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SYNTHESIS AND IDENTIFICATION SOME OF 1, 3-OXAZEPINE DERIVATIVES CONTAINING AZO GROUP

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ABSTRACT

Series of oxazepine compounds were synthesized from Schiff base as azo and azomethine derivatives by using primary amine as a starting material with ethanol in the presence sulfuric acid to give ester. The last ester reacting with hydrazine hydrate to give hyrazone derivatives. The hydrazone derivative reacting with various benzaldehyde derivatives to give azomethin compound, then the schiff bases reacting with maleic, phathalic and succinic anhydride respectively. The chemical structures of synthesized compound were confirmed on the bases of their spectral date (FTIR and HNMR).

KEYWORDS: AZO Compounds, Schiff Bases, Resorcinol

INTRODUCTION

Azo compounds are the important glass in organic chemistry as a starting material for most of compounds. Synthetic azo compounds are widely used in different application fields, such as cosmetic, foods, plastics and in analytical chemistry [(1-9)].

Anils compounds are characterized by the -N=CH-(imine) group which is important in the most of biochemical systems [(10)].

The Schiff bases are used to prepared many heterocyclic compounds, for example oxazepine derivatives which refer to any seven – membered ring containing oxygen and nitrogen atom [(11,12)]. Oxazepine derivative showed various biological activities such as antibacterial and anticonvulsant activity.[(13,14)]

Experimental

All chemical compounds are supplied from (BDH, Fluka) companies in high purity., IR- spectra carried out in college education., H.NMR spectra were carried out on Bruker 2009 specrometer at 400 MH_2 in DMSO- D_6 as solvent in Tahran

SYNTHESIS METHODS

Synthsis of Azo Compound (1)

The azo compound was synthesized from 3- Amino benzoic acid with resorcinol according to Shibatta method[(15).]

Synthesis Ester Derivative (2)

Azo compound (1) was dissolved in (50 ml) of absolute ethanol containing 6 drops of sulfuric acid. The reaction mixture was refluxed with stirring on a water bath at 70 c° for (9 hrs) and monitored by TLC. The mixture was then allowed to cool down to room temperature, the colored precipitate was filtered and recrystallized from ethanol.

Synthesis Hydrazine Derivative (3)

Ester derivative (0.02 mole) was dissolved in (25ml) of absolute ethanol, then added hydrazine hydrate (0.02 mole) drop by drop, the mixture was refluxed with stirring on water bath at 70 c° for (hrs), and monitored by TLC. The mixture was then allowed to cool down to room temperature, the colored precipitate was filtered and recrystallized from ethanol

General Procedure for Synthesis of Schiff Bases (4-8)

Hydrazone derivative (0.02 mole) was dissolved in (20 ml) of absolute ethanol containing two drops of glacial acetic acid, then benzaldehyde derivatives (4-OH,3-CH_3, 4-Cl, 4-Br, 3-Cl and 3-OH) respectively(0.02 mol) was dissolved in (20 ml) of absolute ethanol and added drop wise. The reaction mixture was refluxed with stirring on a water bath at 70 c ° for (6-9 hrs) and monitored by TLC. The mixture was then allowed to cool down to room temperature, the colored precipitate was filtered and recrystallized from ethanol. The physical properties and other characteristic for the synthesized Schiff bases derivatives (4-8) were shown in table 1

General Procedure for the Synthesis of 1, 3–Oxazepine– 4, 7-Dione Derivatives (9-13)

A mixture of Schiff bases derivatives (4-8) (0.02 mole) and maleic anhydride (0.02 mole) in dry benzene (25 ml) was refluxed on a water bath at 60 c ° for (10-14 hrs) and monitored by TLC. The mixture was then allowed to cool down to room temperature.Dried upon filter paper then in oven and recrystallized from ethanol. The physical properties and other characteristics for the synthesized 1,3– Oxazepine derivatives (9-13) were shown in table 2.

General Procedure for The Synthesis of 1,3- Oxazepine -4,7-Dione Derivatives (14-17):

A mixture of Schiff bases derivatives (4-8) (0.02 mole) and phathalic or succinic anhydride (0.02 mole) respectively in (25 ml) of dry benzene was refluxed on a water bath at 60 c ° for (12-17hrs) and monitored by TLC. The mixture was then allowed to cool down to room temperature. Dried in oven and recrystallized from ethanol. The physical properties and other characteristics for the synthesized oxazepine derivatives (14-17) were shown in table 2.

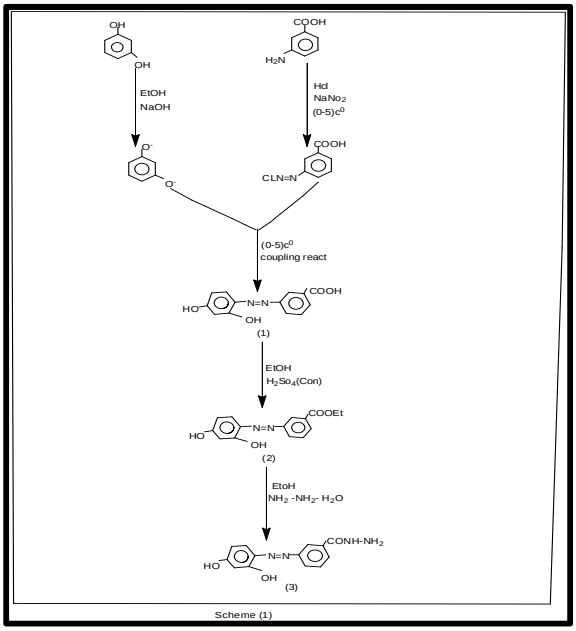


Figure 1

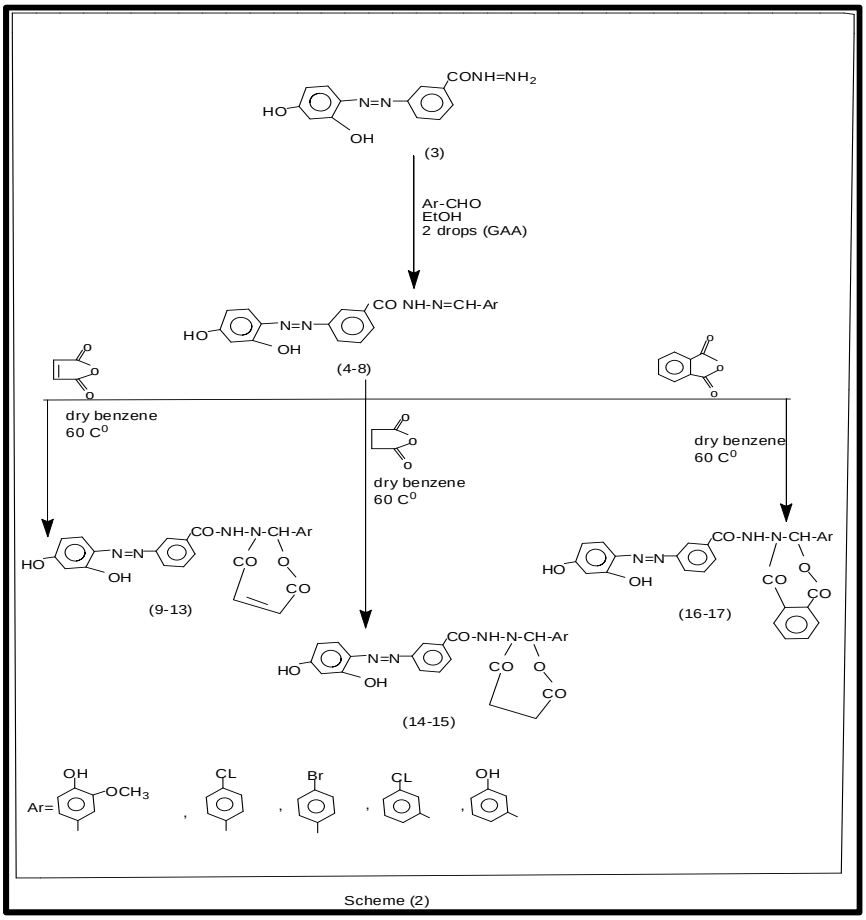


Figure 2

All physical properties in Table (1, 2):

Table 1: Physical Properties for the Compounds (1-8)

Comp. No.	M.F	M. Wt	M.P/C°	Color	RF	Solvent
1	$C_{13}H_{10}N_2O_4$	258	280-282	Orang	0.54	Ethanol
2	$C_{15}H_{14}N_2O_4$	286	237-239	Red	0.35	Ethanol
3	$C_{13}H_{12}N_4O_3$	272	176-178	Dark Red	0.46	Ethanol
4	$C_{21}H_{18}N_4O_5$	406	180-182	White	0.81	Ethanol
5	$C_{20}H_{15}N_4O_3Cl$	430	185-187	Yellow	0.53	Ethanol
6	$C_{20}H_{15}N_4O_3Br$	438	227-229	Brown	0.82	Ethanol
7	$C_{20}H_{15}N_4O_3Cl$	430	221-223	Yellow	0.72	Ethanol
8	$C_{20}H_{16}N_4O_4$	376	214-216	Brown	0.43	Ethanol

Table 2: Physical Properties for the Compounds (9-17)

Comp. No.	M.F	M.WT	M.P/C°	Color	RF	Solvent
9	$C_{25}H_{20}N_4O_8$	504	138-140	Orange	0.71	Benzene
10	$C_{24}H_{17}N_4O_6Cl$	528	210-212	Green	0.53	Benzene
11	$C_{24}H_{17}N_4O_6Br$	537	145-147	Brown	0.68	Benzene
12	$C_{24}H_{17}N_4O_6Cl$	528	125-127	Brown	0.62	Benzene
13	$C_{24}H_{18}N_4O_7$	474	103-105	Yellow	0.45	Benzene
14	$C_{29}H_{22}N_4O_8$	554	110-112	White	0.55	Benzene
15	$C_{28}H_{19}N_4O_6Cl$	578	135-137	Brown	0.61	Benzene
16	$C_{24}H_{17}N_4O_6Br$	537	163-165	Brown	0.77	Benzene
17	$C_{24}H_{18}N_4O_7$	474	120-122	Yellow	0.82	Benzene

RESULTS AND DISCUSSIONS

The synthesized compounds were identified y several techniques methods as spectral methods to give indicators for the results in this study:

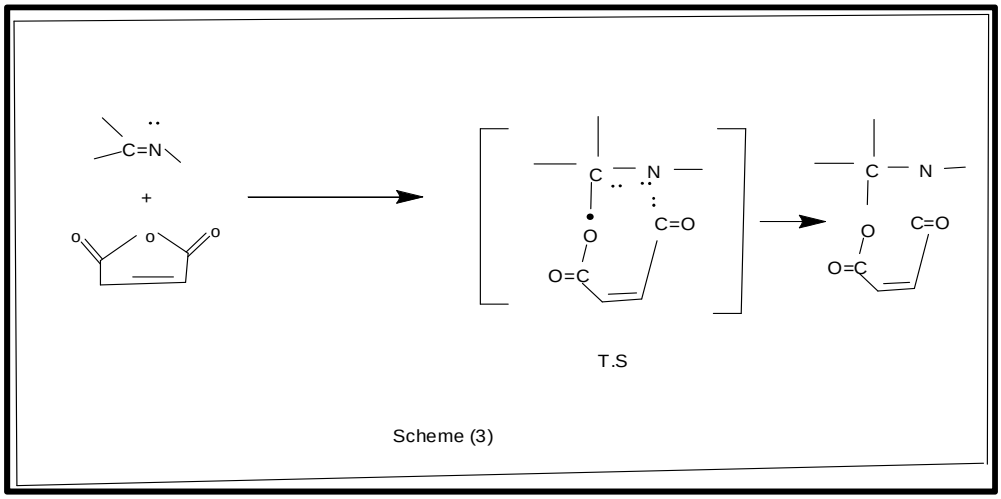
From FT.IR Spectra

Which gave many bands indicated to synthesized compounds, Schiff bases derivatives (4-8), figure 4 Were synthesized through condensation reaction between the hydrazone derivative (3) and some of benzaldehyde derivatives (vaniline, 4-Cl benzaldehyde, 4-Br benzaldehyde 3- Clbenzaldehyde and 3- Hydroxybenzaldehyde) respectively in the presence of glacial acetic acid as catalyst in absolute ethanol.

FTIR spectra of Schiff bases derivatives (4-8), figures (4-8) provide good evidence that the condensation reactions proceeded successfully and produced the Schiff bases, by appearing the medium bands at 1624 – 1668 cm $^{-1}$ assigned to the stretching vibration of imine group (C=N), also the spectra showed disappearance the two bands at 3329 and 3277 cm $^{-1}$ for asymmetric and symmetric stretching vibrations of (NH_2) group. other characteristic bands shown in table 3.

1,3 -Oxazepine derivatives (9-13) (14-15) and (16-17) were prepared via introducing of the synthesized Schiff bases derivatives (4-8) in (2+5=7) cyclo addition reaction with maleic, phathalic and succinic anhydrides respectively, in dry benzene

The mechanism of this reaction are shown in scheme (3)



Scheme (3)

Figure 3

The FT.IR data of the synthesized 1,3 –oxazepine derivative(9-12),figure (9-12) provide good evidence that the cyclo addition reactions proceeded successfully and produced the desired products by appearing bands at the range 1695 – 1710 cm $^{-1}$ attributed to the stretching vibration of (CO) lactone group. Other bands were summarized in table 3.The FT.IR data of the synthesized 1,3-oxazepine derivatives (9-12) provide good evidence that the cycloaddition reactions proceeded successfully and produced the desired products by appearing the sharp bands at the range (1691-1697 cm^{-1}) which belong to the stretching vibration of(C=O) lactone group. Other bands were summarized in table 4.

Table 3: FTIR Data of the Prepared Compounds (1-8) In Cm^{-1}

Comp. No.	FTIR Bands
(1)	3500-2500 ($_{OH}$) carboxylic and ($_{OH}$) phenolic, 1695 ($_{C=O}$) carboxylic, 1458 ($_{N=N}$)
(2)	3300-3400 ($_{OH}$) phenolic,1718 ($_{C=O}$) ester,1473 ($_{N=N}$)
(3)	3427, 3379, ($_{OH}$) phenolic, 3329, 3277, 3194 ($NH_{2\ asy.}$ $NH_{2\ SY.}$NH),1471(N=N)
(4)	3381($_{OH}$) phenolic, 3232 ($_{NH}$),1668 ($_{CH=N}$),1460 ($_{N=N}$)
(5)4-Cl	3421 ($_{OH}$) phenolic, 1624 ($_{CH=N}$),1487 ($_{N=N}$),($_{C-CL}$) 700
(6)4-Br	3317 ($_{OH}$) phenolic, 3209 ($_{NH}$),1624 ($_{CH=N}$), 1479 ($_{N=N}$) 813,($_{C-Br}$)
(7)3-Cl	3431 ($_{OH}$) phenolic, 1629 ($_{CH=N}$), 1475 ($_{N=N}$) 756 ($_{C-CL}$)
(8)	3423 ($_{OH}$) phenolic, 1624 ($_{CH=N}$), 1438 ($_{N=N}$)

Table 4: FTIR Data of the Prepared Compounds (9-17) In Cm^{-1}

Comp. No.	FTIR Bands
(9)	
(10)	3433 ($_{OH}$) phenolic, 3211 ($_{NH}$),1707 ($_{C=O}$) lactone 1593 ($_{C=O}$) lactam, 1483 ($_{N=N}$)
(11)	3244 ($_{OH}$) phenolic and ($_{NH}$),1708 ($_{C=O}$) lactane 1591 ($_{C=O}$) lactam,1462 ($_{N=N}$)
(12)	3256 ($_{OH}$) phenolic and ($_{NH}$), 1701 ($_{C=O}$) lactone 1568 ($_{C=O}$) lactame, 1467 ($_{N=N}$)
(13)	3348 ($_{OH}$) phenolic, 3217 ($_{NH}$), 1695 ($_{C=O}$) lactone (1589) ($_{C=O}$) lactame, 1460 ($_{N=N}$)
(14)	3358 ($_{OH}$) phenolic, 3254 ($_{NH}$), 1697 ($_{C=O}$) lactone, 1591 ($_{C=O}$) lactone, 1408 ($_{N=N}$)
(15)	3431 ($_{OH}$) phenolic, 1691 ($_{C=O}$) lactone, (1587)lactame 1404 ($_{N=N}$).
(16)	3485 ($_{OH}$) phenolic, 3103 ($_{NH}$), 1697 ($_{C=O}$) lactone, 1583 ($_{C=O}$) lactame
(17)	3207 ($_{OH}$) phenolic, 3161 ($_{NH}$), 1695 ($_{C=O}$) lactone, 1587 ($_{C=O}$) lactame

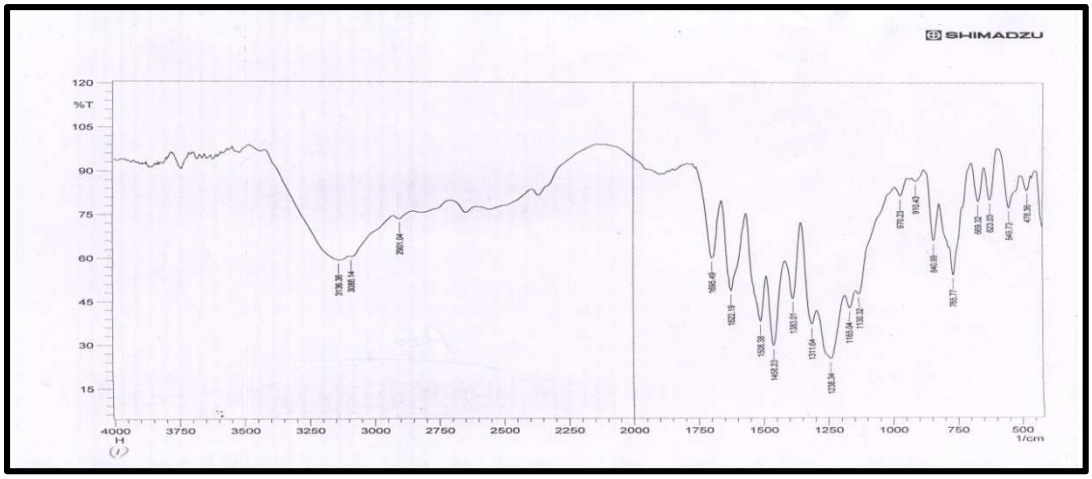


Figure 4: FTIR Spectrum of the Compound (1)

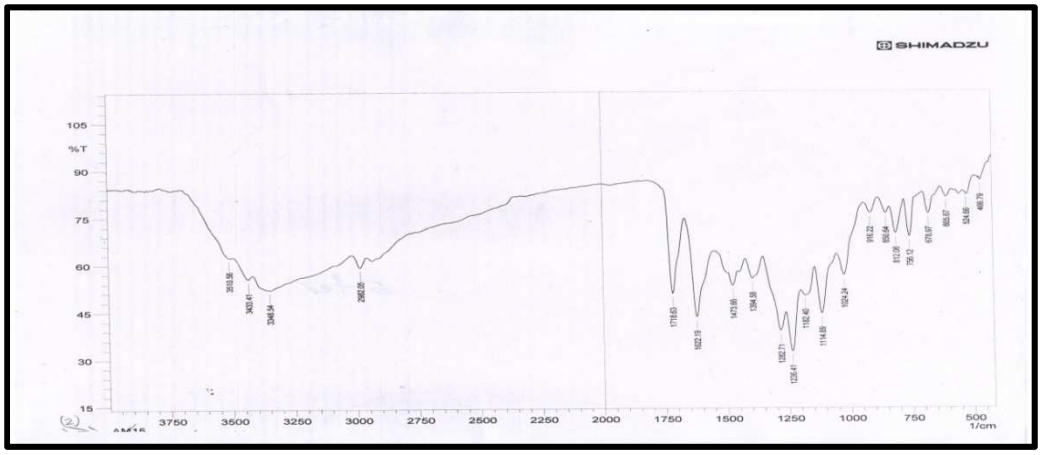


Figure 5: FTIR Spectrum of the Compound

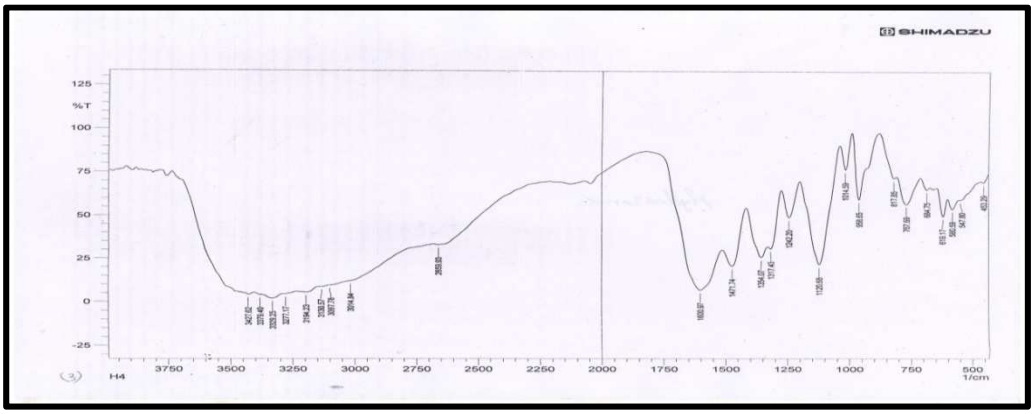


Figure 6: FTIR Spectrum of the Compound (3)

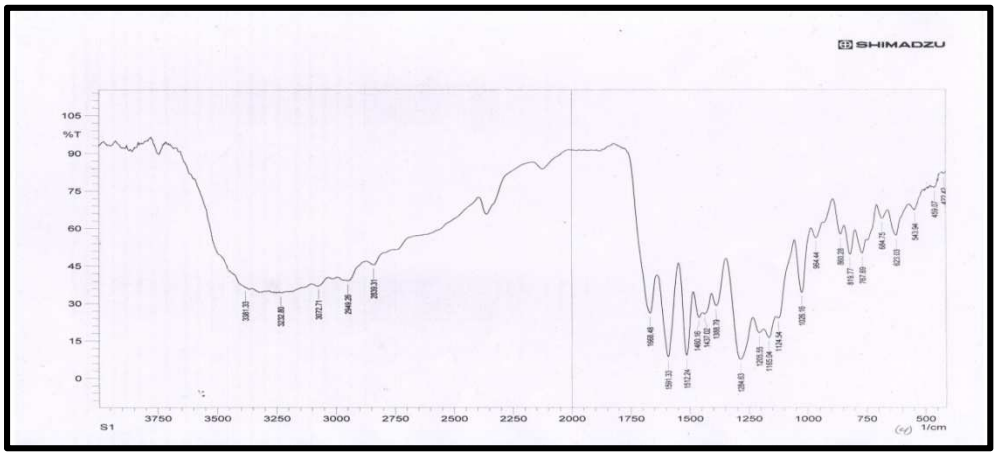


Figure 7: FTIR Spectrum of the Compound (4)

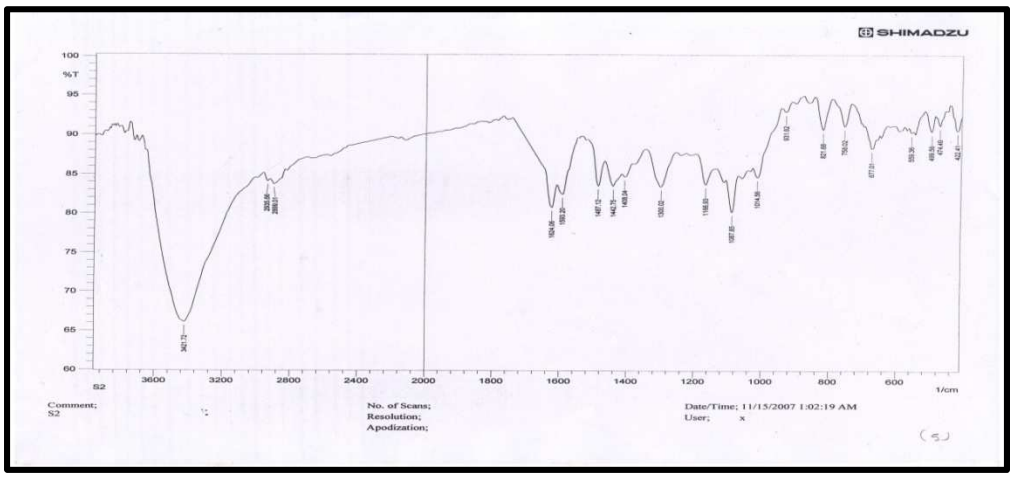


Figure 8: FTIR Spectrum of the Compound (5)

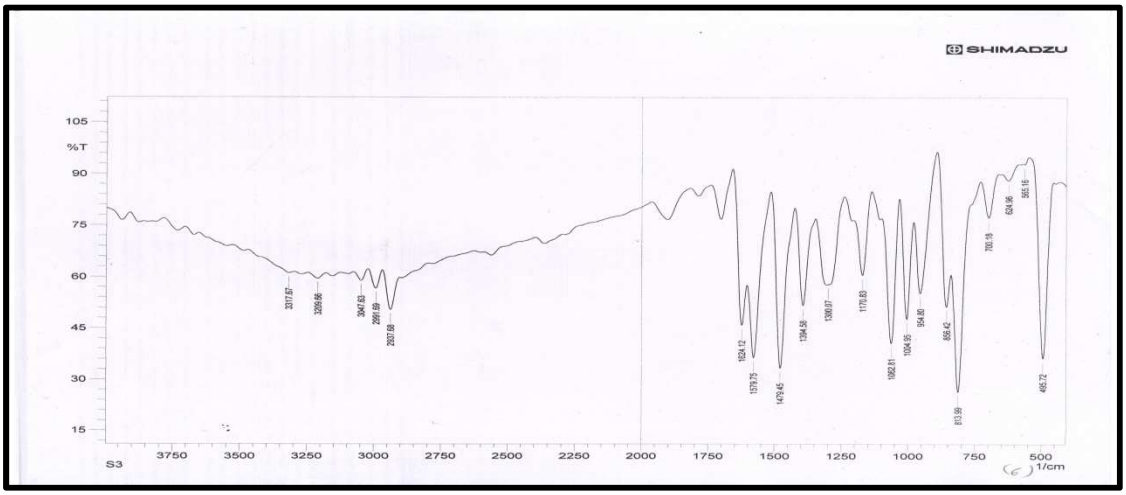


Figure 9: FTIR Spectrum of the Compound (6)

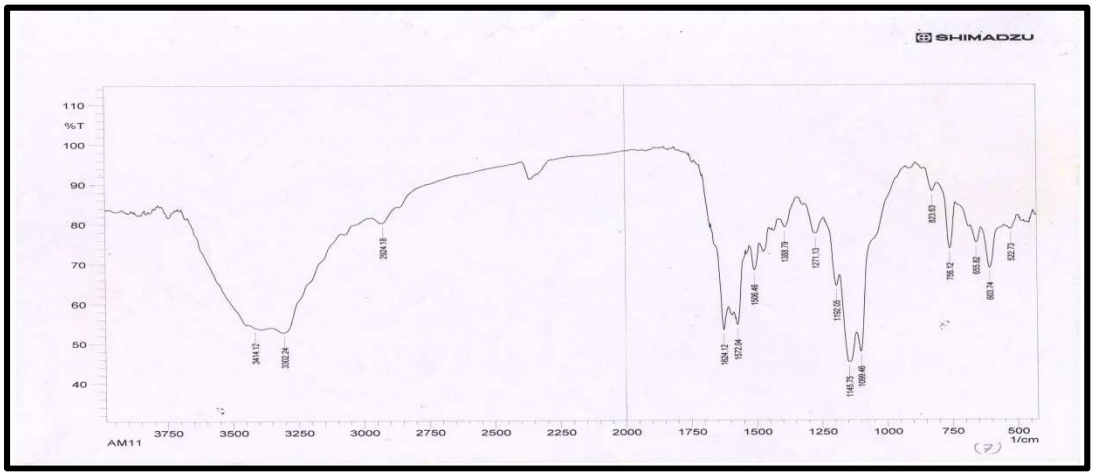


Figure 10: FTIR Spectrum of the Compound (7)

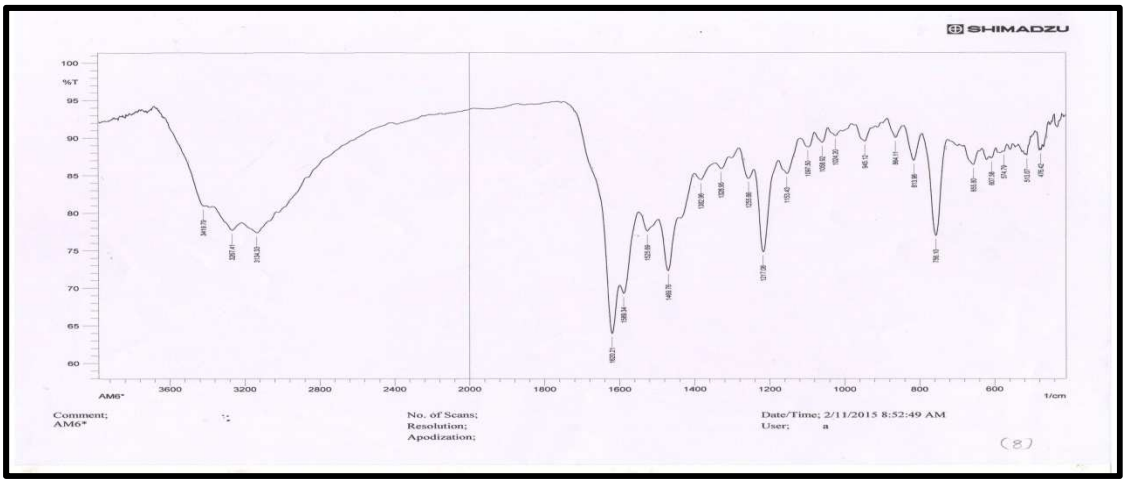


Figure 11: FTIR Spectrum of the Compound (8)

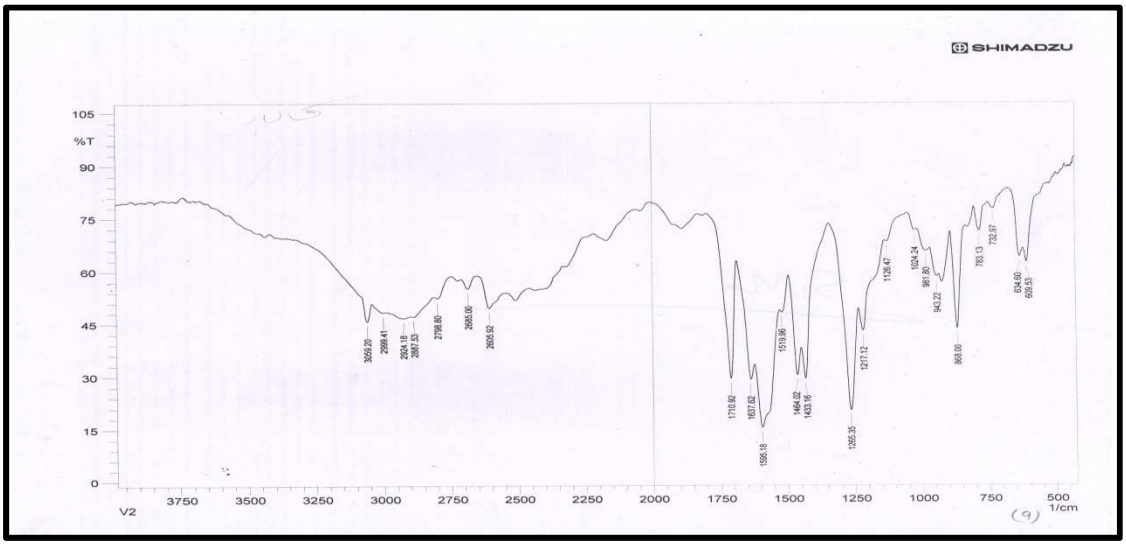


Figure 12: FTIR Spectrum of the Compound (9)

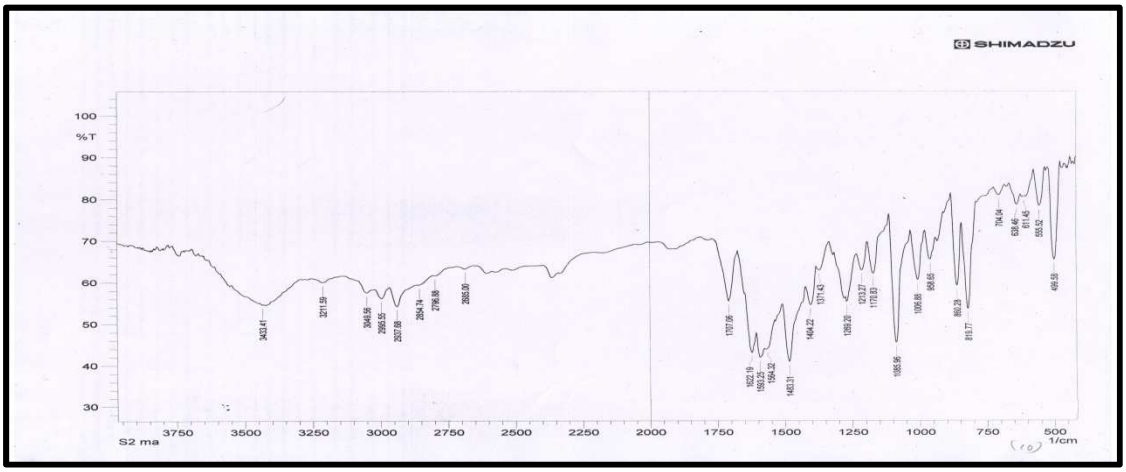


Figure 13: FTIR Spectrum of the Compound (10)

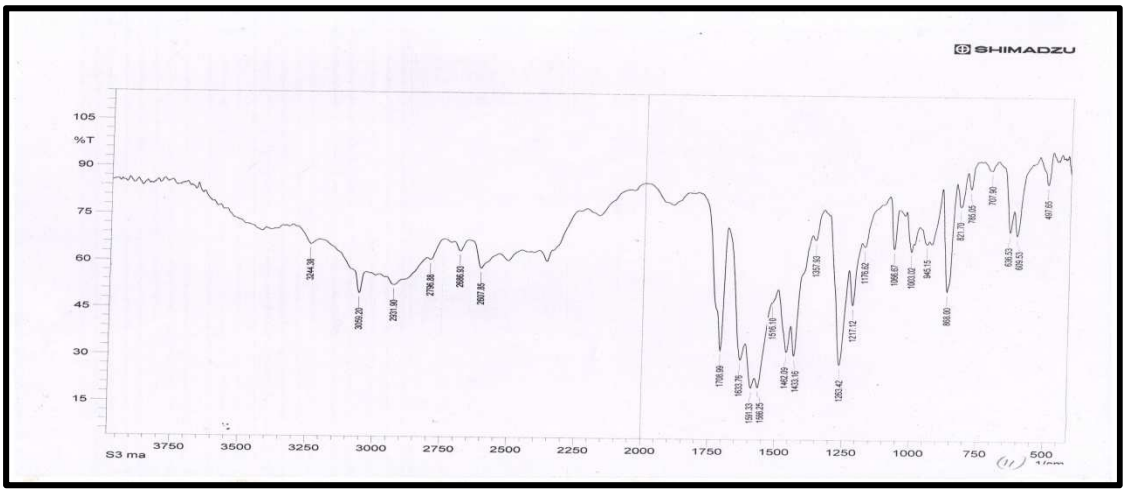


Figure 14: FTIR Spectrum of the Compound (11)

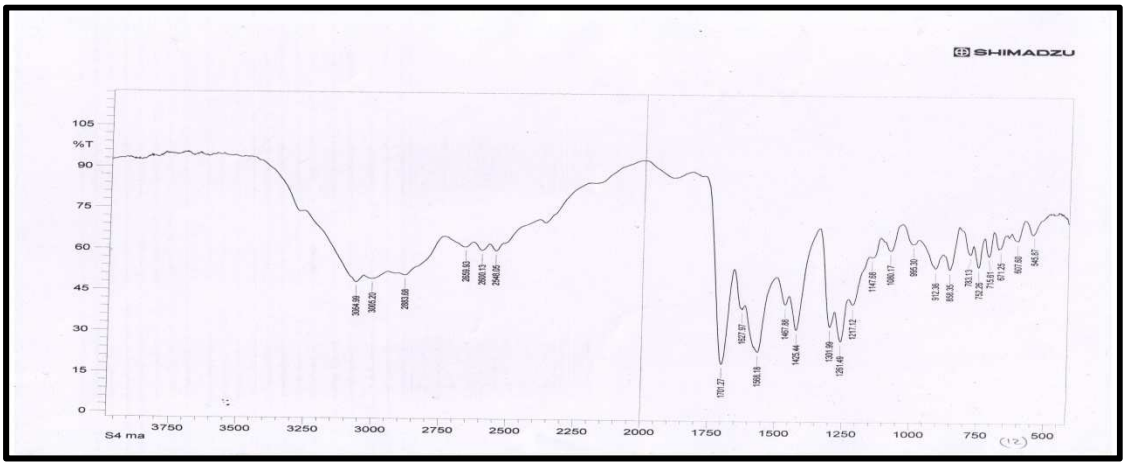


Figure 15: FTIR Spectrum of the Compound (12)

H.NMR spectra of derivative (1 and 2), HNMR spectrum, figure 13 (400 MH_2, DMSO) of compound(1) appeared the following signals at ϭ(ppm) :2.4 (DMSO solvent, 8, 6.3- 6.4 (d) OH phenolic, 7.6- 8.3 (m, H aromatic 12.2, (s, H proton of carboxylic acid)

H.NMR spectrum, figure 14 (400 MH_2, DMSO) of compound (2) appeared the following signals at ϭ(ppm) : 2.4 (DMSO solvent), 1-1.3 (t, 3Hproton 0 4.3 (9, 2H, -OCH_2), 6.2-6.4 (H phenolic), and (7.4 – 8.3) (m, H aromatic). Table 5..

Table 5

Comp. No.	^{1}HNMR Signals
(1)	ϭ(12.2) O-H proton carboxylic (S), ϭ (6.3 - 6.4) O-H proton of phenolic (d), ϭ (7.6 -8.3) proton of aromatic ring (m) ϭ 2-4 (proton of DMSO solvent.
(2)	ϭ (7.4-8.3) proton of aromatic ring (m), ϭ (6.2 -6.4) proton of phenolic (d), ϭ 4.2 proton of (CH_2) (q). ϭ (1-1.3) proton of CH_3 (t).

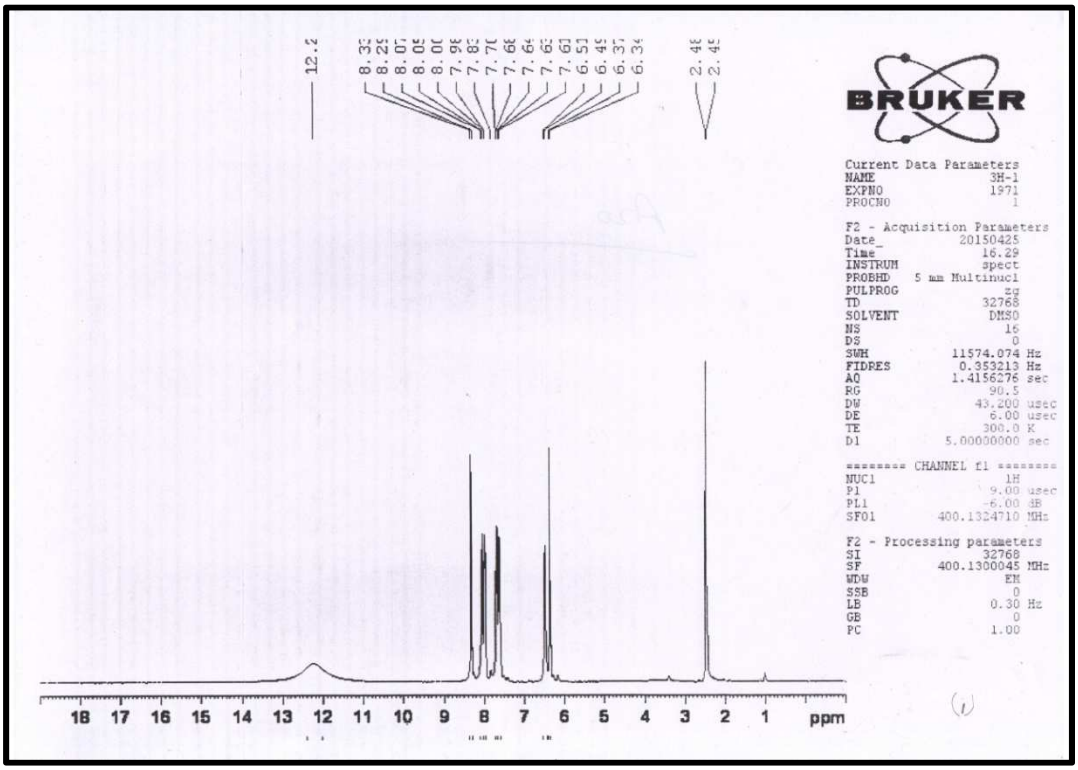


Figure 16: HNMR Spectrum of the Compound (18)

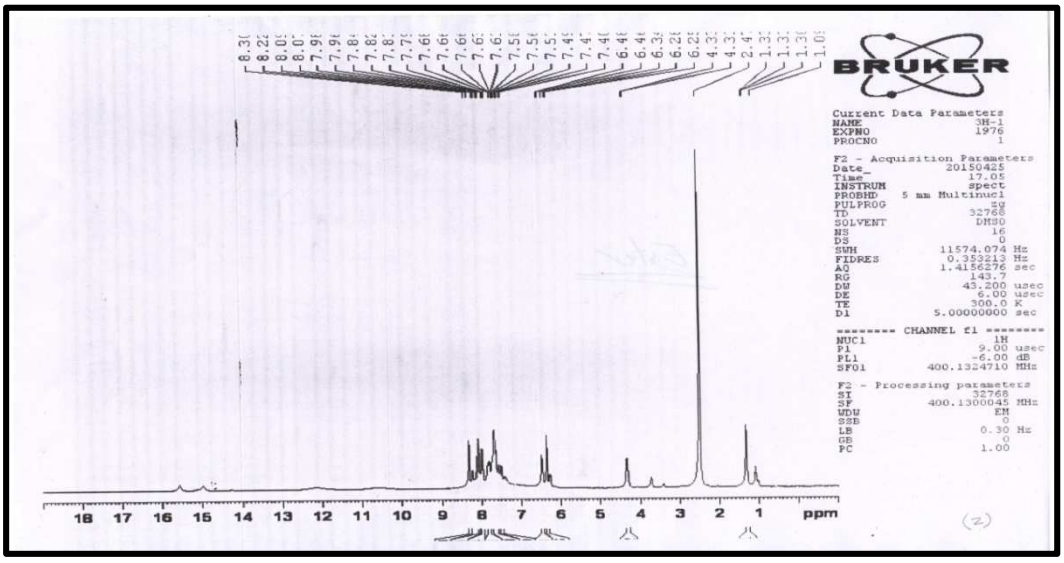


Figure 17: HNMR Spectrum of the Compound (19)

CONCLUSIONS

- Azo compound (1) depend on the PH solution
- All cycloaddition reactions for the synthesis of oxazepine derivatives required relatively long time for completion

ACKNOWLEDGEMENTS

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