry	Substrate	<i>t</i> / min	Entry	Substrate	<i>t</i> / min
1	3-Hydroxybenzaldehyde	2	14	2,4-Dihydroxybenzaldehyde	2
2	4-Hydroxybenzaldehyde	1	15	4-(Diethylamino)benzaldehyde	3
3	3-Chlorobenzaldehyde	2	16	α -Bromocinnamaldehyde	3
4	Furfural	1	17	3,5-Dibromo-4-hydroxybenzaldehyde	2
5	4-Hydroxy-3-methoxybenzaldehyde	2	18	4-(Dimethylamino)cinnamaldehyde	3
6	3-Bromo-4-hydroxybenzaldehyde	2	19	2-Ethoxybenzaldehyde	3
7	4-Nitrobenzaldehyde	2	20	4-(Dimethylamino)benzaldehyde	2
8	3-Bromobenzaldehyde	1	21	2-Hydroxyacetophenone	1
9	3-Nitrobenzaldehyde	3	22	3,5-Dimethoxybenzaldehyde	2
10	2-Nitrobenzaldehyde	3	23	4-Methoxycinnamaldehyde	1
11	4-Methoxybenzaldehyde	1	24	4-Ethoxybenzaldehyde	1
12	4-Chlorobenzaldehyde	2	25	4-Methylbenzaldehyde	2
13	4-Chloro-3-nitrobenzaldehyde	1			

Moreover, the structures of the products were elucidated by LC–MS, ¹H-NMR, ¹³C-NMR, IR, and CHN analysis. The ¹H-NMR spectra of all the compounds was quite simple and the azomethine group (–N=CH–Ar) of all the synthesized Schiff bases was found in the region of 7.4–8.9 ppm. The aromatic protons ap-

peared as a multiplet in the region of 6.74–7.90 ppm depending on the aromatic substituent. In IR spectrum, -N=C- appears in the region 1511–1545 cm^{-1} .

TABLE II. Effect of different amounts of catalyst on the yield of 1-[(4-hydroxyphenyl)-methylidene]amino}-9,10-anthraquinone

Entry	Catalyst, mol %	Reaction time, min	Yield, %
1	Free	20	50
2	0.5	10	70
3	1	1	87
4	1.5	1	87

TABLE III. Comparison with other catalysts used for the synthesis of Schiff base

Entry	Catalyst	Solvent	Reaction Time	Yield, %	Ref.
1	$\text{Mg}(\text{ClO}_4)_2$	1,2-Dichloroethane	8 h	80	30
2	$\text{SiO}_2/\text{P}_2\text{O}_5$	–	13–26 min	88	31
3	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	MeOH/EtOH/DMF	20–30 min	60–88	32
4 ^a	Montmorillonite K-10	–	1–3 min	80	33
5	ZnCl_2	1,2-Dichloroethane	8 h	46	30
6	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	1,2-Dichloroethane	8 h	65	30
7	TiCl_2	1,2-Dichloroethane	8 h	35	30

^aUnder microwave conditions

CONCLUSION

Based of the excellent yields, short reaction time, easy work-up, solvent-free facile and environment greener reaction, it could be concluded that dodecatungstosilicic acid/ P_2O_5 is a very useful catalyst for the synthesis of Schiff bases.

SUPPLEMENTARY MATERIAL

Analytical and spectral data for the synthesized compounds are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

ЕФИКАСНА СИНТЕЗА И СПЕКТРОСКОПСКА КАРАКТЕРИЗАЦИЈА ШИФОВИХ БАЗА КОЈЕ САДРЖЕ 9,10-АНТРАЦЕНДИОНСКИ СТРУКТУРНИ ФРАГМЕНТ

GHULAM FAREED^{1,2}, MUHAMMAD ALI VERSIANI², NIGHAT AFZA¹, NAZIA FAREED², MUHAMMAD IRFAN ALI¹ и МАНВООВ АЛИ КАЛХОРО¹

¹Pharmaceutical Research Center, PCSIR Laboratories Complex Karachi, Shahrāh-e-Dr. Salim-uz-Zaman Siddiqui, Karachi-75280, Sindh, Pakistan и ²Department of Chemistry, Federal Urdu University of Arts, Science and Technology, Ghulshan-e-Iqbal, Karachi-75300, Sindh, Pakistan

Развијен је нов поступак за синтезу Шифових база које садрже антрахинонски фрагмент, употребом додекаволфрамсилицијумове киселине/ P_2O_5 , у одсуству органских растварача, на собној температури. Реакција је готова у периоду 1–3 min у одличном

приносу. Утврђено је да је поступак ефикаснији, једноставнији и безбеднији. Структуре синтетисаних Шифових база одређене су $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, LC-MS, FT-IR и CHN анализама.

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