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SYNTHESIS, CHARACTERIZATION AND KINETIC STUDIES OF SOME OXAZEPINE AND OXAZEPANE DERIVATIVES

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ABSTRACT

1,3-Bis(2-hydroxy-benzylidene)-Thiourea and 1,3-Bis-(dimethylamino-benzylidene)-Thiourea were prepared by condensation of Thiourea with one equivalent and two equivalent of substituted benzaldehyde. These Schiff-bases were reacted with one equivalent of Maleic , Succinic and Phthalic anhydride in absolute ethanol to give 7-membered heterocyclic ring system of 2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3] oxazpine-3-carbothioic acid amide and 2-(4-Dimethylamino-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioiacid amide, 1,3-Bis(2-hydroxy-benzylidene)-Thiourea and 1,3-Bis-(dimethylamino-benzylidene)-Thiourea were reacted with two equivalent of Maleic and Succinic anhydride in same solvent to give 2 (7-membered) heterocyclic ring system of 2-(2-hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbothioyl]-2,3-dihydro-[1,3]oxazepine-a,7-dione and 2-(4-Dimethylamino-phenyl)-3-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepine-3- carbothioyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione. The constants of reaction velocity for (Schiff-bases)with Maleic , Succinic and Phthalic anhydride were studied and showed that the reaction wsa first – order one .Some of thermodynamic characteristics were evaluated and showed differences among the prepared compounds . The final products were identified by their melting points, elemental analysis, IR, 1H NMR and UV-Visible spectra.

Introduction:-

The synthesis of 2-phenyl -1,3-oxazepine by irradiation of 4-phenyl-2-oxa-3-aza bicyclo[3.2.0]-hepta-3,6-diene[1] , and the discovery of the central nervous system(CNS) activity of 1,4- benzodiazepine [2] encourage the chemists to look for more effective ways to build up the 7- membered heterocyclic ring systems from already available materials. One of these ways which has been discovered recently, involves direct addition of maleic anhydride to the (C=N) double bond of Schiff bases and number of 2,3-diaryl-2,3-dihydro-1,3-oxazepine-4,7-diones were prepared and characterized. [3-4].Pyrylium tetrafluroborate

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underwent ring expansion on treatment with excess sodiumazide in anhydrous 1,4-dioxane to give 58-96% substituted 1,3-oxazepine. Furthermore, thermal rearrangement of ketovinylazirines gave substituted 1,3-oxazepines. [5-6] However , Biginelli s initial one-pot method of refluxing a β-keto ester , aryl aldehyde and urea with a catalytic amount of acid frequently afforded low (20-60%) yields of the desired target molecules[7]. While optimizing the reaction conditions of the Biginelli reaction, we found that treatment of β-keto ester , aryl aldehyde and urea with KSF montmorillonite in methanol afforded DHPMs in good to excellent yields [8].A simple, efficient and cost-effective method has been developed for the synthesis of 3,4-dihydropyrimidin-2(1H) –ones by a one-pot three component cyclocondensation reaction of 1,3-dicarbonyl compound, aldehyde, and urea ,thiourea using benzyltriethylammonium chloride as the catalyst, under solvent-free conditions: the scope of this protocol is utilized for the synthesis of mitotic kinesin EG5 inhibitor monastrol. [9]

Experimental:-

Melting points were recorded with Gallenkamp melting points Apparatus and were uncorrected . Elemental analysis was carried out in perkin-Elmer 2400 CHN Elemental analyzer table (1,5) , FT-IR spectra were recorded on FT-IR spectrophotometer -8400s Shimadza (KBr) table (2,6) their 1H-NMR spectra were recorded with BRUKER-AC-200MHZFT-NMR table (3,7) and UV-Visible spectra were recorded (in ethanol) On Schimadza Reco- 160 Spectrophotometer table (4,8) .

Preparation of (2-hydroxy-benzylidene)-Thiourea (Schiff-base):- To a solution of 0.05 mole (3.6 g) of thiourea in 30 ml of absolute ethanol, 0.05 mole (6.1g) of O- hydroxy benzaldehyde was added and refluxed 2hr. Where by a yellow crystalline solid was precipitated. The solid was filtered and recrystallized from ethanol.

Preparation of 2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioic acid amide:-

In a 100 ml round bottom flask equipped with double surface condenser fitted with calcium chloride guard tube was placed a mixture of 0.01 mole (1.52 g) of (2-hydroxy-benzylidene)-thiourea and 0.01mole (0.98 g) maleic anhydride in 20 ml of absolute ethanol. The reaction mixture was refluxed in water bath at 78 ° C for 2 hr.

The solvent was then removed and the resulting solid which recrystallized from anhydrous THF.

Preparation of 2-(2-Hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbothioyl]-2,3-dihydro-[1,3]oxazepine-4,7-dion:-

A mixture of (0.01 mole) (2.84g)of 1,3-Bis(2-hydroxy-benzylidene)-thiourea and (0.02mole) (1.96 g) of maleic anhydride in 30 ml of absolute ethanol was refluxed on a water bath for 3hr. The solvent was then removed and the crystalline solid was recrystallized from anhydrous 1,4-dioxan.

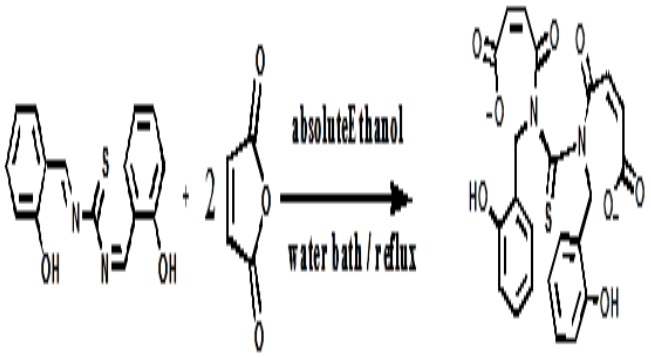
This experiment was repeated using the same amounts of the reactance to obtain other derivatives.

Discussion:-

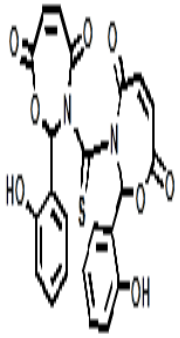
It is known that Schiff bases react smoothly with acid chlorides and anhydrides to give the corresponding addition products.(5,6,9)

The reaction is followed by the appearance of (N=CH) absorption band at (1600-1615) cm^{-1} the disappearance of both (C=O) absorption band at (1670-1687) cm^{-1} and (-NH2) absorption bands at (3400,3655) cm^{-1} in their IR spectra.

In this paper, the reaction of the maleic, Succinic and phthalic anhydrides with 1,3-Bis(2-hydroxy-benzylidene)-thiourea to gives the dipolar intermediate [11A] which collapses to the 7-membered heterocyclic ring system.[11B] is presented.



11A



11B

Scheme 1

This is indicated by the appearance of the characteristic C=O (lacton-lactam) absorption band at 1700cm^{-1} in the IR spectra of the addition products[11B].

It is impressive to note that the two absorption band at (1800-1955)cm^{-1} in the IR spectra of pure maleic ,Succinic, and phthalic anhydride have disappeared when the anhydride became part of the 7-membered ring system of the 2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioic acid amide and 2-(2-Hydroxy-phenyl)-3-[2-(2-

hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbothioyl]-2,3-dihydro-[1,3]oxazepine-4,7-dion.

The new absorption bands of the (C=O) group in the IR spectra of the addition products [11B] appear at (1665-1710)cm^{-1}, this attributed to the fact that the structures of the addition products are combination of the lacton-lactam structure.[10,11] .

The UV spectra 2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioic acid amide and 2-(2-Hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbothioyl]-2,3-dihydro-[1,3]oxazepine-4,7-dion show absorption maxima at (230-305)nm , and at (308-440)nm due to charge transfer of the aryl group and the cyclic 7-membered structure [11B].

2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioic acid amide and 2-(2-Hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbothioyl]-2,3-dihydro-[1,3]oxazepine-4,7-dion are identified by their melting points ,elemental analysis (table 1,5),IR spectra (table 2,6) , 1H NMR spectra (table 3,7) and UV spectra (table 4,8). It is noticeable that the values of C-Hstr. (benzylic) absorption bands are rather high. This is in fact explained by the shift towards longer wavelength that takes place when the benzylic carbon is linked to three electron-withdrawing groups, phenyl, O and N in the title compounds.

The reaction of maleic and succinic anhydride with various Schiff bases is a sort of cycloaddition reaction.Cycloaddition is a ring formation that results from the addition of bonds to either δ or π with formation of new δ bonds. This class of reactions and its reverse encompasses a large number of individual types. Huisgen [12] has formulated a useful classification of diverse cycloaddition in terms of the number of the new δ bond. The ring size of the product, and the number of atoms in the components taking part in the cycloaddition. This cycloaddition reaction is classified as a 2 + 5-7, and it is the first cycloaddition of this type, although in principle, one would predict that the butadiene cation might add to an olefin through a (4n+2) transition state to yield the cyclohexenyl cation [13].

Calculation of the Reaction Velocity:

A first-order reaction equation was applied to the reaction of Schiff-bases with Maleic, Succinic and Phthalic anhydrides. It proved to be useful to calculation the reactions velocity under vaying temperutures (213-253)k with (10) k increase.

The value of K was calculated for all reactions by drawing the relation between ln At/Aω with Time.

The relation between lnK with 1/T was then drawn. It shows the effect of temperature on the reaction velocity in order to obtain the ideal

temperature for the reaction. It was noticed that velocity increases with temperature and that velocity is stable at (353) k.

From the tables (9 -20) we notice that the value of ΔH , ΔS , and ΔG is positive. This proves that the reactions are endothermic and spontaneous. We also notice that the activation energy ΔH stars to increase with deferent used compounds.

Figures (1, 2, 3) show the reaction velocity for deferent compounds.

Al-Hadithi[14][15] found that the (Ethylene Schiff-bases) compounds are needs less energy than those of (Thiourea Schiff-bases), which are in turn ,less energy than the (Urea Schiff-bases) compounds.

Conclusions:-

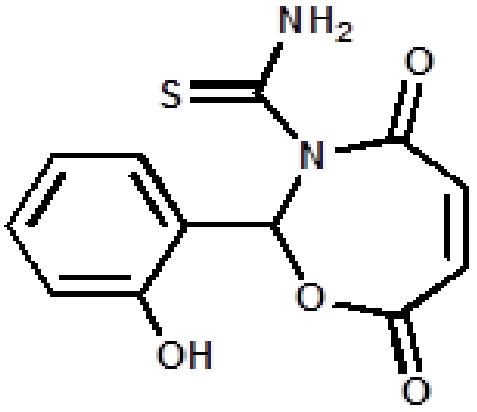
1-The Schiff bases prepared in this research were verified by elemental analysis, IR, 1H NMR and UV-Visible spectra.

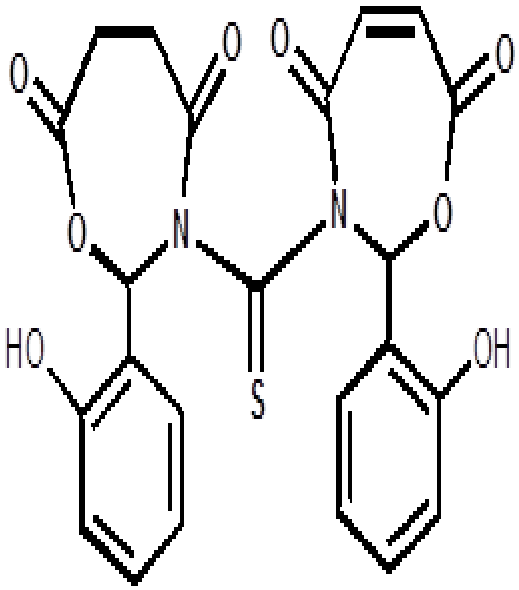
2-The Oxazepines and oxazepanes prepared in this research were verified by elemental analysis, IR, 1H NMR and UV-Visible spectra.

3- A first-order reaction equation was applied to the reaction of Schiff-bases with maleic, succinic, phthalic anhydride. It proves to be useful for the calculation of the reactions velocity under varying temperatures (213-253)k with (10) k increase .

4- The values of ΔH, ΔS, and ΔG are positive. This proves that the reactions are endothermic and spontaneous.

Table (1): Melting points, yield,molecular formula [M.F]. and elemental analysis of thiourea [1,3] oxazepine and thiourea [1,3] oxazepane -4,7- dione (1-9) .





No.	m.p/C°	Yield%	M.F	Calculated			Found		
				C	H	N	C	H	N

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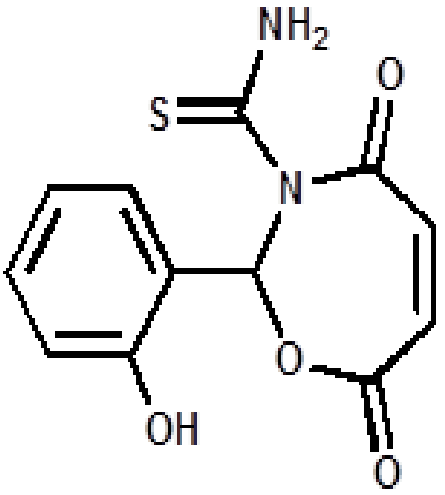
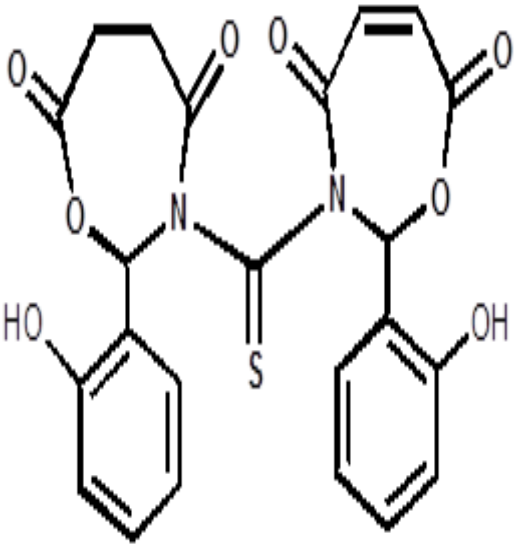
Table (2) The Major IR Absorption (cm^{-1}) of thiourea [1,3] oxazepine and thiourea [1,3] oxazepane -4,7- dione (1-9) .





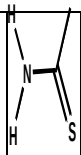
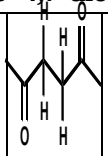
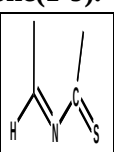
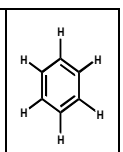
No.	١	٢
O-H str. phenol	3440	٣٤50
C-H str. Benzylic	٣٢00	٣٢10
C-H str. Aromatic	٣٠70	٣٠50
C=O str. Lacton,lactam	١٦75	١٦70
C=C str. Olefin	١٦١٠	-
C=C str. Aromatic	1590,1540	1570,1540
C-N str.	١٤٤٠	١٤٤٠
C-O str. Lacton	١٣٢٠	١٣٣٠
C=S str.	1240	1235
C-H bend. Aromatic	10٠0,770	1030,875

١	٢	٣	٤	٥	٦	٧	٨	٩
154-156	144-146	١٨٢-١٨٠	١٤٠-١٣٨	160-162	176-178	152-154	148-150	170-172
67	٧٥	٨٠	٦٦	٦٠	٧٣	٧٧	٧٠	٧١
$C_{12}H_{10}N_2O_4S$	$C_{12}H_{12}N_2O_4S$	$C_{16}H_{12}N2O_4S$	$C_{18}H_{15}N_2O_5S$	$C_{19}H_{14}N_2O_5S$	$C_{23}H_{16}N_2O_5S$	$C_{22}H_{15}N2O_8S$	$C_{21}H_{16}N_2O_8S$	$C_{26}H_{17}N_2O_8S$
51.79	٥١,٤٢	58.53	58.21	59.68	63.88	56.53	55.26	60.35
3.62	4.32	3.68	4.07	3.69	3.73	3.23	3.53	3.31
10.07	9.99	8.53	7.54	7.33	6.48	5.99	6.14	5.41
51.86	51.52	58.46	58.11	59.60	64.00	٥٦,٦١	55.37	60.26
3.72	4.44	3.69	4.20	3.57	3.71	3.40	3.63	3.44
10.00	9.84	8.41	7.38	7.12	6.35	5.78	6.02	5.32

٩	٨	٧	٦	٥	٤	٣
٣٤55	٣٤45	٣٤30	٣٤20	٣٤25	٣٤٣٠	٣٤30
٣٢20	٣200	٣١90	٣٢10	٣٢٣٠	٣١80	٣٢٠٠
٣٠90	٣٠80	٣٠70	٣٠75	٣٠65	٣٠80	٣٠30
١٢٧٠	١٢65	١٢65	١٢70	١٢80	١٢85	١٢٨٠
١٢15	١٢15	١٢20	-	١٢٢5	-	-
1570,1535	1590,1530	1575,1550	1580,1530	1570,1540	1590,1550	1570,1530
١٤٣٥	١٤45	١٤٤٥	١٤4٠	١٤٣٠	١٤50	١٤3٠
١٣٢٠	١٣٢٠	١٣٢٥	١٣٣٠	١٣١٥	١٣١٠	١٣٢٠
1240	1245	1250	١٢٣٥	1240	1245	1250
1060,800	1040,860	1020,870	1010,860	1055,860	1025,870	1010,850

*** as KBr disc.**

Table (3): The Major ^{1}H NMR Absorptions (ppm) of thiourea [1,3] oxazepine and thiourea [1,3] oxazepane -4,7-dione(1-9).

No.			OH			
1	2.1	6.8 , 6.45	4.8	-	-	6.5-8.0
2	2.15	-	4.9	2.49 , 2.44	-	6.5-7.9
3	2.1	-	4.75	-	-	6.5-8.0
4	-	-	4.8	2.50 , 2.48	8.1	6.5-8.0
5	-	6.85 , 6.43	4.9	-	8.2	6.5-7.8
6	-	-	4.9	-	8.1	6.5-8.0
7	-	6.8 , 6.50	4.85	-	-	6.5-7.9
8	-	6.82 , 6.44	4.7	2.51 , 2.48	-	6.5-7.8
9		6.80 , 6.52	4.85		-	6.5-7.8

***Chemical Shift = δ ** By using DMSO –d_6 as solvent**

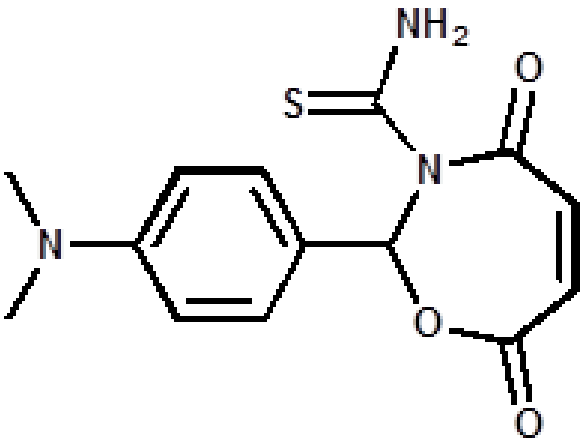
Table (4) The UV-Visible absorption maxima λ (nm) of thiourea [1,3] oxazepine and thiourea [1,3] oxazepane -4,7- dione (1-9) .

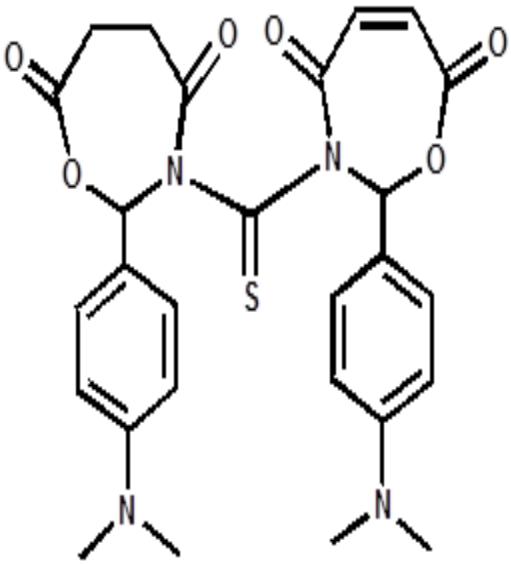
Compound	UV-Visible absorption maxima λ/nm
١	376,310,255 ,231,221
٢	363,300,271 ,238,226
٣	388,320,266 ,230,225

٤	275,309,269 ,235,220
٥	360,303,260 ,231,222
٦	361,300,275 ,230,220
٧	370,306,285 ,234,225
٨	380,308,267 ,235,220
٩	381,302,285 ,235,222

*** By using ethanol abslute.**

Table (5): Melting points,yield,molecular formula [M.F]. and elemental analysis of thiourea [1,3] oxazepine and thiourea [1,3] Oxazepane -4,7- dione (10-18) .





No.	m.p/C°	Yield%	M.F	Calculated			Found		
				C	H	N	C	H	N
10	126-128	55	$C_{14}H_{15}N_3O_3S$	55.07	4.95	13.76	54.92	5.01	13.62
11	133-135	59	$C_{14}H_{17}N_3O_3S$	54.71	5.57	13.67	54.84	5.63	13.61
12	146-148	62	$C_{18}H_{17}N_3O_3S$	60.83	4.82	11.82	60.93	4.95	١١.٦٩
13	120-122	56	$C_{23}H_{26}N_4O_3S$	62.99	5.98	12.78	63.12	6.06	12.64
14	129-131	70	$C_{23}H_{24}N_4O_3S$	63.28	5.54	12.83	63.33	5.54	12.65
15	188-190	76	$C_{27}H_{26}N_4O_3S$	66.65	5.39	11.51	66.74	5.45	11.47

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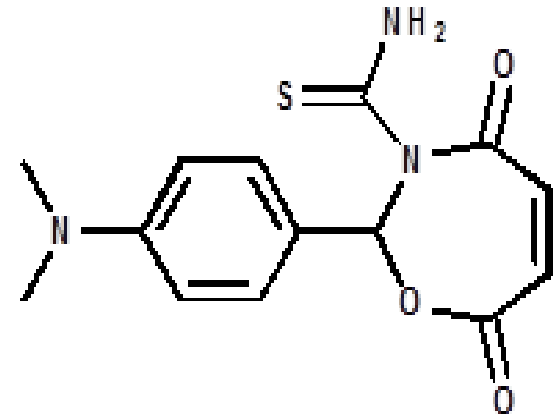
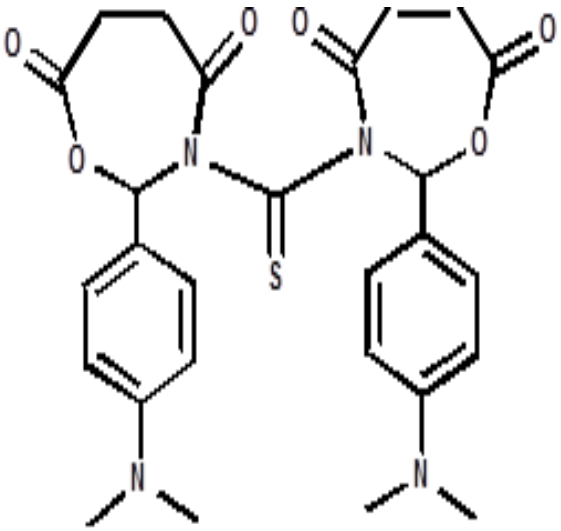
18	17	16
169-171	170-172	174-176
71	77	73
$C_{31}H_{28}N_4O_6S$	$C_{27}H_{28}N_4O_6S$	$C_{27}H_{26}N_4O_6S$
63.69	60.43	60.66
4.83	5.26	4.90
9.58	10.44	10.48
63.73	60.53	60.73
4.92	5.31	4.99
9.51	10.30	10.31

Table (6) The Major IR Absorption (cm^{-1}) of thiourea [1,3] oxazepine and thiourea [1,3] oxazepane -4,7- dione (10-18) .





No.	١٠	١١	١٢	١٣	١٤	١٥	١٦	١٧	١٨
N-H str. amide	٣٣٣٠,3200	3340,3210	3350,3220	-	-	-	-	-	-
C-H str. Aromatic	٣٠60	٣٠75	٣٠70	٣٠65	٣٠40	٣٠80	٣٠65	٣٠75	٣٠٢٠
C=O str. acton,lactam	1680,1630	1680,1640	1670,1630	1685,1660	1670,1645	1680,1655	1675,1660	1690,1660	1680,1640
C=C str. Olefin	١٦٢٥	-	-	-	١٦20	-	١٦١5	١٦3٠	١٦٢5
C=C str. Aromatic	1590,1520	1565,1530	1580,1540	1570,1550	1580,1540	1585,1530	1580,1550	1575,1560	1590,1540
C-N str.	1340,1010	1350,1010	1350,1030	1360,1020	1340,1030	1360,1030	1365,1010	1375,1025	1350,1030
C-O str. Lacton	١٢80	١٢٨٠	١٢70	١٢65	١٢80	١٢7٠	١٢7٥	١٢9٠	١300
C=S str.	1230	1245	1240	1235	1230	1240	1240	1235	1230

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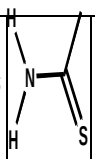
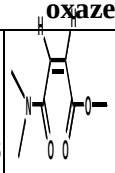
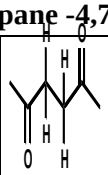
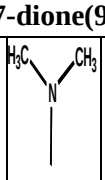
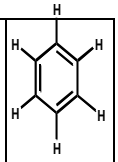
Table (7) : The Major ^{1}H NMR Absorptions (ppm) of thiourea [1,3] oxazepine and thiourea [1,3] oxazepane -4,7-dione(9-18).

No.						
10	2.1	6.9 , 6.5	-	2.80	-	6.4 -7.9
11	2.1	-	2.49 , 2.51	2.75	-	6.5 -7.8
12	2.0	-	-	2.75	-	6.4 -7.8
13	-	-	2.52 , 2,50	2.73	8.0	6.4-7.8
14	-	6.75 , 6.40	-	2.70	8.1	6.4 -76
15	-	-	-	2.81	8.0	6.4 -7.9
16	-	6.9 , 6.55	-	2.75	-	6.4 -7.7
17	-	6.70 , 6.50	2.52 , 2.49	2.7	-	6.5 -7.8
18	-	6.80 , 6.55		2.77	-	6.6 -7.9

***Chemical Shift = δ ** By using DMSO –d_6 as solvent**

Table (8) The UV-Visible absorption maxima λ (nm) of thiourea [1,3] oxazepine and thiourea [1,3] oxazepane -4,7- dione (10-18) .

Compound	UV-Visible absorption maxima λ/nm
١٠	352,306,254 ,236,223
١١	350,300,251 ,231,228
١٢	349,302,249 ,233,221
١٣	339,301,256 ,239,222
١٤	351,309,271 ,230,227
١٥	350,310,277 ,236,223
١٦	359,300,271 ,236,225
١٧	358,311,274 ,233,220
١٨	355,505,285 ,240,229

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Table (9): Thermodynamic values for the reaction of (A) with maleic anhydride calculated from the effect of temperature on K, Ea, Δ H, Δ S and Δ G value (1)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔGJ K,mol^{-1}
313	0.0043	56083.1	53485.2	-207.23	118348.19
323	0.0092	56083.1	53402.2	-207.73	120498.99
333	0.0312	56083.1	53319.2	-208.24	122663.12
343	0.045	56083.1	53536.2	-208.67	124810.01
353	0.057	56083.1	53153.2	-209.21	127004.33

Table (10): Thermodynamic values for the reaction of (B) with maleic anhydride calculated from the effect of temperature on K, Ea, Δ H, Δ S and Δ G value (2)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG KJ,mol^{-1}
313	0.0041	56033.3	53435.4	-208.04	118551.92
323	0.0089	56033.3	53352.4	-208.57	120720.51
333	0.0311	56033.3	53569.4	-209.07	122889.71
343	0.047	56033.3	53186.4	-209.5	125039.9
353	0.052	56033.3	5310.4	-210.04	127247.52

Table (11): Thermodynamic values for the reaction of (C) with maleic anhydride calculated from the effect of temperature on K, Ea, Δ H, Δ S and Δ G value (3)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG jK,mol^{-1}
313	0.0047	54066.2	51468.3	-212.19	117883.77
323	0.012	54066.2	51385.3	-212.64	120068.02
333	0.0372	54066.2	51302.3	-213.22	122304.26
343	0.048	54066.2	51219.3	-213.65	124501.25
353	0.061	54066.2	51136.3	-214.19	126745.37

Table (12): Thermodynamic values for the reaction of (D) with maleic anhydride calculated from the effect of temperature on K, Ea, Δ H, Δ S and Δ G value (4)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG K,mol^{-1}
313	0.0045	54705.3	52107.4	-211.36	118263.08
323	0.0098	54705.3	52024.4	-211.88	120461.64
333	0.0361	54705.3	51941.4	-212.39	122667.27
343	0.043	54705.3	51858.4	-212.82	124855.66
353	0.058	54705.3	51775.4	-213.36	127091.48

Table (13): Thermodynamic values for the reaction of (A) with succinic anhydride calculated from the effect of temperature on K, Ea, Δ H , Δ S and Δ G value (1)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔGJK,mol^{-1}
313	0.00037	57414.42	54816.52	-209.70	120452.62
323	0.0081	57414.42	54733.52	-210.12	122611.97
333	0.021	57414.42	54650.52	-210.72	124820.28
343	0.0382	57414.42	54567.52	-211.22	127015.98
353	0.040	57414.42	54484.52	-211.69	129306.4

Table (14): Thermodynamic values for the reaction of (B) with succinic anhydride calculated from the effect of temperature on K, Ea, Δ H , Δ S and Δ G value (2)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔGj K,mol^{-1}
313	0.0032	56298.9	53701	-210.78	119675.14
323	0.0086	56298.9	53618	-211.30	121867.9
333	0.028	56298.9	53535	-211.80	124064.4
343	0.0352	56298.9	53452	-212.30	126270.9
353	0.047	56298.9	53369	-212.77	128476.81

Table (15): Thermodynamic values for the reaction of (C) with succinic anhydride calculated from the effect of temperature on K, Ea, Δ H , Δ S and Δ G value (3)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔGJ K,mol^{-1}
313	0.0049	53659.5	51061.6	-215.09	118384.77
323	0.0087	53659.5	50978.6	-215.63	120627.09
333	0.032	53659.5	50895.6	-216.12	122863.56
343	0.044	53659.5	50812.6	-216.62	125113.26
353	0.0521	53659.5	50729.6	-217.09	127362.37

Table (16): Thermodynamic values for the reaction of (D) with succinic anhydride calculated from the effect of temperature on K, Ea, Δ H , Δ S and Δ G value (4)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔGJ K,mol^{-1}
313	0.0035	58456.9	55858.1	-206.41	120464.43
323	0.0084	58456.9	55775.1	-206.90	122603.8
333	0.037	58456.9	55692.1	-207.41	124759.63
343	0.042	58456.9	55609.1	-207.84	126898.22
353	0.053	58456.9	55526.1	-208.37	129080.71

Table (17): Thermodynamic values for the reaction of (A) with phthalic anhydride calculated from the effect of temperature on K, Ea, Δ H , Δ S and Δ G value (1)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG K,mol^{-1}
313	0.0031	54896.6	52298.3	-218.33	120635.59
323	0.0079	54896.6	52215.3	-218.86	122907.08
333	0.024	54896.6	52132.3	-219.38	125185.84
343	0.0321	54896.6	52049.3	-219.80	127440.07
353	0.042	54896.6	51966.3	-220.35	129749.85

Table (18): Thermodynamic values for the reaction of (B) with phthalic anhydride calculated from the effect of temperature on K, Ea, Δ H , Δ S and Δ G value (2)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG K,mol^{-1}
313	0.0034	57112.3	54514.4	-213.85	121449.45
323	0.0097	57112.3	54431.4	-214.37	123672.91
333	0.033	57112.3	54348.4	-214.89	125906.77
343	0.042	57112.3	54265.4	-215.31	128116.73
353	0.051	57112.3	54182.4	-215.85	130377.45

Table (19): Thermodynamic values for the reaction of (C) with phthalic anhydride calculated from the effect of temperature on K, Ea, Δ H , Δ S and Δ G value (3)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG K,mol^{-1}
313	0.0045	52539	49941.1	-219.59	118672.77
323	0.014	52539	49858.1	-220.1	120950.4
333	0.0351	52539	49775.1	-220.62	123241.56
343	0.042	52539	49692.1	-221.01	125498.53
353	0.053	52539	49609.1	-221.58	127826.84

Table (20): Thermodynamic values for the reaction of (D) with phthalic anhydride calculated from the effect of temperature on K, Ea, Δ H , Δ S and Δ G value (4)

T .k	K,h^{-1}	Eaj mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG K,mol^{-1}
313	0.0042	52075.86	49477.96	-220.24	118413.08
323	0.011	52075.86	49394.96	-220.78	120706.9
333	0.0312	52075.86	49311.96	-221.27	122994.87
343	0.04	52075.86	49228.96	-221.71	125275.49
353	0.048	52075.86	49145.96	-222.27	127607.27

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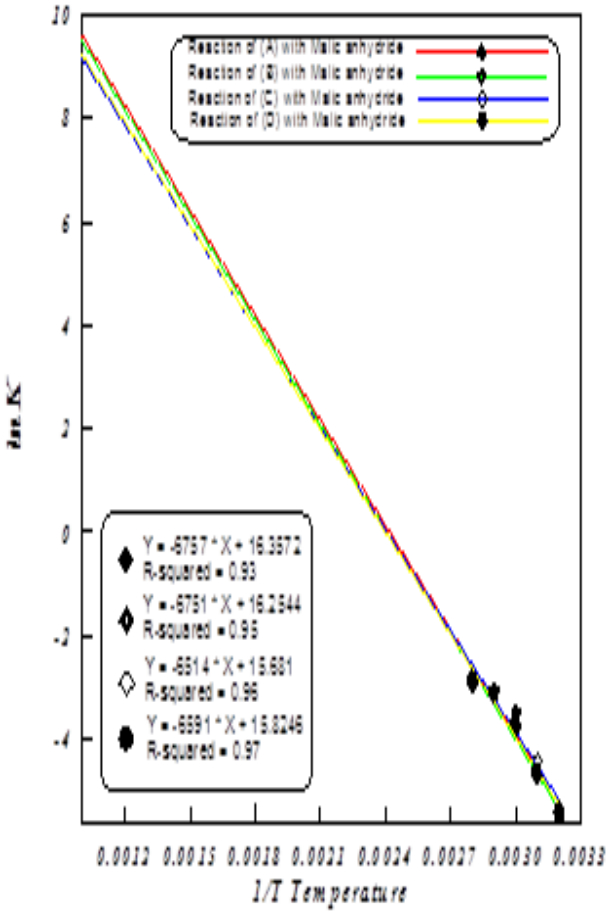

Fig (1): The relationship between lnK and 1/T of reaction A,B,C and D with maleic anhydride.

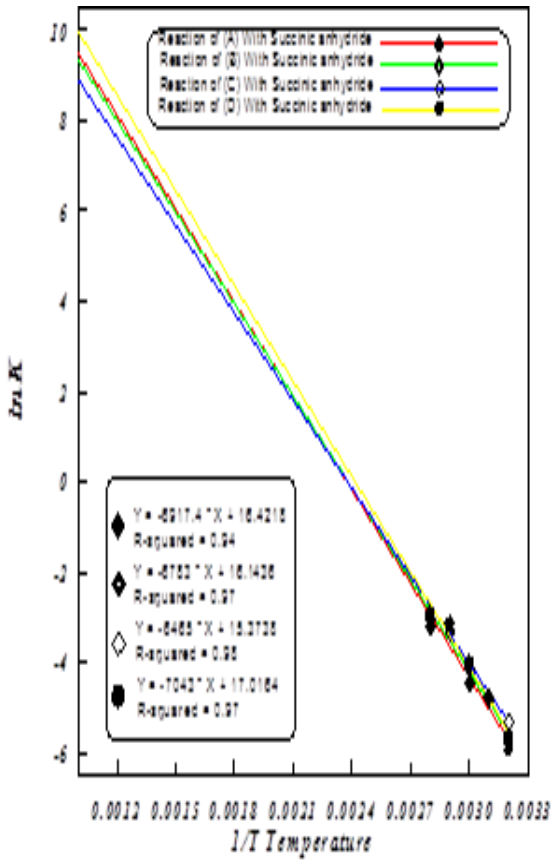

Fig (2) :The relationship between lnK and 1/T of reaction A,B,C and D with succinic anhydride.

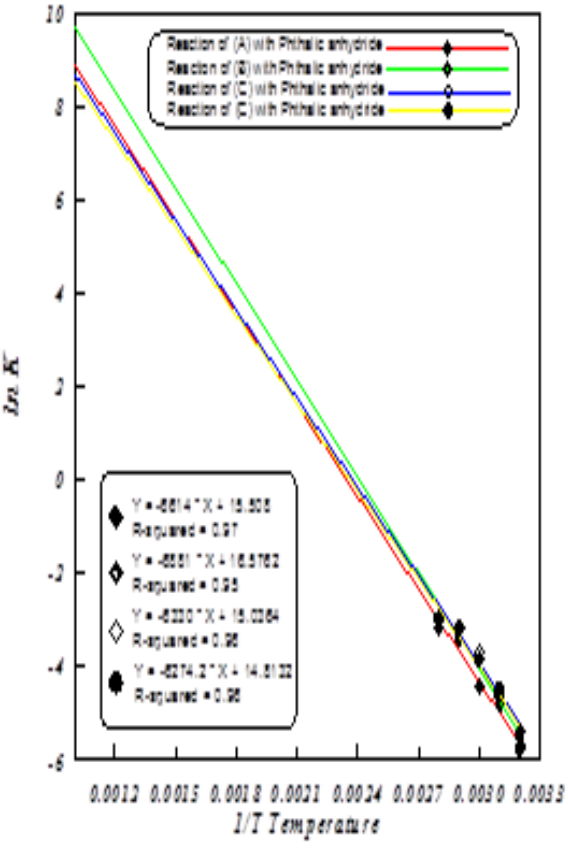

Fig (3):The relationship between lnK and 1/T of reaction A,B,C and D with phthalic anhydride.

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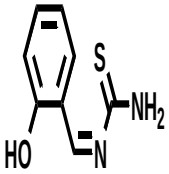
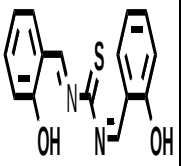
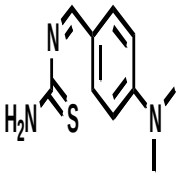
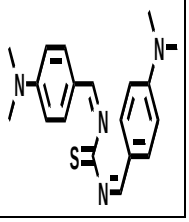
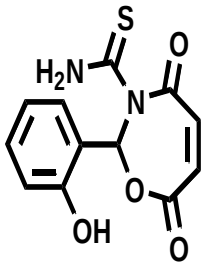
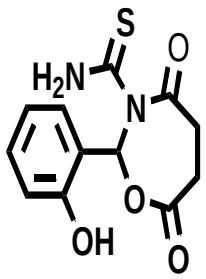
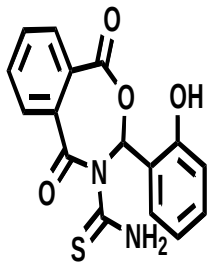
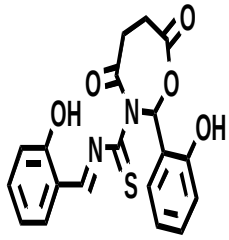
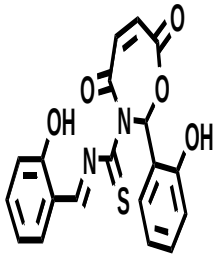
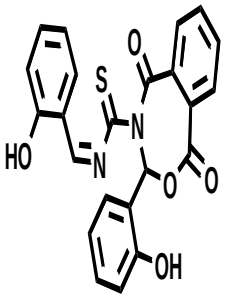
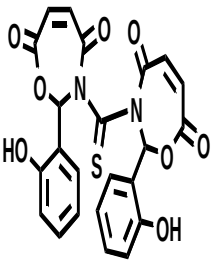
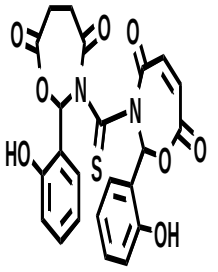
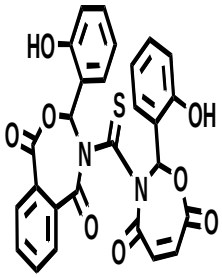
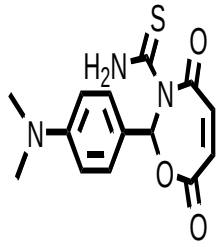
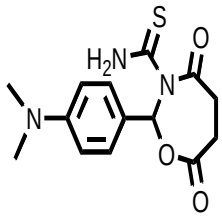
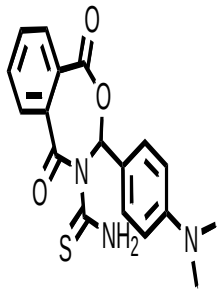
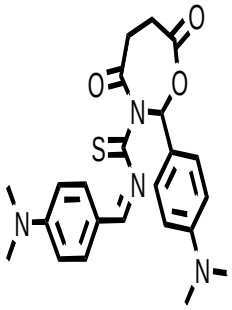
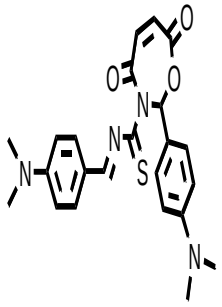
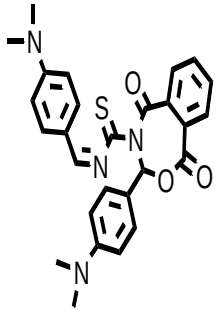
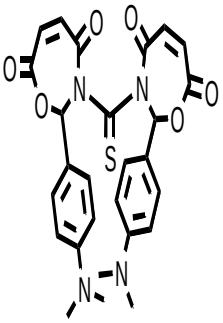
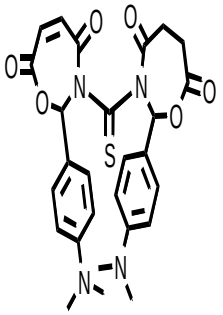
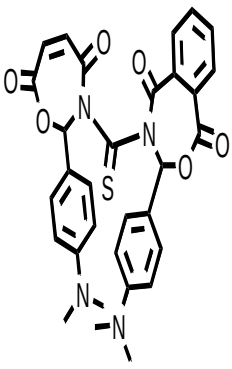
Table(21); The Schiff bases prepared in this research .

No.	Schiff-Bases Name	Structure
A	(2-Hydroxy-benzylidene)-thiourea	
B	1,3-Bis-(2-hydroxy-benzylidene)-thiourea	
C	(4-Dimethylamino-benzylidene)-thiourea	
D	1,3-Bis-(4-dimethylamino-benzylidene)-thiourea	

Table(22); The oxazepines and oxazepanes prepared in this research.

No.	Name of compounds	Structure
1	2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3] oxazepine-3-carbothioic acid amide	
2	2-(2-Hydroxy-phenyl)-4,7-dioxo-[1,3] oxazepane-3-carbothioic acid amide	
3	7-(2-Hydroxy-phenyl)-5,9-dioxo-5,9-dihydro-6-oxa-8-aza-benzocycloheptene-8-carbothioic acid amide	
4	2-(2-Hydroxy-phenyl)-4,7-dioxo-[1,3] oxazepane-3-carbothioic acid 2-hydroxy-benzylideneamide	
5	2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioicacid 2-hydroxy -benzylideneamide	
6	7-(2-Hydroxy-phenyl)-5,9-dioxo-5,9-dihydro-6-oxa-8-aza-benzocycloheptene-8-carbothioic acid 2-hydroxy-benzylideneamide	
7	7-(2-Hydroxy-phenyl)-5,9-dioxo-5,9-dihydro-6-oxa-8-aza-benzocycloheptene-8-carbothioic acid 2-hydroxy-benzylideneamide	
8	2-(2-Hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7 -dioxo-[1,3]oxazepane-3-carbothioyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione	

9	7-(2-Hydroxy-phenyl)-8-[2-(2-hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioyl]-7,8-dihydro-6-oxa-8-aza-benzocycloheptene-5,9-dione	
10	2-(4-Dimethylamino-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioic acid amide	
11	2-(4-Dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepane-3-carbothioic acid amide	
12	7-(4-Dimethylamino-phenyl)-5,9-dioxo-5,9-dihydro-6-oxa-8-aza-benzocycloheptene-8-carbothioic acid amide	
13	2-(4-Dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepane-3-carbothioicacid4-dimethyl amino-benzylideneamide	
14	2-(4-Dimethylamino-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioic acid 4-dimethylamino-benzylideneamide	
15	7-(4-Dimethylamino-phenyl)-5,9-dioxo-5,9-dihydro-6-oxa-8-aza-benzocycloheptene-8-dimethyl carbothioic acid 4-dimethylamino-benzylideneamide	
16	2-(4-Dimethylamino-phenyl)-3-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbothioyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione	
17	2-(4-Dimethylamino-phenyl)-3-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepane-3-carbothioyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione	
18	7-(4-Dimethylamino-phenyl)-8-[2-(4-dimethylamino-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbothioyl]-7,8-dihydro-6-oxa-8-aza-benzocycloheptene-5,9-dione	

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تخليق ودراسة طيفية وحركية لبعض مشتقات الاوكزازبين والاوكزازبان

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الخلاصة:-

تم تحضير قواعد شيف ٣,١-بس(٢-هيدروكسي-بنزيليدين)- ثايو يوريا و٣,١- بس(ثنائي مثيل أمينو- بنزيليدين)- ثايويوريا من تكاثف الثايويوريا مع مول واحد ومولين من البنزالديهايد المعوض. فوعلت قواعد شيف هذه مع مول واحد من انهيدريدات الماليك، السكسنيك والفثاليك وتم الحصول على نظام حلقي غير متجانس (سباعي الحلقة) وعند مفاعلة قواعد شيف مع مولين من الانهيدريدات أنفة الذكر أعطى نظام حلقي غير متجانس (بحلقتين سباعيتين). قد شخصت المركبات المحضرة بتحليل العناصر، والطرق الطيفية (أطياف الأشعة فوق البنفسجية ،أطياف الأشعة تحت الحمراء وطيف الرنيين النووي المغناطيسي) وقد أسهمت نتائج التشخيص بالطرق المختلفة في إثبات الصيغ التركيبية للمركبات المحضرة كما درست ثوابت سرع التفاعلات للمركبات المحضرة (قواعد شيف) مع انهيدريدات المالك، والسكسنيك والفثاليك فأظهرت بان التفاعل من الدرجة الأولى ، كما حسبت بعض الخواص الثرموديناميكية والتي أظهرت اختلافاً لهذه الخواص بين المركبات المحضرة.