



# Synthesis Characterization of Some New Heterocyclic Compounds

## Containing 1, 3-Oxazepine Ring

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### ABSTRACT

*In this work a series of 1, 3-oxazepine derivatives have been synthesized throughout two steps. First step synthesis of imines derivatives (A<sub>1</sub>-A<sub>7</sub>) via the condensation reaction of 4-hydroxy benzaldehyde with different substituted amines by using catalytic amount of glacial acetic acid, while the second step involves reactions of the prepared imines (A<sub>1</sub>-A<sub>7</sub>) via maleic anhydride by [2+5] cycloaddition in dry benzene and refluxing it to produce 1, 3 - oxazepine - 4, 7 - dione derivatives (A<sub>1m</sub>-A<sub>7m</sub>) respectively. The prepared compounds were characterized by C.H.N.S micro analysis, some physical properties and spectral methods (IR , H<sup>1</sup>-NMR).*

**Keywords:** Schiff base, heterocyclic, 1, 3 – oxazipine, glacial acetic acid.

## تحضير وتشخيص بعض المركبات الغير المتجانسة الجديدة المحتوية على حلقة

### ١، ٣-أوكسازيين

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### المخلص

تم تحضير سلسلة من مشتقات ١، ٣ - الأوكسازيين من خلال خطوتين الأولى: يتضمن تحضير مشتقات الأيمين (A<sub>7</sub>-A<sub>1</sub>) من تفاعل ٤ - هيدروكسي بنزالديهايد مع امينات معوضة مختلفة وباستخدام حامض الخليك الثلجي. الخطوة الثانية: يتضمن تفاعل الأيمينات المحضرة (A<sub>7</sub>-A<sub>1</sub>) مع حامض المالك اللامائي من خلال الغلق الحلقي من نوع [5+2] في البنزين الجاف والتصعيد لينتج مشتقات 3,1- الأوكسازيين - 4, 7 - دايون (A<sub>7m</sub>-A<sub>1m</sub>)، شخست المركبات المحضرة باستخدام التحليل الدقيق للعناصر (C.H.N.S) وبعض الخصائص الفيزيائية والطرق الطيفية (IR, NMR-H<sup>1</sup>).

الكلمات الدالة: قواعد شف، حلقات غير متجانسة ، ١، ٣ - أوكسازيين وحامض الخليك الثلجي.

## 1. INTRODUCTION

Schiff bases was prepared in (1864) for the first time by German scientist (Hugo Schiff) [1]. Schiff bases having a double bond (-CH = N-) are usually prepared from the condensation process between aldehyds or ketone with primary amines [2, 3]. The properties of Schiff bases are characterized by their colors [4, 5], and they have the ability to form colored complexes with

most transition metals ions [6]. As well as Schiff bases have the ability to form inter and intra hydrogen bonds [7]. The Oxazepine are unsaturated compounds of seven membered heterocyclic rings as it includes five atoms of carbon, an atom of oxygen and one atom of nitrogen. Also contains double bond and that is one of the compounds unsaturated. Oxazepine is non - aromatic compound because it is seven membered that is not- planar and take the shape of boat to increase stability of these compounds and the chelating polymers of these compounds are very important in industrial in order to remove the heavy metals such as ( $\text{Cu}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Pb}^{+2}$  and  $\text{Ni}^{+2}$ ) [8].

## 2. Experimental

Melting points were determined in open glass capillaries using apparatus and the readings were uncorrected. IR spectra were recorded as KBr disk on Shimadzu infrared Spectrophotometer Fourier Transform FT- IR 8400S.  $\text{H}^1$  - NMR spectra were recorded on a Bruker Ultra shield 400MHZ instrument using DMSO as solvent and TMS as an internal standard. Elemental analysis wer carried out on a Eurovetro, EA 3000A, Italy. All reagents were supplied from (Aldrich, BDH and Fluka) and used without further purification.


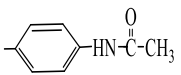
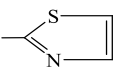


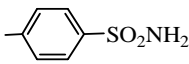
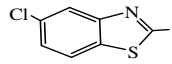
### 2.1 Synthesis of Schiff bases ( $\text{A}_1$ - $\text{A}_7$ )[9, 10].

A series of Schiff bases were prepared from the reaction of (0.01) mole of (4-hydroxy benzaldehyde), with (0.01) moles of different amines in (25) ml of absolute ethanol and few drops of glacial acetic acid. These mixtures were refluxed for (3-4) hours, and cooled; the precipitates were obtained, filtered and recrystallized from ethanol. Physical properties of the products were listed in Table (1) .


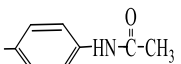
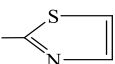


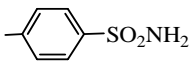
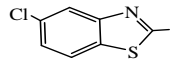
### 2.2 Synthesis of Oxazepine ( $\text{A}_1\text{m}$ - $\text{A}_7\text{m}$ )[11-13].

A mixture of Schiff base (0.001) mole and (0.001) mole of maleic anhydride was dissolved in (20) ml of dry benzene, the mixture was refluxed for (4- 5) hrs. on water bath, and the mixture was cooled. The precipitate formed was filtered and recrystallized from suitable solvent. Physical properties of the products were listed in Table (2) .

**Table (1):** Physical and analytical data of the prepared compounds (A<sub>1</sub> - A<sub>7</sub>)

Comp. No.	R	M.P. °C	Yield %	Color	(C.H.N) (cal/found)/ %			
					C	H	N	S
A <sub>1</sub>		74-75	65	Yellow	72.72 72.71	5.05 5.10	14.14 14.16	-
A <sub>2</sub>		199- 200	90	Light brown	70.86 70.81	5.51 5.50	11.02 11.11	-
A <sub>3</sub>		109- 110	88	Brown	58.82 58.80	3.92 3.89	13.72 13.76	15.68 15.61
A <sub>4</sub>		180- 182	75	Milky	72.73 72.71	5.05 5.11	14.14 14.18	-
A <sub>5</sub>		91-93	86	Milky	66.33 66.31	4.52 4.51	21.10 21.18	-
A <sub>6</sub>		223- 225	78	Yellow	56.52 56.49	4.34 4.30	10.14 10.19	11.59 11.52
A <sub>7</sub>		89-91	75	Light yellow	58.23 58.26	3.11 3.18	9.70 9.60	11.09 11.12

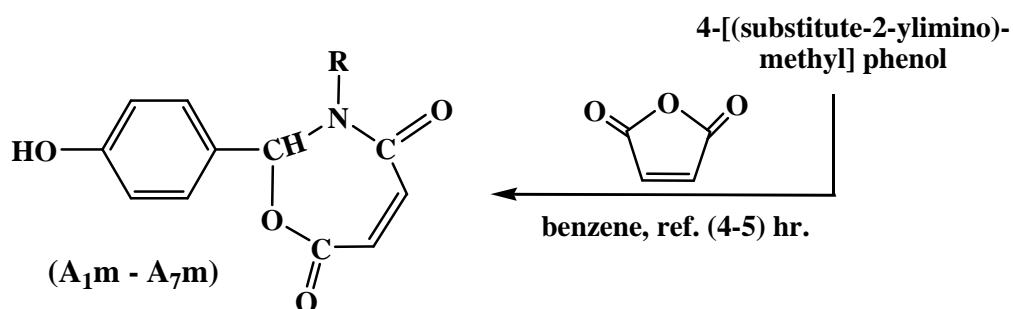
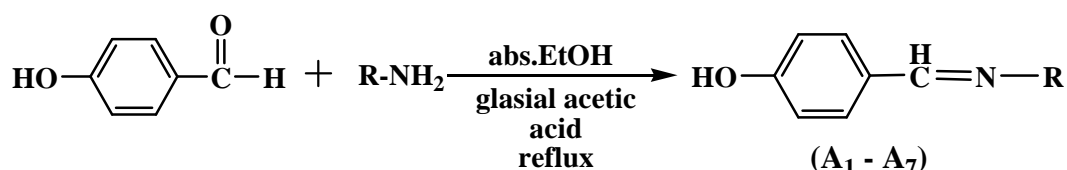
**Table (2):** Physical and analytical data of the prepared compounds (A<sub>1m</sub> - A<sub>7m</sub>)

Comp. No.	R	M.P. °C	Yield %	Color	(C.H.N) (cal/found)/ %			
					C	H	N	S
A <sub>1m</sub>		98-100	73	Orange	64.86 64.80	4.05 4.11	9.45 9.41	-
A <sub>2m</sub>		184-186	70	Yellow	78.26 78.22	4.34 4.31	7.60 7.59	-
A <sub>3m</sub>		143-145	50	Brown	55.62 55.61	3.31 3.33	9.27 9.25	10.59 10.51
A <sub>4m</sub>		132-134	65	Yellow	64.86 64.80	4.05 4.11	9.45 9.40	-
A <sub>5m</sub>		155-156	70	Orange	60.60 60.58	3.70 3.69	14.14 14.18	-
A <sub>6m</sub>		157-159	62	Yellow	54.54 54.58	3.74 3.80	7.48 7.49	8.55 8.51
A <sub>7m</sub>		119-121	63	Green	55.88 55.75	2.84 2.97	7.24 7.44	8.27 8.19

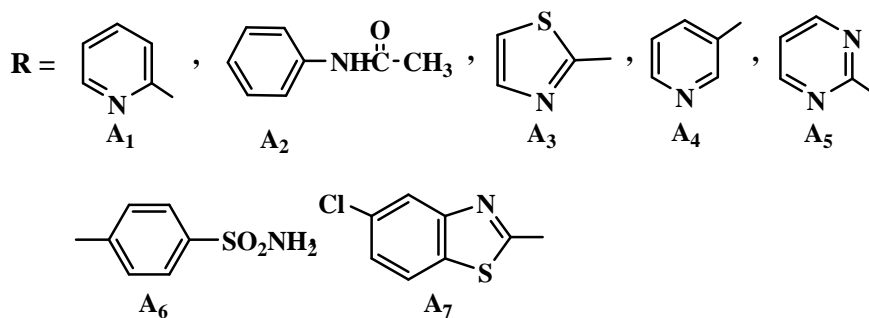
### 3. Results and Discussion

Schiff bases (A<sub>1</sub>-A<sub>7</sub>) were prepared from the condensation reaction of (4 - hydroxy benzaldehyde) with different primary aromatic amines in absolute ethanol in the presence of glacial acetic acid. The compounds (A<sub>1</sub>-A<sub>7</sub>) were reacted with maleic anhydride in dry benzene to give (A<sub>1m</sub>-A<sub>7m</sub>). The work is shown in **Scheme (1)**. These compounds were then characterized by elemental analysis, IR spectral studies and H<sup>1</sup>-NMR spectral studies. The IR spectra of the Schiff bases are recorded in the solid state using the KBr disc. The spectra of Schiff Bases (A<sub>1</sub>-A<sub>7</sub>) showed prominent band at (1654-1595) cm<sup>-1</sup> attributed to the azomethine group [14, 15] and the disappearance of (C=O) group band which was shown at (1666) cm<sup>-1</sup>. IR spectra of oxazepine compounds (A<sub>1m</sub>-A<sub>7m</sub>) in **Table (3)** showed the bands at (1729-1697) cm<sup>-1</sup> of (C=O) lactone and bands at (1698-1668) cm<sup>-1</sup> for (C=O) lactame and disappearance of (C=N) group. The formation

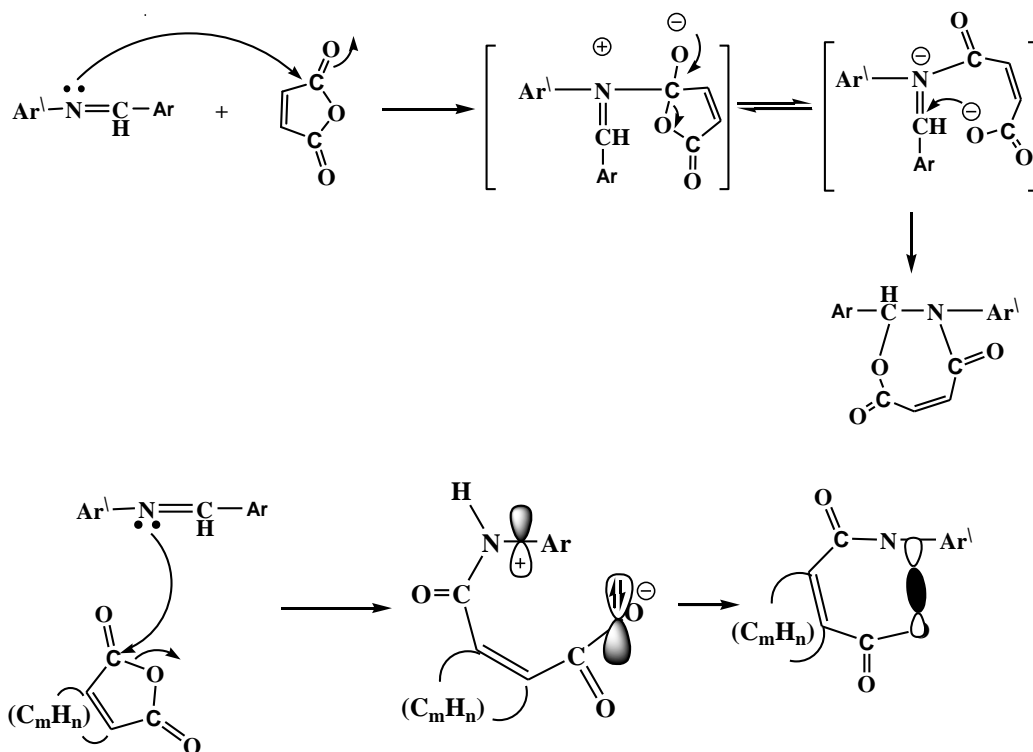
of the oxazepine compound and their mechanism are shown in schemes (1) and (2) .



2-(4-hydroxyphenyl) - 3 - (substitute) - 2,3 - dihydro - 1,3 - oxazepine - 4,7 - dione



**Scheme (1)**



i - m = 0 , n = 2 , maleic  
 ii - m = 4 , n = 4 , phthalic

**Scheme (2)**

**Table (3):** The characteristic infrared bands for the synthesized compounds (cm<sup>-1</sup>)

Comp. No.	v (O-H)	v (C=O) amide	v (C=O) ester	v (C-H) arom.	v (C=C) arom.	v (C=N)
A <sub>1</sub>	3380	-	-	3091	1598	1654
A <sub>2</sub>	3440	-	-	3057	1519	1598
A <sub>3</sub>	3378	-	-	3024	1508	1595
A <sub>4</sub>	3437	-	-	3057	1577	1624
A <sub>5</sub>	3315	-	-	3030	1539	1614
A <sub>6</sub>	3443	-	-	3070	1601	1651
A <sub>7</sub>	3345	-	-	3043	1535	1647
A <sub>1m</sub>	3455	1716	1683	3095	1508	-
A <sub>2m</sub>	3488	1710	1681	3074	1604	-
A <sub>3m</sub>	3365	1720	1693	3074	1612	-
A <sub>4m</sub>	3390	1729	1698	3068	1582	-
A <sub>5m</sub>	3386	1698	1680	3101	1558	-
A <sub>6m</sub>	3486	1725	1668	3072	1600	-
A <sub>7m</sub>	-	1705	1683	3060	1593	-

arom.: aromatic

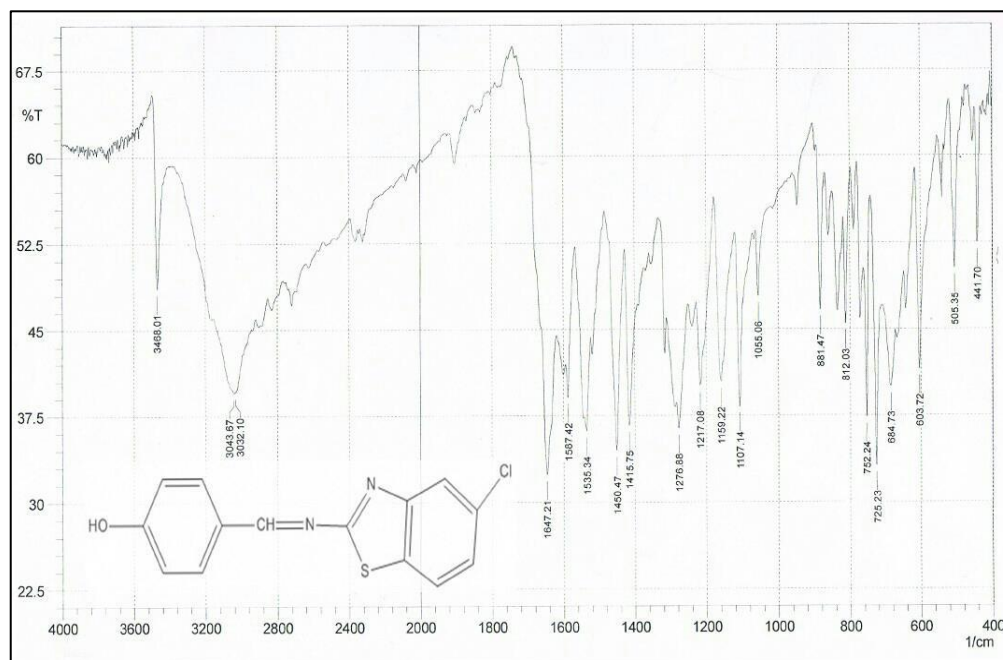
The H<sup>1</sup>-NMR, spectra of the all oxazepine derivatives shows the following signal peaks but especially for (A<sub>1m</sub> and A<sub>7m</sub>) were exhibited in Tables (4). The signal peaks are as follows: doublet signal peaks for single proton of the (CH=CH) group attached to the two carbonyl groups in the oxazepin ring at (6.00-6.30) ppm and another doublet peaks for the second proton in the same group at (6.40-6.60) ppm that overlapped with benzene ring protons peaks and with protons of the (R) groups attached to the oxazepin ring; multiplet peaks at the range (6.00-8.00) ppm for the benzene ring protons and the (R) groups; singlet peak at (7.70-8.00) ppm for one proton of the group (-N-CH-O-) and finally singlet peak at (9.50-10.60) ppm for phenolic (-OH).



**Table (4):** The  $H^1$ -NMR Spectra Data ( $\delta$ , ppm) of the oxazepines

Comp. No.	DMSO	O - H	CH = CH	Aromatic	N - CH - O
A <sub>1</sub> m	2.5 (s)	9.78 (s, 1H)	(6.06-6.47) (s, 2H)	(6.69-8.46) (m, 8H)	8.59 (s, 1H)
A <sub>7</sub> m	2.5 (s)	9.78 (s, 1H)	(6.53-6.27) (s, 2H)	(6.91-7.96) (m, 7H)	7.98 (s, 1H)

s: singlet, m: multiplet



**Fig. (1):** FT-IR spectra of compound (A<sub>2</sub>m)

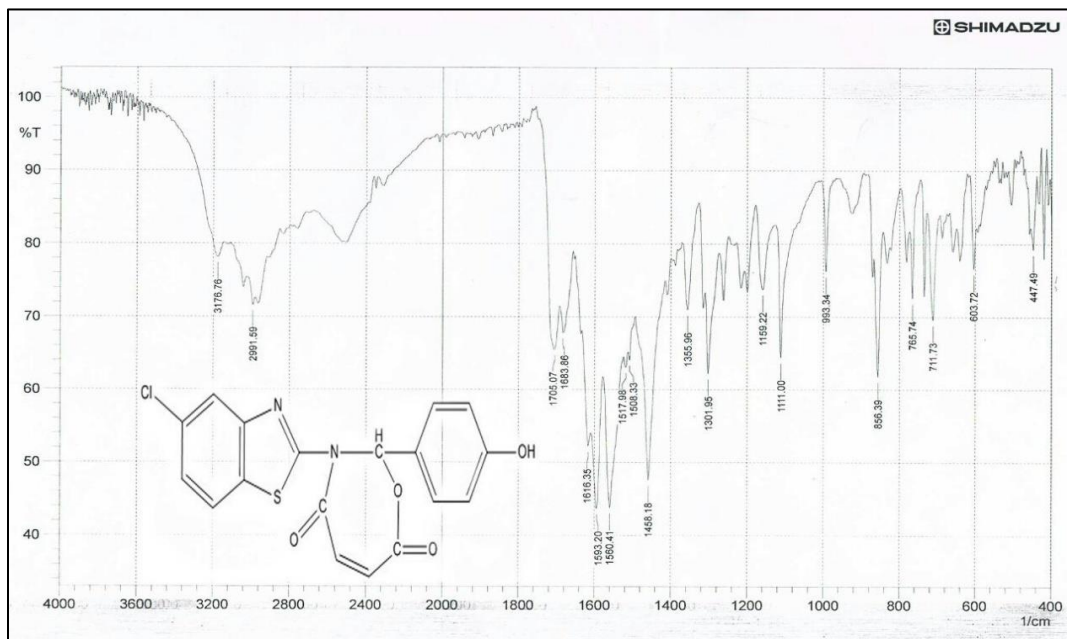


Fig. (2): FT-IR spectra of compound (A7m)

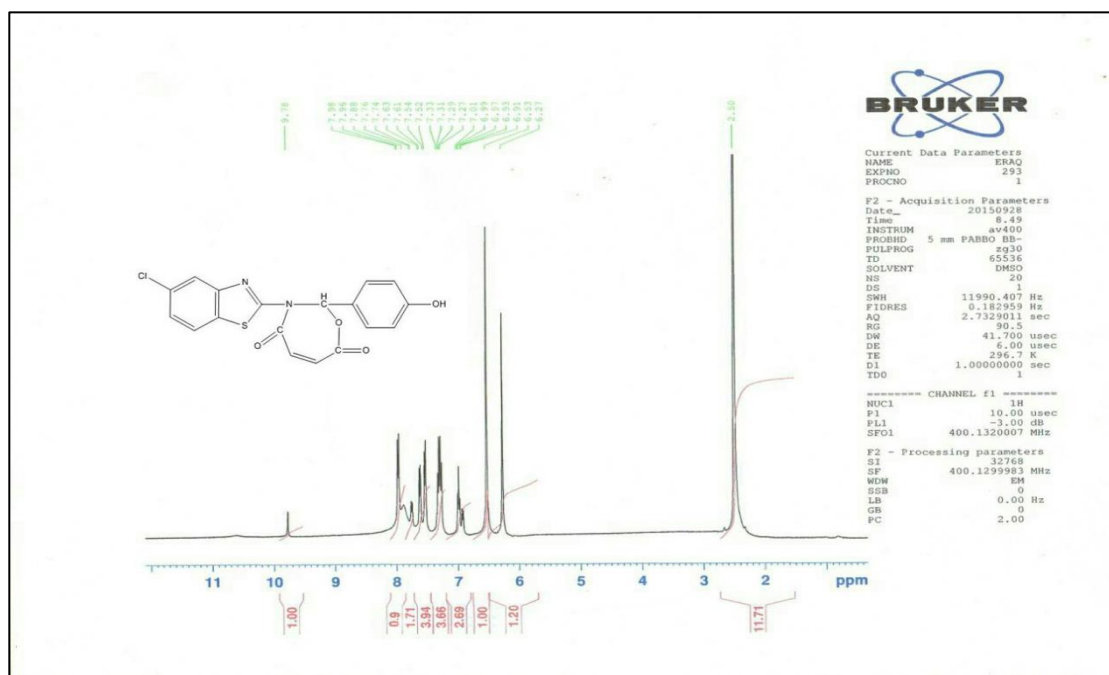
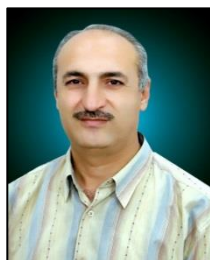


Fig. (3):  $^1\text{H}$ -NMR spectra of compound (A7m)

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