

Synthesis of New Pyrazoline - Phenoxathiin Derivatives

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Abstract:

Phenoxathiin was prepared by the reaction of diphenyl ether with sulfur in the presence of anhydrous aluminum chloride. This work comprised the synthesis of new phenoxathiin derivatives containing heterocyclic moieties. These heterocyclic compounds were synthesized in three groups. The first group was made up of 2-(oxoalken-1-yl) phenoxathiin derivatives (**3a-3j**) obtained from the reaction of 2-acetylphenoxathiin with different aromatic aldehyde in the presence of sodium hydroxide. The other two groups involved compounds produced from the reaction of (**3a-3j**) with hydrazine hydrate in acetic acid to get 2-(1-acetyl pyrazolin-3-yl) phenoxathiin derivatives (**4a-4j**), and phenyl hydrazine in the presence of piperidine to afford 2-(1-phenyl pyrazolin-3-yl) phenoxathiin derivatives (**5a-5j**). All these compounds of two groups above were substituted in position (5) in pyrazoline ring with different aryl groups according to aromatic aldehyde used in the preparation of the first group series compounds.

Keywords: Phenoxathiin, Oxoalken derivatives, Pyrazoline.

Introduction:

Phenoxathiin is given as the preferred name by Patterson and Capell [1-3]. Most widely method of preparation of phenoxathiin has been used alkyl phenoxathiin oxides by Ferrario [4-10] and dioxides of cycloalkyl phenoxathiins and their halogen derivatives have been recommended as modifiers in plastic materials, intermediates antioxidants and as rubber and gum inhibitors [11-13]. Several of crystalline phenoxathiin cation radicals have allowed us to be studying the chemistry of the cation radical in homogenous solution. Several of phenoxathiin compounds are reddish brown dyes on cotton [14].

Alkylated phenoxathiin has excellent oxidative stability and excellent anti-wear properties, so they are beneficial as lubricant additives, lubricant base stocks, or intermediates to lubricant base stock to improve viscosity and wear properties [15]. In biological field, they are used in many drugs as bacteriostatic, fungicides, anthelmintic, insecticides and antiviral agents such as distemper virus, influenza virus, hepatitis virus, neurotropic virus and especially influenza and herpetic viruses [16]. The phenoxathiin and its derivatives are used subunits to prepared different compounds example dihydroazulenes (DHAS)[17].

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Polyimides were readily prepared by the polycondensations of phenoxathiin diamines with aromatic diacyl chlorides and aromatic diamines with new phenoxathiin diacyl chlorides [18]. The acetyl derivatives are obtained by the action of acetyl chloride on the amino acid. Phenoxathiin derivatives have recently gained attention owing to their fluorescent properties [19,20]. Organometallic derivatives of phenoxathiin have been prepared with different elements such as lithium and silicon [21-31].

Materials and Methods:

FT-IR spectra were recorded on [SHIMADZU] FT-IR 8400s spectrophotometer; Solid samples were run in KBr disc, Liquid were run as smears. UV spectra were recorded on UV-Visible Spectrophotometer [SHIMADZU] UV-160A. ¹H-NMR spectra were recorded on ultra shield 300 MHz with tetramethyl silane as internal standard. Melting points were determined in a [Gallen Kamp] melting point apparatus with sample contained in open capillary glass tube in an electrically heated metal block apparatus. Thin Layer Chromatography [TLC] was performed on pre-coated plastic sheet with 0.25 mm layer of silica-gel F254. Spots were detected with iodine vapour.

General procedure for synthesis of phenoxathiin and its derivatives phenoxathiin (1)

A mixture of 188.6 g. (1.1 mol) of phenyl ether, 25.6 g. of sulfur (flowers) and 51.0g. (0.38 mol) of anhydrous aluminum chloride, maintained on steam bath for 4 hrs.

The reaction mixture was poured slowly, with stirring, into ice bath to which (25 ml.) of concentrated hydrochloric acid was added. After the two layers were separated the water layer was discarded and the (phenyl ether-phenoxathiin) layer dried overnight with calcium chloride, this mixture was distilled at (5 mm.) pressure from a 500-ml special Claisen flask. After removal of the phenyl ether the fraction boiling at (140-160°C / 5mm.), phenoxathiin was collected at (150-152)°C. The product was crystallized from methyl alcohol, m.p.(56-57)°C, yield 80%.

2-acetylphenoxathiin (2)

A mixture of (22.9 g, 0.114 mol) phenoxathiin, (9.7 g, 0.155 mol, 8.8 ml) acetyl chloride and carbon disulphide (120 ml) was stirred while anhydrous aluminum chloride (15.5 g, 0.116 mol) was added in small portions. The red mixture was stirred for (2 hrs.) at room temperature and refluxed on the water bath for a further (24 hours), the mixture was cooled, poured on to a mixture of ice and hydrochloric acid, product was crystallized once from ethanol and twice from petroleum ether b.p. (80-100)°C, m.p. 112°C, yield 52.5%. IR: 1665 cm⁻¹ (C=O)str.

Part One

2-(oxoalken-1-yl) phenoxathiin derivatives (3a-3j)

A mixture of (3g, 0.013 mol) 2-acetyl phenoxathiin and (1.56 g , 0.0147 mol) of appropriate benzaldehyde in (80 ml) of ethanol and (1.5ml) of (1% NaOH) solution was refluxed for (2 hrs). The reaction mixture was poured in cold water, the precipitate filtered off and

recrystallized from (ethanol-water) (3:1) to give (3a-3j). FT-IR spectra of these compounds showed (C=O) str. band at (1670-1685) cm^{-1} and (1608-1600) cm^{-1} aliphatic (C=C) str. Table (1) represent the physical data of compounds (3a-3j). Characteristic bands of FT-IR spectra of compounds (3a-3j) are listed in Table (2).

Part Two

2-(1-acetylpyrazolin-3-yl)

phenoxathiin derivatives (4a-4j)

To a solution of 2-(3-phenyl-1-oxypropen-1-yl) phenoxathiin (3a) (0.313 g, 0.001 mol) in acetic acid (96%, 1 ml) hydrazine hydrate (0.4 ml, 0.008 mol) was added and the mixture was refluxed for 5 hrs., the product separated and out on cooling was crystallized from (ethanol-water) (3:1) to give (4a), the following compounds were prepared in this manner. FT-IR of these compounds showed absorption bands at (1460-1585) cm^{-1} aromatic (C=C) str., (1597-1612) cm^{-1} (C=N) str. and (1227-1258) cm^{-1} (C-N) str. Table (3) represent the physical data of compounds (4a-4j). Characteristic bands of FT-IR spectra of compounds (4a-4j) are listed in Table (4).

Part Three

2-(1-phenylpyrazolin-3-yl)

phenoxathiin derivatives (5a-5j)

To a solution of 2-(3-phenyl-1-oxypropen-1-yl) phenoxathiin (3a) (1.65 g, 0.005 mol), phenyl hydrazine (0.830 g, 0.007 mol) in ethanol (80 ml) and few drops of piperidine were refluxed for 3 hrs. On concentration and cooling, gummy deposit separated out, this was crystallized from (ethanol-water) (3:1) to give (5a), the following compounds were prepared in

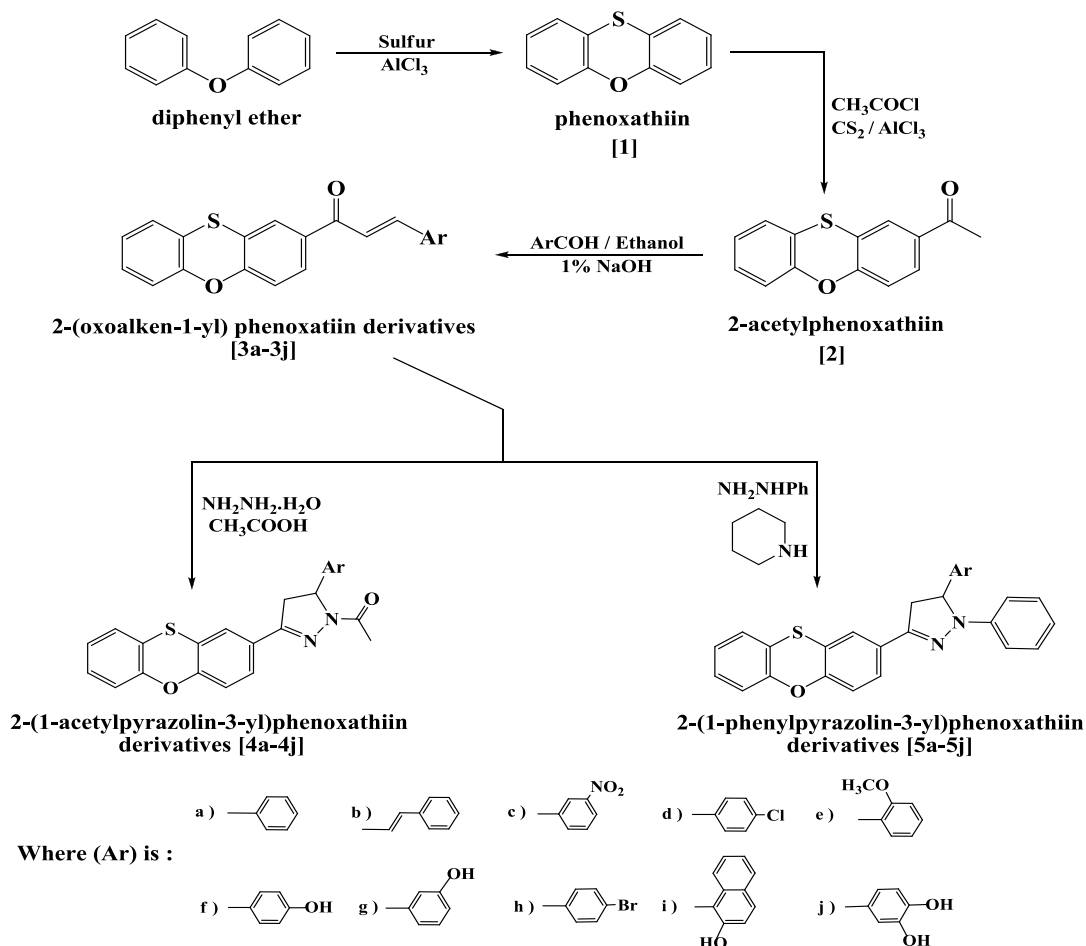
this manner. FT-IR spectra of this compound and the following compounds showed absorption bands at (1460-1600) cm^{-1} aromatic (C=C) str., (1681-1682) cm^{-1} (C=N) str. and (1249-1355) cm^{-1} (C-N) str. Table (5) represent the physical data of compounds (5a-5j). Characteristic bands of FT-IR spectra of compounds (5a-5j) are listed in Table (6).

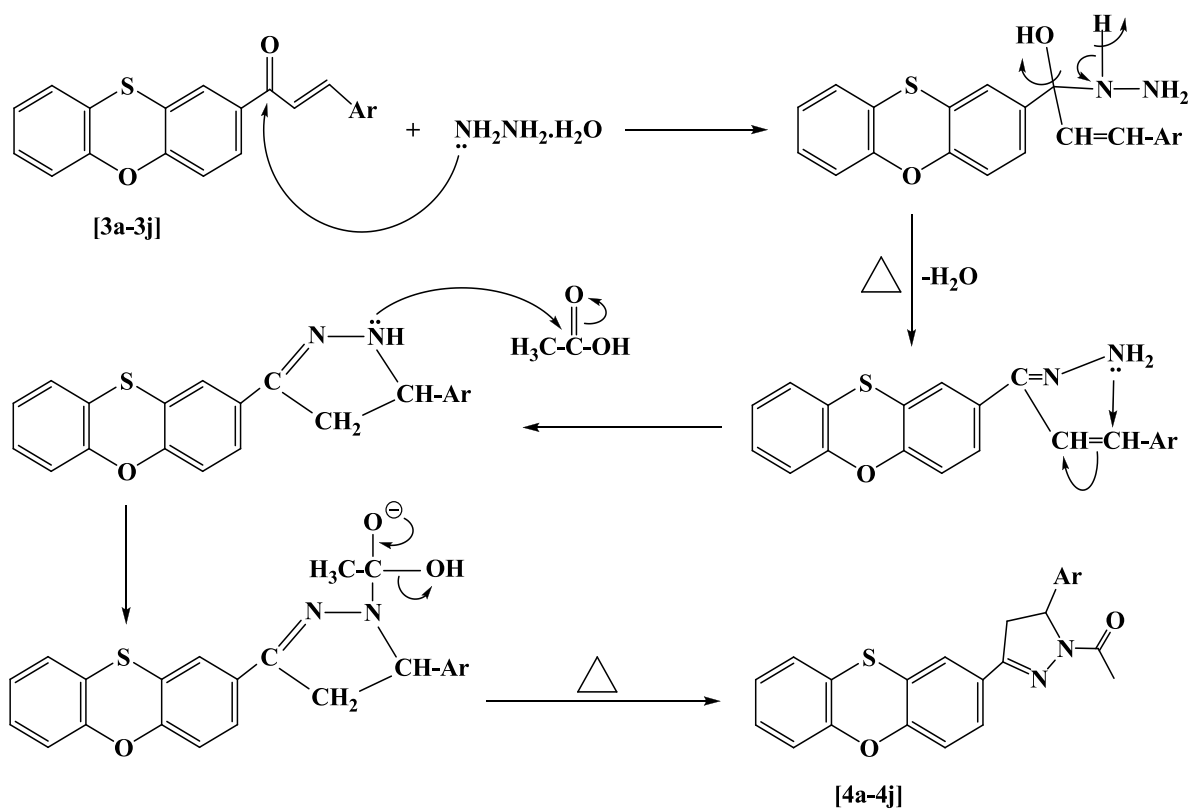
Results and Discussion:

Phenoxathiin reacted with acetyl chloride in dry carbon disulfide in presence of anhydrous aluminum chloride to get 2-acetyl phenoxathiin through Friedel Crafts acylation method. FT-IR spectrum of phenoxathiin showed strong bands at 3063 cm^{-1} aromatic (C-H) str., 1585 cm^{-1} and 1450 cm^{-1} assigned to the aromatic stretching system (C=C) str., 1219 cm^{-1} and 1026 cm^{-1} assigned to asym. and sym. (C-O-C) str. The $^1\text{H-NMR}$ spectrum showed signals between δ (6.8-7.3) ppm assigned to aromatic protons. FT-IR spectrum of compound (2) showed weak bands at 3078 cm^{-1} for aromatic (C-H) str., 2962 cm^{-1} , 2931 cm^{-1} and 2877 cm^{-1} aliphatic (C-H) str. of (CH₃) acetyl group, strong bands at 1674 cm^{-1} (C=O) str., two bands at 1558 cm^{-1} and 1465 cm^{-1} aromatic system (C=C) str. and 756 cm^{-1} (C-H) aromatic ring. The $^1\text{H-NMR}$ spectrum showed a signal at δ 2.6 ppm assigned to the three protons of the acetyl group and signals between δ (7.0-7.3) ppm assigned to aromatic protons. Through nucleophilic addition reaction as the typical reaction of aldehydes and ketones, compound (2) undergoes the characteristic condensation reaction with different kinds of aromatic

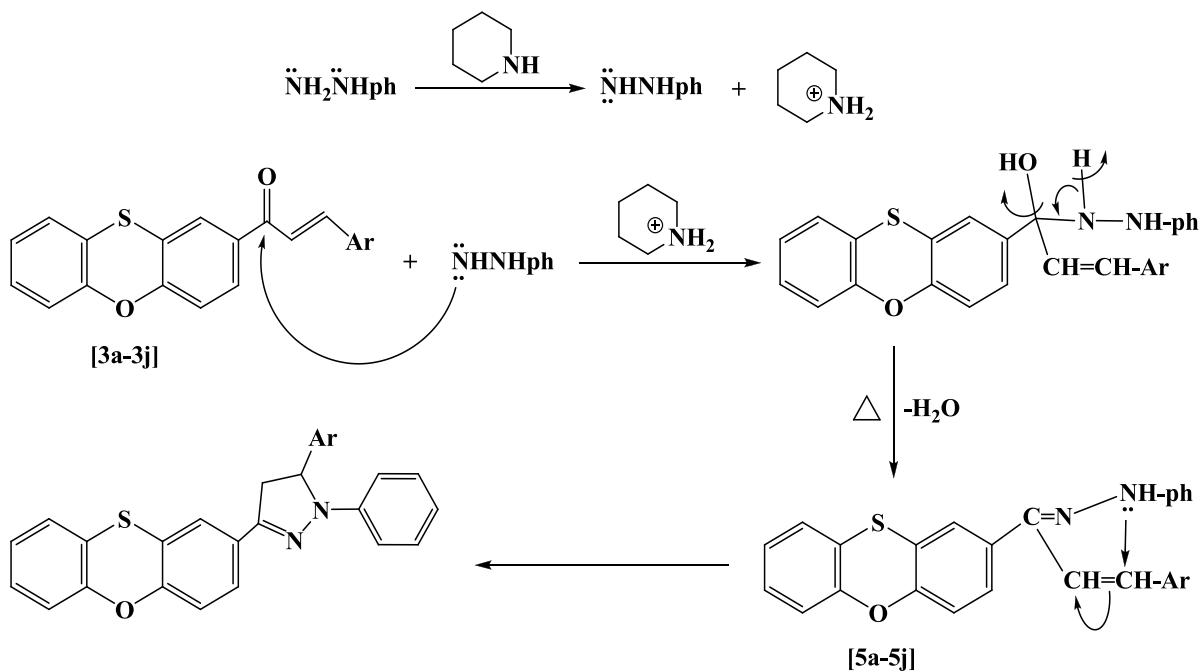
aldehydes in ethanol instead of 1% NaOH solution as a catalyst to afford (3a-3j). The IR spectra of compounds aliphatic (C=C)str. The $^1\text{H-NMR}$ spectrum showed a signal at δ 2.6 ppm assigned to aliphatic three protons of methoxy group, signals between δ (7.0-7.3) ppm assigned to both olefinic H1 and H2 respectively and a signals at δ 7.5 ppm and δ 7.9 ppm assigned to aromatic protons. The additive property of the exocyclic (C=C) in (3) conjugated with the carbonyl group promoted us to investigate their behavior towards the action of hydrazine hydrate, phenyl hydrazine react with (3) in presence of glacial acetic acid giving mono acetyl pyrazine (4a-4j). The structure of [4] has been established from IR spectra and UV. FT-IR spectrum showed absorption band at 3040 cm^{-1} aromatic (C-H)str, 2970 cm^{-1} , 2915 cm^{-1}

(3a-3j) showed absorption bands at $(1670-1648)\text{cm}^{-1}$ (C=O)str., $(1670-1685)\text{cm}^{-1}$ and $(1600-1608)\text{cm}^{-1}$ and 2800 cm^{-1} aliphatic (C-H)str. Strong bands at 1665 cm^{-1} (C=O)str and 1600 cm^{-1} (C=N)str, 1550 cm^{-1} aromatic (C=C)str. Phenyl hydrazine reacted with (3) in ethanol in presence of piperidine giving 2-phenyl pyrazoline (5a-5j). The structure of these compounds was established from IR and UV. FT-IR spectrum showed reactivity medium weak bands at 3055 cm^{-1} aromatic (C-H)str, 2975 cm^{-1} and 2865 cm^{-1} aliphatic (C-H)str. Strong bands at 1620 cm^{-1} (C=N)str, 1600 cm^{-1} (C=C)str. The $^1\text{H-NMR}$ spectra for [5a] showed a signal at δ 1.2 ppm assigned to aliphatic protons (two H4 and H5) of pyrazoline ring respectively and a signal at δ (6.6-7.5)ppm assigned to aromatic protons.



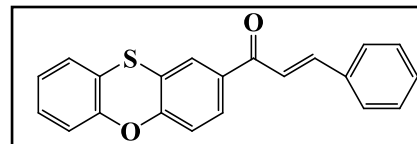


Reaction mechanism for the formation of compounds [4a-4j]



Reaction mechanism for the formation of compounds [5a-5j]

Table (1) represent the physical data of compounds (3a-3j)



Comp. No.	Scientific name	m.p. °C	Yield %	Color of crystal	Chemistry structure
3a	2-(3-phenyl-1-oxoprop-1-en-1-yl) phenoxathiin	100-102	73.0	Yellowish	
3b	2-(5-phenyl-1-oxypentadien-1-yl) phenoxathiin	102-104	53.0	Light-yellow	
3c	2-[3-(3-nitrophenyl)-1-oxoprop-1-en-1-yl] phenoxathiin	92-94	65.0	Yellow	
3d	2-[3-(4-chlorophenyl)-1-oxoprop-1-en-1-yl] phenoxathiin	94-96	45.2	Deep-yellow	
3e	2-[3-(2-methoxyphenyl)-1-oxoprop-1-en-1-yl] phenoxathiin	96-98	60.0	Deep-yellow	
3f	2-[3-(4-hydroxyphenyl)-1-oxoprop-1-en-1-yl] phenoxathiin	103-105	67.0	Reddish	
3g	2-[3-(3-hydroxyphenyl)-1-oxoprop-1-en-1-yl]phenoxathiin	102-104	67.2	Yellow-reddish	
3h	2-[3-(4-bromophenyl)-1-oxoprop-1-en-1-yl] phenoxathiin	106-108	55.9	Yellow	
3i	2-[3-(2-hydroxy-1-naphthyl)-1-oxoprop-1-en-1-yl] phenoxathiin	92-94	53.9	Black	
3j	2-[3-(3,4-dihydroxyphenyl)-1-oxoprop-1-en-1-yl] phenoxathiin	93-95	66.0	Brown	

Table (2) Infrared absorption data for compounds (3a-3j)

Comp. No.	Chemistry structure	FTIR spectral data cm^{-1}				
		$\nu(\text{C}=\text{O})$	$\nu(\text{C-H})$ aromatic	$\nu(\text{C-H})$ olefinic	$\nu(\text{C}=\text{C})$	other bands
3a		1680	3076	3018	1608	-
3b		1681	3090	3010	1600	(C-H) olefinic 3010
3c		1681	3070	2977	1600	(NO ₂) 1535 1350
3d		1674	3078	3009	1600	(C-Cl) 1095
3e		1674	3078	3008	1600	(C-O-C) 1249 1026
3f		1674	3078	3009	1600	(O-H) 3433
3g		1674	3075	3030	1600	(O-H) 3440
3h		1674	3078	3009	1600	(C-Br) 632
3i		1674	3078	3008	1600	(O-H) 3409
3j		1674	3078	3009	1600	(O-H) 3471

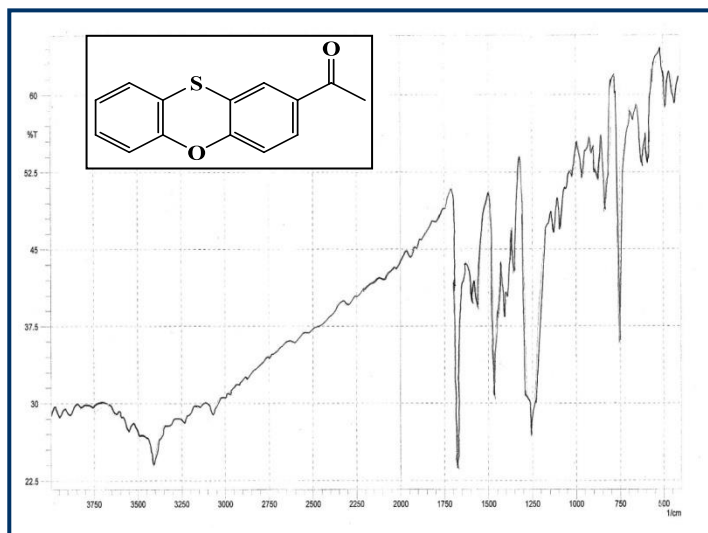


Fig.(1): FT-IR spectrum for compound (2)

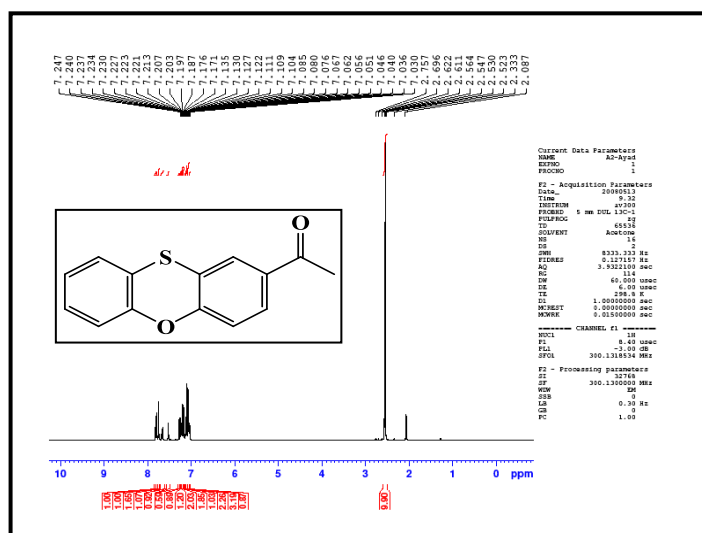


Fig.(2): ¹H-NMR spectrum for compound (2)

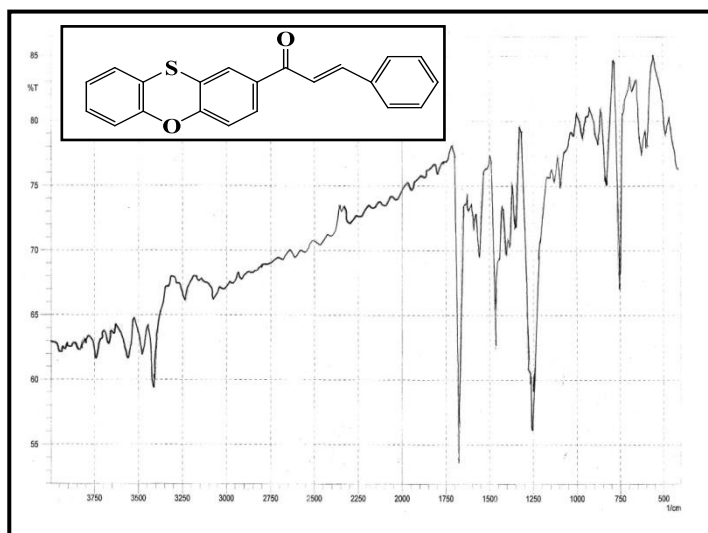


Fig.(3): FT-IR spectrum for compound (3a)

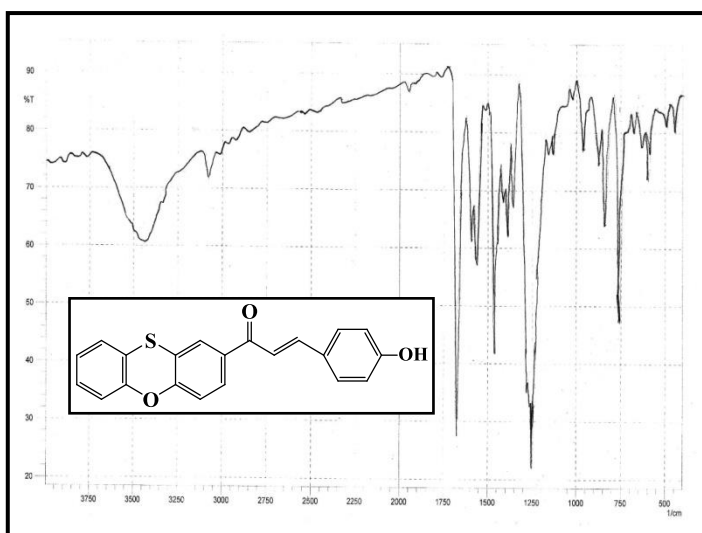


Fig.(4): FT-IR spectrum for compound (3f)

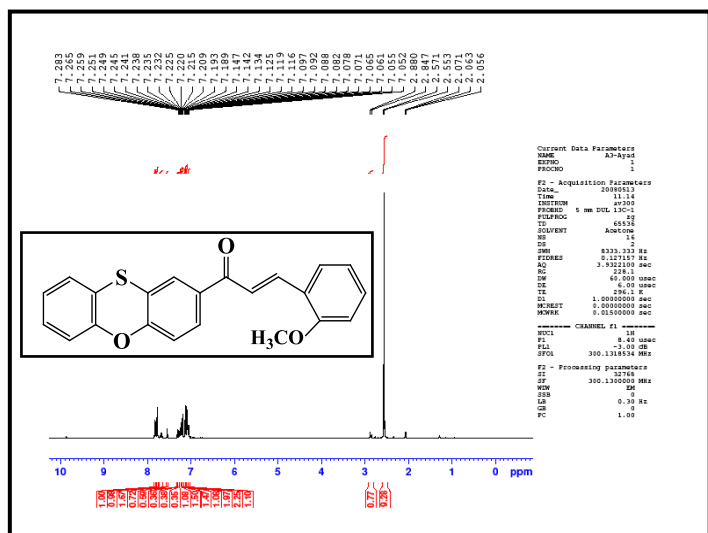


Fig.(5): ¹H-NMR spectrum for compound (3e)

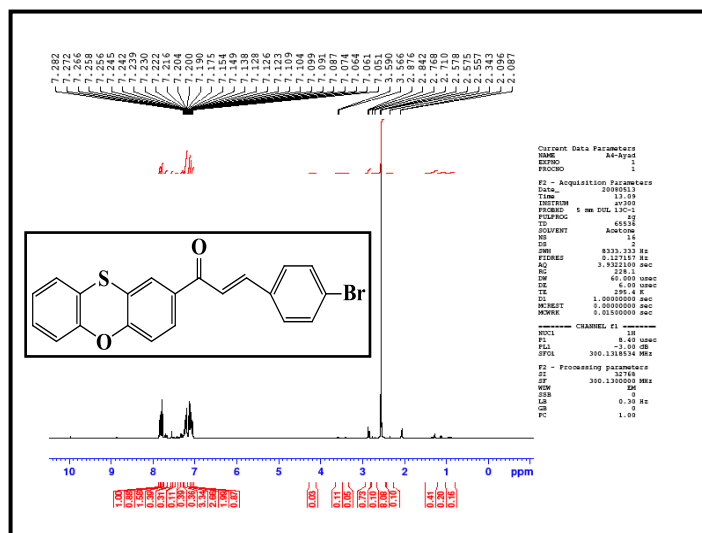
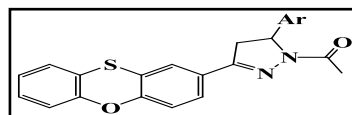


Fig.(6): ¹H-NMR spectrum for compound (3h)

Table (3) represent the physical data of compounds (4a-4j)



Comp. No.	Scientific name	m.p. °C	Yield %	Color of crystal	Chemistry structure
4a	2-(1-acetyl-5-phenylpyrazolin-3-yl) phenoxathiin	155-157	46.1	Yellow-brown	
4b	2-(1-acetyl-5-styrenyl pyrazolin-3-yl) phenoxathiin	182-184	47.8	Yellow-brown	
4c	2-[1-acetyl-5-(3-nitrophenyl) pyrazolin-3-yl] phenoxathiin	110-112	64.1	Yellow-brown	
4d	2-[1-acetyl-5-(4-chlorophenyl) pyrazolin-3-yl] phenoxathiin	115-117	86.0	Brown	
4e	2-[1-acetyl-5-(2-methoxyphenyl) pyrazolin-3-yl] phenoxathiin	118-120	87.8	Dark-yellow	
4f	2-[1-acetyl-5-(4-hydroxyphenyl) pyrazolin-3-yl] phenoxathiin	116-118	88.0	Yellow-reddish	
4g	2-[1-acetyl-5-(3-hydroxyphenyl) pyrazolin-3-yl] phenoxathiin	117-119	79.8	Yellow	
4h	2-[1-acetyl-5-(4-bromophenyl) pyrazolin-3-yl] phenoxathiin	121-123	80.2	Pale yellow	
4i	2-[1-acetyl-5-(2-hydroxynaphthyl) pyrazolin-3-yl] phenoxathiin	122-124	58.4	Black	
4j	2-[1-acetyl-5-(3,4-dihydroxy phenyl) pyrazolin-3-yl] phenoxathiin	132-134	81.2	Deep yellow	

Table (4) Infrared absorption data for compounds (4a-4j)

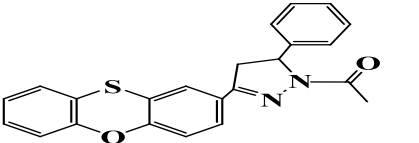
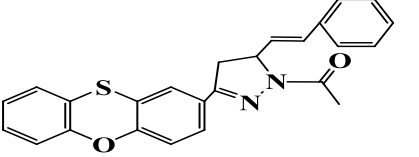
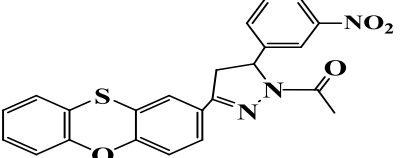
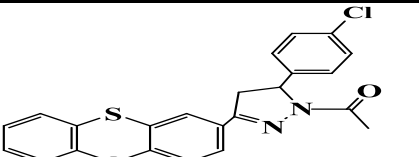
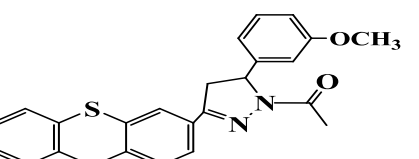
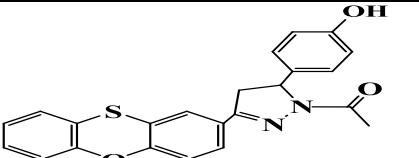
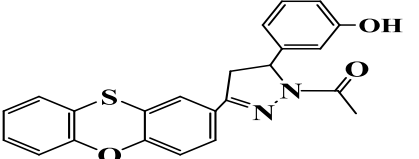
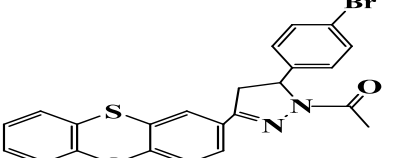
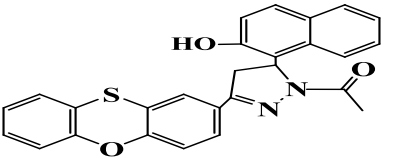
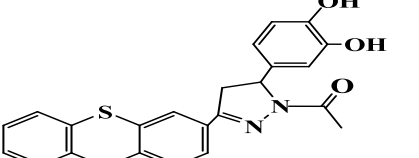
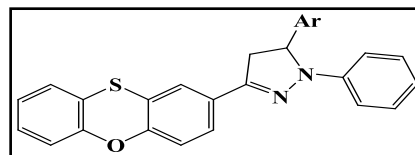
Comp. No.	Chemistry structure	FTIR spectral data cm^{-1}						other bands
		$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{H})$ aromatic	$\nu(\text{C}-\text{H})$ aliphatic	$\nu(\text{C}=\text{C})$ aromatic	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	
4a		1681	3078	2923 2854	1500 1465	1604	1258	-
4b		1674	3062	2923 2862	1551 1466	1604	1227	(C-H) olefinic 3030
4c		1682	3086	2923 2854	1585 1550	1605	1257	(NO ₂) 1500 1350
4d		1682	3078	2932 2870	1558 1465	1605	1257	(C-Cl) 705
4e		1682	3078	2924 2870	1566 1466	1612	-	(C-O-C) 1257 1018
4f		1674	3070	2924 2854	1574 1460	1597	1257	(O-H) 3417
4g		1684	3078	2932 2862	1575 1466	1605	1257	(O-H) 3418
4h		1682	3070	2935 2855	1566 1466	1597	1257	(C-Br) 625
4i		1674	3047	2932 2854	1570 1465	1597	1258	(O-H) 3479
4j		1682	3078	2932 2870	1575 1465	1605	1258	(O-H) 3472

Table (5) represent the physical data of compounds (5a-5j)



Comp. No.	Scientific name	m.p. °C	Yield %	Color of crystal	Chemistry structure
5a	2-(1,5-diphenylpyrazolin-3-yl) phenoxathiin	86-88	38.9	Red	
5b	2-[1-phenyl-5-styrenyl pyrazolin-3-yl] phenoxathiin	90-92	73.1	Red	
5c	2-[1-phenyl-5-(3-nitrophenyl) pyrazolin-3-yl] phenoxathiin	94-96	71.0	Reddish	
5d	2-[1-phenyl-5-(4-chlorophenyl) pyrazolin-3-yl] phenoxathiin	93-95	82.2	Reddish	
5e	2-[1-phenyl-5-(2-methoxy phenyl) pyrazolin-3-yl] phenoxathiin	112-114	70.7	Red	
5f	2-[1-phenyl-5-(4-hydroxy phenyl) pyrazolin-3-yl] phenoxathiin	126-128	74.5	Red	
5g	2-[1-phenyl-5-(3-hydroxy phenyl) pyrazolin-3-yl] phenoxathiin	114-116	77.3	Brown	
5h	2-[1-phenyl-5-(4-bromophenyl) pyrazolin-3-yl] phenoxathiin	120-122	78.0	Brown	
5i	2-[1-phenyl-5-(2-hydroxy naphthyl) pyrazolin-3-yl] phenoxathiin	150-152	65.0	Black	
5j	2-[1-phenyl-5-(3,4 dihydroxy phenyl) pyrazolin-3-yl] phenoxathiin	167-169	57.3	Brown	

Table (6) Infrared absorption data for compounds (5a-5j)

Comp. No.	Chemistry structure	FTIR spectral data cm^{-1}					
		$\nu(\text{C-H})$ aromatic	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C=C})$ aromatic	$\nu(\text{C=N})$	$\nu(\text{C-N})$	other bands
5a		3065	2930 2850	1566 1470	1681	1249	-
5b		3062	2920 2860	1600 1566 1465	1681	1257	(C-H) olefinic 3020
5c		3050	2960 2910	1597	1682	1250	(NO ₂) 1560 1358
5d		3062	3008 2923 2860	1597 1465	1681	1257	(C-Cl) 700
5e		3063	3008 2910	1589 1466	1681	1350	(C-O-C) 1257 1041
5f		3063	2962 2923 2854	1597 1465	1682	1357	(O-H) 3340
5g		3062	3000 2940 2850	1597 1460	1681	1355	(O-H) 3330
5h		3060	2910 2840	1558 1460	1681	1350	(C-Br) 610
5i		3070	3020 2915	1558 1466	1681	1350	(O-H) 3479
5j		3063	2923 2862	1597 1460	1682	1350	(O-H) 3448

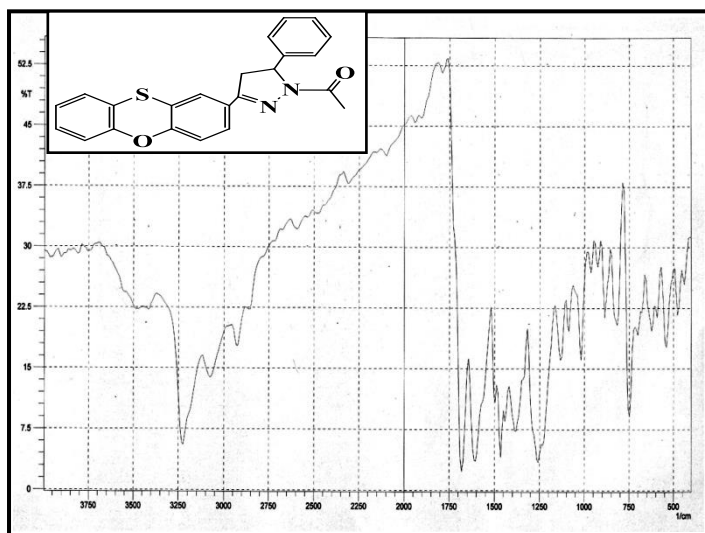


Fig.(7): FT-IR spectrum for compound (4a)

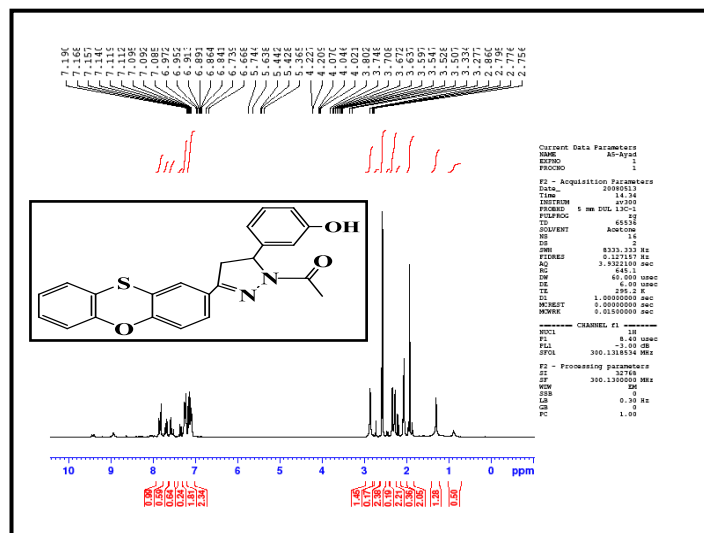


Fig.(8): ¹H-NMR spectrum for compound (4g)

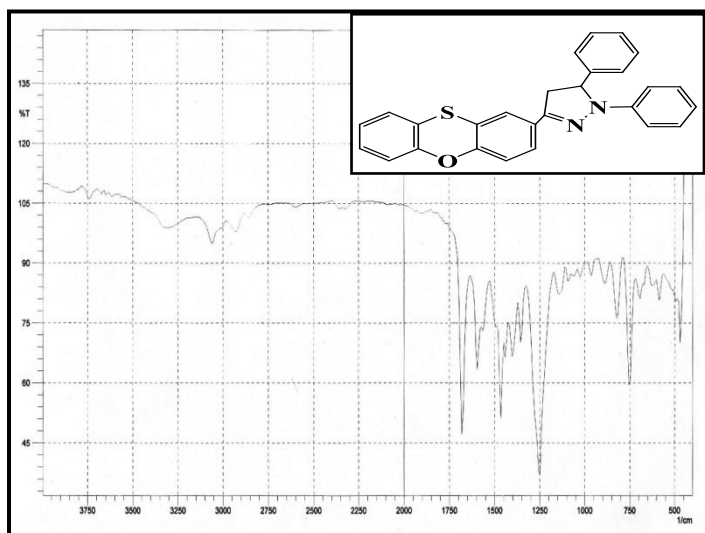


Fig.(9): FT-IR spectrum for compound (5a)

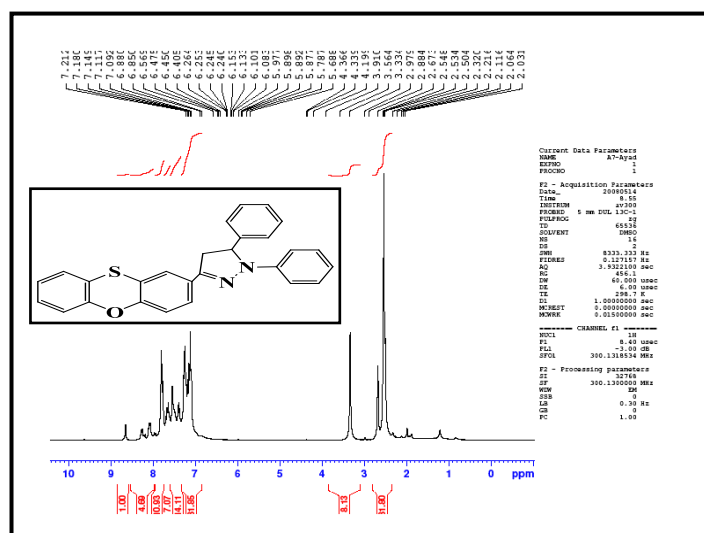


Fig.(10): ¹H-NMR spectrum for compound (5a)

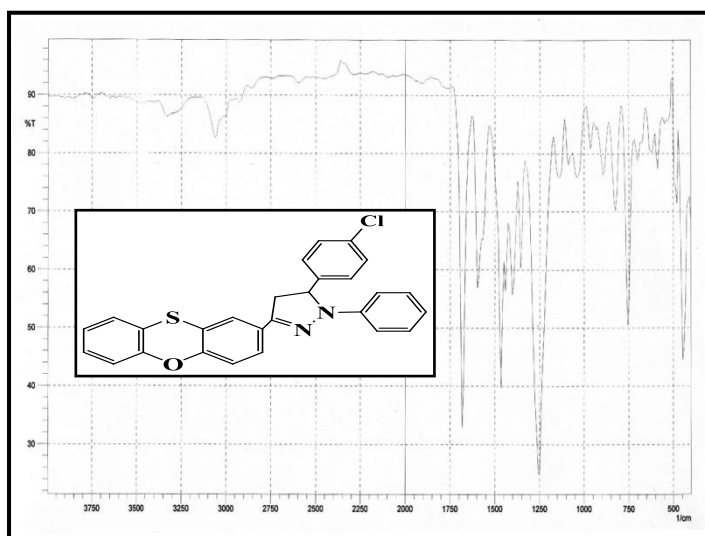


Fig.(11): FT-IR spectrum for compound (5d)

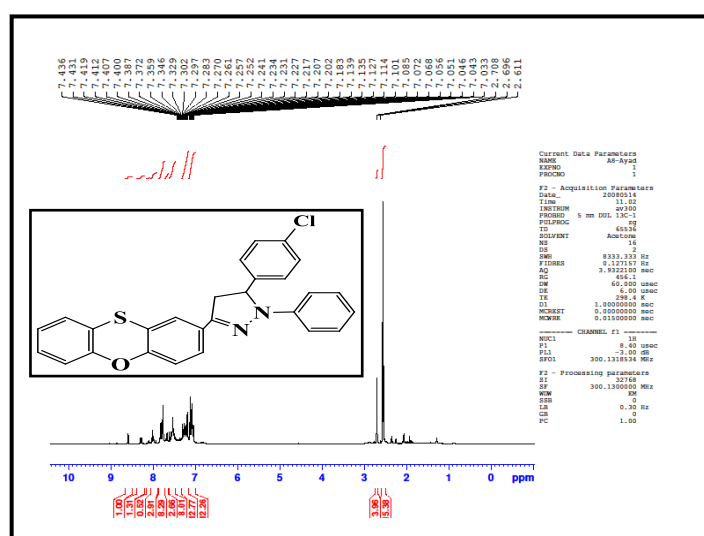


Fig.(12): ¹H-NMR spectrum for compound (5d)

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تحضير مشتقات جديدة للبايرازولين فينوكسيثين

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الخلاصة:

تم تحضير الفينوكسيثين من تفاعل ثنائي فنيل ايثر بوجود كلوريد الالمنيوم الجاف. تضمن البحث تحضير مشتقات جديدة من الفينوكسيثين التي تحتوي على حلقات غير متجانسة. وقد صنفت جميع هذه المركبات المحضرة الى ثلاث مجاميع تحتوي كلاها منها على عشرة مركبات. المجموعة الاولى هي مشتقات ل-2-(أوكسو الكين-1-يل) الفينوكسيثين (3a-3j) والمحضرة من تفاعل 2-أسيتيل فينوكسيثين مع مختلف المركبات العطرية الالدهايدية وبوجود هيدروكسيد الصوديوم. اما مركبات المجموعتين الثانية والثالثة فقد تم تحضيرها عن طريق مفاعلة مركبات المجموعة الاولى (3a-3j) مع كل من الهيدرازين بوجود حامض الخليك للحصول على مشتقات ل-2-(1-أسيتيل بايرازولين-3-يل) للفينوكسيثين (4a-4j), ومع الفينيل هيدرازين بوجود البايبيريدين لتعطي مشتقات ل-2-(1-فنيل بايرازولين-3-يل) فينوكسيثين (5a-5j). جميع مركبات المجموعتين أعلاه معوضة في الموقع (5) في حلقة الباييرازولين بمجاميع أريل وحسب المركبات العطرية الالدهايدية المستخدمة في تحضير مركبات المجموعة الاولى.