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SYNTHESIS AND CHARACTERIZATION OF SOME 3-(2-(6-OXO-1, 3-THIAZINAN-3-YL)-R)-1, 3-OXAZEPINE-4, 7-DIONE AND N-BROMO AMINES 1, 3-OXAZEPINE-1, 4-DIONE DERIVATIVES

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ABSTRACT

This study includes synthesis and characterization of new derivatives of 3-(2-(6-oxo-1, 3-thiazinan-3-yl)-R)-1, 3-oxazepine-4, 7-dione and N-Bromo Amines 1, 3-oxazepine-1, 4-dione Derivatives. via Schiff's bases reactions through one step process in inert solvents. Some different Schiff bases [1, 2, 3, 4] synthesized from reaction of different amines with aldehydes such as (Salicylaldehyde,) in absolute ethanol under reflux. Heterocyclic rings of the1, 3-oxazepine-4, 7-dione prepared the reaction of succinic anhydride with schiffs bases [1, 2, 3, 4] and 3-(2-(6-oxo-1, 3-thiazinan-3-yl)-R)-1, 3-oxazepine-4, 7-dione derivatives prepared by the reaction of 3-Mercaptopropanoic acid with 1, 3-oxazepine-4, 7-dione[A1, A2, A3, A4] in 1, 4-Dioxan. Synthesis of some N-Bromo amine derivatives by the reaction of 1, 3-oxazepine-4, 7-dione[A1, A2, A3, A4] with 2, 4, 4, 6-TBCD (2, 4, 4, 6-tetrabromocyclohexa-2, 5-dienone) in dry benzene, The prepared compounds were characterized by melting point, FT-IR, UV-Vis and 1H- NMR spectra.

KEYWORDS: Schiff Bases, 3-(2-(6-Oxo-1, 3-Thiazinan-3-Yl)-R), 1, 3-Oxazepine-4, 7- Dion, N- Bromo Amines 1, 3-Oxazepine-4, 7-Dione Derivatives

INTRODUCTION

Schiff's Bases act important intermediate compounds in the preparation of some of the biological activity Compounds such as (β-Lactams) and Heterocyclic Compounds [1-4] as well as pharmaceutical materials, anti-bacterial [5, 6], anticancer [7-10] and some of which are effective against cardiovascular cramps and others have effective anti-TB. [11]. Thiazinanones (six-membered heterocycle) are less common in the literature; however, they also show important biological properties as immunopotentiating [12], anti-inflammatory [13], antimalarial and antibacterial [14] activities. We have studied methodologies for the synthesis of thiazolidinones in the past few years [15, 16], especially under nonconventional sonochemistry methodology [17, 18] and it is our first attempt to study the chemistry of thiazinanone ring. So, in this work, we synthesized 15 novel thiazinanones from 2-picolylamine, are aldehydes, and mercaptopropionic acid. This work also aims to explore the antioxidant properties of previously synthesized thiazolidinones [18] and the new thiazinanones. N-bromo compounds have bromine atom attached to nitrogen and have much applications as antibacterial, antifungal and ant HIV [19-24].

MATERIALS AND METHODS

Melting points were recorded with (Stuart) 30 Melting point Apparatus and were uncorrected, UV-Visible spectra were recorded with Schimadsu (UV-1800) spectrophotometer Infrared spectra were recorded as KBr pellets on a Thermo-

Fisher spectrometer. 1H-NMR spectra were recorded on Bruker-500 MHz Spectrometer using DMSO –d6 as a solvent and TMS (Tetra methyl silane (CH3)4Si) as internal standard.

Preparation of Schiff Base1, 3-Bis (2-Hydroxybenzylidene) Urea (5)

25 cm3 of urea ethanolic solution (0.01 mole, 0.60 g) was added to the same volume of the same solvent of (0.02 mole, 2.44 g) of salicylaldehyde. Few drops of 10 % NaOH were added to adjust pH and the obtained mixture then refluxed with stirring for two hours and the obtained funnel, recrystallized from ethanol, and dried at room temperature with 70-80 % yield and its melting point is in the range of 100-102 C_o.

Synthesis of O-Hydroxybenzaldehyde (Salicylaldehydyde) Schiff Bases [1-4]:

A Solution of (0.01 mol) of (Ethylenediamine, P- phenylenediamine), o-phenylenediamine, hydrazine and urea in (40 mL) absolute ethanol was added to (0.02mol) salicylaldehyde in (20 mL) absolute ethanol then the mixture was refluxed for 2h, the mixture was cooled to room temperature, filtered, dried and recrystallized from absolute ethanol [25], physical properties are given in table 1.

SYNTHESIS OF HETEROCYCLIC COMPOUNDS

Synthesis of 1, 3-Oxazepine-4, 7-Dione Derivatives (A1, A2, A3, A4, A5):

In a (100ml)round bottom flask equipped with double surfed condenser fitted with Calcium chloride guard tube, was placed a mixture of 0.01 mole of 2, 2'-(1Z, 1'E)-(1, 2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol and 0.01 mole of maleic anhydride in 10ml of dry benzene. The reaction mixture was refluxed in a water bath for 1.5 hr. The solvent was removed and the resulting solid was recrystallized from THF This experiment was repeated using different Schiff bases (2, 3, 4, 5) in order to obtain other 1, 3-oxazepine (A2, A3, A4, A5).[26]

Synthesis of 1, 3-Thiazinane -6-One-1, 3-Oxazepine -4, 7-Dion Derivatives (B1, B2, B3, B4, B5)

A mixture (0.01 mol) of Schiff bases 1, 3-oxazepine-4, 7-dion (A1, A2, A3, A4, A5) with (0.01 mol, 1.085 g) of (3-Mercaptopropanoic acid) in (20 mL) dry benzene and two drops of (Ammonia), the mixture was refluxed for 6h, the solvent was evaporated then the formed precipitate was recrystallized from absolute ethanol physical properties are given in table(3).

Synthesis of 2, 4, 4, 6_Tetrabromo - 2, 5 Cyclohexadinone (2, 4, 4, 6-TBCD):

A mixture (0.02 mol, 1.88 g) of (phenol) and (0.06 mol, 6.714g) of (potassium bromide) with (0.03 mol, 4.797g) (potassium bromate) in (60 mL) of distilled water and then added to the mixture slowly (8.7 mL) of hydrochloric acid (36%) for 2 h after it was mix move and refluxed for two hours, then the precipitate was filtered and washed with distilled water, physical properties are given bellow. m.p. =121-124, FT-IR:C=C 1581 cm-1, =C-H 3050 cm-1, C-Br 683-702 cm-1, C=H 1381 cm-1, C=0 1679 cm-1. [27].

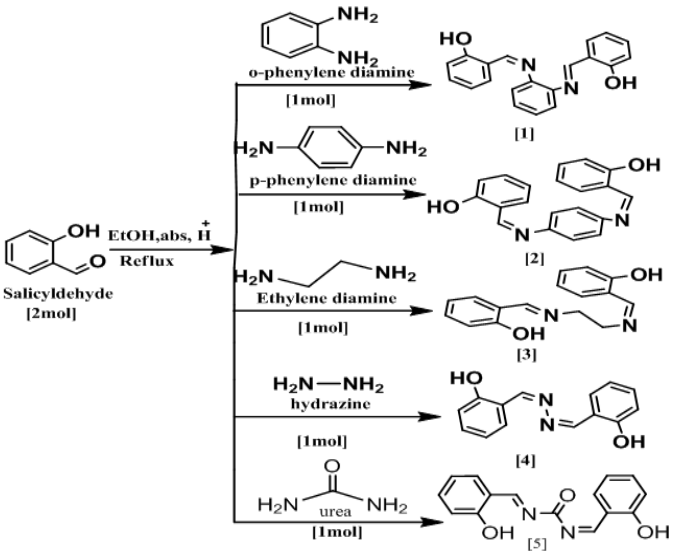
Synthesis of N - Bromo Amines 1, 3-Oxazepine-4, 7-Dion Derivatives (C1, C2, C3, C4, C5)

A Solution of (0.01 mol) of the compound 2, 4, 4, 6- tetra bromo-2, 5- Cyclohexadinone in (20 mL) of dry benzene and then added to a small amount of tri-aluminum chloride (AlCl3) in (100 ml) round bottom flask equipped with magnetic stirrer and condenser and the mixture was refluxed for 15 min, equivalent moles of 1, 3-Oxazepine-4, 7 -dione Derivatives (A1, A2, A3, A4, A5) the same solvent were added to the mix and refluxed for 5 h. Then cold in the ice bath

[29] the colored crystals of derivatives (C1, C2, C3, C4, C5) filtered and washed with distilled water.

RESULTS AND DISCUSSION

Schiff bases prepared by the reaction of salicyldehyde with diamine in absolute ethanol and is shown in scheme (1).



Scheme 1

The prepared compounds were characterized by melting point; Physical properties are given in table 1.

Table 1: Physical Properties of Schiff Bases [1, 2, 3, 4, 5] M. Wt. M.P C_o yield % Colour Molecular Formula Comp

Comp. Symb.	Molecular Formula	Colour	Yield %	M.P C_o	M. Wt.
1	C20H16N2O2	yellow	70	163-165	316.35
2	C20H16N2O2	orange	60	170-172	316.35
3	C16H16N2O2	Greenish yellow	72	128-130	268.31
4	C14H12N2O2	brown	74	308-310	240.26
5	C15H12N2O3	Light green	71	100-102	268.27

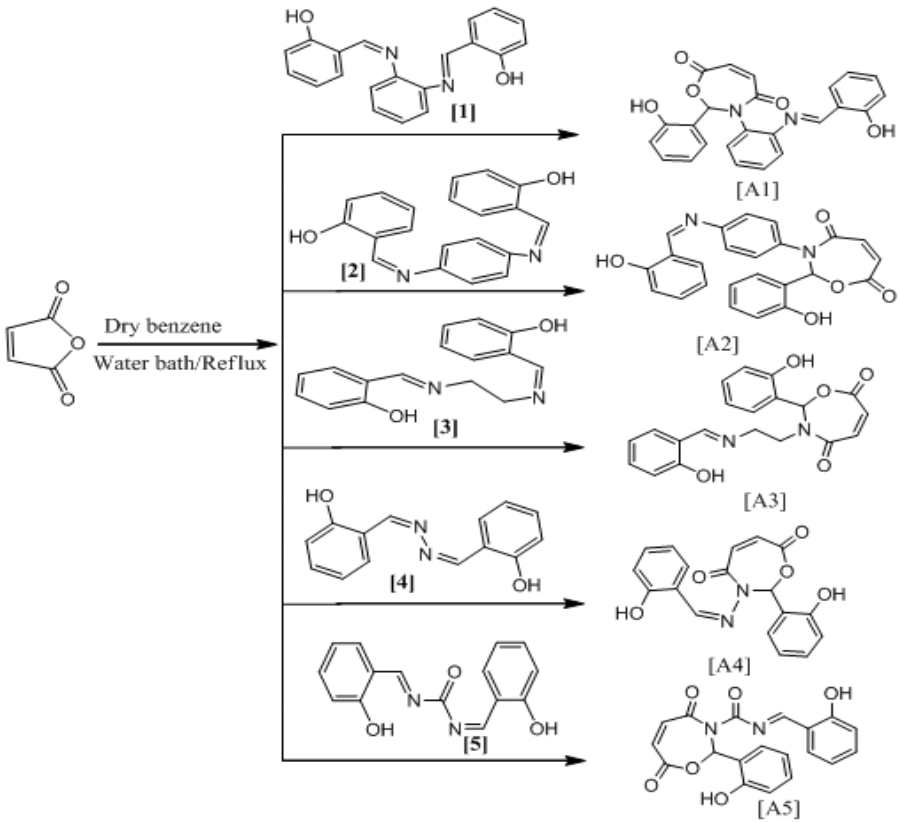
The FT-IR spectrum of Schiff bases showed the disappearance of bands at (3310 -3415cm-1) for amino group, and appear of bands at (3009 –3084) cm-1 for benzene ring, at (2906-2986 cm-1) for methylene groups, at (1230-1280) cm-1 for (C-N), at (1495–1572) cm-1 for (C=C) aromatic ring, FT-IR wave numbers are given in the table 2.

Table 2: FT-IR Spectrum Data of Schiff Bases [1, 2, 3, 4, 5] cm-1

Comp.	ν O-H	ν C-H Arom.	ν C-H Alipha.	ν C=N Imine	ν C-N	ν C=C Arom.
1	3470	3060	-	1630	1275	1495
2	3475	3050	-	1625	1280	1570
3	3465	3030	2905	1650	1230	1572
4	3470	3040	-	1610	1265	1565
5	3466	3042	-	1633	1273	1583

1, 3-oxazepane-4, 7-dione compound compounds [A1, A2, A3, A4, A5] prepared by reaction of Succinic

anhydride compound with Schiff bases [1, 2, 3, 4, 5] by using dry benzene as a solvent. and is shown in scheme(2).



Scheme 2

Table 3: Physical Properties of 1, 3-Oxazepine -4, 7-Dione [A1, A2, A3, A4, A5]
M. Wt. M.P. C₀ Yield % Colour Molecular Formula Compound

Comp.	Mol. Formula	Colour	yield %	M.P. C	M. Wt.
A1	C24H18N2O5	orange	65	176-178	416.43
A2	C24H18N2O5	Greenish yellow	60	171-173	416.43
A3	C20H18N2O5	yellow	75	165-167	368.38
A4	C18H14N2O5	orange	70	170-172	340.33
A5	C19H14N2O6	Light green	71	100-102	366.32

These derivatives were identified by infrared spectroscopy FT-IR Spectra, the table (4) and appeared absorption band (1606 -1624 cm-1) for (C-N Imines), and appeared absorption band at 3455 -3479 cm-1)) for OH phenolic group, and appeared of bands at (3030-3054) cm-1) for (C═C─H) and (1558 -1579cm-1) for aromatic ring, while the absorption bands (1265-1277 cm-1) for (CN), show two bands absorption at (1665- 16765) cm-1)) to (C = O Lactone), and (1730-1755 cm-1), to (C = O Lactam)FT-IR wave numbers are given in the table 3.

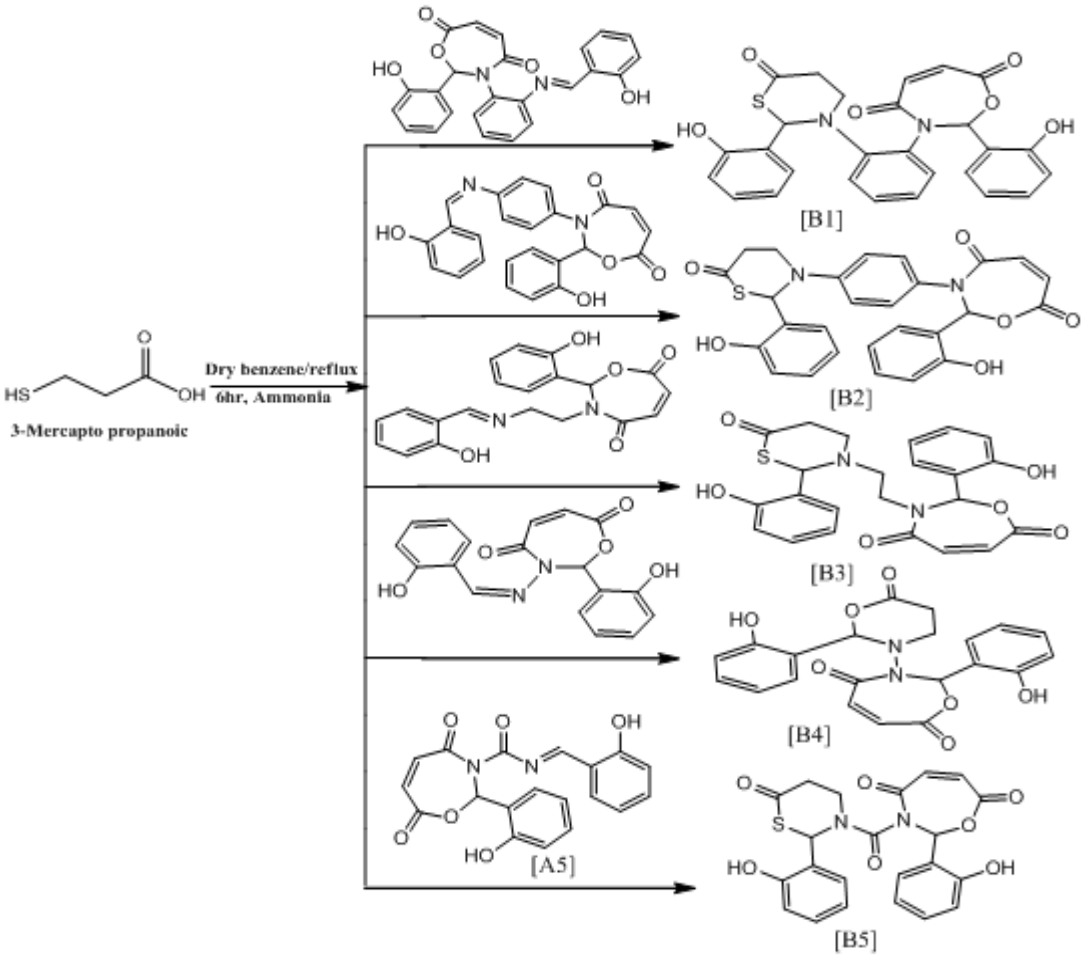
Table 4: FT-IR Spectrum Data of 1, 3-Oxazepine -4, 7-Dion [A1, A2, A3, A4, A5] cm-1

Comp.	ν O-H	ν C-H Arom.	ν C=N Imine	ν C=C Alkene	ν C-N	ν C=C Arom.	ν C=O lactone	ν C=O lactam
A1	3455	3030	1608	1610	1265	1553	1669	1735
A2	3464	3049	1625	1623	1272	1556	1667	1728
A3	3470	3054	1628	1628	1276	1575	1675	1750
A4	3479	3040	1609	1615	1277	1587	1666	1755

A5	3468	3048	1612	1618	1265	1572	1665	1730

1, 3-thiazinane-6-one compound, compounds [B1, B2, B3, B4, B5] prepared by reaction of 3-Mercaptopropanoic acid compound with 1, 3-oxazepine [A1, A2, A3, A4, A5] by using 1, 4 Dioxan as a solvent.

The prepared compounds were characterized by melting point; Physical properties are given in table (5). And is shown in scheme (3).



Scheme 3

Table 5: Physical Properties of 1, 3-Thiazinane-6-One [B1, B2, B3, B4] M. Wt. M.P. C yield % Colour Molecular Formula Compound

Comp.	Mol. Formula	Colour	Yield%	M.P.C	M. Wt.
B1	C27H22N2SO6	yellow	65	178-180	504.46
B2	C27H22N2SO6	orange	68	166-168	504.46
B3	C23H22N2SO6	yellow	74	158-160	456.28
B4	C21H18N2SO6	yellow	62	196-198	428.28
B5	C22H18N2O7S	orange	66	143-145	454.45

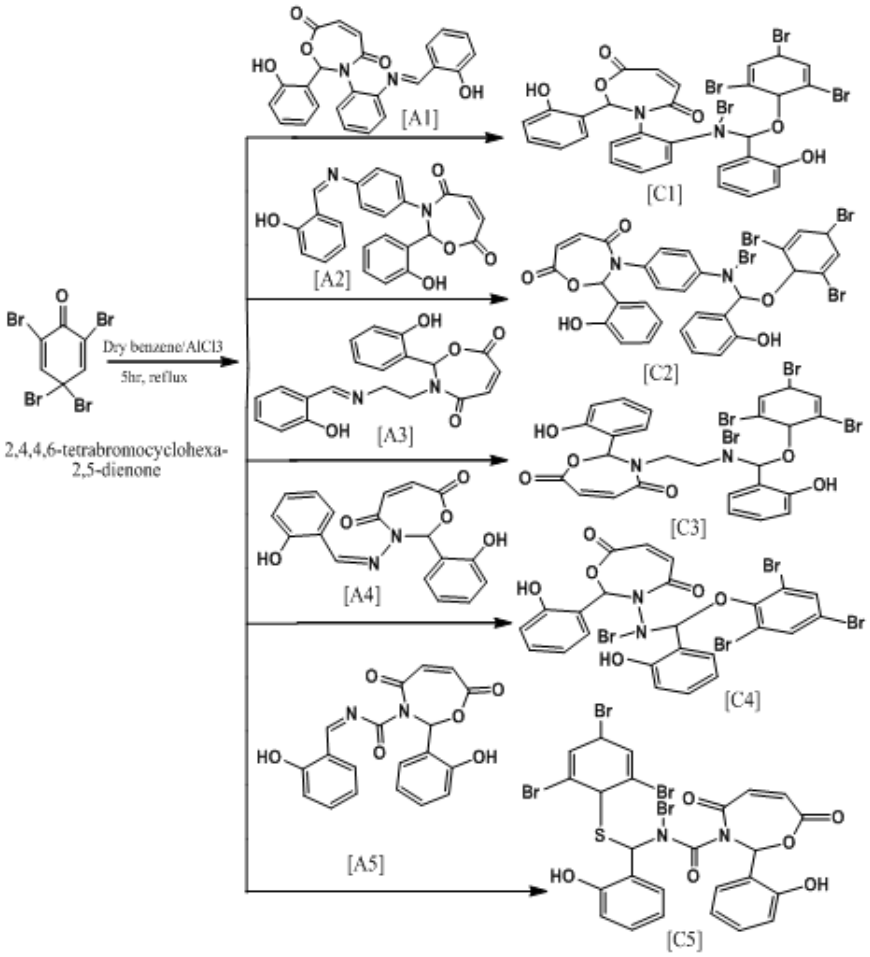
1, 3-Thiazinan-6-one compound compounds [B1, B2, B3, B4, A5] prepared by reaction of 3-mercaptopropanoic Acid compound with 1, 3-oxazepine-4, 7-dione [A1, A2, A3, A4] by using dry benzene as a solvent and ammonia. FT-IR spectrum ms showed bands at (3465-3477) cm-1 for (OH) at (3020 –3055) cm-1 for benzene ring, at (1640-1674) cm-1 for (C=O) lactone and lactam compounds, at (1360-1385) cm-1 for (C-N) and (1628–1615) cm-1 for (C=C) aromatic ring.

These derivatives were identified by infrared spectroscopy FT-IR Spectra in the Table (6).

Table 6: FT-IR Spectrum Data of 1, 3-Thiazine-6-One [B1, B2, B3, B4B5,] cm-1

Comp.	ν O-H	ν C-H Arom.	ν C-N	ν C-S	ν C=C Arom.	ν C=O lactone	ν C=O lactam	λ max1 THF	λ max2 THF
B1	3477	3020	1360	753	1564	1645	1725	370	225
B2	3470	3039	1380	756	1570	1662	1729	325	219
B3	3475	3055	1385	751	1566	1678	1735	350	228
B4	3472	3040	1370	743	1560	1670	1730	340	230
B5	3465	3030	1375	745	1585	1650	1720	345	220

N-bromoamine compounds [C1, C2, C3, C4, C5] prepared by reaction of 2, 4, 4, 6-Tetrabromo-2, 5-cyclohexadienone with 1, 3-Oxazepine -4, 7-dione Derivatives [A1, A2, A3, A4, A5] using benzene as a solvent and AlCl3 as a catalyst. Physical properties are given in table (7).and is shown in scheme (4).



(Scheme 4)

Table 7: Physical Properties of N-Bromo Amines 1, 3-Oxazepine-1, 4-Dione Derivatives [C1, C2, C3, C4, C5] M. Wt. M.P. C Yield % Colour Molecular Formula Compound

Comp.	Mol. Formula	Colour	Yield%	M.P.C	M.Wt.
C1	C30H24Br4N2O6	Light Yellow	66	181-183	828.14
C2	C30H24Br4N2O6	Light Yellow	70	172-174	828.14
C3	C26H24Br4N2O6	orange	73	138-140	780.09

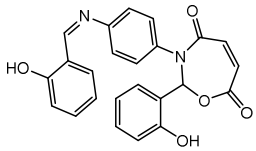
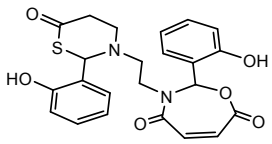
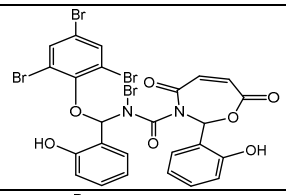
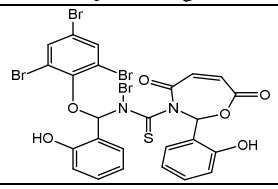
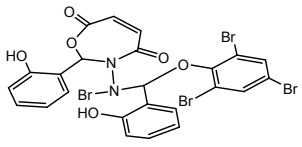
C4	C24H20Br4N2O6	yellow	67	122-124	752.04
C5	C25H18Br4N2O6S	Peggy	64	122-124	794.10

FT-IR spectrums showed bands, at (3435-3455) cm-1 for –OH phenol, at (3039-3058) cm-1 for benzene ring, at (1645-1753(cm-1 for (C=O) for lactone and lactam compounds, at, besides other at (1565-1584) cm-1 for (C=C) aromatic ring [28, 26]. FT-IR spectrum data are given in the table 8.

Table 8: FT-IR Spectrum Data of N-Bromo Amines 1, 3-Oxazepine-1, 4-Dione Derivatives [C1, C2, C3, C4, C5] cm-1

Comp	ν O-H	ν C-H Arom	ν C-N	ν C=C Arom.	ν C=O lactone	ν C=O lactam	ν N C-Br -	C-O-C	λ max1 THF	λmax2 THF
C1	3455	3058	1360	1590	1680	1730	680	1118	324	215
C2	3440	3052	1390	1585	1663	1740	675	1170	390	209
C3	3435	3054	1370	1575	1684	1728	689	1184	257	215
C4	3450	3056	1365	1575	1675	1735	690	1165	343	210
C5	3445	3039	1380	1565	1645	1753	666	1175	268	223

Table 9: It Shows the Chemical Displacements of Some Compounds Prepared by 1HNMR Spectra

Comp. No	Structure	Chemical Shift(δPpm)	No. Proton	Type of Signal	Group
B2		8.85 2.48-2.55 7.20 6.80-8.11 13.03	1 2 1 12	Singlet Singlet Singlet Multi singlet	-N=CH-Het -CO-CH=CH O-CH-Het Aromatic Proton- OH
B3		2.53-2.58 2.30-2.60 3.72-3.83 6.75 6.85-8.30 12.95	2 2 2 1 8 1	Singlet Singlet Singlet Singlet Multi Singlet	-CO-CH=CH -S-CO-CH2- N-CH2 O-CH-Het Aromatic Proton-OH
C1		3.36 2.50-2.54 6.89 6.90-7.85 13.05	1 2 1 10 1	Singlet Singlet Singlet Multi Singlet	-CH-N-Br -CO-CH=CH O-CH-Het Aromatic Proton -OH
C2		3.37 2.53-2.56 6.87 6.88-7.82 12.95	1 2 1 10 1	Singlet singlet Singlet Multi Singlet	-CH-N-Br -CO-CH=CH O-CH-Het Aromatic Proton -OH
C4		3.67 2.50-2.57 6.49 6.88-8.10 12.68	1 2 1 10 1	Singlet Singlet Singlet Multi Singlet	-CH-N-Br -CO-CH=CH O-CH-Het Aromatic Proton -OH

APPLICATIONS

We expect the prepared compounds have pharmaceutical applications in addition to the possibility of their use as anti-bacterial and antifungal

CONCLUSIONS

A new some 1, 3-Oxazepine-4, 7-dione, 1, 3-Thiazin-6-one, and N-bromo amines 1, 3-Oxazepine -4, 7-dione derivatives were synthesized, purified and characterized by melting point, FT-IR, UV-Vis and 1H-NMR spectra.

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