International Journal of Multidisciplinary Research and Development

JEZS 2014; 1(1): 41-45

Received: 03-05-2014
Accepted: 18-05-2014
ISSN: 2349-4182

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Synthesis and Identification of new 4-Amino phenazone derivatives containing azo group

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ABSTRACT
This work involves to synthesis derivatives of 4-Amino phenazone and studies their biological activity. Approach the title synthesis devieatives were prepared by reacting 4-Amino phenazone with Salicylaldehyde to form azo compound.
The second step azo compound reacting with various amines to give Schiff bases. The last Schiff bases reacting with maleic and phthalic anhydride. The chemical structures of the synthesized compounds were confirmed on the basis of their spectral data (FTIR, HNMR spectra and CHN analysis).

Keywords: 4-Amino phenazone, Azo compounds, biological activity.

1. Introduction

Azo days contain at least one nitrogen-nitrogen double bond (N=N), however many different structures are possible. Now a days, synthetic azo compounds are widely used in different application fields, such as cosmetics, foods, pints, plastics, automobile industry and in analytical chemistry [2, 7].

Compounds containing the (-C=N-) azomethine group structure are known as Schiff bases, usually synthesized from the condensation of amines and active carbonyl groups. Schiff bases are well known for their biological applications as antibacterial and antifungal [8].

Both Schiff bases and azo compounds are important structures in the medicinal and pharmaceutical fields [9].

4-Amino antipyrine and derivatives are known for their variety of clinical applications. New kinds of chemotherapeutic agents containing Schiff bases have gained significant attention a many biochemists and of those aminopyrine are commonly administered in travenously to detect liver disease in clinical treatment [10]. The Schiff bases of 4-Amino antipyrine and their derivatives have been extensively investigated because of their biological clinical, pharmacological, analytical and material applications [11, 12].

In this paper azo compound synthesized from 4-Amino phenazone and salicylaldehyde, then series Schiff bases were synthesized from azo compound and aniline derivatives, the last synthesize new oxazapine derivatives from Schiff bases with phathalic anhydride and maleic anhydride respectively. The derivatives were identified by CHN analysis, FTIR spectrum and some derivatives were identified by H-NMR spectrum.

2. Experimental

Reagents such as 4-Amino phenazone, aniline derivatives (2-OH,4-acetyl and 4-NO_2) were of BDH preducts, Salicylaldehyde, 2-amino pyrimidine, phthallic anhydride and maliec anhydride were of Merck products. Absolute ethanol, glacial aceticacid, benzene and methanol were of sigma products. FTIR spectra of the samples were recorded on ashemadzu 8400 using KBr disc. H-NMR spectra (400MHZ) of some samples were recorded in DMSO-d, by employing TMS as internal standard at the AL-othmania University, India.

2.1 Preparation of azo compound

The azo compound was synthesized from 4-Amino phenazone with Salicylaldehyde according to shibatta method [13].

2.2 Preparation of Schiff bases (Th2-Th5).

The Schiff bases were prepared by standard method in which azo compound (0.1) mole dissolved in (30 ml) absolute ethanol taken in around bottom flask and then aniline derivatives were added which were dissolved in the same volume absolute ethanol.

The reaction mixture was refluxed for (3-8 h) and then it was cooled to room temperature. Solid obtained was separated and wash with ethanol and finally dried aver calcium chloride.

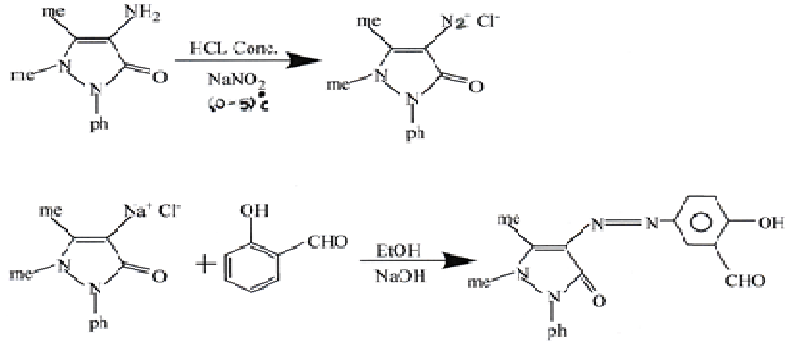
The purity of the preparation Schiff bases were checked by TLC, melting point. (Table) [1].

2.3 Reaction of the Schiff bases derivatives with maleic and phathalic anhydride:

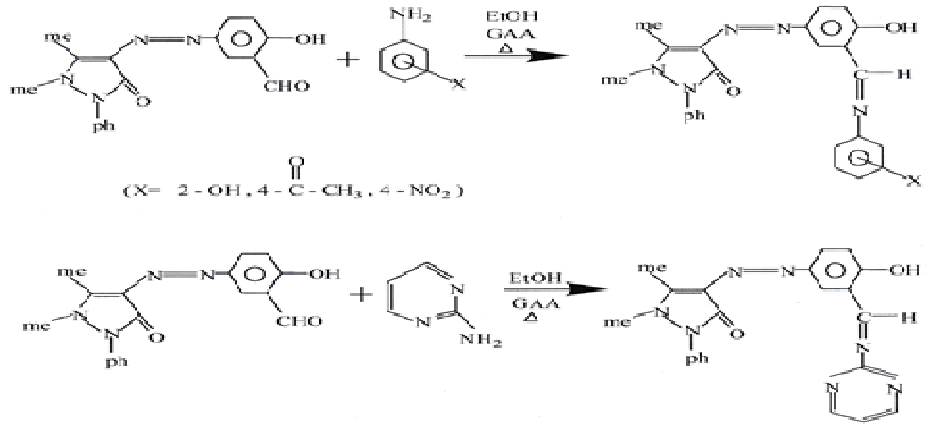
(0.48) mmole of desired imine was dissolved in suitable solvent followed by addition with drop wise the cyclic anhydride refluxing conditions and monitored with (TIC) to determine the completion of the reaction. Filtration or evaporation under reduces pressure, drying and recrystallization by suitable solvent.

2.4 With maleic anhydride:

(0.2 g) (0.48 mmole) of compound was dissolved in dry benzene with stirring flow lmmole of maleic anhydride solution added drop wise with stirring then refluxing at 60 ^{0}c for (3-4 h) the reaction mixture is controlled by TIC technique, after workup the orange precipitate of desired product with percentage yield 70%.

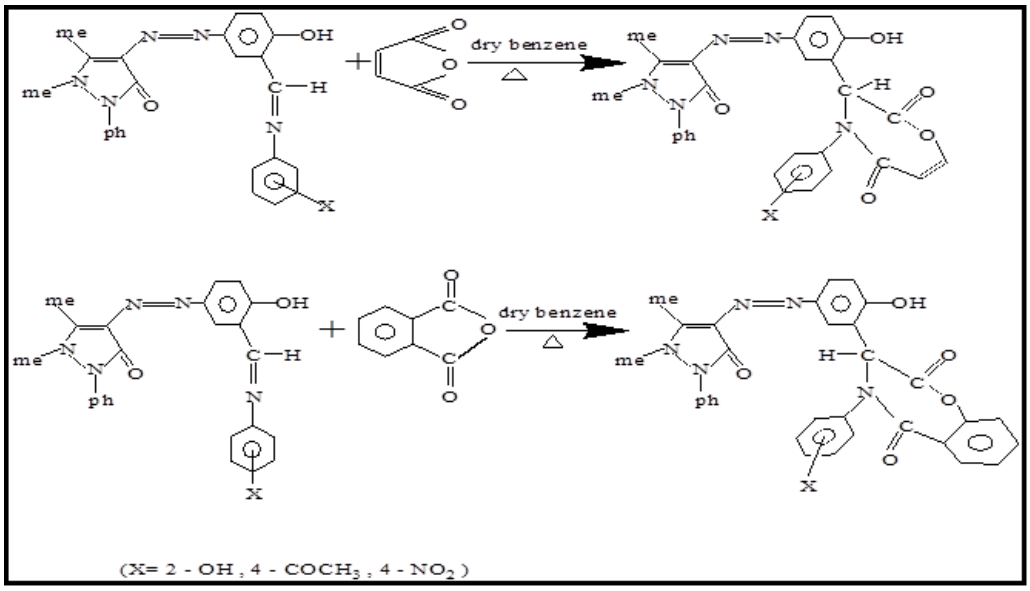


Scheme (1) Synthesis azo compound (Th_1)



Scheme (2) Synthesis Schiff bases derivatives ($Th_2 - Th_5$)

Scheme 1, 2: preparation of azo compounds.



Scheme 3: Synthesis Schiff bases derivatives (Th_2 – Th_5)

3. Results and Discussion

The present work involved three steps

First step: include preparation of azo compound (Th_1) was prepared by reaction of 4- amino phenazone with Salicylaldehyde in the presence sodium nitrite at (0- 5 ^{0}C).

The synthesis of the azo compound was carried out lined in Schem **[1]** and the physical properties for its including melting point and yield % and the azo compound was identified by FTIR spectroscopy

FTIR spectra of compound (Th_1) showed characteristic absorption bands (3421) Cm^{-1} , 2854 Cm^{-1}, 1715 Cm^{-1}, 1593 Cm^{-1} due to ν(OH), νCH aldehyde, ν C=O aldehyde and ν N=N respectively **[14]**.

Second step: The second step include preparation of new four Schiff bases (Th_2- Th_5) were prepared by reaction of azo compound (Th_1) with different amines.

The synthesis of these compounds was carried out lined in Schem (2) and the physical properties for Schiff bases (Th_2- Th_5) including melting points, yield % RF and CHN analysis (Table .1)

FTIR spectrum of compounds (Th_2- Th_5) showed characteristic absorption bands, (3430,1596,1620) Cm^{-1} due to ν (OH) ν N=N and (H-C=N-) respectively and appesence the (C-H) aldehyde and carbonyl group Table(2) .

Third step: the third step including preparation of new oxazepine derivatives (Th_6 –Th_{13}) were prepared by reaction Schiff bases(Th_2- Th_5) with maleic and phathalic anhydride respectively, the physical properties and CHN analysis are listed in Table (1), Scheme (3)

FTIR spectrum of the compounds (Th_6- Th_{13}) showed new b absorption bands (1720 and 1745) Cm^{-1} due to vibration stretching of cyclic ester

HNMR spectrum:

HNMR spectrum of compounds showed many single at different positions the HNMR spectrum of azomethine derivatives showed singlet single at (8.4 - 9.1) PPm for proton of azomethine group (-CH=N) (Th_2 and Th_4) but in the oxazepine derivatives showed many signals such as signal at(9.8-11.8) **[15]** PPm due to proton of amide in oxazepine derivatives, doublet signal at (4.8-5.8) PPm due to (CH=CH) alkene of maleic anhydride, multiplate signal at (6.7-7.92) PPm due to phenylning attacked to amide doublet signal at 8.3-8.5 PPm due to phenyl ring adjacent of to oxazepine ring in derivatives (Th_6 and Th_7) Table(3).

Table (1): Physical properties and CHN analysis data.

Comp.	M.F	M.wt	M.p(c°)	Rf: BenzMeOH)(4:1)	C%	Calc. ExpH%	N%
TH_1	$C_{18}H_{16}N_4O_3$	336	192-194	0.82	------	------	-----
TH_2	$C_{24}H_{21}N_5O_3$	427	130-132	0.72	67.447 67.385	4.918 4.823	16.393 16.255
TH_5	$C_{22}H_{19}N_7O_2$	413	121-123	0.65	63.922 63.857	4.600 4.45	23.728 23.601
TH_3	$C_{26}H_{23}N_5O_3$	453	102-124	0.58	68.874 68.973	5.077 5.023	15.452 15.423
TH_4	$C_{24}H_{20}N_6O_4$	456	113-115	0.68	63.157 63.053	4.385 4.298	18.421 18.372
TH_6	$C_{32}H_{25}N_5O_6$	575	93-95	0.77	66.782 66.634	4.347 4.289	12.173 12.013
TH_7	$C_{28}H_{23}N_5O_6$	524	125-127	0.62	-----	------	-----
TH_8	$C_{30}H_{25}N_5O_6$	551	192-194	0.44	65.335 65.291	4.537 4.498	12.704 12.668
TH_9	$C_{34}H_{27}N_5O_6$	601	122-124	0.38	-------	-------	------
TH_{10}	$C_{28}H_{22}N_6O_7$	554	128-130	0.8	60.649 60.513	3.971 3.884	15.162 15.034
TH_{11}	$C_{32}H_{24}N_6O_7$	604	134-136	0.6	------	-----	----
TH_{12}	$C_{26}H_{21}N_7O_5$	511	119-121	0.53	61.056 60.928	4.109 4.042	19.178 19.016
TH_{13}	$C_{30}H_{23}N_7O_5$	561	148-150	0.43	-----	------	-----

Table2: FT-IR data (cm^{-1}) of compounds (Th_1-Th_{13})

Comp.no	νN=N	νO-H	$\nu C\text{-}H_{arom}$	$\nu C{=}O_{lactom}$	$\nu C\text{-}O_{lactone}$	others
Th_1	1593	3421	3030	1550		$C\text{-}H_{aldeh.}$2854
Th_2	1590	3430	3020	1560		νC=O 1715
Th_3	1585	3425	3035	1570		νC=N 1620
Th_4	1587	3435	3050	1562		νC=N 1610
Th_5	1575	3440	3055	1540		νC=N 1630
Th_6	1591	3430	3070	1545	1730	νC=N 1615
Th_7	1588	3418	3030	1565	1740	
Th_8	1592	3380	3053	1530	1743	
Th_9	1595	3410	3040	1545	1728	
Th_{10}	1593	3405	3058	1555	1720	
Th_{11}	1583	3403	3070	1560	1745	
Th_{12}	1585	3392	3065	1565	1735	
Th_{13}	1593	3410	3075	1555	1742	

Table 3: ^{1}HNMR data (ppm) of compounds (Th_2, Th_4, Th_6,Th_7)

Compound	Data of ^{1}HNMR
Th_2	1H,CH=N,S, 8.4PPm ,2H,2OH ,S,12.0-12.4ppm ,7H,2phenyl,m,7.1-8.0ppm.
Th_4	1H,CH=N,S,9.1ppm 6.1H,OH,S,11.9ppm,S7H,2phenyl m,6.9-7.8ppm.
Th_6	1H,CH_{cyclic}, S, 9.8ppm,2H,2OH,S,11.3-12.1ppm &CH=CH_{cyclic} ,d,4.8-5.5ppm.
Th_7	1H,CH_{cyclic}, S, 10.3ppm,1H,S,11.8ppm,proton of phenyl 6.7-8.5ppm.

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