A Synthesis of Thiopyran Pyridinium Perchlorate Compounds

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Abstract

Asynthesis of four pyridinium perchlorate compounds have been prepared from reaction one mole pyrylium salt (product already) with one mole cysteine in room temp. and diagnosed spectrally (FT-IR., ^{1}H-NMR) in addition to the accurate quantitative elemental analysis.

Asynthesis of sixteen Thiopyranpyridinium perchlorate compounds from reaction one mole from pyridinium compounds produced with one mole pyrylium salt (product already) under zero temp. very good yields that were diagnosed spectrally (FT-IR., ^{1}H-NMR) in addition to the accurate quantitative elemental analysis.

Keyword: Thiopyran pyridinium perchlorate compounds.

Introduction

Thiopyran Pyridinium compounds are compounds of a Di-6-member hetrocyclic ring with a six-π-electron system. The one hetro atom is an sp^2- hybridised trivalent nitrogen in the form of an nitronium ion and also hetro atom is an sp^2- hybridised trivalent salphid without ion.(1)

Pyrylium compounds are compound of a 6-member hetrocyclic ring with a six-π-electron system. The hetro atom is an sp^2- hybridised trivalent oxygen in the form of an oxonium ion. The pyrylium cation can be combined with nucleophilic anion trihalides (except the fluoride ion) and with most complex anions of low polarisability and weak nucleophilic properties, Chloroferrate Chloroalumnate, Fluoroborate …. etc. However, stable crystalline forms of the Pyrylium compounds are obtained as prechlorate(2,3,4)

The pyrylium cation reaction with primary (mono amine compounds)(5,6,7) and (Di amino compounds) product pyrydinium and Bis-Pyrydinium diagnosing them spectrally IR, UV and NMR in addition to the accurate quantitative elemental analysis (5,6,7,8)

The Pyrylium cation reaction with aqueous solution of sodium sulphide in acidic medium, product six thiopyrylium perchlorate(5,7). Synthesis 1, 2, 4, 6- tetra phenyl thiopyran benzene from reaction 2, 4, 6-Tri phenyl thiopyrylium with PhLi.(9-12). Airm of the work asynthesis of thiopyrran pyridinium perchlorate compounds and studying of biological evaluation.

Experimental

Instrumentation:

Used Shimadzu FT-IR spectrophotometer-(8300), by using KBr disc., C.H.N.: Element Analysis, (Elmer 240 B-perken) and ^{1}HMR spectrophotometer Bruker Ac-200 MH_2 by using DMSO-d_6 as solvent. were made at chemistry department, Al-Albyt University, and Jordon

First step: preparation Pyridinium Compound: (13-14)

Amixture of (2,4,6-tri-phanyl pyrylium prechlorate) (0.0088mol) and cysteine (0.0088mol) in (40mol) ethanol was refluxed for (6hr) and showed dissolved color red. After cooling the solution was filtered and recrystallized from ethanol to give yield (80.5%) m.p. (207-208)C^0, they were diagnosed spectally (FT-IR ,^{1}H-NMR) in Table (3) and (4) in addition to the accurate quantitative C.H.N(see. Table (1)).

Table (1)
Characterization data for the synthesized of Pyridinium compounds.

No.	*Formula (M.Wt)*	*M.P. ^0C*	*Yield%*	*Analysis Clcd (found)*				
				C%	*H%*	*N%*	*S%*	*Br%*
A	$C_{28}H_{26}O_8NSCl$ (585.81)	207-208	80.6	57.40 57.24	4.44 4.24	2.39 2.25	5.47 5.41	
B	$C_{26}H_{20}O_6NSCl_2Br$ (638.85)	223-224	84	48.88 48.67	3.13 2.95	2.19 1.98	5.02 4.74	11.10 11.03
C	$C_{27}H_{24}O_6NSCl$ (525.80)	245-246	80.5	61.67 60.82	4.56 3.98	2.66 2.46	6.10 6.04	
D	$C_{26}H_{21}O_8N_2SCl$ (570.55)	200-201	88	54.73 54.66	3.68 3.47	4.91 4.87	5.62 5.51	

Second: prepare Thiopyran Pyridinium compound:

Amixture(4,6-Diphanyl-2-(3.4-dimethoxy-phanyl) Pyridinium perchlorate (0.0053mol) Dissolved in (20 ml) Ethanol and [1-(carboxy-mercapto-methyl)-2,4,6-triphanyl Pyridinium prechlorate] (0.0053mol) Dissolved in (20 ml) Acetone was refluxed for about(12hr) at water bath and showed color golden brown. After cooling, adding diethyiether and filtered off then washed with (10ml) ethanol then recrystallized from acetic aced to give yield (88%), m.p.(232-234)^oC. They were diagnosed spectrally (FT-IR, ^{1}H-NMR) IN Table (5) and (6) in addition to the accurate quantitative C.H.N(see. Table (2)).

Table (2)
Characterization data for the synthesized of Thiopyran Pyridinium compounds.

Co. No.	*Pyridinium No.*	*Formula (M.Wt)*	*M.P. ^0C*	*Yield %*	*Analysis Clcd /found*					
					C%	*H%*	*N%*	*S%*	*Cl%*	*Br%*
1	A	$C_{49}H_{43}O_8NSCl$ (841.01)	250-251	84.3	69.97 69.69	5.11 4.87	1.67 1.57	3.81 3.76	4.22 4.18	----
2	A	$C_{49}H_{41}O_8NSCl_2Br$ (954.36)	255-256	90	61.66 61.37	4.30 4.11	1.47 1.38	3.36 3.24	7.43 7.19	8.37 8.05
3	A	$C_{51}H_{47}O_{10}NSCl$ 901.03	267-268	85.4	67.98 67.68	5.22 5.00	1.55 1.41	3.56 3.44	3.93 3.76	----
4	A	$C_{49}H_{42}O_{10}N_2SCl$ 886.02	209-210	80	66.42 65.99	4.74 4.44	3.16 3.02	3.62 3.54	4.00 3.89	----
5	B	$C_{49}H_{34}O_6NSCl_3Br_2$ (1030.71)	251-252	84	57.10 56.62	3.30 2.97	1.36 1.26	3.11 3.05	10.32 10.17	15.50 15.27
6	B	$C_{51}H_{40}O_8NSCl_2Br$ (973.38)	264-265	89	62.67 62.39	4.09 3.89	1.43 1.30	3.28 3.21	7.25 7.07	8.17 8.08
7	B	$C_{49}H_{35}O_8N_2SCl_2Br$ (962.37)	246-247	91	61.15 60.80	3.64 3.38	2.91 2.88	3.33 3.19	7.37 7.21	8.30 8.16
8	B	$C_{49}H_{37}O_6NSCl_2Br$ (918.36)	244-245	81	64.08 63.79	4.03 3.75	1.53 1.09	3.49 3.40	7.72 7.38	8.70 8.65
9	C	$C_{51}H_{42}O_8NSCl$ (864.03)	232-234	88	70.89 70.47	4.86 4.67	1.63 1.54	3.71 3.28	4.10 4.02	----
10	C	$C_{49}H_{36}O_6NSCl_2Br$ (917.36)	245-246	80.2	64.15 63.85	3.92 3.55	1.53 1.50	3.49 2.41	7.73 7.64	8.71 8.55
11	C	$C_{49}H_{38}O_6NSCl$ (804.01)	215-216	87	73.19 72.86	4.73 4.39	1.74 1.67	3.99 3.56	4.41 4.38	----
12	C	$C_{49}H_{37}O_8N_2SCl$ (849.02)	237-238	79	69.31 68.88	4.36 4.09	3.30 3.24	3.78 3.59	4.18 4.19	----
13	D	$C_{49}H_{36}O_{10}N_3SCl$ (894.03)	228-229	86	65.82 65.42	4.03 3.86	4.70 4.66	3.59 3.47	3.97 3.78	----
14	D	$C_{49}H_{38}O_8N_2SCl$ (850.02)	219-220	84.2	69.23 68.88	4.47 4.39	3.30 3.24	3.77 3.46	4.17 4.11	----
15	D	$C_{51}H_{42}O_{10}N_2SCl$ (910.04)	254-255	87	67.31 66.89	4.62 4.42	3.08 3.01	3.52 3.45	3.90 3.87	----
16	D	$C_{49}H_{35}O_8N_2SCl_2Br$ (962.37)	239-240	80.9	61.15 60.72	3.64 3.37	2.91 2.87	3.33 3.27	7.37 7.32	8.30 8.18

Results and Discussion

A Synthesis used two steps, as follows:

The first step preparing Pyridinium Compound : [15]

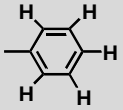
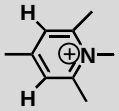
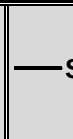
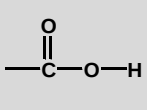
Got reaction(0.0088 mol) of Pyrylium prechlorate with(0.0088 mol) of the Compounds content primary Amine and Sulfide, to give a Pyridinium prechlorate interview and yield were very good the appearance of (N=C) absorption band at (1621-1682) cm^{-1} , the appearance of (C-N) absorption band at (1305-1379) cm^{-1}, the disappearance of both (NH_2) absorption band at (3400, 3200) cm^{-1} and (-S=C) absorption band at (1523-1580) cm^{-1} in their I.R. spectra, the appearance of (S-H) absorption band at (7.33-7.30) S in their 1H.N.M.R. spectra.(see Tables (3) (4) and Fig.(1), also explained mechanism and formula the following (Scheme (1)).

Table (3)
IR. Spectra of Pyridinium compounds.

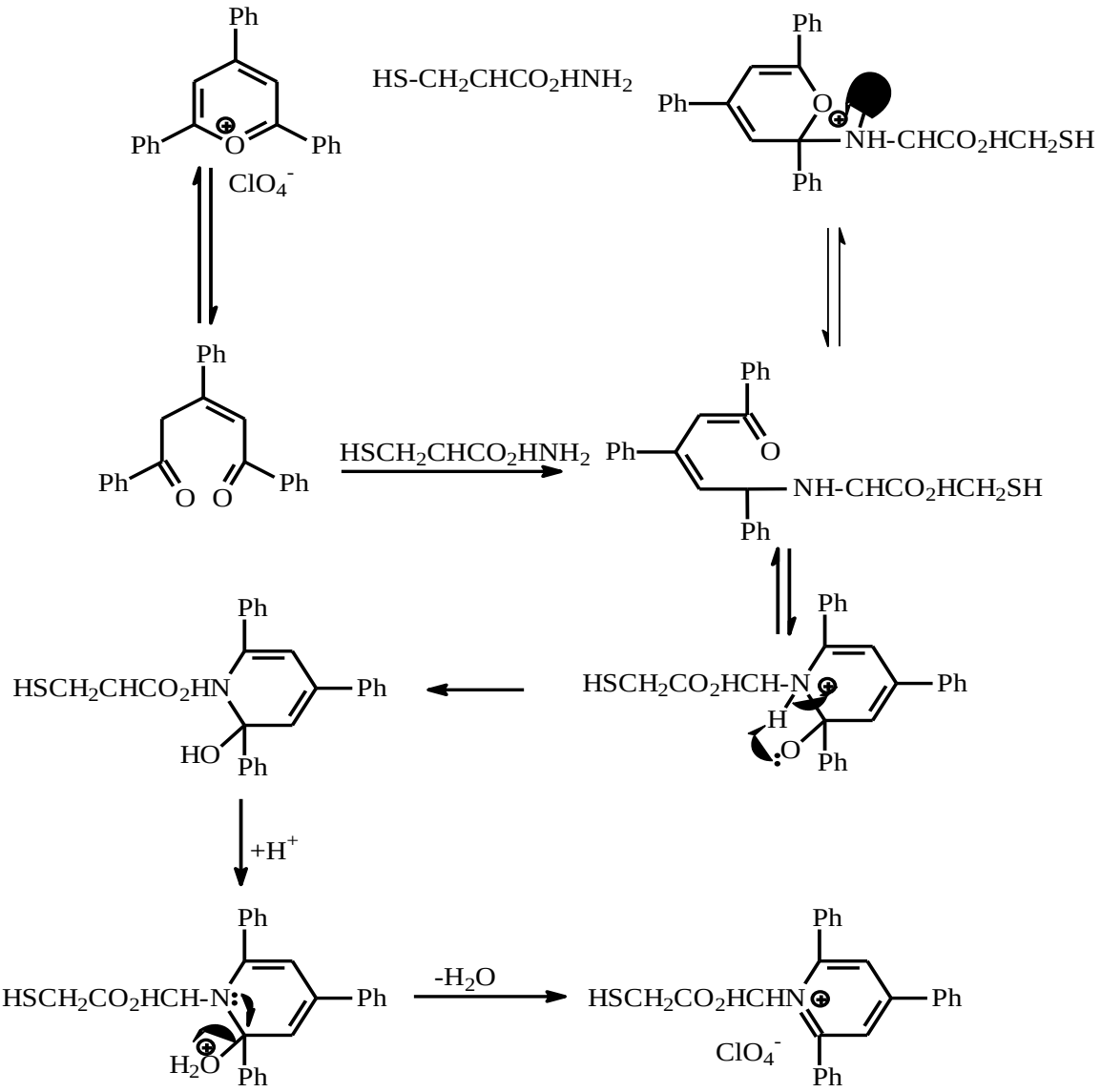
No.	*C-N*	*C=N*	*C-H phenyl*	*ClO_4^-*	*C=C*	*C-H pyridinium*	*S-C*	*Other*	
								group	*cm^{-1}*
A	1376	1682.6	669, 672.1	1087.1	1453.1, 1402	862.3	1270	COOH	3642
B	1305.1	1674.1	642. 683	1086.2	1478.3, 1462.1	892	1259.9	Cl, Br COOH	790,568 3554
C	1305.7	1621.7	623, 686.6	1087.8	1450.4 ,1490.9	877.6	1245.9	OCH_3 COOH	1274.9 3632
D	1322.2	1660	609.9, 684	1081	1467, 1432.1	859.6	1288.1	NO_2 COOH	1342 3582

**** using KBr disc.***

Table (4)
^{1}H-NMR Spectra of Pyridinium compounds.

No.Comp.					*Other*
A	(7.73),(7.70)M (7.69)M	(8.37) S	(7.33) S	(8.71) S	OCH_3 (3.81),(4.15) CH (1.63)

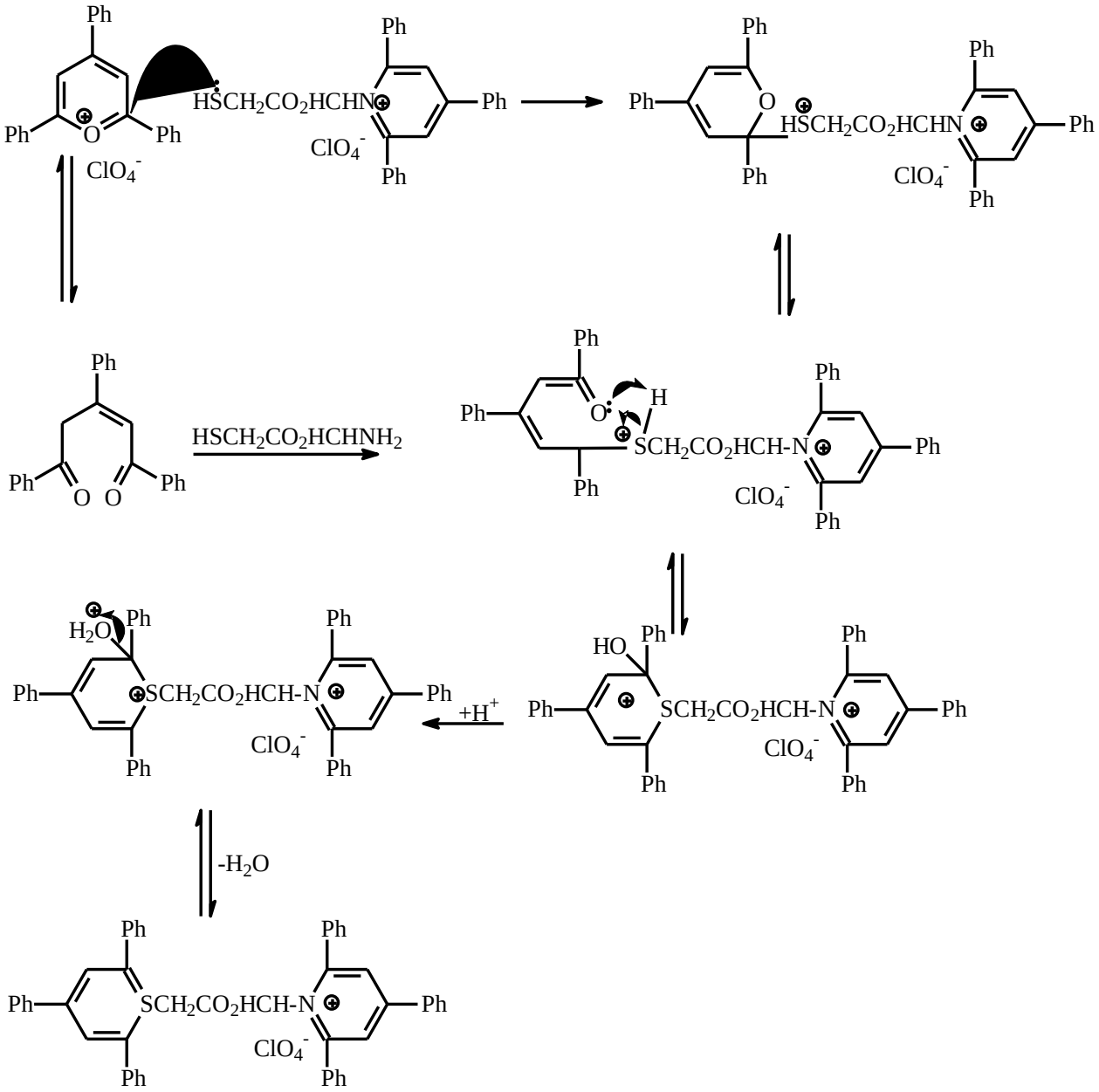
***** By using DMSO-d_6 solvent***



Scheme (1).

Second prepare Thiopyran Pyridinium compound:

Got reaction one mol of Pyrylium prechlorate with one mol of the Pyridinium prechlorate, to give a Thiopyran Pyridinium silt. Interview and yield very good, the appearance of (N=C) absorption band at (1644, 1591) cm^{-1}, the appearance of (C-N) absorption band at (7.33-7.30) S in their 1H-NMR. Spectra (see Table (6) (7)) and Fig.(2-5), also absorption band at (1393-1342) cm^{-1}, the appearance of (S=C) absorption band at (1523-1580) cm^{-1} the disappearance of (S-C) absorption band at (1245-1295) cm^{-1} in their I.R. spectra, the disappearance of (S-H) explained mechanism and formula the following (Scheme (2)).


Ph
Ph
O
Ph
ClO4-
HSCH2CO2HCHN
Ph
ClO4-
Ph
Ph
O
HSCH2CO2HCHN
Ph
ClO4-
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O O
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HSCH2CO2HCHNH2
Ph
O
H
Ph
SCH2CO2HCH-N
Ph
ClO4-
Ph
Ph
H2O
Ph
Ph
SCH2CO2HCH-N
Ph
ClO4-
Ph
+H+
HO
Ph
Ph
SCH2CO2HCH-N
Ph
ClO4-
Ph
-H2O
Ph
Ph
SCH2CO2HCH-N
Ph
ClO4-
Ph

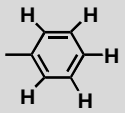
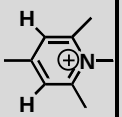
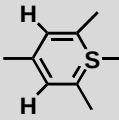
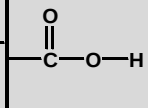
Scheme (2).

Table (5)
IR. Spectra of Thiopyran Pyridinium compounds.

No.	C-N	C=N	C=S	C-H Pyridinium	C-H Thiopyrinium	C-H Phenyl	ClO_4^-	C=C	Other	
									group	cm^{-1}
1	1380.1	1611.3 1552.1	1561	839.9	919.3	653 701	1080.4	1496 1523.1	OCH_3	1249.1 3448.1
2	1352.4	132, 1580.4	1574.4	890	922.1	660 683	1089.1	1469.1 1521.5	OCH_3 C-Cl C-Br COOH	1230.3 776.1 572 3528
3	1350.2	1610.5 1562.3	1577.3	880.1	943.6	686 690	1083.3	1459.3 1534.1	OCH_3 C-Cl C-Br COOH	1255.1 795.3 556.9 3501
4	1353.9	1623.8 1596.9	1550.7	893.4	931.6	623 702	1088.5	1404 1496 1461	OCH_3 NO_2 COOH	1257 1340.4 3388.7
5	1393.2	1636.3 1562	1563	834	948.2	680.1	1086.5	1473.8 1569	C-Cl C-Br COOH	782.2 569 3529.1
6	1350	1619.4 1580	1561.2	894	957	685	1088.9	1469.2, 1589	OCH_3 C-Cl C-Br COOH	1218.2 763 582 3531
7	1345.3	1644, 1552	1573.1	881	948.1	695	1082	1586, 1477.9	NO_2 C-Cl C-Br COOH	1245 784.1 591 3535.1
8	1352.6	1622, 1550	1582.3	879.1	938.9	688	1085	1565, 1454.3	C-Cl C-Br COOH	787.3 553.4 3543
9	1352	1620, 1552	1561	882	948	697	1086.4	1587,15 08,1482	OCH_3 COOH	1227 3525
10	1340.9	1590.3 1610	1562.1	881.1	939.5	685	1083.0	1490, 1586.2	C-Cl C-Br COOH	771.4 565 3470
11	1340.4	1591.6 1627.8	1561.2	881.4	948.9	682	1087.6	1404, 1496	COOH	3483
12	1367	1644, 1515	1582	882.1	934.1	677	1082.4	1577, 1490.1	NO_2 COOH	1298 3546
13	1361.1	1654 1586.4	1557.9	848.1	932	603 795,3	1088.6	1478 1509.2	NO_2 COOH	1322.1 3379
14	1388.4	1630 1571.5	1587.1	877.3	940.1	609.1 688	1086.1	1489 1533.6	NO_2 COOH	1319.4 3467
15	1396.4	1622 1566.3	1575.7	825.5	896.8	619.1 686,6	1083.9	1475.4 1434.9	OCH_3 NO_2 COOH	1224.7 1278.7 3060.8
16	1359.7	1631 1550,7	1587.3	835.1	881.4	881 835	102.22	1488 1407	C-Cl C-Br NO_2 COOH	779.2 565 1244 3462

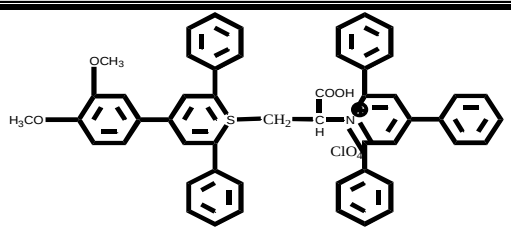
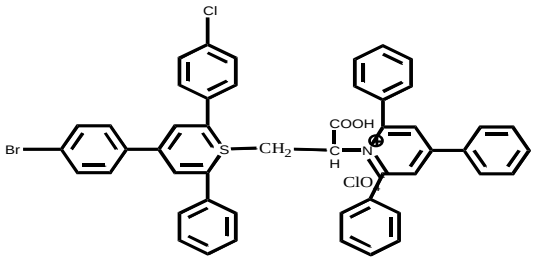
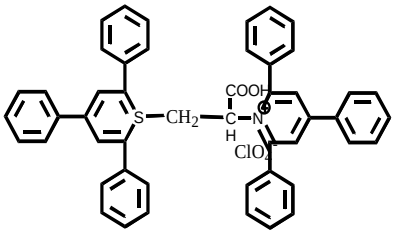
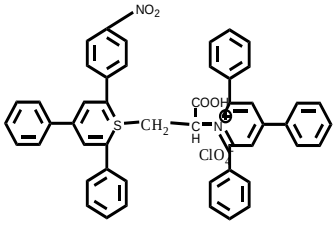
**** using KBr disk.***

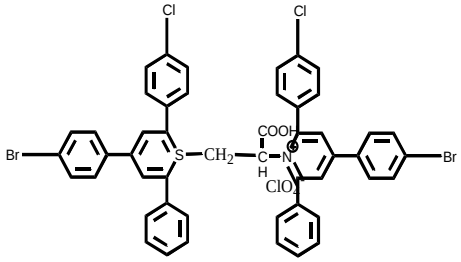
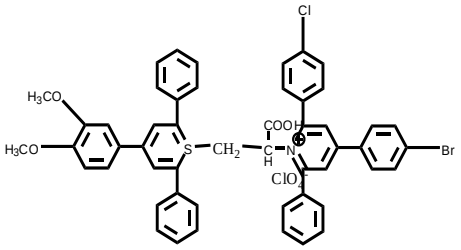
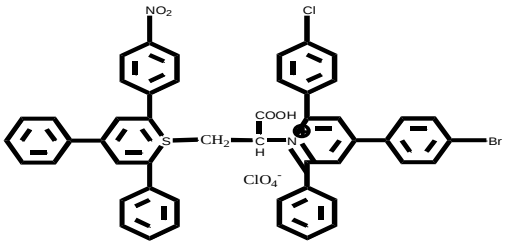
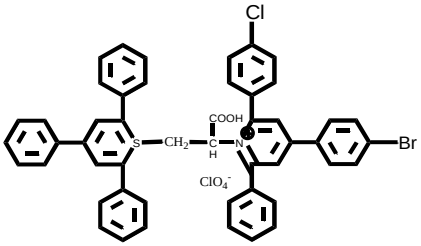
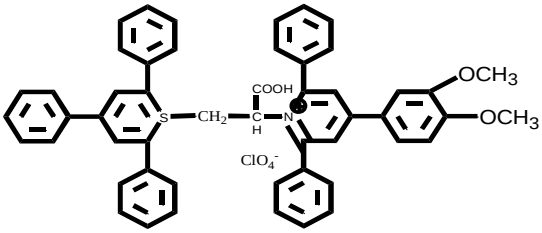
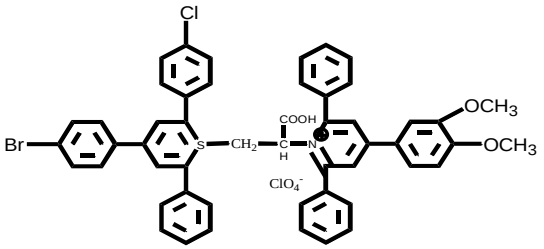
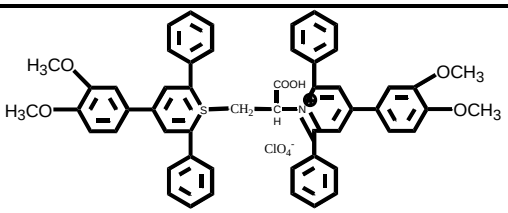
Table (6)
^{1}H-NMR Spectra of Thiopyran Pyridinium compounds.

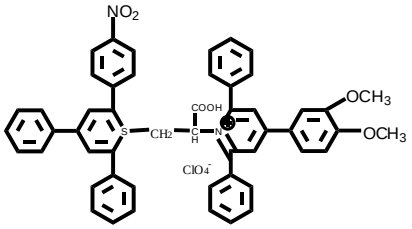
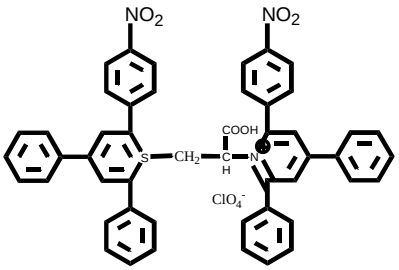
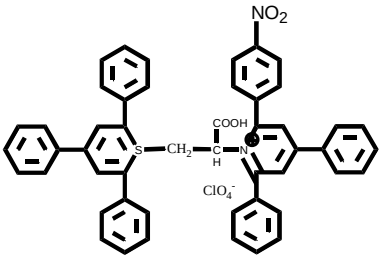
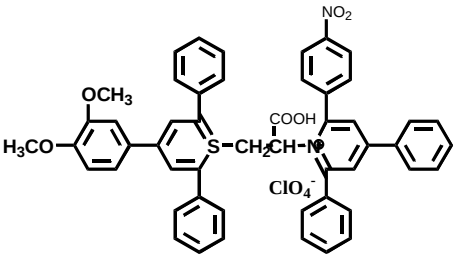
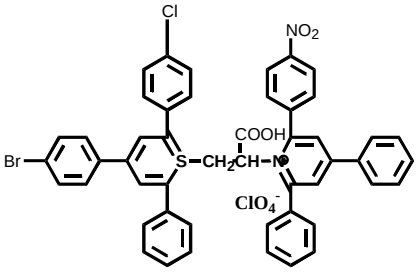
No. Comp.					*Other*
1	(7.97),(7.13)M	(7.90) S	(6.72) S	(8.09) S	OCH_3 (3.91),(3.66) CH (1.64)
6	(8.36),(8.35)M (7.74),(7.33)M	(8.55) S	(7.23) S	(8.17) S	OCH_3 (3.82),(4.15) CH (1.63)
7	(7.74),(7.66)M (7.49).(7.11)M	(8.36) S	(6.99) S	(8.77) S	CH (3.48)

***** By using DMSO-d_6 solve.***

Table (7)
Name and Structure of compounds (1-16).

No. Compounds	*Name*	*Structure*
1	1-{1-Carboxy-2-[4-(3,4-dimethoxy-phenyl)-2,6-diphenyl-1λ^4--thiopyran-1-yl]-ethyl}-2,4,6-triphenyl-pyridinium; perchlorate	
2	1-{2-[4-(4-Bromo-phenyl)-2-(4-chloro-phenyl)-6-phenyl-1λ^4-thiopyran-1-yl]-1-carboxy-ethyl}-2,4,6-diphenyl-pyridinium; perchlorate	
3	1-[1-Carboxy-2-(2,4,6-triphenyl-1λ^4-thiopyran-1-yl)-ethyl]-2,4,6-triphenyl-pyridinium ; perchlorate	
4	1-{1-Carboxy-2-[2-(4-nitro-phenyl)-4,6-diphenyl-1λ^4-thiopyran-1-yl]-ethyl}-2,4,6-triphenyl-pyridinium; perchlorate	

5	4-(4-Bromo-phenyl)-1-{2-[4-(4-bromo-phenyl)-2-(4-chloro-phenyl)-6-phenyl-1λ^4-thiopyran-1-yl]-1-carboxy-ethyl}-2-(4-chloro-phenyl)-6-phenyl-pyridinium; perchlorate	
6	4-(4-Bromo-phenyl)-1-{1-carboxy-2-[4-(3,4-dimethoxy-phenyl)-2,6-diphenyl-1λ^4-thiopyran-1-yl]-ethyl}-2-(4-chloro-phenyl)-6-phenyl-pyridinium; perchlorate	
7	4-(4-Bromo-phenyl)-1-{1-carboxy-2-[2-(4-nitro-phenyl)-4,6-diphenyl-1λ^4-thiopyran-1-yl]-ethyl}-2-(4-chloro-phenyl)-6-phenyl-pyridinium; perchlorate	
8	4-(4-Bromo-phenyl)-1-[1-carboxy-2-(2,4,6-triphenyl-1λ^4-thiopyran-1-yl)-ethyl]-2-(4-chloro-phenyl) -6-phenyl-pyridinium; perchlorate	
9	1-[1-Carboxy-2-(2,4,6-triphenyl-1λ^4-thiopyran-1-yl)-ethyl]-4-(3,4-dimethoxy-phenyl)-2,6-diphenyl- pyridinium; perchlorate	
10	1-{2-[4-(4-Bromo-phenyl)-2-(4-chloro-phenyl)-6-phenyl-1λ^4-thiopyran-1-yl]-1-carboxy-ethyl}-4-(3,4 -dimethoxy-phenyl)-2,6-diphenyl-pyridinium; perchlorate	
11	1-{1-Carboxy-2-[4-(3,4-dimethoxy-phenyl)-2,6-diphenyl-1λ^4-thiopyran-1-yl]-ethyl}-4-(3,4-dimethoxy-phenyl)-2,6-diphenyl pyridinium; perchlorate	

12	1-{1-Carboxy-2-[2-(4-nitro-phenyl)-4,6-diphenyl-1λ⁴-thiopyran-1-yl]-ethyl}-4-(3,4-dimethoxy-phenyl)-2,6-diphenyl-pyridinium; perchlorate	
13	1-{1-Carboxy-2-[2-(4 nitro-phenyl)-4,6-diphen yl-1λ⁴-thiopyran-1-yl]ethyl}-2-(4-nitro-phenyl)-4,6 -diphenyl-pyridinium; perchlorate	
14	1-[1-Carboxy-2-(2,4,6-triphenyl-1λ⁴-thiopyran-1-yl)-ethyl]-2-(4-nitro-phenyl)-4,6-diphenyl-pyridinium; perchlorate	
15	1-{1-Carboxy-2-[4-(3,4-dimethoxy-phenyl)-2,6-diphenyl-1λ⁴-thiopyran-1-yl]-ethyl}-2-(4-nitro-phenyl)-4,6-diphenyl-pyridinium perchlorate	
16	1-{2-[4-(4-Bromo-phenyl)-2-(4-chloro-phenyl)-6-phenyl-1λ⁴-thiopyran-1-yl]-1-carboxy-ethyl}-2-(4-nitro-phenyl)-4,6-d Pyridinium; perchl	

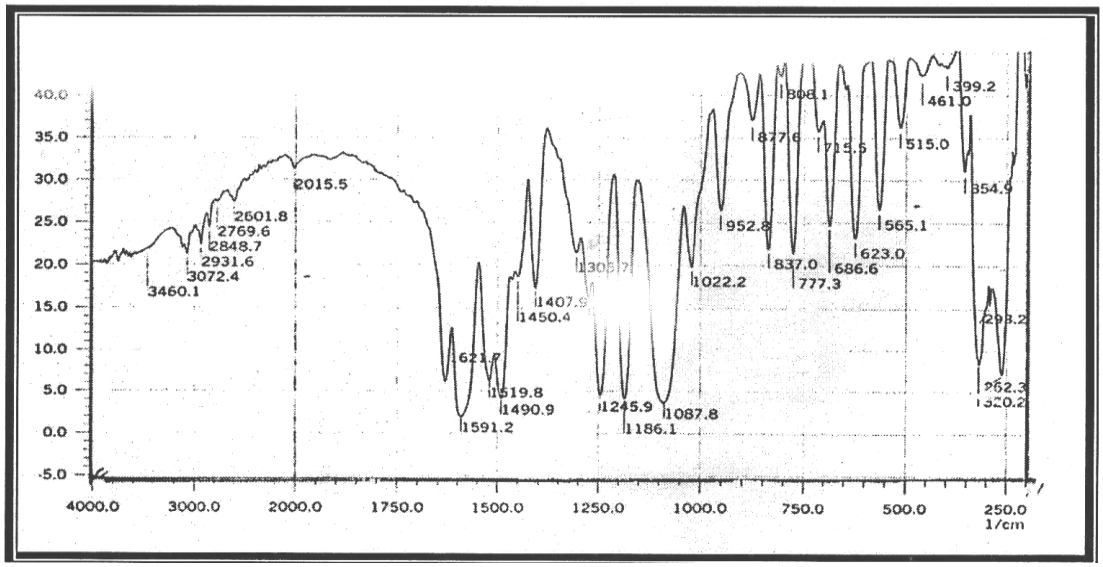


Fig. (1) Spectra I.R for Comp. (A).

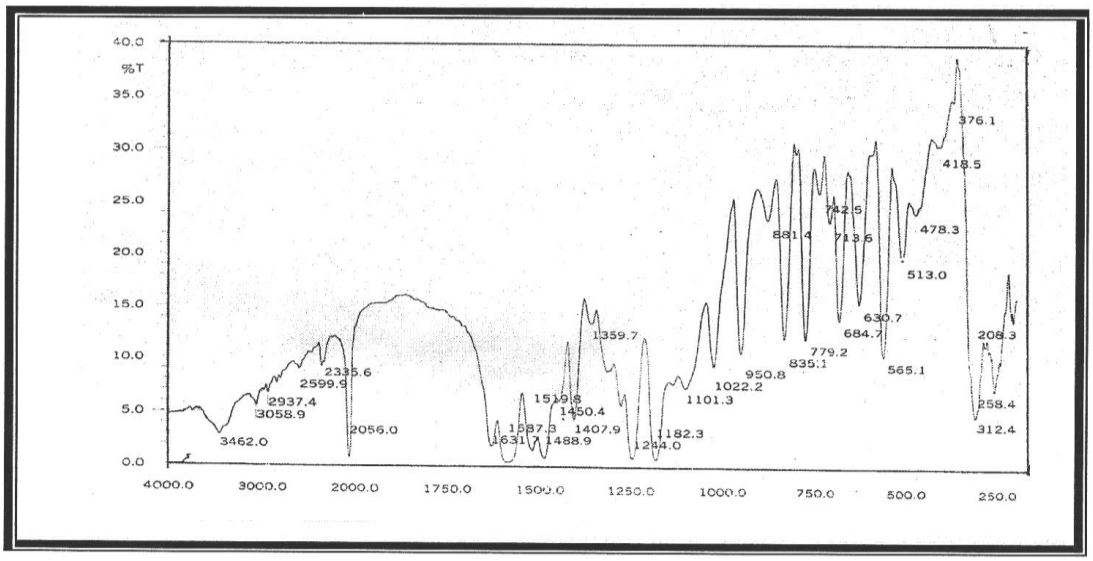


Fig. (2) Spectra I.R for Comp. (1).

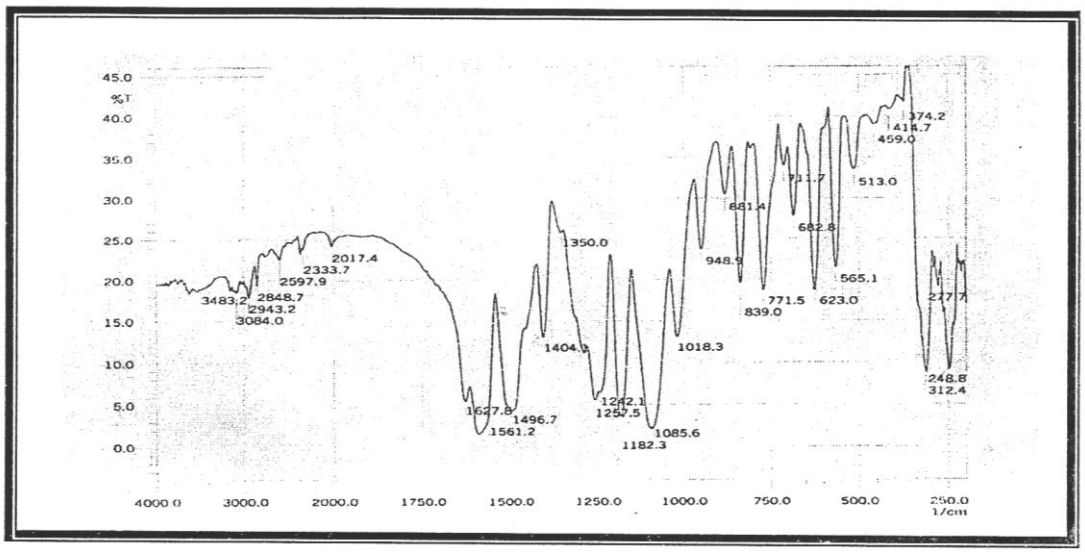


Fig. (3) Spectra I.R for Comp. (3).

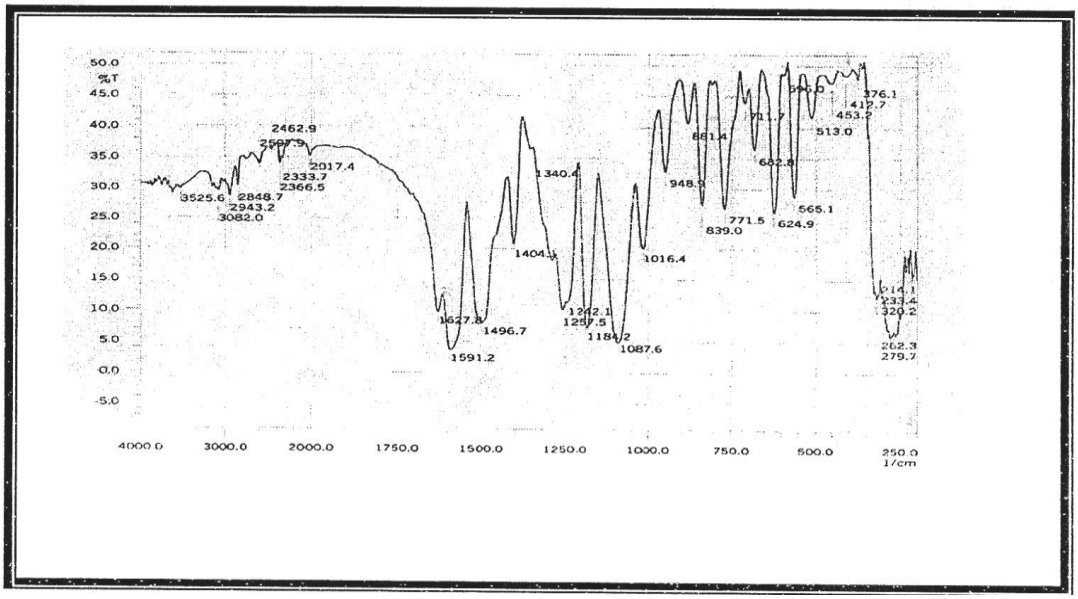


Fig. (4) Spectra I.R for Comp. (12).

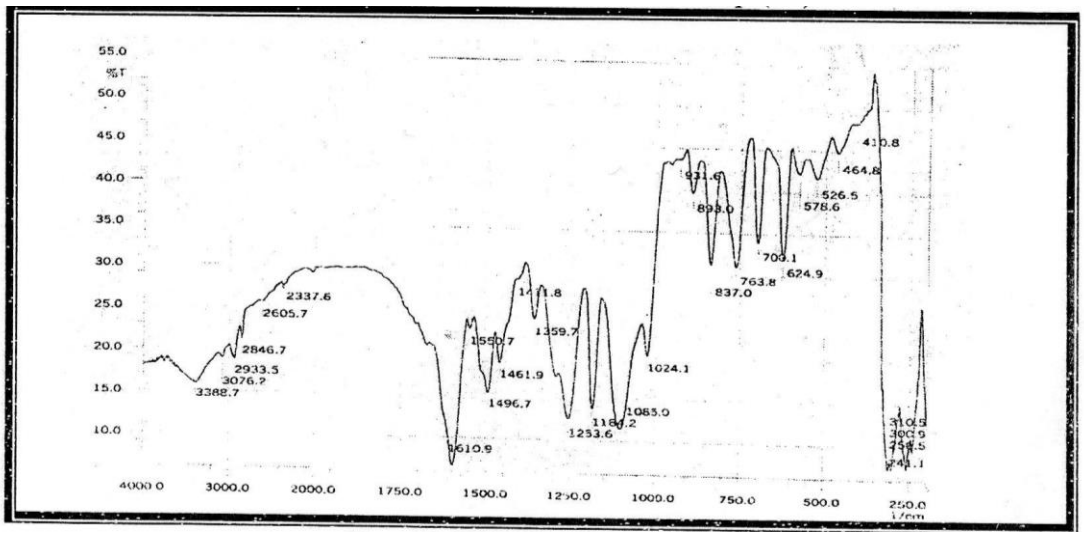


Fig. (5) Spectra I.R for Comp. (16).

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الخلاصة

تم تحضير اربع مركبات من مركبات البريدينيوم وذلك من خلال مفاعلة واحد مول من املاح البايريليوم (المحضرة مسبقا) مع مول واحد من الـ (٢-امينواثلين ثايول) في درجة حرارة الغرفة وتم تشخيصها طيفيا بوساطة طيف (الاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي والتحليل الكمي للعناصر).

ومن خلال مركبات البريدينيوم المحضرة تم مفاعلة واحد مول من مركبات البريدينيوم مع واحد مول من املاح البايريليوم (المحضرة مسبقا) في درجة حرارة اقل من (الصفر المئوي) ومن خلال هذه العملية تم الحصول على ستة عشر مركبا من مركبات الثايوبايرين بايريدينيوم بركلورات بمنتوج جيد جدا وتم تشخيصها طيفيا بوساطة طيف (الاشعة تحت الحمراء وطيف الرنين النووي المغناطيسي والتحليل الكمي للعناصر).