MICROWAVE ASSISTED SYNTHESIS & CHARACTERIZATION OF BENZADIAZE PINIUM PICRATES

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ABSTRACT

Cleaning up the environment and, more importantly, preventing pollution volutions for worrying problems, approaching responsible research studying risk and precaution. Scientific organizations as IUPAC and the Organization for are important issues in today's world. There is the necessity for science to provide Economic Co-operation and Development (OECD) utilize their global perspective to contribute toward the enhancement of education in the field of Sustainable Chemistry and advance the public understanding of scientific methods and new technologies for a sustainable development. In order to respect this concept, in 1991, the Environmental Protection Agency (EPA) has introduced the Green Chemistry [1-2].

Green Chemistry is the design of chemical products and processes that reduces or eliminates the use and generation of hazardous substances.

Keywords :- Schiffbase, metal salts, salicyaldehyde, antimicrobial activity.

INTRODUCTION

Green Chemistry has demonstrated, over the course of the past decade, how fundamental scientific methodologies can protect human health and the environment in an economically beneficial manner. Significant progress is being made in several key research areas, such as catalysis, the design of safer chemicals and environmentally benign solvents, and the development of renewable feedstock. Advances in science and technology can address the challenges of global environmental sustainability, which include the release of persistent organic pollutants, climate change, bio-accumulation of contaminants, atmospheric distillation, endocrine disruption and ozone depletion. Achieving sustainability requires an intricate balance between resource use, economic growth and environmental impact. Green chemistry is a growing field of research that ddresses many of these concerns by combining the critical clements of vironmental improvement, cconomic competitiveness and social responsibility. Green chemistry began as a program of the US Environmental Protection

Agency the carly 1990s with the goal of achieving pollution prevention through a sience-based, non-regulatory and economically driven approach [3-10].

To address the issue of implementing sustainability, green chemistry seeks to integrate a new generation of scientific and engineering technologies with economic behavior by analyzing the processes and the materials used in production and development to enhance resource use and faster environmental improvement. The global chemical enterprise provides compelling examples of this relationship.

It is true that more environmentally sound, scientifically viable chemical alternatives to current technologies are being researched and developed, but to be effective, the economic viability of these alternatives must also be demonstrated. Scientists, engineers, policy makers, and especially industry leaders will need to be educated about the availability of alternative technologies and it must be proven that they are both environmentally sustainable and economically sound. This will require an effective system of information dissemination.

Green Chemistry Applied to Environmental Challenges

Green chemistry provides options for addressing the world's most pressing challenges to sustainability, which include population growth, energy production and use, food production, global climate change, toxics in the environment, and non-renewable resource depletion. Green chemistry research has focused on technologies that reduce or eliminate the use or generation of toxic and hazardous materials, as well as on cenlacing non-renewable feed stocks with renewable materials. Green chemistry tries to reduce the toxicity of a product at the most Gundamental level - the molecular level. It attempts to reduce hazards hat have a negative impact on human health and the environment. Adoption of green chemistry will improve the future of industrial science and technology in several important ways.

Microwave assisted organic reaction enhancement (MORE) is now a days a well-established technique for synthesis of various heterocycles. All thermally driven reaction can be accelerated by microwave. The spectacular results viz. shorter reaction time, experimental simplicity selectivity of products and easy work up etc were obtained giving clear indication on the potentialities of this technique over conventional heating [11-13]. The reactions under MWI can be carried out under solvent less solid phase making it a environmentally benign

process. Thus microwave induced organic synthesis becomes a part of green chemistry [14-15]. Now-a-days it is also termed as e-chemistry because it is easy economic, effective and eco-friendly.

EXPERIMENT

All commercially available chemicals were purchased from Fluka and Lancaster Chemical Co. and used as received without further purification.

The microwave irradiations were performed using a commercial / kitchen microwave oven model BMO: 700T (BPL- make). All reactions were monitored by analytical thin layer chromatography using silica gel 60 F precoated plates. and spots were detected either by UV-absorption or iodine. The melting points were determined on a Gallen kamp melting point apparatus and are corrected.

All compounds were analysed satisfactorily for C, H and N using Carl-Ebra 1106 elemenial analyser in micro analytical laboratory.

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 and AVANCE DPX-200 spectrometers and were taken in DMSO-d, and CDCI, at 200 and 400 MHz The chemical shifts are reported in ppm relative to internal tetramethylsilane (6 - 0.00), Multiplicities are described by using the following abbreviations: s = singlet, d=doublet, t = triplet, m = multiplet, br= broad.

FT-IR spectra were obtained on a Bruker Vektor 22 in the range of 400 to 4000 cm" (2.5 % pellets in KBr).

The ultraviolet spectra were obtained on a Perkin-Elmer Model 350 spectrophotometer using absolute methanol as solvent.

SYNTHESIS PROCEDURES

The synthesis of different derivatives of mesomeric betaines involved the following general procedures:

General procedure for the preparation of the 2,4-dimethyl-5H- I. benzo|b||1,4]diazepin-1-picrates (1-18)

Solutions of the diaminobenzene derivatives (1.0 mmol) in ethanol (20 mL) were treated with penkane-2,4-dione (0.1 ml, 1.0 mmol) and a few drops of 0.5 g of picric acid (50% water). The reactions started immediately where upon the color changed to dark violet.

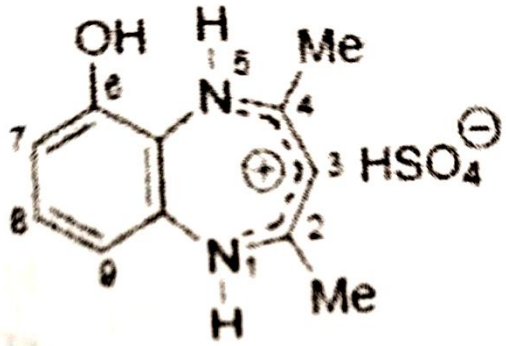
The mixtures were stirred for 30min at room temperature. After concentrating the cathanolic solutions to 20% of its original volume, addition of diethyl ether precipitated solids which were filtered off and washed with diethyl ether to give intensely violet solids, respectively.

6-Hydroxy-2,4-dimethyl-5H-benzo[b] [1,4] diazepin-1-ium hydrogen sulfate (1)

2,3-Diaminophenol (0.124 g, 1 mmol) was used.

Yield: 0.24 g (92 %).

m.p.: 468-470 K



Spectroscopic Data:

^{1}H-NMR (200 MHz, DMSO-d_6) δ = 1. 80 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 4. 32(s, 1H, 3-H), 5.99 (d, *J*= 8.2 Hz, 1H, 9-H), 6.54 (d, *J* = 8.2 Hz, 1H, 7-H), 6.79 (t, *J* = 8.2 Hz, 1H, 8-H), 9.12 (s, 1H, NH), 9.62 (s, 1H, NH), 10.75 (s, 1H, OH).

^{13}C-NMR (50 MHz, DMSO-d_6) δ = 24.1 (CH3), 24.2 (CH3), 95.8 (C-3), 113.7 116.3, 120.3, 129. 8, 136.2, 149.9, 175.2, 176.6.

UV λ_{max} (H,O) 362, 492 nm, λ_{max} (MeOH) 368, 496 nm; λ_{max} (MeCN) 366, 520 nm.

IR (KBr) $\tilde{\nu}$ = 3283, 3050, 1623, 1605, 1519, 1448.

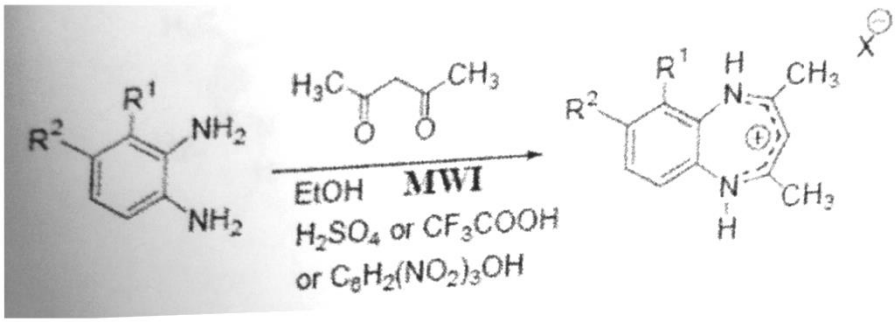
Analytical Data:

Calculated for $C_{11}H_{14}N_2O_5S$ (286.31): C, 46.1, H, 4.9, N, 9.8,

Found: C, 45.7, H, 4.9; N, 9.6.

RESULT AND DISCUSSION

The diamines were reacted with stoichiometric amounts of 2.,4-pentanedione in ethanol at room temperature in the presence of sulfuric acid or trifluoroacetic acid to give the corresponding 1,5-benzodiazepinium salts 1-15 in high yields as intensely violet solids, respectively. It proved to be advantageous to conduct the condensation of the less reactive a-carboxy derivative (v) to 14 in hydrochloric acid Anion exchange to hydrogen sulfate was then accomplished with excess sulfuric acid.



1, 4, 7, 10, 12, 14: X =HSO_4

2, 5, 8, 11, 13, 15: X = CF_3COO

3, 6, 9 : X = Picrate

		R^1	R^2
(i)	1, 2, 3	OH	H
(ii)	4, 5, 6	H	OH
(iii)	10, 11	H	SH
(iv)	14, 15, 16	H	COOH
(v)	12, 13	COOH	H
(vi)	7, 8, 9	H	OMe

Moreover, reaction of the 1,2-diaminobenzenes (i, ii & vi) with acetylacetone in ethanol in the presence of picric acid gave the 1,5- benzodiazepinium picrates 3, 6 & 9 as intensely violet crystals. The presence of picric acid proved to be advantageous in comparison with other acids because the resulting salts readily precipitate from the reaction mixture and are analytically pure after washing with diethyl ether (Scheme-4.12) Not unexpected, the products are protonated due to the strong acıdıty of picric acid (p^{Ka}0.25).

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