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Synthesis and Spectral Charactrization of Some Pyrimidinones

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ABSTRACT

The phase- transfer catalysis PTC technique was followed to achieve the reaction, using 50% NaOH aqueous solution as a base, benzene as a solvent, and tetrabutyl ammonium bromide TBAB as a catalyst, to afford the pyrimidinone compounds.

Keywords: Pyrimidinones, Diarylidene acetone.

تشييد والخواص الطيفيه لبعض البيريميدنيونات

الملخص

تم تحضير سلسلة من الاسيتونات ثنائية الاريلادين (6-42) وتم تكثيفها مع اليوريا. اتبعت تقنية التحفيز بانتقال الطور لانجاز التفاعل باستخدام 50% محلول هيدروكسيد الصوديوم المائي قاعدة والبنزين مذيباً وملح بروم الامونيوم رباعي البيوتيل حافزاً لإعطاء مركبات البيريميدنيونات.

INTRODUCTION

Pyrimidinones were synthesised by the reaction of diarylidene acetone (DAA) with urea using NaOH as a base and benzene as a solvent. Diarylidene acetone (DAA) was synthesis by a Claisen-Schmidt reaction. The products always, has at least one double bond conjugated to both a carbonyl group and an aromatic ring (Kappe *et al*., 1993). Pyrimidinones show versatile biological activities including: anticancer (El-Gazzar *et al*., 2007), antifungal (Ismail and Koreish, 1992), antimalarial (Tinsley *et al*., 1981), antibacterial, antihypertensive, antitumor (Kappe *et al*., 1993), anti-inflammatory (Ataby and Eldin, 1999), and antimicrobial effects (Mishra and Moorth, 2008).

EXPERIMENTAL

Melting points were determined by Gallenkamp apparatus- England Ultra- Violet spectra were obtained using Shimadzu UV- Vissible spectrophotometer UV- 1650.

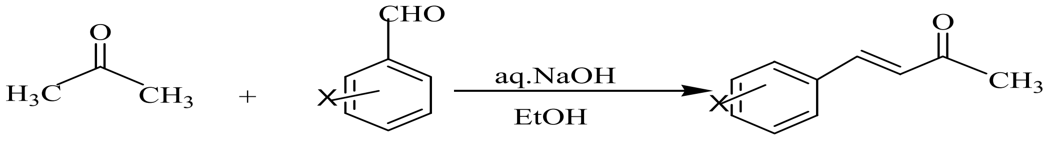
Fourier-Transform Infrared spectra were recorded on Brucker Tensor spectrophotometer (Japan).

Nuclear magnetic resonance ^{1}H- NMR, ^{13}C-NMR spectra were registered at 400 MHz Brucker spectrometer by using tetramethyl silane (TMS) as an internal standard, and $CDCl_3$ as a solvent.

Preparation of Substituted benzalacetone (1-5) (Vogel, 1981):

General procedure:

Place 42g (40ml) of pure substituted benzaldehyde and 63.5 gm (80ml) of pure acetone in a 250 ml, wide- mouthed bottle or bolt- head flask equipped with a mechanical stirrer immerse the reaction vessel in a bath of cold water add slowly from a dropping funnel 10ml of 10 % Sodium hydroxide solution was added. Render the upper organic layer, extract the lower aqueous layer, wash the later with 20ml of water and dry with a little anhydrous magnesium sulphate. filtered and the solvent evaporated. The physical properties and spectral data of compounds(1-5) were listed in Table (1 and 2).



(1-5)

Table 1: The physical properties of arylidene acetone (1-5):

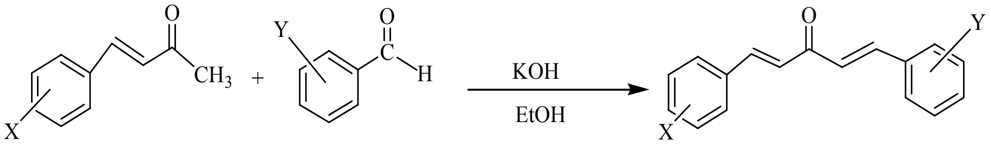
Compd. No.	X	m.p °C	Yield %	Colour
1	H	38-39	71	Yellow
2	4-OCH_3	51-53	71	Yellow
3	4-NO_2	>300	67	Violet
4	4-Cl	123-124	50	Pale yellow
5	4-Br	193-194	60	Pale yellow

Table 2: The spectral data of arylidene acetone (1-5):

Compd. No.	UV($CHCl_3$) λmax (nm)	I.R(KBr), υ cm^{-1}			
		C=O str.	C=C str.	C=C str.	Others
1	292	1666	1626	1591	- - - -
2	322	1631	1610	1421	C–O–C (sym.,asy)1028,1246
3	332	1662	1595	1516	N=O(sym.,asym.) 1346,1595
4	336	1649	1601	1491	- - - -
5	340	1649	1630	1487	- - - -

Preparation of diarylidene acetone (DAA)(6-42):

To a cold stirred mixture of benzaldehyde or substituted benzaldehyde (5.2 gm, 0.03 mole) and benzylideneacetone (4.3 gm, 0.03 mole) in (50 ml) absolute ethanol potassium hydroxide (1 gm) was added in a small portion to the mixture in a period of (15 min). The stirring was continued for further (1hr) at room temperature (Marrel *et al.*, 1992) and (Vogel, 1981). The physical properties were listed in Table (3).



(6-42)

Table 3: The physical properties of compounds(6-42)

Compd. No.	X	Y	m.p C°	Yield %	colour
6	H	H	98-100	50	Yellow
7	H	4-F	108-110	63	Yellow
8	H	2,6-diCl	137-140	34	Dark Yellow
9	H	4-Cl	108-110	12	Yellow
10	H	3-NO_2	130-132	90	Pale Yellow
11	H	3-Br	89-90	38	Yellow
12	H	4-Br	118-120	31	Yellow
13	H	2-NO_2	90-91	38	Dark Yellow
14	H	2-Cl	88-91	40	Yellow
15	H	2,4-di Cl	120-122	78	Pale Yellow
16	4-OCH_3	4-F	90-92	53	Dark Yellow
17	4-OCH_3	3-Br	118-120	56	Yellow
18	4-OCH_3	2-Cl	90-93	70	Yellow
19	4-OCH_3	4-Cl	130-132	94	Pale Yellow
20	4-OCH_3	2,4-diCl	87-89	50	Dark
21	4-OCH_3	3-NO_2	118-120	20	Yellow
22	4-OCH_3	4-OCH_3	102-104	90	Pale Yellow
23	4-NO_2	2,4-diCl	120-122	88	Dark brown
24	4-NO_2	4-Cl	181-184	9	Dark Yellow
25	4-NO_2	4-F	162-164	13	brown
26	4-NO_2	2-Cl	247-251	12	Dark brown
27	4-NO_2	2,6-diCl	115-117	16	Yellow
28	4-NO_2	4-Br	233-235	8	Dark brown
29	4-NO_2	4-OCH_3	204-206	6	Dark brown
30	4-Cl	4-Cl	172-175	72	Yellow
31	4-Cl	3-Br	125-126	46	Pale Yellow
32	4-Cl	2,6- diCl	157-158	46	Pale Yellow
33	4-Cl	3-NO_2	159-161	67	Pale Yellow
34	4-Cl	2,4- diCl	159-161	77	Yellow
35	4-Cl	4-F	152-154	78	Yellow
36	4-Cl	2-Cl	123-124	62	Pale Yellow
37	4-Br	4-OCH_3	178-180	50	Yellow
38	4-Br	2-Cl	174-175	25	Pale Yellow
39	4-Br	4-F	177-180	50	Yellow
40	4-Br	4-Cl	182-184	65	Yellow
41	4-Br	2,6- diCl	154-156	91	Yellow
42	4-Br	3-Cl	173-174	23	Pale Yellow

Preparation of 4-aryl-6-[(E)-2-arylvinyl]-3,4-dihydropyrimidine-2(1H)-one (General procedure) (Vogel, 1981)

In a 100mL round- bottomed flask equipped with magnetic stirrer, a mixture of (3ml) of (50%) sodium hydroxide solution, (25ml) of benzene, (0.3 gm) of tetrabutyl ammonium bromide (TBAB) and (0,0025 mole) of urea was stirred for (5min) at room temperature then a (0.0025 mole) of (DAA) was added drop wise to the reaction mixture. Stirring was continued at (20-50 C°)until no further change in the color of the reaction was observed, the benzene layer was separated and washed three times(10mL)of water to remove the base and the catalyst, then was dried over anhydrous magnesium sulfate, filtered and evaporated, finally the residue obtained was recrysallized from ethanol. Some physical properties of these compounds were listed in Table (4).

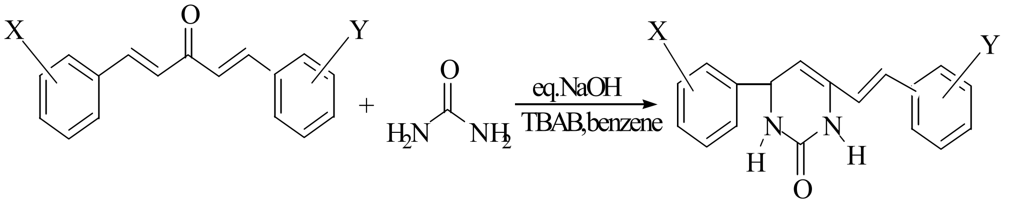


Table 4: The physical properties of compounds (43- 68):

Compd. No.	X	Y	m.pc°	Yield %	colour
43	H	3-NO$_2$	180-183	75	Dark Yellow
44	H	4-F	99-100	15	Yellow
45	H	2,6-diCl	155-157	20	Brown
46	H	H	70-73	50	Yellow
47	H	4-Cl	142-144	35	Orange
48	H	3-Br	80-82	50	Yellow
49	H	4-Br	225-226	33	Dark Orange
50	H	2-Cl	159-161	50	Yellow
51	H	2,4-diCl	131-132	33	Yellow
52	4-OCH$_3$	3-NO$_2$	134-136	3	Brown
53	4-OCH$_3$	4-F	97-99	25	Yellow
54	4-OCH$_3$	4-OCH$_3$	197-198	40	Yellow
56	4-OCH$_3$	4-Cl	100-102	57	Yellow
57	4-NO$_2$	4- OCH$_3$	140-142	50	Yellow
58	4-OCH$_3$	2,4-diCl	82-83	13	Dark Yellow
59	4-OCH$_3$	3-Br	89-90	13	Yellow
60	4-OCH$_3$	2-Cl	182-184	50	Yellow
61	3-Br	4-Cl	140-141	50	Yellow
62	4-Cl	2-Cl	78-80	43	Pale Yellow
63	4-Cl	4-F	159-161	90	Yellow
64	4-Cl	2,4-diCl	143-144	33	Yellow
65	4-Br	4-OCH$_3$	156-158	33	Yellow
66	4-Br	4-F	65-66	33	Yellow
67	4-Br	4-Cl	179-182	53	Yellow
68	4-Br	2,6-diCl	161-162	33	Yellow

Table 5:The spectral data of compounds (43-68) :

Compd.No.	UV($CHCl_3$) λ max (nm)	I .R (KBr) , υ(cm^{-1})			
		C=O str.	C=C str.	N-H str.	Others
43	328	1645	1595	3377	(sym., asy.)=1344,1408 N=O
44	340	1643	1587	3242	
45	302	1641	1639	3219	- - - - -
46	336	1651	1626	3417	- - - - -
47	262	1651	1601	3346	- - - - -
48	338	1645	1622	3390	- - - - -
49	328	1616	1595	3350	- - - - -
50	332	1648	1604	3296	- - - - -
51	328	1620	1600	3377	- - - - -
52	326	1668	1622	3423	N=O (sym., asy.) 1350, 151 C-O–C (sym., asy.) 1024,1254
53	350	1666	1616	3480	C–O–C (sym., asy.) 1028,1254
54	350	1655	1631	3402	C–O–C (sym., asy.) 1030,1252
55	340	1650	1600	3475	C–O–C (sym., asy.) 1031,1251
56	352	1649	1620	3419	N-O (sym., asy.) 1340,1510 C–O–C (sym., asy.) 1254
57	334	1668	1618	3446	C–O–C (sym., asy.) 1030,1252
58	336	1651	1604	3310	C–O–C (sym., asy.) 1030,1252
59	350	1670	1653	3064	C–O–C (sym., asy.) 1252
60	332	1639	1617	3415	- - - - -
61	328	1640	1615	3415	- - - - -
62	332	1670	1626	3413	- - - - -
63	328	1653	1616	3435	- - - - -
64	340	1650	1598	3416	C–O–C= (sym., asy.) 1032,1250
65	338	1649	1624	3384	- - - - -
66	330	1653	1601	3394	- - - - -
67	332	1649	1603	3417	- - - - -
68	332	1649	1581	3417	- - - - -

Table 6: ^{1}H-NMR spectral data for pared compounds (46-64):

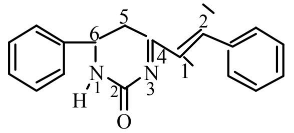
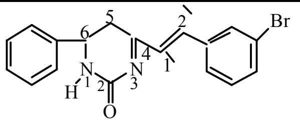
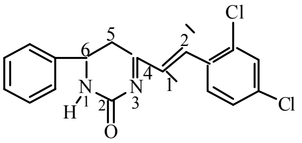
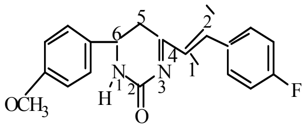
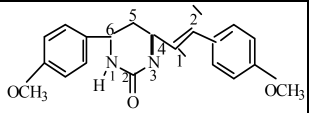
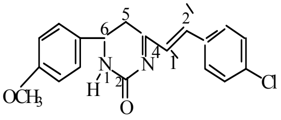
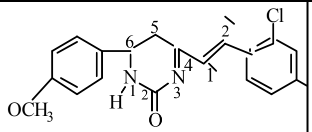
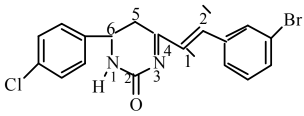
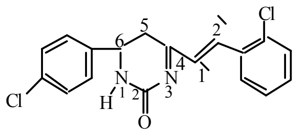
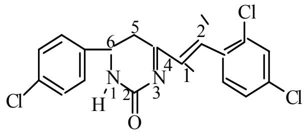
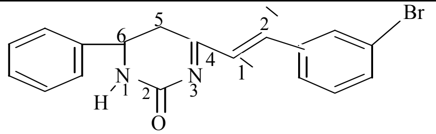
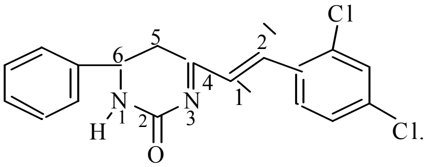
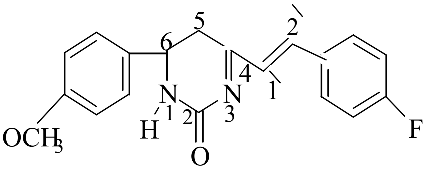
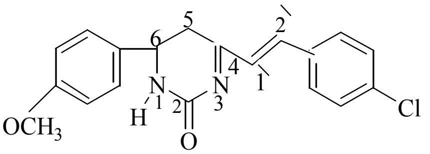
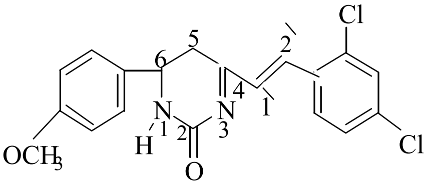
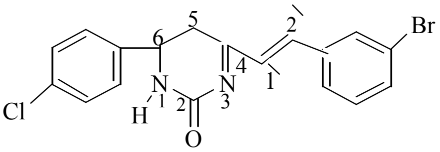
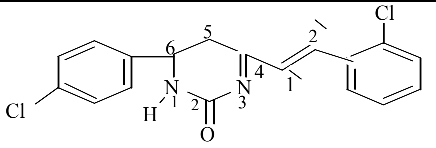
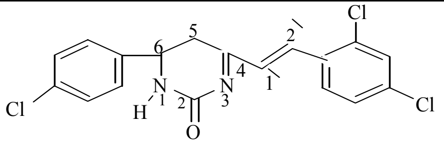
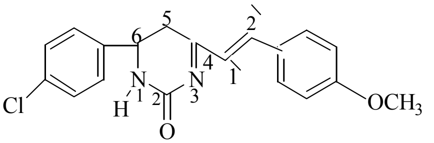
Compd. No.	Structures	Methylene Protons (C_5), (2H)	Methine Proton (C_6), (1H)	Nitrogen Proton (1H)	Olefinic C_{1}\` (1H)	Protons C_{2}\` (1H)	Aromatic Protons	OCH_3 Protons
46		(2.4),(m)	(3.3),(s)	(4.1),(s)	(6.9),(d)	(7.2),(d)	(7-7.6),(m)	- - - - - -
48		(2.4),(m)	(3.4),(s)	(4.4),(s)	(6.4),(d)	(6.8),(d)	(7.6-7.8),(m)	- - - - - -
51		(2.2),(m)	(3.4),(s)	(4.5),(s)	(6.1),(d)	(6.8),(d)	(7.2-7.4),(m)	- - - - - -
53		(2.4),(m)	(3.4),(s)	(4.5),(s)	(6.9),(d)	(7.2),(d)	(7.68-7.70),(m)	(3.8)s,(3H)
54		(2.3),(m)	(3.6),(s)	(3.7),(s)	(6.2),(d)	(6.9),(d)	(7.68-7.41),(m)	(3.8)s,(6H)
55		(2.1),(m)	(3.5),(s)	(3.7),(s)	(6.9),(d)	(7.1),(d)	(7.5-7.6),(m)	(3.87)s,(3H)
57		(2.2),(m)	(3.7),(s)	(4.4),(s)	(6.5),(d)	(7.1),(d)	(7.59-7.67),(m)	(3.88)s,(3H)
60		(2.4),(m)	(3.4),(s)	(4.4),(s)	(6.6),(d)	(7.1),(d)	(7.8-7.9),(m)	- - - - -
61		(2.2),(m)	(3.2),(s)	(4.4),(s)	(6.7),(d)	(6.8),(d)	(7.9-8.3),(m)	- - - - -
63		(2.3),(m)	(4.8),(s)	(4.8),(s)	(6.8),(d)	(7.1),(d)	(7.3-7.4),(m)	- - - - - -

Table 7: ^{13}C-NMR data for some of the prepared compounds (Pyrimidinones)

Compd. No.	Structures	Olefinic Carbons	Aliphatic Carbons	Aromatic Carbons	Carbonyl Carbons	$O\underline{C}H_3$
48		C'_1, C'_2 (128,129) C4 (126)	C_5 (123) C_6 (127)	(130-143)	188.5	—
51		C'_1, C'_2 (130,132) C4 (126)	C_5 (127) C_6 (128)	134-145	193	—
53		C'_1, C'_2 (114,131) C4 (161)	C_5 (76) C_6 (77)	(142,143)	188.5	55
55		C'_1, C'_2 (132,133) C4 (123)	C_5 (125) C_6 (127)	(141-143)	188.5	55
57		C'_1, C'_2 (130,141) C4 (123)	C_5 (125) C_6 (127)	(142-143)	161	55
60		C'_1, C'_2 (129,130) (–)C4	C_5 (127) C_6 (128)	(137-138)	188	—
61		C'_1, C'_2 (132,133) C4 (127)	C_5 (127) C_6 (128)	(134-139)	—	—
63		C'_1, C'_2 (132,133) C4 (128)	C_5 (127) C_6 (130)	(141.5 -141.9)	197	—
64		C'_1, C'_2 (131,132) C4 (128)	C_5 (127) C_6 (130)	(141-143)	188.8	55

RESULTS AND DISCUSSION

The structures of the products were established on the basis of spectroscopic data as in Table (2,4 and 5). The (IR) spectra of compounds(1-6) showed bands in the range of (1670-1616) cm^{-1}which belongs to the stretching vibration of carbonyl group (C=O) (Al- Hajjar and Jarrar, 1980), while the bands in the range (1653-1581) cm^{-1} related to stretching vibration of carbon- carbon double bond (υC=C), other broad absorption bands appeared in the range of (3480-3219) cm^{-1} due to the stretching vibration of (N-H) bond, The compound (54) is taken as a representative model for the discussion of the ^{1}H-NMR spectra.

The ^{1}H-NMR spectrum of compound (63), showed a multiplet signal at δ(2.3) ppm (2H) attributed to the protons of methylene group at C_5 of pyrimidinone ring. Another signal at δ(3.6) ppm (1H) referred to the benzylic protone at C_6 of pyrimidinone ring and singlet signal at (3.7) ppm related the proton attached to nitrogen while the singlet signal at δ(3-8) ppm (6H) referred to the methoxy group protons, The doublet signal at δ(6.8) ppm (1H) referred to the olefinic proton at C_1 of styryl group. Finally, the multiple signal at $^{\delta}$ (6.9, 7.7) ppm referred to the olefinic proton at C_2 of styryl group and aromatic proton Table (5). The ^{13}C-NMR spectrum of compound (55), showed a line at δ (141-143) ppm due to the aromatic carbons. Finally, the line at δ(188) ppm attributed to the carbonyl carbon. Table (6).

The ^{1}H-NMR data for the compounds (46, 48, 51, 54, 55, 57, 61, 63) are shown in Table (5) and the ^{13}C-NMR data for the compounds (57, 60, 64, 66, 69, 70, 72, 73) are shown in Table (6) . The (UV) spectra showed (λ max) in the range of (290-354) nm.

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