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SYNTHESIS, CHARACTERIZATION AND KINETIC STUDIES OF SOME OXAZEPINE AND OXAZEPANE FROM REACTION OF ETHYLIMINO AND DIETHYLIMINO WITH MALEIC, SUCCINIC AND PHTHALIC ANHYDRIDE

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ABSTRACT: Ethylimino and Di Ethylimino were prepared by condensation of Ethylene diamine with one equivalent and tow equivalent of substituted benzaldehyde. These ethylimino were reacted with one equivalent of maleic , succinic and phthalic anhydride in absolute ethanol to give 7-membered heterocyclic ring system of 3-(2-amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3] oxazepine and 3-(2-amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3] oxazepane. Diethylimino were reacted with tow equivalent of maleic and succinic anhydride in same condition to give 2(7-membered) heterocyclic ring system of 2-(2-hydroxy-phenyl)-3-{2-[2-(2-hydroxy-phenyl) -4,7-dioxo -[1,3] oxazepine-3-yl]-ethyl}-2,3-dihydro-[1,3]oxazepine-4,7-dione and 2-(2-hydroxy-phenyl)-3-{2-[2-(2-hydroxy-phenyl) -4,7 -dioxo -[1,3] oxazepane-3-yl]-ethyl}-2,3-dihydro-[1,3]oxazepane-4,7-dione. Kinetic Studies of reaction of Ethylimino and DiEthylimino with maleic , Succinic and phthalic anhydride proved to A first-class equation was applied to the reaction.

Keywords : Schiff bases; oxazepine and oxazepane; synthesis; properties ; kinetic studies.

Introduction

The synthesis of 2-phenyl -1,3-oxazepine by irridiation of 4-phenyl-2-oxa-3-aza bicyclo[3.2.0]-hepta-3,6-diene(1)was studied by Toshio Makai with other workers.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(3), involves direct addition of maleic anhydride to the (C=N) double bond of schiffs bases and anumber of 2,3-diaryl-2,3-dihydro-1,3-oxazepine-4,7-diones were prepared and characterized.(3-8)

Pyrylium tetrafluroborate 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. (9-14)

Materials and methods

Starting material and solvent were used without further purification. Melting points were recorded on Gallenkamp melting points Apparatus and were uncorrected . Elemental analysis was carried out in Al-Qaqah state company on perkin-Elmre 2400 CHN Elemental analyzer . FT-IR spectra were recorded on FT-IR spectrophotometer -8400s Shimadza (KBr) and UV-Visible spectra were recorded (inethanol) On Schimadza Reco- 160 Spectrophotometer.

Preparation of 2-[(2-Amino-ethylimino)-Methyl]-phenol.(Schiff-base):-

To a solution of o.o5 mole of Ethylene diamine in 30 ml of Ethanol (absolute) was added o.o5 mole or o.1 mole of substituted benzaldehyde and refluxed 2hr. Whereby ayellow crystalline solid separated out . The solid was filtered and recrystallized from ethanol.

Preparation of 3-(2-Amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3]oxazepine 4,7-dione:-

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 of 2-[(2-Amino-ethylimino)-Methyl]-phenol and 0.01mole maleic anhydride in 20 ml of Ethanol absolute. The reaction mixture was refluxed in water bath at 78C° 3he, the solvent was then removed and the resulting solid was recrystallized from anhydrous THF.

Preparation of 2-(2-hydroxy-phenyl)-3-{2-[2- hydroxy-phenyl)-4,7-dioxo-[1,3] oxazepine-3-yl]-ethyl}2,3-dihydro-[1,3] oxazepine-4,7-dione:-

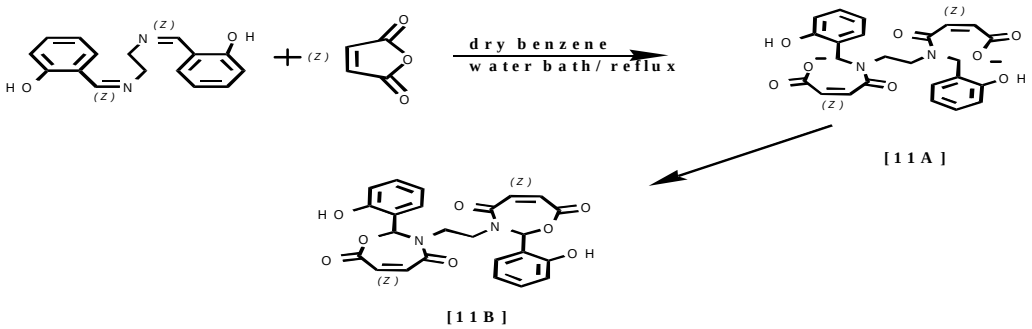
A mixture of(0.01 mole) of 3-(2-Amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3]oxazepine 4,7-dione and (0.002 mole) of maleic anhydride in Ethanol absolute was refluxed on a water bath for 3hr. The solvent was then removed and the crystalline solid was recrystallized from anhydrous 1,4-dioxan.

This experiment was repated using the same amounts of the reactance to obtain other derivatves.

Result and discussion

It is known that Schiff bases react smoothly with acid chlorides and anhydrides to give the corresponding addition products.(5-7)

In this paper, the reaction of the Maleic and Succinic anhydride with(2-[(2-Amino-ethylimino)-Methyl]-phenol 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 addition

products[11B] as shown in tables(2,3,4).

It is impressive to note that the two absorption band at (1800-1950)cm-1 in the IR spectra (Tables 2,3,4) of pure Maleic anhydride have disappeared when the anhydride became part of the 7-membered ring system of the 3-(2-Amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3]oxazepine 4,7-dione and2-(2-hydroxy-phenyl)-3-{2-[2- hydroxy-phenyl)-4,7-dioxo-[1,3] oxazepine-3-yl]-ethyl}2,3-dihydro-[1,3] oxazepine-4,7-dione.The new absorption bands of the (C=O) group in the IR spectra of the addition products [11B] appear at (1670-1700)cm-1, this attributed to the fact that the structures of the addition products are combination of the lacton-lactam structure.(8,9) .

The UV spectra (Tables 5,6) of 3-(2-Amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3]oxazepine 4,7-dione and 2-(2-hydroxy-phenyl)-3-{2-[2-hydroxy-phenyl)-4,7-dioxo-[1,3] oxazepine-3-yl]-ethyl}2,3-dihydro-[1,3] oxazepine-4,7-dione show absorption maxima at (240-310)nm , and at (310-445)nm due to charge transfer of the aryl group and the cyclic 6-membered structure [11B].

3-(2-Amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3]oxazepine 4,7-dione and 2-(2-hydroxy-phenyl)-3-{2-[2-hydroxy-phenyl)-4,7-dioxo-[1,3] oxazepine-3-yl]-ethyl}2,3-dihydro-[1,3] oxazepine-4,7-dione are identified by their m.ps,elemental analysis (table 1),IR spectra (table 2) and UV spectra (table 5). It is noticeable that the values of C-Hstr. (benzylic) absorption bands are rather high.This is in fact explained by the shift towared 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 C=N 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 (10) has formulated a useful classification of diverse cycloaddition in terms 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 woud predict that the butadienyl cation might add to an olefin through a (4n+2) transition state to yield the cyclohexenyl cation (11).

A first-order 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(313-253)k with (10) k interval.

T=2.303/k log A/A-X

Ln At/Aw = kt

K= Rate constant

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

In order to obtained the ideal temp. For the reaction and to study the effect of temp. on reaction velocity relation between Lnk and 1/T was than draw. . It was noticed that velocity increases with temperature and that velocity is stable at (353) k .

From the tables (7 -18) we notice that the value of ΔH , ΔS , and ΔG is positive. This proves that the

reactions are indotherm and auto. We also notice that the activation ΔH stars to increase with deferent used compounds

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

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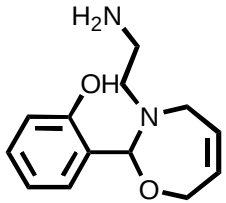
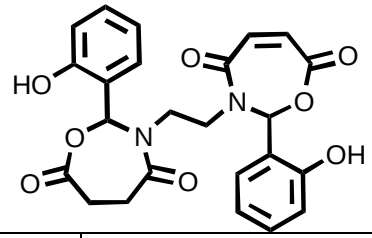
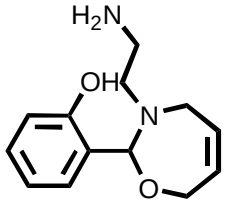
Table (1) Melting point ,percentage yield, molecular formula and elemental analysis of 3-(2-Amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3]oxazepine 4,7-dione and 2-(2-hydroxy-phenyl)-3-{2-[2- hydroxy-phenyl)-4,7-dioxo-[1,3] oxazepine-3-yl]-ethyl}2,3-dihydro-[1,3] oxazepine-4,7-dione:-

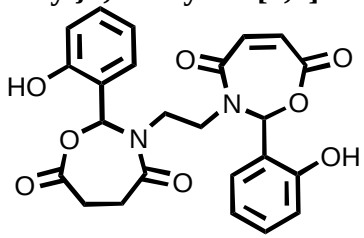




Compound	m.p/C°	Yield%	Mwt.	M.F	Calc.			Found		
					C	H	N	C	H	N
1	114-116	66	264.38	$C_{13}H_{20}N_2O_2$	66.07	8.53	11.85	65.98	8.63	11.75
2	116-118	62	262.26	$C_{13}H_{19}N_2O_2$	66.64	7.74	11.96	66.70	7.71	11.88
3	96-98	81	312.32	$C_{17}H_{20}N_2O_2$	71.81	7.09	9.85	71.69	7.11	9.79
4	104-106	89	366.37	$C_{20}H_{20}N_2O_5$	65.21	5.47	7.60	65.26	5.50	7.60
5	108-110	76	368.38	$C_{20}H_{18}N_2O_5$	65.57	4.95	7.65	65.59	5.51	7.71
6	115-117	70	416.43	$C_{24}H_{20}N_2O_5$	69.22	4.84	6.73	69.25	4.88	6.61
7	120-122	63	468.46	$C_{24}H_{24}N_2O_8$	61.53	5.15	5.98	61.55	5.20	5.83
8	119-121	69	466.44	$C_{24}H_{22}N_2O_8$	61.80	4.75	6.01	61.85	4.78	6.00
9	125-127	58	516.50	$C_{28}H_{24}N_2O_8$	65.11	4.68	5.42	65.12	4.66	5.40

Table (2) The major IR absorption (cm-1)of 3-(2-Amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3]oxazepine 4,7-dione and 2-(2-hydroxy-phenyl)-3-{2-[2- hydroxy-phenyl)-4,7-dioxo-[1,3] oxazepine-3-yl]-ethyl}2,3-dihydro-[1,3] oxazepine-4,7-dione:

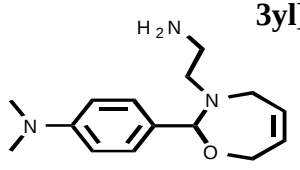


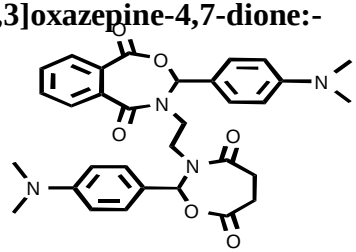


Compound	O-H str.phenol	C-H str. Benzylic	C-H str. Olefin	C=O str. Lacton,lactam	C=C str. Olefin	C=C str. Aromatic	C-N str.	C-O str. Lacton,	C-H bend. Aromatic
1	3440	3230	3080	1680	1610	1580,1540	1440	1320	1020,770
2	3435	3200	3090	1670	1620	1580,1540	1430	1330	1010,870
3	3440	3190	3100	1675	1600	1580,1560	1450	1320	1030,900
4	3435	3180	3120	1680	1605	1585,1555	1440	1330	1050,970
5	3450	3210	3100	1690	1610	1570,1560	1435	1325	1060,770
6	3450	3200	3090	1685	1620	1580,1560	1430	1325	1070,780
7	3430	3200	3080	1670	1620	1585,1560	1450	1320	1010,800
8	3440	3210	3070	1660	1600	1575,1540	1435	1340	1020,850
9	3430	3220	3100	1670	1600	1580,1535	1440	1330	1060,820

*** as KBr disc.**

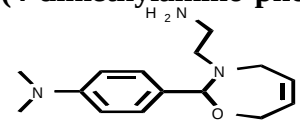
Table (3) Melting point ,percentage yield, molecular formula and elemental analysis of{4-[3-(2-amino-ethyl)-2,3,4,7-tetrahydro-[1,3]oxazepine-2-yl]-phenyl-dimethyl-amine and (Diethyl amino-phenyl)-3-{2-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepane-3yl]-ethyl}-2,3-dihydro-[1,3]oxazepine-4,7-dione:-

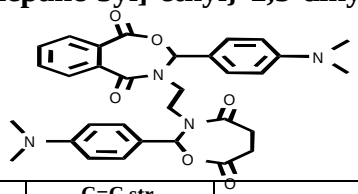




Compound	m.p/C°	Yield%	Mwt.	M.F	Calc.			Found		
					C	H	N	C	H	N
10	180-182	72	291.35	$C_{15}H_{25}N_3O$	68.40	9.57	15.95	68.58	9.54	15.88
11	152-154	77	289.33	$C_{15}H_{23}N_3O$	68.93	8.87	16.08	69.00	8.82	16.00
12	220-222	65	339.39	$C_{19}H_{25}N_3O$	73.28	8.09	13.08	73.22	8.03	13.41
13	170-172	81	420.50	$C_{24}H_{30}N_4O_3$	68.22	7.16	13.26	68.26	7.18	13.20
14	164-166	72	422.52	$C_{24}H_{28}N_4O_3$	68.55	6.71	13.32	68.59	6.77	13.29
15	212-214	80	470.56	$C_{28}H_{30}N_4O_3$	71.47	6.43	11.91	71.52	6.41	11.86
16	172-174	82	518.56	$C_{28}H_{30}N_4O_6$	64.85	5.83	10.80	64.88	5.91	10.79
17	191-193	68	520.58	$C_{28}H_{32}N_4O_6$	64.60	6.20	10.76	64.66	6.29	10.71
18	200-202	66	568.62	$C_{32}H_{34}N_4O_6$	67.35	6.01	9.82	67.39	6.11	9.73

Table (4)The major IR absorption (cm-1)of{4-[3-(2-amino-ethyl)-2,3,4,7-tetrahydro-[1,3]oxazepine-2-yl]-phenyl-dimethyl-amine and (Diethyl amino-phenyl)-3-{2-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepane-3yl]-ethyl}-2,3-dihydro-[1,3]oxazepine-4,7-dione:-





Compound	N-H str. amine	C-H str. Olefin	C=O str. Lacton,lactam	C=C str. Olefin	C=C str. Aromatic	C-N str.	C-O str. Lacton
10	3400ى3270	3050	1680ى1650	1620	1590ى1510	1350ى1020	1280
11	3440ى3200	3070	1670ى1655	1620	1580ى1550	1340ى1010	1275
12	3390ى3200	3080	1680ى1640	1610	1590ى1540	1360ى1020	1270
13	3380ى3210	3100	1690ى1645	1600	1595ى1540	1370ى1030	1275
14	3400ى3220	3090	1680ى1650	1600	1570ى1530	1360ى1010	1280
15	3410ى3220	3080	1690ى1640	1610	1580ى1540	1380ى1015	1280
16	3400ى3220	3090	1680ى1650	1620	1590ى1540	1375ى1025	1290
17	3400ى3210	3085	1685ى1640	1615	1570ى1540	1375ى1030	1295
18	3420ى3200	3080	1690ى1650	1620	1570ى1540	1380ى1020	1300

*** as KBr disc.**

nm of3-(2-Amino-ethyl)-2-(2-hydroxy-phenyl)-[1,3]oxazepine 4,7-dione and 2-(2-/Table (5) The UV-Visible absorption maxima λ hydroxy-phenyl)-3-{2-[2- hydroxy-phenyl)-4,7-dioxo-[1,3] oxazepine-3-yl]-ethyl}2,3-dihydro-[1,3] oxazepine-4,7-dione

Compound	UV-Visible absorption maxima λ/nm In ethanol solvent
1	377,300,269,235,220
2	269,311,278,233,226
3	380,316,272,293,222
4	370,320,266,252,225
5	382,319,265,259,230
6	365,300,260,241,220
7	372,301,265,244,225
8	360,300,261,298,226
9	375,301,275,236,221

nm of{4-[3-(2-amino-ethyl)-2,3,4,7-tetrahydro-[1,3]oxazepine-2-yl]-phenyl-dimethyl-/Table (6) The UV-Visible absorption maxima λ amine and (Diethylamino-phenyl)-3-{2-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepane-3yl]-ethyl}-2,3-dihydro-[1,3]oxazepine-4,7-dione:

Compound	UV-Visible absorption maxima λ/nm In ethanol solvent
10	340,300,255,230,220
11	346,300,250,229,221
12	345,302,266,239,223
13	339,306,252,229,223
14	349,299,256,241,228
15	358,295,246,236,222
16	341,288,251,244,220
17	350,306,260,241,230
18	361,305,249,236,221

Table (7)1-Ethelyne diamine -1-mol salicylaldehyde + Maleic anhydride Thermodynamic value of reaction of (A) with Maleic anhydride through of temperature effect 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	0.0241	19944.9	17343	-306.64	113321.32
323	0.0361	19944.9	17264	-307.17	116479.91
333	0.0542	19944.9	17181	-307.59	119608.47
343	0.066	19944.9	17098	-308.167	122799.28
353	0.0761	19944.9	17015	-308.645	125966.68

Table (8) 1-Ethelyne diamine -2-mol salicylaldehyde + Maleic anhydride Thermodynamic value of reaction of (B) with Maleic anhydride through of temperature effect 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	0.0221	25373.1	22775.2	-306.72	118778.56
323	0.0331	25373.1	22692.2	-307.24	121930.72
333	0.0521	25373.1	22609.2	-307.75	125089.95
343	0.0642	25373.1	22526.2	-308.24	128252.52
353	0.0731	25373.1	22443.2	-308.71	131417.83

Table (9) 1-Ethelyne diamine -1-mol -4-N,Ndimethyle + Maleic anhydride Thermodynamic value of reaction of (C) with Maleic anhydride through of temperature effect 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	0.0282	22426.6	19828.7	-305.48	115600.44
323	0.0441	22426.6	19745.7	-306	118583.7
333	0.065	22426.6	19662.7	-306.51	121730.53
343	0.0721	22426.6	19579.7	-307.0	124880.7
353	0.0851	22426.6	19496.7	-307.48	128037.14

Table (10) 1-Ethelyne diamine- 2mol-4-N,Ndimethyle + Maleic anhydride Thermodynamic value of reaction of (D) with Maleic anhydride through of temperature effect 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	0.0252	26186.5	23588.6	-304.99	119050.47
323	0.0421	26186.5	23505.6	-305.51	122185.33
333	0.0633	26186.5	23422.6	-306.01	125323.93
343	0.0741	26186.5	23339.6	-306.50	128469.1
353	0.092	26186.5	23256.6	-306.98	131620.54

Table (11) 1-Ethelyne diamine -1-mol salicylaldehyde +Succinic anhydride Thermodynamic value of reaction of (A) with Succinic anhydride through of temperature effect 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	0.0221	25190.5	22592.6	-298.8	116117
323	0.0342	25190.5	22509.5	-307.1	121702.3
333	0.051	25190.5	22426.6	-307.89	124953.37
343	0.063	25190.5	22343.6	-308.39	128120.77
353	0.0742	25190.5	22295.6	-308.84	131316.12

Table (12) 1-Ethelyne diamine -2-mol salicylaldehyde + Succinic anhydride Thermodynamic value of reaction of (B) with Succinic anhydride through of temperature effect 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	0.0263	23430.9	20833	-306	116611
323	0.0372	23430.9	20750	-306.71	119817.3
333	0.057	23430.9	20667	-307.60	123097.8
343	0.066	23430.9	20584	-308.09	126258.8
353	0.081	23430.9	20501	-308.57	124426.21

Table (13) 1-Ethelyne diamine -1-mol -4-N,Ndimethyle+Succinic anhydride Thermodynamic value of reaction of (C) with Succinic anhydride through of temperature effect 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	0.0293	23115.5	20517.6	-305.74	116214
323	0.041	23115.5	20434.6	-306.26	119356
333	0.062	23115.5	20351.6	-306.26	122506.01
343	0.071	23115.5	20268.6	-306.77	125658.78
353	0.089	23115.5	20185.6	-307.74	128817.82

Table (14) 1-Ethelyne diamine -2-mol -4-N,Ndimethyle+ Succinic anhydride Thermodynamic value of reaction of (D) with Succinic anhydride through of temperature effect 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	0.0278	23978.7	21380.8	-305.48	116996.04
323	0.043	23978.7	21297.8	-306	120135.8
333	0.061	23978.7	21214.8	-306.51	120217.53
343	0.072	23978.7	21131.8	-307.00	126432.8
353	0.0911	23978.7	21048.8	-307.48	129589.24

Table (15) 1-Ethelyne diamine -1-mol salicylaldehyde + Phthalic anhydride Thermodynamic value of reaction of (A) with Phthalic anhydride through of temperature effect 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	0.023	25398	22800.1	-306.36	118690.78
323	0.0361	25398	22717.1	-306.88	121839.34
333	0.054	25398	22634.1	-307.38	124991.64
343	0.067	25398	22551.1	-307.87	128150.51
353	0.078	25398	22468.1	-308.35	131315.65

Table (16) 1-Ethelyne diamine -2-mol salicylaldehyde + Phthalic anhydride Thermodynamic value of reaction of (B) with Phthalic anhydride through of temperature effect 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	0.0282	22891.4	20293.5	-306.72	116296.86
323	0.0341	22891.4	20210.5	-307.24	119449.02
333	0.058	22891.4	20127.5	-307.75	122608.25
343	0.062	22891.4	20044.5	-308.24	125770.82
353	0.083	22891.4	19961.5	-308.7	128932.6

Table (17) 1-Ethelyne diamine -1-mol -4-N,Ndimethyle + Phthalic anhydride Thermodynamic value of reaction of (C) with Phthalic anhydride through of temperature effect 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	0.0271	24211.1	21613.2	-305.35	117187.75
323	0.043	24211.1	21530.2	-305.88	120329.44
333	0.063	24211.1	21447.2	-306.38	123471.74
343	0.077	24211.1	21364.2	-306.87	126620.61
353	0.087	24211.1	21281.2	-307.35	129775.75

Table (18) 1-Ethelyne diamine -2-mol -4-N,Ndimethyle + Phthalic anhydride Thermodynamic value of reaction of (D) with Phthalic anhydride through of temperature effect 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	0.0261	23779.5	21181.6	-287.89	111291.17
323	0.04	23779.5	21098.6	-288.41	114255.03
333	0.059	23779.5	21015.6	-288.92	117225.96
343	0.073	23779.5	20932.6	-289.41	120200.23
353	0.081	23779.5	20849.6	-289.89	123180.77

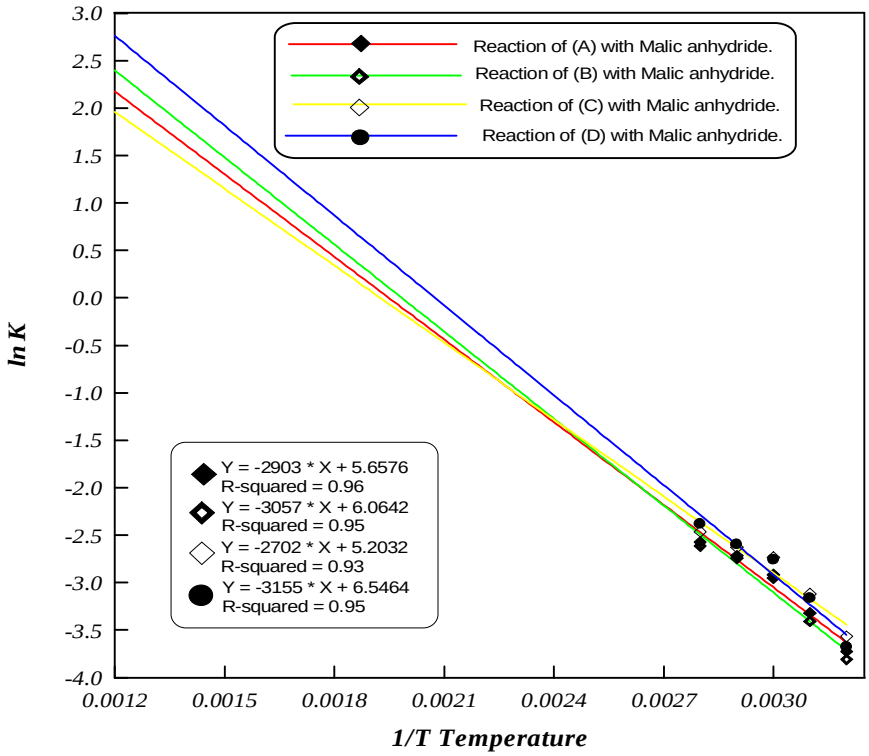


Fig (1)
The relationship between lnK and 1/T of reaction A, B, C and D With Maleic anhydride.

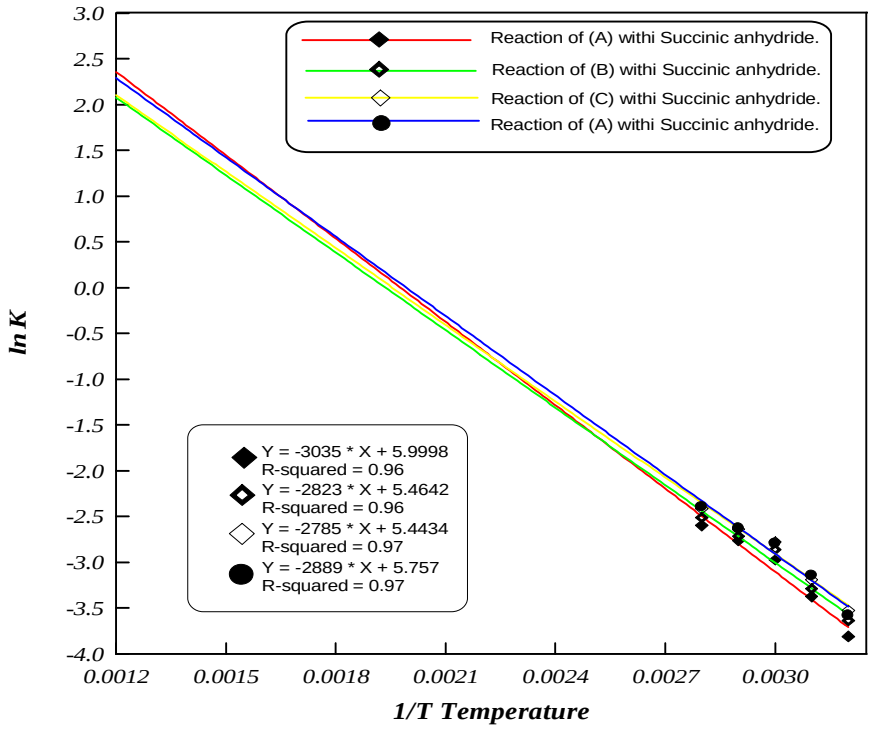


Fig (2)
The relationship between lnK and 1/T of reaction A, B, C and D With Succinic anhydride.

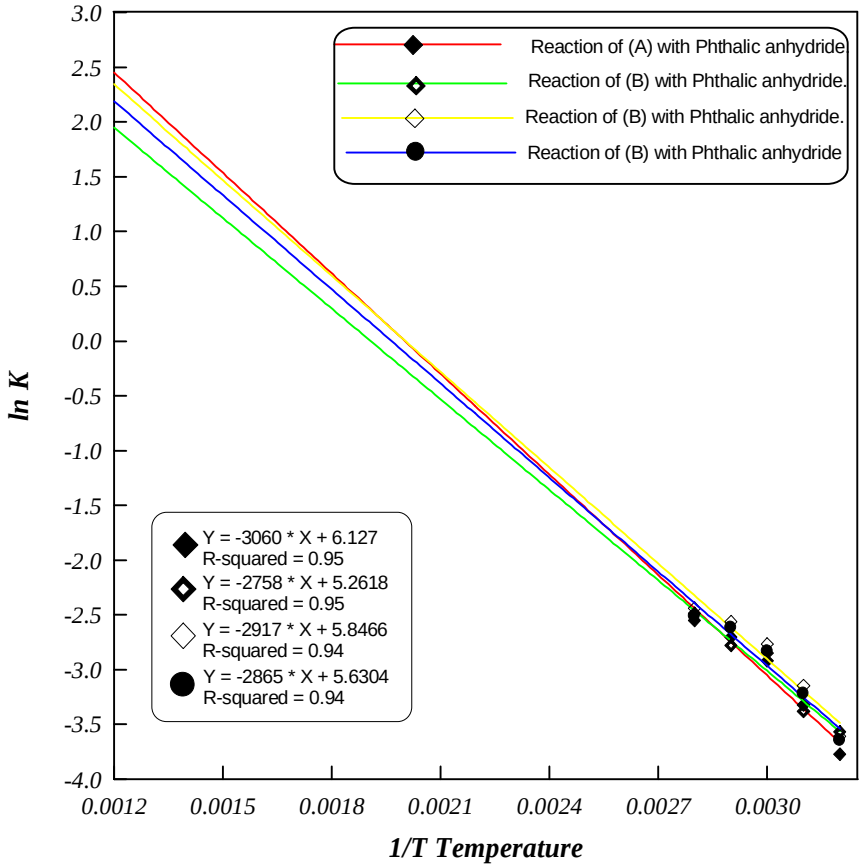
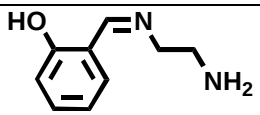
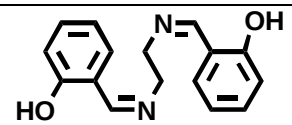
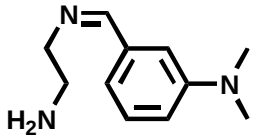
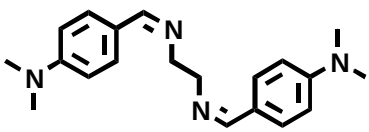
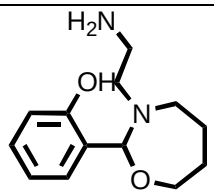
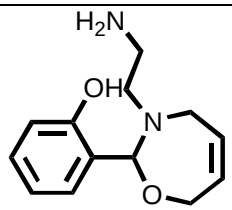
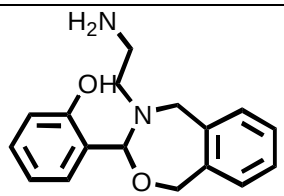
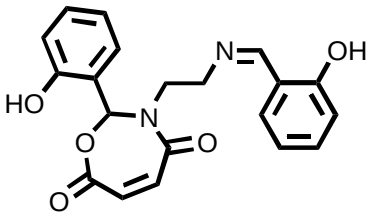
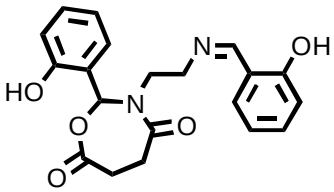
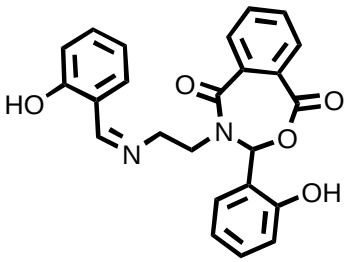
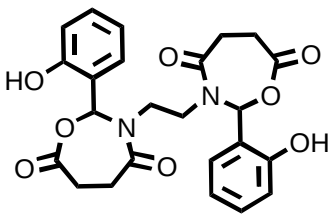
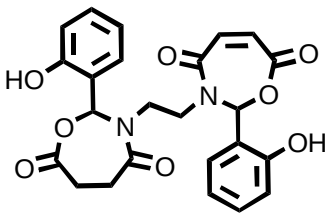
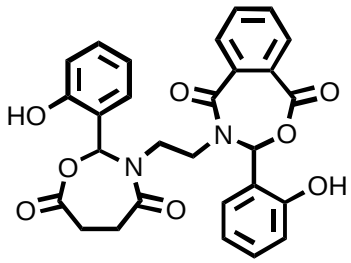
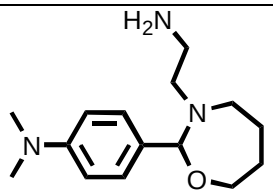
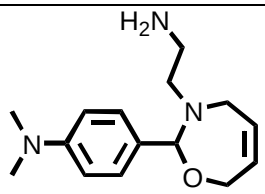
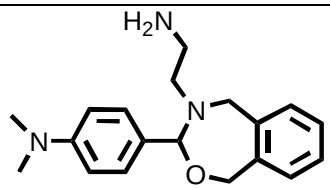
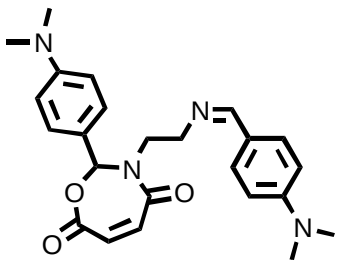
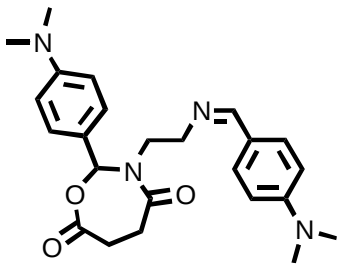
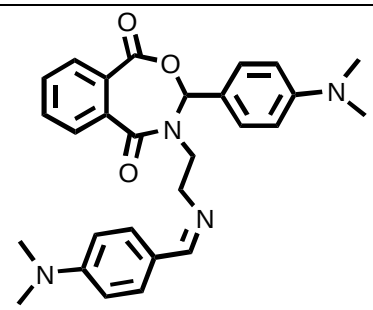
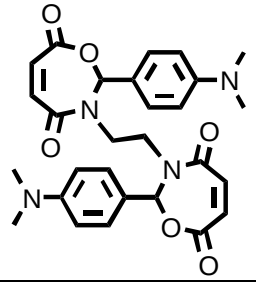
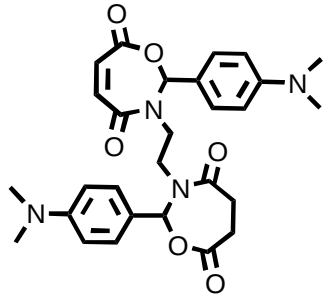
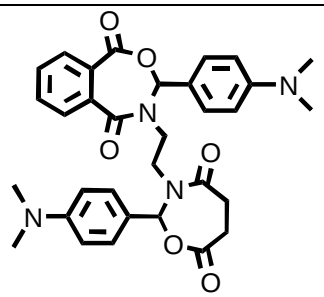


Fig (3)
The relationship between lnK and 1/T of reaction A, B, C and D With Phthalic anhydride.

No.	Schiff-Bases Name	Structure
A	**2-[(2-Amino-ethylimino)-methyl]-phenol**	
B	**2-({2-[(2-hydroxy-benzylidene)-amino] -ethylimino}-methyl)-phenol**	
C	**N^1-(3-Dimethylamino-benzylidene) -ethane-1,2-diamine**	
D	**N-(4-Dimethylamino-benzylidene)-N'-(4-Dimethylamino-benzylidene)-ethane-1,2 -diamine**	

No.	Name of compounds	Structure
1	2-[3-(2-Amino-ethyl)-[1,3]oxazepan-2-yl]-phenol	
2	2-[8-(2-Amino-ethyl)-5,7,8,9-tetrahydro-6-oxa -8-aza-benzocyclohepten-7-yl]-phenol	
3	2-[8-(2-Amino-ethyl)-5,7,8,9-tetrahydro-6-oxa -8-aza-benzocyclohepten-7-yl]-phenol	
4	3-{2-[(2-Hydroxy-benzylidene)-amino]-ethyl}-2 -(2-hydroxy-phenyl)-2,3-dihydro-[1,3]oxazepine -4,7-dione	
5	3-{2-[(2-Hydroxy-benzylidene)-amino]-ethyl}- 2-(2-hydroxy-phenyl)-[1,3]oxazepane-4,7-dione	
6	8-{2-[(2-Hydroxy-benzylidene)-amino]-ethyl}- 7-(2-hydroxy-phenyl)-7,8-dihydro-6-oxa-8-aza- benzocycloheptene-5,9-dione	
7	2-(2-Hydroxy-phenyl)-3-{2-[2-(2-hydroxy-phenyl)- 4,7-dioxo-[1,3]oxazepane-3-yl]-ethyl}-2,3-dihydro- [1,3]oxazepane-4,7-dione	
8	2-(2-Hydroxy-phenyl)-3-{2-[2-(2-hydroxy-phenyl)- 4,7-dioxo-[1,3]oxazepan-3-yl]-ethyl}-2,3-dihydro-[1,3] oxazepine-4,7-dione	

9	7-(2-Hydroxy-phenyl)-8-{2-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepan-3-yl]-ethyl}-7,8-dihydro-6-oxa-8-aza-benzocycloheptene-5,9-dione	
10	{4-[3-(2-Amino-ethyl)-[1,3]oxazepan-2-yl] -phenyl}-dimethyl-amine	
11	{4-[3-(2-Amino-ethyl)-2,3,4,7-tetrahydro-[1,3]oxazepin-2-yl]-phenyl}-dimethyl-amine	
12	{4-[8-(2-Amino-ethyl)-5,7,8,9-tetrahydro-6-oxa-8-aza -benzocyclohepten-7-yl]-phenyl}-dimethyl-amine	
13	3-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-2-(4-dimethylamino-phenyl)-2,3-dihydro-[1,3]oxazepine -4,7-dione	
14	3-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-2 -(4-dimethylamino-phenyl)-[1,3]oxazepane	
15	8-{2-[(4-Dimethylamino-benzylidene)-amino]-ethyl}-7-(4-dimethylamino-phenyl)-7,8-dihydro-6-oxa-8-aza -benzocycloheptene-5,9-dione	

16	2-(4-Dimethylamino-phenyl)-3-{2-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepine-3-yl]-ethyl}-2,3-dihydro-[1,3]oxazepine-4,7-dione	
17	2-(4-Dimethylamino-phenyl)-3-{2-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepan-3-yl]-ethyl}-2,3-dihydro-[1,3]oxazepine-4,7-dione	
18	7-(4-Dimethylamino-phenyl)-8-{2-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepan-3-yl]-ethyl}-7,8-dihydro-6-oxa-8-aza-benzocycloheptene-5,9-dione	

تحضير وتشخيص ودراسة الصفات الفيزياوية والثرموديناميكية لمركبات الاوكسازبين والاوكسازبان من تفاعل اثيل ايماينو وثنائي اثيل ايماينو مع انهيدريدات الماليك والسكسنيك والفثاليك .

وليد فرج حمادي محمد عبد الكريم طلك عيد صالح محمد

***Email*: mohamed_alhadithi@yahoo.com**

الخلاصة :-

تم تحضير قواعد شيف (اثيل ايمانيو و ثنائي اثيل ايماينو) من تكثيف ثنائي أمينو اثلين مع مول واحد ومولين من البنزالديهايد المعوض . فوعلت قواعد شيف هذه مع مول واحد من انهيدريدات كل من الماليك والسكسنيك 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) . وقد شخصت المركبات المحضرة بتعيين درجات انصهارها، تحليل العناصر، أطياف الأشعة فوق البنفسجية ,أطياف الأشعة تحت الحمراء 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 والفثالك فأظهرت بان التفاعل من الدرجة الأولى , كما حسبت بعض الخواص الثرموديناميكية فأظهرت اختلافاً بين المركبات المحضرة.