Synthesis, Characterization and Kinetic Studies of Oxazepine and Oxazepane from reaction of 1,3-Bis(2-hydroxy-benzylidene)-urea and 1,3-Bis-(dimethylamino-benzylidene)-urea with maleic, Succinic and phthalic anhydride

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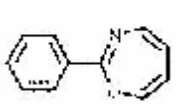
Abstract

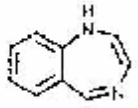
1,3-Bis(2-hydroxy-benzylidene)-urea and 1,3-Bis-(dimethylamino-benzylidene)-urea were prepared by condensation of urea with one equivalent and two equivalent of substituted benzaldehyde. These Schiff bases were reacted with one equivalent of maleic , succinic and phthalic anhydride in absolute ethanol to give 7 membered heterocyclic ring system of 2-(2-Hydroxy phenyl)-4,7-dioxo-4,7-dihydro-[1,3] oxazepine-3-carboxylic acid amide and 2-(4-Dimethylamino-phenyl) 4,7 dioxo-4,7-dihydro-[1,3]oxazepine-3-carboxylic acid amide and 1,3-Bis(2-hydroxy-benzylidene)-urea and 1,3-Bis-(dimethylamino-benzylidene)-urea 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]oxazepin-3-carbonyl]-2,3-dihydro-[1,3]oxazepin-4,7-dione and 2-(4 Dimethylamino-phenyl)-3-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepine 3 carbenyl] 2,3 dihydro-[1,3]oxazepin-4,7-dione. Kinetic Studies of reaction of 1,3-Bis(2-hydroxy-benzylidene)-urea and 1,3-Bis (dimethylamino-benzylidene)-urea with maleic , Succinic and phthalic anhydride proved to A first-class equation was applied to the reaction.

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[4] , and the discovery of the central nerveus system(CNS) activity of 1,4- benzodiazepine [5] encouraged on 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.[5-6]



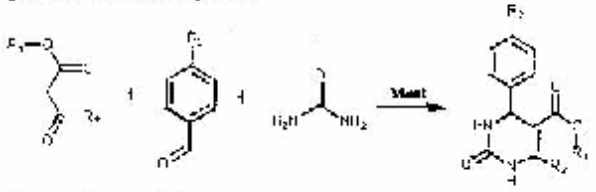
2-phenyl-1,3-oxazepine



1,4-benzodiazepine

Pyrylium tetrafluoroborate 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 acetovinylazirines 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, Linated found that treatment of β-keto ester , aryl aldehyde and urea with KSF montmorillonite in methanol afforded DHPMs in good to excellent yields [8]



Experimental

Melting points were recorded on Gallenkamp melting points apparatus and were uncorrected . Elemental analysis was carried out in Al-Qaqah state company on perkin-Elmer 2400 CHN Elemental analyzer FT-IR spectra were recorded on FT-IR spectrophotometer -8400s Shimadzu (KBr) and UV-Visible spectra were recorded (in ethanol) On Schimadzu Reco- 160 Spectrophotometer.

Preparation of (2-hydroxy-benzylidene)-urea (Schiff-base)

(1,2 Hydroxy-benzylidene)-urea and 1,3-Bis(2-hydroxy-benzylidene)-urea were prepared by condensation of urea with substituted benzaldehyde . To a solution of 0.05 mole of urea in 30 ml of Ethanol (absolute) ,0.05 mole or 0.1 mole of substituted benzaldehyde was added and refluxed 2hr, yellow

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crystalline solid separated out . The solid was filtered and recrystallized from ethanol.

Preparation of 2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carboxylic acide amide

In a 100 ml round bottom flask equiped with adoubl surface condener fitted with calcium chloride guard tube , a mixture of 0.01 mole of (2-hydroxy-benzylidene)-urea and 0.01mole maleic anhydride in 20 ml of absolute ethanol was placed. The reaction mixture was refluxed in water bath at 78C° for 3hr, 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-carbonyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione

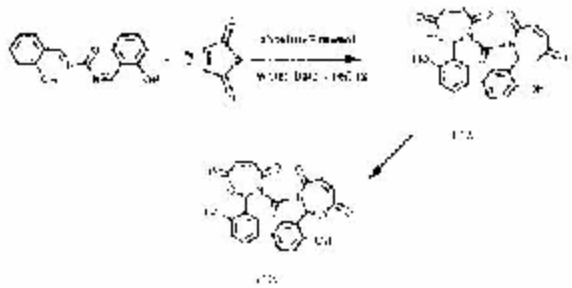
A mixture of (0.01 mole) of 1,3 Bis(2 hydroxy-benzylidene)-urea and (0.002 mole) of maleic anhydride in absolute ethanol was refluxed on a water bath for 3hr. The solvent was then removed and the crystalline solid was recrystallized from anhydrous 1,4-dioxan.

This experiment was repated 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 acdition products[5,6,9]

In this paper, the reaction of the maleic succinic and phthalic anhydrides with1,3-Bis(2-hydroxy-benzylidene)-urea to gives the dipolar intermediate [11A] which collapses to the 7- membered heterocyclic ring system,[11B] is presented



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].

It is impressive to note that the two absorption band at (1800-1950) cm^{-1} in the IR spectra of pure maleic ,succinic , and pathalic 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-carboxylic acide amide and 2-(2-Hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepin-3-carbonyl]-2,3-dihydro-[1,3]oxazepin-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 thet 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-carboxylic acide amide and 2-(2-Hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbonyl]-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].

2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carboxylic acid amide and 2-(2-Hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbonyl]-2,3-dihydro-[1,3]oxazepin-4,7-dione are identified by their m.ps,elemental analysis (table 1),IR spectra (table 2) and UV spectra (table 3). It is noticeable that the values of C-Hstr. (benzylic) absorption bands are rather high. This is in fact explained by the shift toward 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 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 he 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].

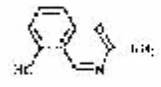
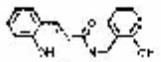
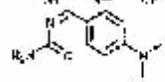
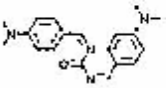
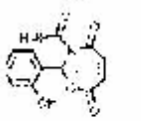
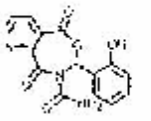
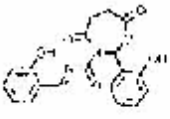
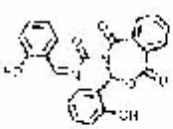
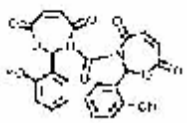
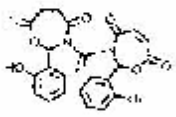
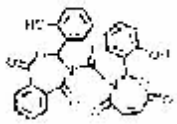
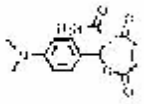
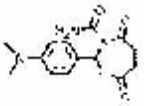
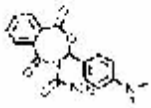
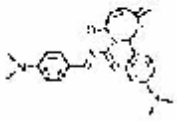
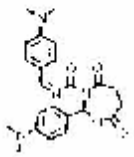
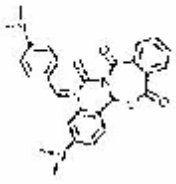
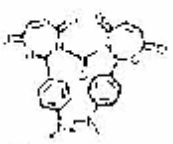
Calculation the Reaction Velocity

A first-class 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 vayring temperatures(213-253)k with (10) k increase.

The value of K was calculated for all reactions by drawing the relation between ln A_t/A_∞ with Time.

Relation 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 (7 -18) we notice that the value of ΔH , ΔS , and ΔG is positive. This proves that the reactions are endothermic and auto. We also notice that the activation ΔH stars to increase with deferent used compounds. Figurers (1, 2 , 3) show the reaction velocity for different compounds

No.	Schiff-Bases Name	Structure
A	(3-Hydroxy-benzylidene)-urea	
B	1,3-Bis-(2-hydroxy-benzylidene)-urea	
C	(4-Dimethylamino-benzylidene)-urea	
D	1,3-Bis-(4-dimethylamino-benzylidene)-urea	
1	2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3] oxazepine-3-carboxylic acid amide	
2	2-(2-Hydroxy-phenyl)-4,7-dioxo-4,7-dihydro-[1,3] oxazepane-3-carboxylic acid amide	
3	7-(2-Hydroxy-phenyl)-5,9-dioxo-5,9-dihydro-6-oxa-8-aza-benzocycloheptene-8-carboxylic acid amide	
4	2-(2-Hydroxy-phenyl)-4,7 dioxo 4,7 dihydro [1,3]oxazepine-3-carboxylicacid3-hydroxy -benzylidenearnide	
5	2-(2-Hydroxy-phenyl)-1 7-dioxo-[1,3]oxazepane 3 carboxylic acid 2-hydroxy-benzylidenearnide	
6	7-(2-Hydroxy-phenyl)-5,9-dioxo-5,9 dihydro 6 oxa-8-azabenzocycloheptene-8-carboxylicacid2-hydroxybenzylidenearnide	
7	2-(2-Hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbenyl]-2,3-dihydro-[1,3]oxazepine-4,7 dione	
8	2 (2-Hydroxy-phenyl)-3-[2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepane-3-carbonyl]-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-carbonyl -7,8-dihydro-6-oxa-8-azabenzocycloheptene-5,9-dione	
10	2-(4-Dimethylamino-phenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carboxylic acid amide	
11	2-(4-Dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepane-3-carboxylic acid amide	
12	7-(4-Dimethylamino-phenyl)-5,9-dioxo-5,9-dihydro-6-oxa-8-aza-benzocycloheptene-8-carboxylic acid amide	
13	2-(4-Dimethylamino-phenyl)-4,7-dioxo-4,7-dihydro-[1,3] oxazepine-3 carboxylicacid4 dimethylamino-benzylidenearnide	
14	2-[4-Dimethylamino-phenyl) 4,7-dioxo-[1,3]oxazepane 3 carboxylic acid4-dimethylamino benzylidenearnide	
15	7-(4-Dimethylamino-phenyl) 5,9 dioxo 5,9 dihydro-6-oxa-8-aza-benzocycloheptene-8-carboxylic acid 4-dimethylamino-benzylidenearnide	
16	2-(4-Dimethylamino-phenyl)-3-[2-(4-dimethylaminophenyl)-4,7-dioxo-[1,3]oxazepine-3-carbonyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione	

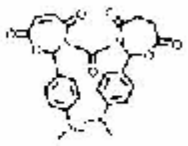
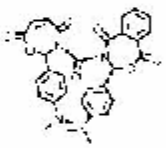
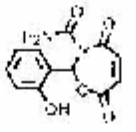
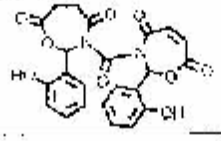
17	2-(4-Dimethylamino-phenyl)-3-[2-(4-dimethylamino-phenyl)-4,7-dioxo-[1,3]oxazepane-3-carbonyl]-2,3-dihydro-[1,3]oxazepine-4,7-diene	
18	7-(4-Dimethylamino-phenyl)-8-[2-(4-dimethylaminophenyl)-4,7-dioxo-4,7-dihydro-[1,3]oxazepine-3-carbonyl] 7,8 dihydro-6-oxa-8-aza-benzocycloheptene-5,9-dione	

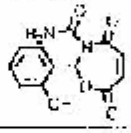
Table (1): Melting point ,percentage yield,molecular formula and elemental analysis of 2-(2-hydroxy-phenyl)-4,7-dioxo-4,7dihydro-[1,3]oxazepine-3-carboxylic acid amide and 2-(2-hydroxy-phenyl)-3-[2-(2-hydroxy-phynyl)-4,7-dioxo-[1,3]oxazepine-3-carbonyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione.





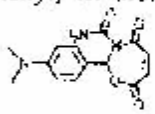
Compound	m.p/C°	%Yield	Molecular Formula	Calc.			Found		
				C	H	N	C	H	N
1	170-172	78	$C_{12}H_{10}N_2O_5$	54.97	3.83	10.68	55.03	3.89	10.59
2	156-158	69	$C_{12}H_{12}N_2O_4$	54.55	4.58	10.60	54.63	4.69	10.55
3	206-208	77	$C_{16}H_{12}N_2O_5$	61.54	3.87	8.97	61.67	3.85	8.86
4	220-222	81	$C_{19}H_{16}N_2O_6$	61.95	4.38	7.61	62.10	4.45	7.58
5	160-162	80	$C_{19}H_{14}N_2O_6$	62.30	3.85	7.65	62.47	3.90	7.56
6	164-166	80	$C_{22}H_{16}N_2O_6$	66.34	3.87	6.73	66.51	3.96	6.60
7	198-200	85	$C_{20}H_{16}N_2O_5$	59.49	3.47	6.03	59.62	3.57	5.92
8	216-218	78	$C_{20}H_{18}N_2O_6$	59.23	3.89	6.03	59.36	3.94	5.89
9	211-213	73	$C_{24}H_{18}N_2O_6$	63.04	3.53	6.01	63.17	3.62	63.05

Table (2): The major IR absorption (cm^{-1})of 2-(2-hydroxy-phenyl)-4,7-dioxo-4,7dihydro-[1,3]oxazepine-3-carboxylic acid amide and 2-(2-hydroxy-phenyl)-3-[2 (2 hydroxy-phynyl)-4,7-dioxo-[1,3]oxazepine-3-carbonyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione.



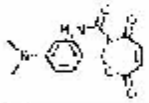
Compound	O-H str.phenol	C-H str. Benzylic	C-H str. Aramatic	C=O str. Lacton,lactam	C=C str. Olefin	C=C str. Aromatic	C=N str.	C-O str. Lacton,	C-H bend. Aromatic
1	3450	3210	3050	1670	1610	1580,1540	1430	1310	1010,770
2	3435	3220	3070	1675	-	1580,1530	1440	1320	1020,870
3	3440	3200	3060	1680	-	1580,1540	1450	1310	1010,900
4	3430	3190	3063	1670	-	1585,1555	1445	1330	1020,870
5	3450	3230	3050	1675	1620	1570,1530	1430	1325	1050,800
6	3440	3200	3090	1680	-	1580,1540	1450	1320	1010,850
7	3455	3180	3080	1670	1610	1575,1530	1440	1325	1020,800
8	3450	3190	3050	1660	1630	1570,1590	1435	1330	1040,860
9	3435	3210	3080	1670	1610	1580,1535	1430	1320	1060,800

Table (3): Melting point ,percentage yield,molecular formula and elemental analysis of 2-(4-Dimethylamino-phenyl)-4,7-dioxo-4,7dihydro-[1,3]oxazepine-3-carboxylic acid amide and 2-(4-Dimethylamino -phenyl)-3-[2-(4-Dimethylamino -phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbonyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione.



Compound	m.p/C°	Yield%	Molecular Formula	Calc.			Found		
				C	H	N	C	H	N
10	174-176	82	$C_{11}H_{11}N_3O_4$	58.13	5.23	14.53	58.20	5.19	14.66
11	180-182	80	$C_{14}H_{17}N_3O_4$	57.72	5.88	14.42	57.69	5.92	14.53
12	193-195	77	$C_{18}H_{17}N_3O_4$	63.71	5.05	12.38	63.85	5.09	12.43
13	112-114	85	$C_{21}H_{26}N_4O_4$	65.39	6.30	13.26	65.29	6.34	13.20
14	125-127	76	$C_{23}H_{24}N_4O_4$	65.70	5.75	13.33	65.78	5.80	1325
15	140-142	88	$C_{27}H_{26}N_4O_4$	68.93	5.57	11.91	69.01	5.66	11.85
16	128-130	81	$C_{27}H_{20}N_4O_4$	62.54	5.05	10.81	62.60	5.11	10.77
17	136-138	73	$C_{27}H_{22}N_4O_7$	62.20	5.42	10.76	62.32	5.59	10.65
18	216-218	82	$C_{31}H_{28}N_4O_7$	65.49	6.96	9.85	65.61	5.03	9.73

Table (4): The major IR absorption (cm^{-1})of of 2-(4-Dimethylamino-phenyl)-4,7-dioxo-4,7dihydro-[1,3]oxazepine-3-carboxylic acid amide and 2-(4-Dimethylamino -phenyl)-3-[2-(4-Dimethylamino -phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbonyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione.



Compound	N-H str. amide	C-H str. Aramatic	C=O str. Lacton,lactam	C=C str. Olefin	C=C str. Aromatic	C-N str.	C-O str. Lacton,
10	3340,3220	3070	1680,1640	1620	1580,1520	1350,1020	1275
11	3350,3230	3060	1670,1650	-	1585,1540	1340,1010	1280
12	3340,3225	3080	1680,1650	-	1570,1550	1360,1020	1290
13	-	3075	1675,1650	-	1590,1540	1380,1010	1280
14	-	3050	1680,1655	1615	1580,1550	1370,1000	1270
15	-	3065	1690,1645	-	1575,1540	1370,1030	1290
16	-	3070	1685,1640	1610	1590,1560	1375,1020	1275
17	-	3080	1680,1660	1620	1585,1550	1385,1025	1300
18	-	3090	1670,1650	1620	1570,1540	1380,1020	1295

Table(5): The UV-Visible absorption maxima λ/nm of2-(2-hydroxy-phenyl)-4,7-dioxo-4,7dihydro-[1,3]oxazepine-3-carboxylic acid amide and2-(2-hydroxy phenyl) 3 [2-(2-hydroxy-phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbonyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione.

Compound	UV-Visible absorption maxima λ/nm
1	360, 303, 260, 231, 222
2	275, 309, 269, 235, 220
3	388, 320, 266, 230, 225
4	376, 310, 255, 231, 221
5	380, 308, 267, 235, 220
6	363, 300, 271, 238, 226
7	370, 306, 285, 234, 225
8	361, 300, 275, 230, 220
9	391, 302, 285, 235, 222

Table (6): The UV-Visible absorption maxima λ/nm of2-(4-Dimethylamino-phenyl) 4,7 dioxo 4,7dihydro-[1,3]oxazepine-3-carboxylic acid amide and 2-(4-Dimethylamino -phenyl)-3-[2-(4-Dimethylamino -phenyl)-4,7-dioxo-[1,3]oxazepine-3-carbonyl]-2,3-dihydro-[1,3]oxazepine-4,7-dione.

Compound	UV-Visible absorption maxima λ/nm
10	352, 306, 254, 236, 223
11	350, 300, 251, 231, 228
12	349, 302, 249, 233, 221
13	339, 301, 256, 239, 222
14	351, 309, 271, 230, 227
15	355, 305, 285, 240, 229
16	359, 300, 271, 236, 225
17	350, 310, 277, 236, 223
18	358, 311, 274, 233, 220

Table (7): Thermodynamic values of reaction of (A) with Malic anhydride through of temperature effect on K, Ea, Δ H , Δ S and Δ G value (1)

T k	K h^{-1}	Ea j mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0011	725.2	69944.1	-198.08	131947.14
323	0.0027	72562	69868.1	-198.62	134015.36
333	0.010	72562	69778.1	-199.10	136078.4
343	0.0211	72562	69695.1	-199.56	138141.18
353	0.031	72562	69512.1	-200.1	140247.2

Table (8): Thermodynamic values of reaction of (B) with Malic anhydride through of temperature effect on K, Ea, Δ H , Δ S and Δ G value (2)

T k	K h^{-1}	Ea j mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.001	76443	73845.1	-150.03	133324.49
323	0.0025	76443	73762.1	-150.55	135309.75
333	0.011	76443	73679.1	-151.06	137302.09
343	0.0232	76443	73596.1	-151.49	139297.17
353	0.033	76441	735.3.1	-152.02	141296.16

Table (9): Thermodynamic values of reaction of (C) with Malic anhydride through of temperature effect on K, Ea, Δ H , Δ S and Δ G value (3)

T k	K h^{-1}	Ea j mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0014	72625	70027	-196.60	131249.9
323	0.0036	72625	69914.1	-196.12	133290.86
333	0.016	72625	69886.1	-196.63	135334.89
343	0.031	72625	69778.1	-197.05	137366.25
353	0.038	72625	69695.1	-197.60	139447.9

Table (10): Thermodynamic values of reaction of (D) with Malic anhydride through of temperature effect on K, Ea, Δ H , Δ S and Δ G value (4)

T k	K h^{-1}	Ea j mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0013	71961	69593	-197.56	130855.48
323	0.0037	71961	69510.1	-197.77	132889.83
333	0.018	71961	68527.1	-198.20	134952.67
343	0.032	71961	68844.1	-198.70	136996.2
353	0.039	71961	6876[illegible].1	-199.25	139096.35

Table (11): Thermodynamic values of reaction of (A) with Succinic anhydride through of temperature effect on K, Ea, A H , A S and A G value (1)

T k	K h^{-1}	Ea j mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0012	71321.9	68724	-198.93	130489.09
323	0.0029	71321.9	686[illegible].1	-199.43	132530.89
333	0.012	71321.9	68535	-199.94	134588.92
343	0.027	71321.9	68473	-200.37	136626.39
353	0.032	71321.9	68392	-200.91	138713.23

Table (12): Thermodynamic values of reaction of (A) with Succinic anhydride through of temperature effect on K, Ea, A H , Δ S and Δ G value (1)

T k	K h^{-1}	Ea j mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0014	71247.2	68649.3	-199.75	131170.99
323	0.0032	71247.2	68566.3	-200.27	133253.51
333	0.0097	71247.2	68482.3	-200.80	135319.7
343	0.024	71247.2	68400.3	-201.190	137409.5
353	0.034	71247.2	68317.3	-201.76	139503.93

Table (13): Thermodynamic values of reaction of (A) with Succinic anhydride through of temperature effect on K, Ea, A H , A S and A G value (1)

T k	K h^{-1}	Ea j mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0016	69778.1	67180.2	-201.43	130022.79
323	0.0037	69778.1	67097.2	-201.96	132330.25
333	0.019	69778.1	67014.2	-202.45	134423.33
343	0.031	69778.1	66931.2	-202.88	136519.04
353	0.037	69778.1	66848.2	-203.40	138648.4

Table (14): Thermodynamic values of reaction of (A) with Succinic anhydride through of temperature effect on K, Ea, A H , A S and A G value (1)

T k	K h^{-1}	Ea j mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0015	70948.4	68350.5	-198.03	130033.39
323	0.0036	70948.4	68267.5	-198.62	132421.76
333	0.017	70948.4	68184.5	-199.10	134488.8
343	0.032	70948.4	68101.5	-199.56	136550.58
353	0.036	70948.4	68018.5	-200.1	138633.8

Table (15): Thermodynamic values of reaction of (A) with Phthalic anhydride through of temperature effect on K, Ea, A H , A S and A G value (1).

T k	K h^{-1}	Ea j mol^{-1}	ΔH $Jmol^{-1}$	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0012	74630	58860.1	-206.35	132169.35
323	0.0026	74630	58780.1	-202.76	134280.04
333	0.0[illegible]	74630	58699.1	-203.26	136384.68
343	0.022	74630	58616.1	-203.71	138488.63
353	0.032	74630	58533.1	-204.25	140626.29

Table (16): Thermodynamic values of reaction of (B) with Phthalic anhydride through of temperature effect on K, Ea, A H , Δ S and Δ G value (1)

T k	K h^{-1}	Ea j mol^{-1}	ΔH Jmol^{-1}	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0014	72210	69612.1	-198.92	131877.13
323	0.0027	72210	69529.1	-199.41	133944.93
333	0.014	72210	69446.1	-199.94	135026.12
343	0.027	72210	69363.1	-200.37	138090.01
353	0.061	72210	69280.1	-200.91	140201.37

Table (17): Thermodynamic values of reaction of (C) with Phthalic anhydride through of temperature effect on K, Ea, A H , A S and A G value (3)

T k	K h^{-1}	Ea j mol^{-1}	ΔH Jmol^{-1}	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0015	70467	67859	-199.73	130290.85
323	0.0035	70467	67786.1	-200.27	135473.31
333	0.015	70467	67703.1	-200.86	136569.5
343	0.033	70467	67620.1	-201.20	136631.7
353	0.037	70467	67537.1	-201.75	138751.85

Table (18): Thermodynamic values of reaction of (D) with Phthalic anhydride through of temperature effect on K, Ea, A H , A S and A G value (4)

T k	K h^{-1}	Ea j mol^{-1}	ΔH Jmol^{-1}	ΔS $J.K^{-1}mol^{-1}$	ΔG J K,mol^{-1}
313	0.0017	69271.8	66673.9	-203.26	130231.68
323	0.0036	69271.8	66590.9	-203.9	135437
333	0.017	69271.8	66507.9	-204.[illegible]	136483.19
343	0.031	69271.8	66424.9	-204.61	136571.85
353	0.036	69271.8	66341.9	-205.[illegible]	138749.2

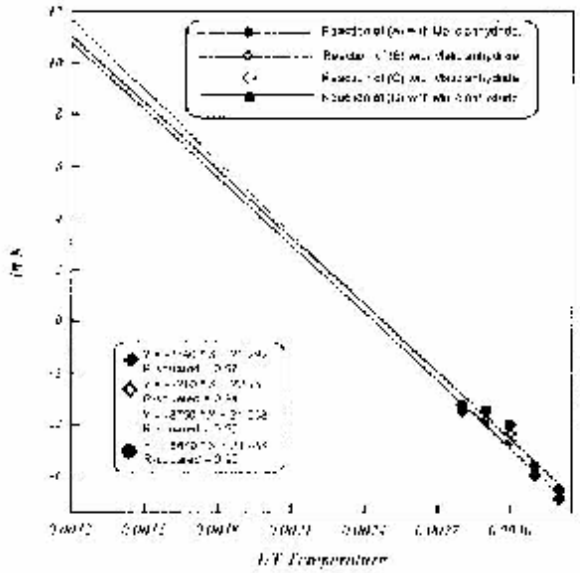


Figure (1): The relation shipe between lnK and 1/T of reaction A,B,C and D with Maleic anhydride.

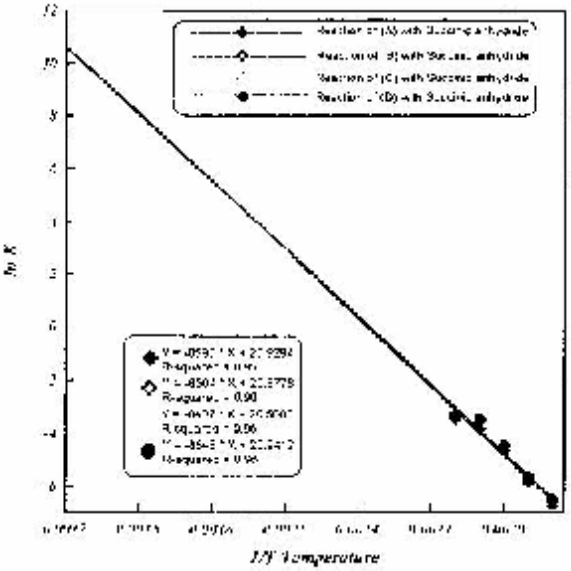


Figure (2): The relation shipe between lnK and 1/T of reaction A,B,C and D with Succinic anhydride.

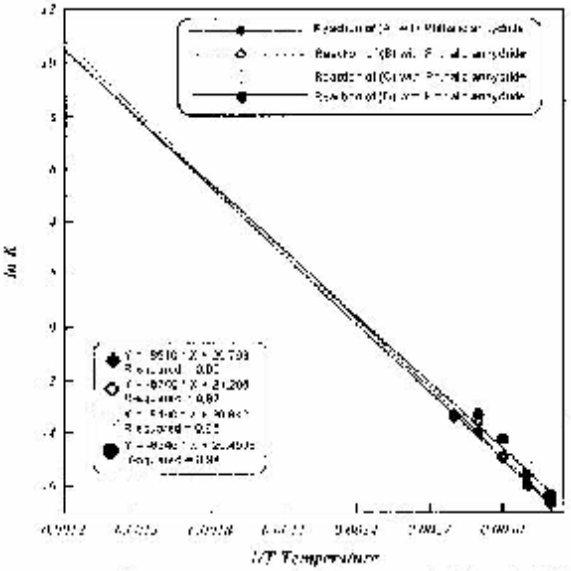


Figure (3): The relation shipe between lnK and 1/T of reaction A,B,C and D with Phthalic anhydride.

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الخلاصة

تم تحضير قواعد شيف 1,3- بس(2- هيدروكسي- بنزليدين)-يوريا و1,3- بس(ثنائي مثيل أمينو- بنزاليدين)-يوريا من تكثيف اليوريا مع مول واحد ومولين من الالديهايد 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 آنفة الذكر أعطي نظام حلقي غير متجانس (بس-أوكسازيبين). وقد شخصت المركبات المحضرة بتعيين درجات انصهارها، تحليل العناصر، أطياف الأشعة فوق البنفسجية، وأطياف الأشعة تحت الحمراء، وقد أسندت نتائج التشخيص بالطرق المختلفة في إثبات الصيغ التركيبية للمركبات المحضرة. كما درست ثوابت سرع التفاعلات للمركبات المحضرة (قواعد شيف) مع انهيدريدات الماليك والسكسنيك والفثاليك فأظهرت أن التفاعل من الدرجة الأولى، كما حسبت بعض الدوال الثرموديناميكية وأظهرت اختلافاً بين المركبات المحضرة.