P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
2018,12 (1) :66-74

Synthesis and Characterization of new 3-(2-(6-oxo-1,3-thiazinan-3-yl)-R)-1,3-oxazepane-4,7-dione and *N*-Bromo Amines 1,3-oxazepane-4,7-dione Derivatives.

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ARTICLE INFO

Received: 12 / 12 /2017
Accepted: 14 / 5 /2018
Available online: 27/11/2018
DOI: 10.37652/juaps.2022.171572

Keywords:
Schiff's bases.
3-(2-(6-oxo-1,3-thiazinan-3-yl)-R),1,3-oxazepane-4.
7-dione.
N- bromo amines derivatives.

ABSTRACT

This study includes synthesis and characterization of new derivatives of 3-(2-(6-oxo-1,3-thiazinan-3-yl)-R)-1,3-oxazepane-4,7-dione and *N*-Bromo amines 1,3-oxazepane-4,7-dione derivatives. Schiff's bases reactions through one step process in inert solvents. Some employing Schiff's bases [1- 4]; in addition, synthesized by the reaction of different amines with (Salicylaldehyde) in absolute ethanol under reflux. Heterocyclic rings of 1,3-oxazepane-4,7-dione prepared by the reaction of succinic anhydride with Schiff's bases [1-4] and 3-(2-(6-oxo-1,3-thiazinan-3-yl)-R)-1,3-oxazepane-4,7-dione derivatives were prepared by the reaction of 3-mercaptopropanoic acid with 1,3-oxazepane-4,7-dione[A_1-A_4] in 1,4-dioxan. Synthesis of some *N*-bromo amine derivatives by the reaction of 1,3-oxazepane-4,7-dione[A_1-A_4] with 2,4,4,6-TBCD (2,4,4,6-tetrabromocyclohexa-2,5-dienone) in dry benzene; The prepared compounds were identified by melting point, FT-IR, UV-Vis and ^{1}H- NMR spectroscopy.

INTRODUCTION

Schiff's bases act important intermediate compounds in the preparation of some biological activan 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.

Our 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 the first attempt to study the chemistry of thiazinanone ring.

There for, in this work, our synthesized (16) new novelty derivatives from 2-picolylamine, aldehydes, and mercaptopropionic acid. This work also aims to explore the antioxidant properties of previously synthesized thiazolidinones and the new thiazinanones. *N*-bromo compounds have bromine atom attached to nitrogen and have much applications as antibacterial, antifungal and anti HIV .

MATERIALS AND METHODS

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Melting points were recorded with (Stuart) 30 Melting point Apparatus and were uncorrected, UV-Visible spectra were recorded with Schimadsu (UV-1800) spectrophotometerInfrared spectra were recorded as KBr pellets on a Thermo-Fisher spectrometer. ^{1}H-NMR spectra were recorded on Bruker-500 MHz Spectrometer using DMSO –d^{6} as a solvent and TMS (Tetramethylsilane $SiMe_4$ as internal standard.

Synthesis of *O*-Hydroxybenzaldehyde (Salicylaldehydyde) Schiff'sbases [1-4]:

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

Synthesis of Heterocyclic Compounds.

Synthesis of 1,3-Oxazepane-4,7-dione Derivatives (A_1-A_4):

In a (100ml) round bottom flask equipped with double surface condenser fitted with calcium chloride guard tube, was placed a mixture of (0.01 mole) of 2,2'-(1*Z*,1'*E*)-(1,2-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene) diphenol and (0.01 mole) of succinic 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) in order to obtain other 1,3-oxazepane (A_2 , A_3 , A_4)[26].

Synthesis of 1,3-Thiazinane -6-one Derivatives (B_1, B_2, B_3, B_4):

A mixture (0.01 mol) of Schiff's bases (A_1, A_2, A_3, A_4) 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 table3. [28].

Synthesis of 2,4,4,6-Tetrabromo-2,5 –Cyclohexadien-1-one (2,4,4,6-TBCD):

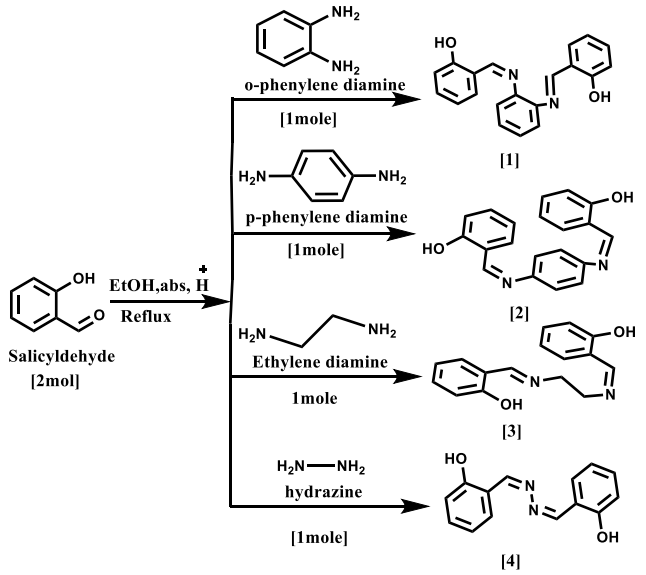
A mixture (0.02 mole, 1.88 g) of phenol and (0.06 mole, 6.714g) of (KBr) with (0.03 mole, 4.797g) ($KBrO_3$) in (60 mL) of distilled water and then added to the mixture slowly (8.7 mL) of hydrochloric acid (36%) for 2 h after it was mix move and refluxed for 2h, then the precipitate was filtered and washed with distilled water , Physical properties are given bellow. m.p. =121-122° , FT-IR:C=C 1581 cm^{-1}, =C-H, 3050 cm^{-1}, C-Br 683-702 cm^{-1}, =CH, 1381 cm^{-1}, C=O, 1679 cm^{-1}. [27].

Synthesis of *N*-bromoaminesDerivatives: (C_1, C_2, C_3, C_4):

A Solution of (0.01 mol) of the compound 2,4,4,6-tetrabromo-2,5- cyclohexadinone in (20 mL) of dry benzene added to a small amount of aluminum trichloride ($AlCl_3$) in (100 mL) round bottom flask equipped with magnetic stirrer and condenser The mixture was refluxed for 15 min, then equivalent moles of 1,3-Oxazepane-4,7-dione derivatives (A_1, A_2, A_3, A_4) 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 (C_1, C_2, C_3, C_4)filtered and washed with distilled water and dried .[28]

RESULTS AND DISCUSSION

Schiff's bases were prepared by the reaction of salicyldehyde with diamines compounds in absolute ethanol [29-31]as shown in scheme 1.



(Scheme 1). Structure for prepared (1, 2, 3, 4) compounds.

The prepared compounds were characterized by their Physical properties such as melting points and colors (table 1.)

Table 1. Physical properties of Schiff's bases [1- 4] :

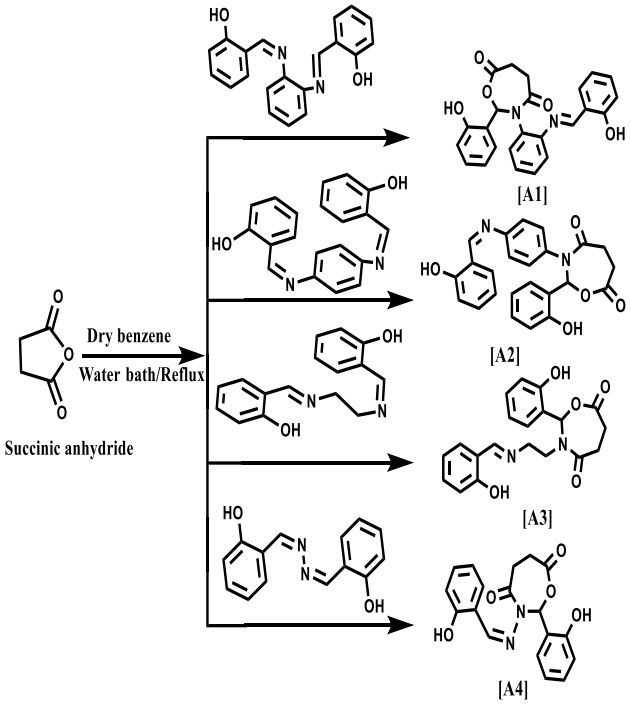
Comp.	Molecular Formula	M. Wt.	M . P C∘	yield %	Colour
1	$C_{20}H_{16}N_2O_2$	316.35	161-163	70	yellow
2	$C_{20}H_{16}N_2O_2$	316.35	168-170	60	orange
3	$C_{16}H_{16}N_2O_2$	268.31	126-128	72	Greenish yellow
4	$C_{14}H_{12}N_2O_2$	240.26	306-308	74	Brown

The FT-IR spectrum of Schiff bases showed the disappearance of bands at (3310 -3415 cm^{-1}) for amino groups, and appear once of bands at (3009 –3084) cm-1 for aromatic C-H, 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, are given in the table 2. [28]

Table 2. FT-IR spectrum data of Schiff's bases [1-4]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	3035	-	1610	1265	1565

1,3-oxazepane-4,7-dione: compounds **[A_1, A_2 , A_3 and A_4]** prepared by reaction of Succinic anhydride with Schiff bases **[1,2,3,4]**in dry benzene as a solvent. and is shown in scheme**(2).**



(Scheme 2). Structure for prepared (A_1, A_2, A_3, A_4) compounds.

Table 3. Physical properties of 1,3-oxazepane -4,7-dione[A_1-A_4] M.Wt. M.P. C° yield % Colour Molecular Formula Compound.

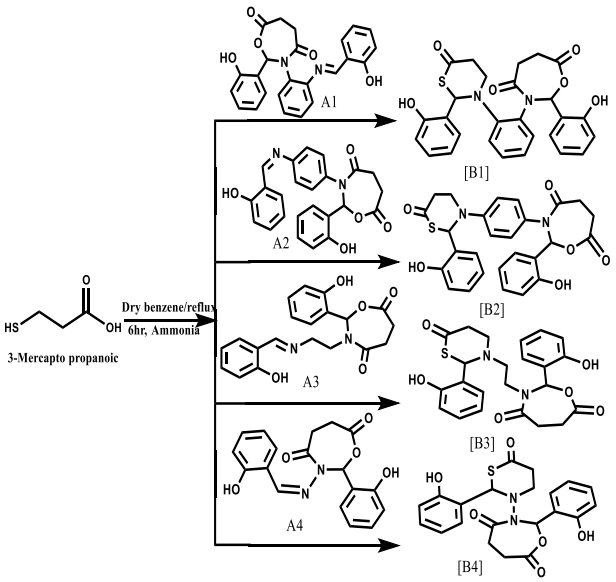
Comp.	M.F.	Colour	M.P. C°	yield %	M.Wt.
A_1	$C_{24}H_{20}N_2O_5$	orange	176-178	65	416.43
A_2	$C_{24}H_{20}N_2O_5$	Greenish yellow	171-173	60	416.43
A_3	$C_{20}H_{20}N_2O_5$	yellow	165-167	75	368.38
A_4	$C_{18}H_{16}N_2O_5$	orange	170-172	70	340.33

These derivatives were identified by FT-IR spectra.The appearance of absorption band at (1606-1624 cm^{-1}) due to (C-N) of Imines(C=N), and absorption band at (3460 -3474 cm^{-1}) for OH phenolic group, while the of bands at (3018-3052 cm^{-1}) for aromatic (C─H) and (1558 -1579cm^{-1}) for aromatic ring, while the absorption bands (1275-1282 cm^{-1}) for (CN), and the two bands absorption at(1661- 1676) cm^{-1}) due to (C = O Lactone), and (1723-1759 cm^{-1}),due to (C = O Lactam).FT-IR wave numbers are given in the table 4.

Table 4. FT-IR spectrum data of 1,3-oxazepane -4,7-dion [A_1-A_4]cm^{-1}

Comp.	ν O-H	ν C-H Arom.	ν C=N Imine	ν C-N	ν C=C Arom.	ν C=O lactone	ν C=O lactam
A_1	3460	3020	1610	1275	1558	1665	1725
A_2	3465	3045	1620	1270	1565	1661	1723
A_3	3474	3052	1624	1280	1570	1676	1755
A_4	3470	3035	1600	1282	1579	1674	1759

,3-thiazinane-6-one : compounds [B_1, B_2, $B_3$and B_4] prepared by reaction of 3-mercaptopropanoic acid with 1,3-oxazepane [A_1, A_2, A_3, A_4] in 1,4 dioxan as a solvent. The prepared compounds were characterized by their physical properties in table (5). and is shown in scheme(3).



(Scheme 3). Structure for prepared (B_1, B_2, B_3, B_4) compounds.

Table 5. Physical properties of 1,3-thiazinane-6-one[B_1-B4].

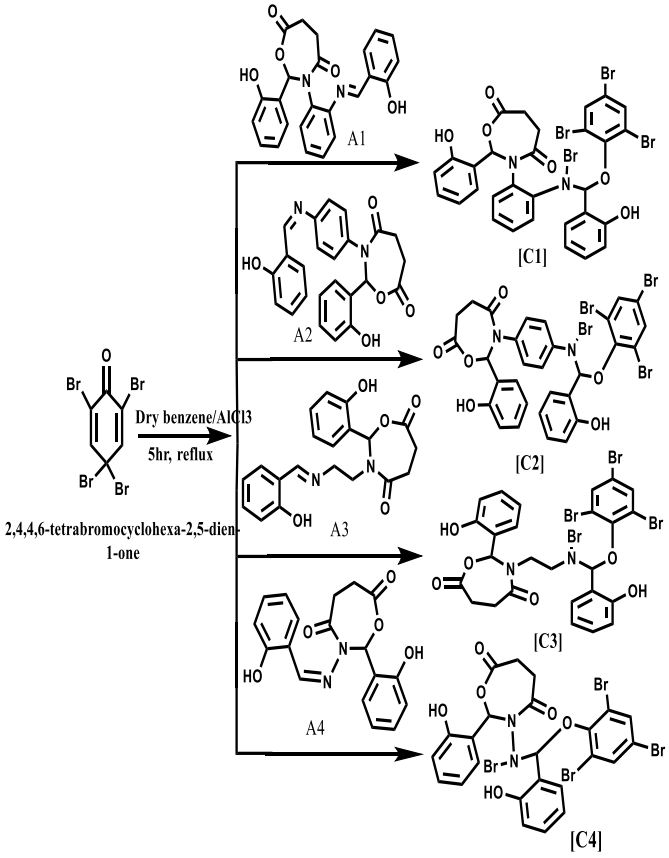
Comp.	M.F.	M.Wt.	M.P.C	Yield%	Colour
B_1	$C_{27}H_{24}N_2SO_6$	504.46	178-180	65	yellow
B_2	$C_{27}H_{24}N_2SO_6$	504.46	166-168	68	orange
B_3	$C_{23}H_{24}N_2SO_6$	456.28	158-160	74	yellow
B_4	$C_{21}H_{20}N_2SO_6$	428.28	196-198	62	yellow

The spectra showed bands at (3470-3480) cm^{-1} for (OH) and (3023 –3050) cm^{-1} for benzene whereas the band at(1666-1674) cm^{-1} for (C=O) lactone and lactam compounds, at (1187-1282) cm^{-1} for (C-N) and (1465–1615) 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 [B_1-B_4]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
B_1	3480	3023	1367	753	1564	1640	1720	369	225
B_2	3476	3035	1384	756	1570	1666	1725	315	219
B_3	3470	3050	1390	751	1566	1672	1741	355	228
B_4	3475	3045	1377	743	1560	1674	1734	346	230

N-Bromoamine, compounds **[C_1, C_2, C_3, C_4]** were prepared by reaction of 2,4,4,6-Tetrabromo-2,5-cyclohexadienonewith 1,3-Oxazepane-4,7-dione derivatives **[A_1, A_2, A_3, A_4]** using benzene as a solvent and $AlCl_3$ as a catalyst scheme (4). physical properties are given in table **(7).**



Scheme 4. Structure for prepared (C_1, C_2, C_3, C_4) compounds.

Table 7. Physical properties of N-bromo amine compounds [C_1-C_4] M. Wt. M.P. C° yield % Colour Molecular Formula Compound.

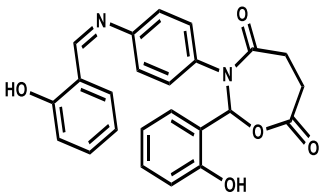
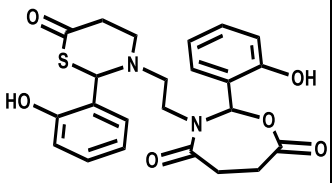
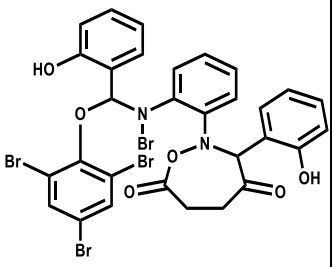
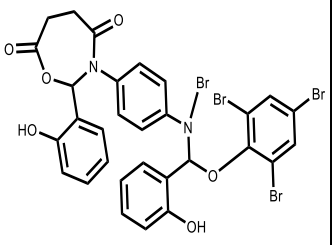
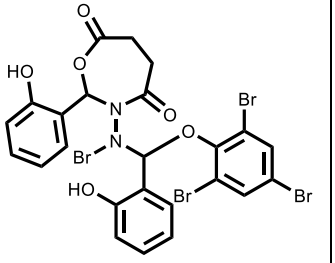
Comp.	Mol. Formula	M.Wt.	M.P.C	Yield%	Colour
C_1	$C_{30}H_{24}Br_4N_2O_6$	828.14	181-183	66	Light Yellow
C_2	$C_{30}H_{24}Br_4N_2O_6$	828.14	172-174	70	Light Yellow
C_3	$C_{26}H_{24}Br_4N_2O_6$	780.09	138-140	73	orange
C_4	$C_{24}H_{20}Br_4N_2O_6$	752.04	122-124	67	yellow

FT-IR spectra showed bands at (1118-1184)cm^{-1} for (C-O-C), at(3415-3424cm^{-1}) for OH phenolic at (3039-3058) cm^{-1} for benzene ring, at (1660-1745cm^{-1}) for (C=O)for lactone and lactam compounds, besides other at (1570-1592) 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-bromoamine compounds[C_1-C_4]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
C_1	3477	3065	1366	1590	1680	1732	688	1118	328	218
C_2	3491	3072	1394	1582	1660	1745	670	1170	395	205
C_3	3485	3084	1375	1570	1692	1729	683	1184	252	212
C_4	3473	3056	1360	1576	1674	1738	694	1165	340	219

Table. 9: shows the chemical shifts in ^{1}HNMR spectra of some compounds prepared.

Comp.No	Structure	Chemical shift (ppm)
B_2		δ = 2.49-2.65 ppm (tt, 4H, -CH_2CH_2-), δ = 5.40ppm (s, 2H, -2OH), δ = 6.99-8.11 ppm (m, 12H, ArH), δ = 6.94 ppm (s, 1H, N-CH-O), δ = 8.87 ppm (s, 1H, -CH=N)
B_3		δ = ppm (tt, 4H, -$COCH_2CH_2N$-),δ = 2.30-2.60 ppm (tt, 4H, -CH_2CH_2-), δ = 5.40ppm (s, 2H, -2OH), δ = ppm (s, 1H, -S-CH-N), δ = 6.85-8.22 ppm (m, 8H, ArH), δ = ppm (s, 1H, N-CH-O)
C_1		δ = 2.40-2.45 ppm (tt, 4H, -CH_2CH_2-), δ = ppm (s, 1H, N-CH-CO) , δ = ppm (s, 1H, N-CH-O) , δ = ppm (s, 1H, CH-O), δ = ppm (s, 2H, -2OH), δ = ppm (m, 14H, ArH)
C_2		δ = ppm (tt, 4H, -CH_2CH_2-), δ = ppm (s, 1H, Br-N-CH-O) , δ = ppm (s, 1H, N-CH-O) , δ = ppm (s, 1H, CH-O), δ = ppm (s, 2H, -2OH), δ = 6.95-7.66 ppm (m, 14H, ArH , C=CH)
C_4		δ = ppm (tt, 4H, -CH_2CH_2-), δ = ppm (s, 1H, Br-N-CH-O) , δ = ppm (s, 1H, N-CH-O) , δ = ppm (s, 1H, CH-O), δ = ppm (s, 2H, -2OH), δ = 6.88-8.10 ppm (m, 10H, ArH , C=CH)

CONCLUSIONS

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

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P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
2018,12 (1) :66-74

تحضير وتشخيص بعض مشتقات 3-(2 -(-6- ثيازينان -3- يل)- R) -3,1-اوكسازبان-7,4 دايون و - N - بروموامين -3,1- اوكسازبان -7,4- دايون الجديدة .

وليدفرج حمادي[1] صفا عبدالسلام عبدالجبار [2]

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الخلاصة :-

تضمنت الدراسة تحضير بعض المشتقات 3-(2-(6- اوكسو -3,1- ثيازينان-3- يل) -R-)-3,1- اوكسازبان -7,4- دايون , N- بروموامين -3,1- اوكسازبان -7,4- دايون. من تفاعل قواعد شيف الثنائية الامين (1-4) المحضرة من تفاعل الامينات الثنائية مع السلسلديهايد في الايثانول المطلق والتصعيد لمدة ساعتان .

حضرت المركبات الحلقية الغير متجانسة 3,1- اوكسازبان -7,4- دايون من تفاعل انهيدريد السكسنيك الحلقي مع قواعد شيف(1-4) ومشتقات 3-(2-(6-اوكسو -3,1- ثيازينان -3- يل)-R) ,3- اوكسازبان-7,4- دايون . من تفاعل 3- مركبتو حامض البروبانويك مع مشتقات 3,1- اوكسازبان 7,4- دايون (B_1-B_4) في 4,1- دايوكسان كمذيب .

حضرت مشتقات N- بروموامين (C_1- C_4) من تفاعل 1, 3- اوكسازبان - 7,4- دايون (A_1-A_4) مع (2 ,4 ,4 ,6) - رباعي بروموسايكلو هكسا - 5, 2 - دايون) في البنزين الجاف .

شخصت جميع المركبات الحلقية الغير متجاسة المحضرة بواسطة درجة الانصهار ,طيف الاشعة فوق البنفسجية (U-Vis) ,الاشعة تحت الحمراء(FT-IR) و طيف الرنين النووي المغناطيسي (^{1}HNMR) .

كلمات مفتاحية :- قواعد شيف ، 3 - (2 - (6 - اوكسو -3,1- ثيازينان-3- يل) - R، 3,1 - اوكسازبان - 7,4 - دايون , ومشتقات N-بروموامين.