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Research Article

SYNTHESIS AND CHEMICAL STUDY OF NEW SULFONE COMPOUNDS

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Abstract

A series of sulfide , sulfoxide and sulfone compounds [1-15] were synthesized via condensation of benzoyl derivatives bromide with sulfur compounds like (mercapto benzoic acid) to yield sulfide compounds , in the next step ,sulfone compounds have been synthesized by oxidation of sulfide compounds by hydrogen peroxide to produce series of new sulfone compound . All steps of reactions followed by TLC and the structures of all compounds [1-15] were confirmed by chemical techniques like (FT.IR, H.NMR, {(C.H.N)-analysis} & melting points .

Keywords: sulfoxide , sulfone , thio , sulfur compounds , alkylation.

Introduction

The importance of sulfur compounds has long been recognized in the field of synthetic organic chemistry. organo sulfur chemistry has played a prominent role in our laboratory , which is bearing sulfur atom constitute the core structure of a number of biologically interesting compounds ,some of them are thiadiazole ,thiazepine , which are structural subunits of several biologically active compounds[1-4] . they have reported to demonstrate awide range of pharmacological activities[5] such asantifungal[6] ,antimicrobial[7,8] ,anticonvunsant[9] ,antitumor[10] ,antiviral[11]& their several derivatives are in clinical use . Sulfid&sulfone compounds have abroad range in synthesis of drugs via incorporation with other organic compounds to yield pharmaceutical drugs .

Sulfur compounds have been used extensively in the field of medicinal chemistry, where they occupy a central position in the development of new and novel therapeutic agents.

Experimental:

All chemicals used were supplied from BDH & Merck - company.

All measurements were carried out by :

1 – Melting points : electro thermal 9300 , melting point engineering LTD , U.K
2 – FT . IR spectra : fourrier transform infrared shimadzu 8300 – (FT . IR), KBr disc
3 – H.NMR-spectra: in DMSO- solvent , in Canada .
4- (C.H.N) – analysis : in Canada

Synthesis of Compounds [1-5]

A mixture of acetophenone (0.1 mole , 12g)with bromine (10 ml) were dissolved in (100ml) methanol with magnetic stirrer for (5hrs) , to produce 89% from compound [1] , which (0.1mole , 19.8 g) reacts with P-mercaptotoluin (0.1mole , 12.4g) in presence of ethanol & magnetic stirrer to yield compound [2] , which (0.1mole , 18g) reacts with (0.1 mole , 10g) of phenyl hydrazine under reflux for (3hrs) in presence ethanol to give compound [3] .To obtain compound[4] , (0,1mole , 33.2g)of compound [3] reacts with hydrogen peroxide under magnetic stirrer to yield compound [4] , which was oxidized by hydrogen peroxide & sodium tungstate toyield 80 % of compound [5] .

Synthesis of Compounds [6-9]

Compound[1] (0.1 mole , 19.8 g) reacts with P-mercapto benzoic acid (0.1mole , 15.4g) in presence of ethanol under magnetic stirrer to yield compound [6] , which (0.1mole , 27.2g) reacts with (0.1 mole , 15g) of P-amino acetanilde in presence of ethanol under reflux to produce compound [7] , which oxidized by hydrogen peroxide to give compound [8] ,then oxidized by hydrogen peroxide with sodium tungstate to yield 76 % compound [9] .

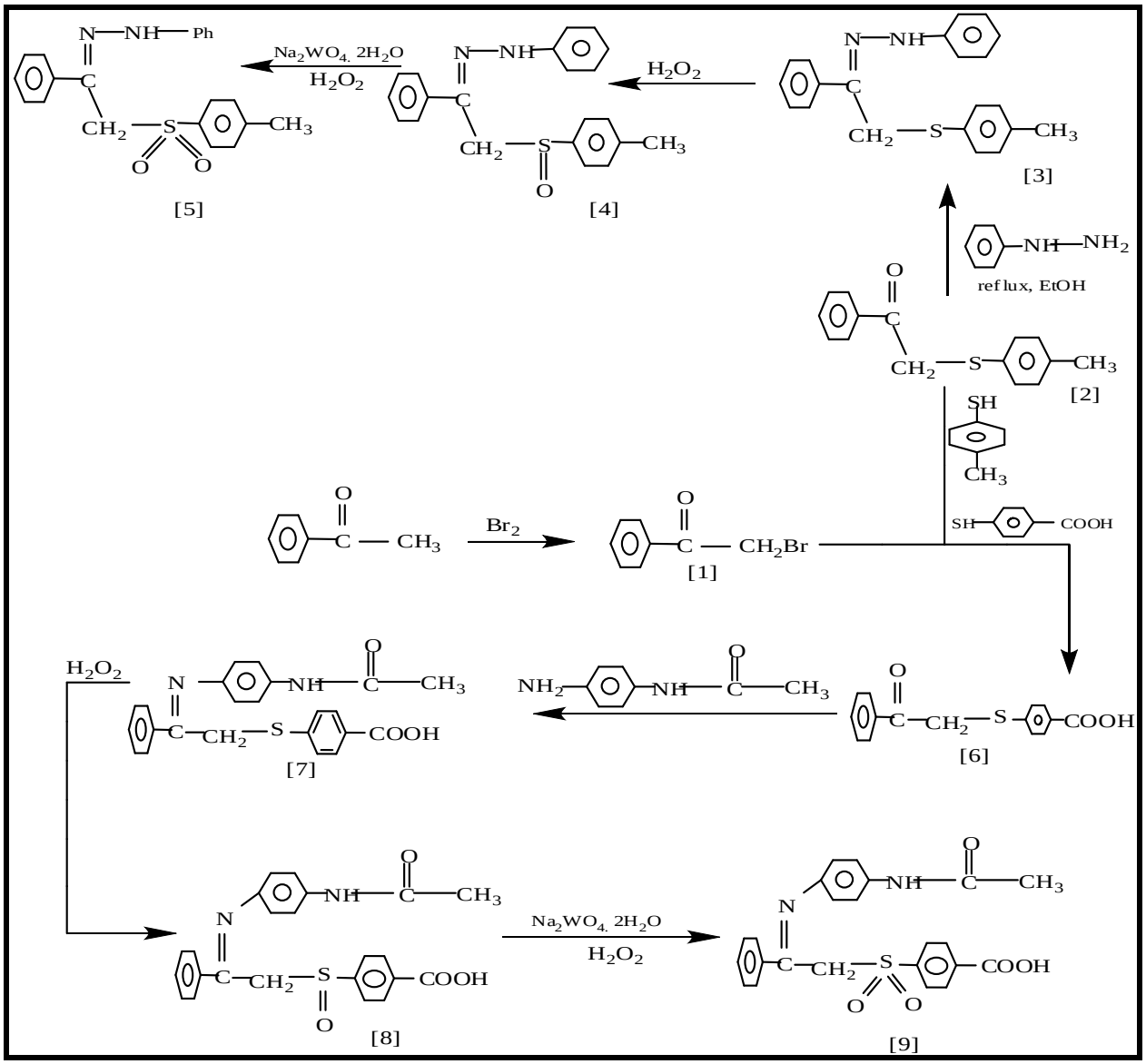
Synthesis of Compounds [10-12]

A mixture of 2-chloro aniline (0.1 mole , 12.7 g) with 2-mercapto acetophenon (0.1mole , 15.2 g) were reacted under reflux in presence of ethanol to yield compound [10] , which refluxed in presence of ethanol with sodium acetate to produce compound [11] , which oxidized by hydrogen peroxide to yield 79% of compound [12] .

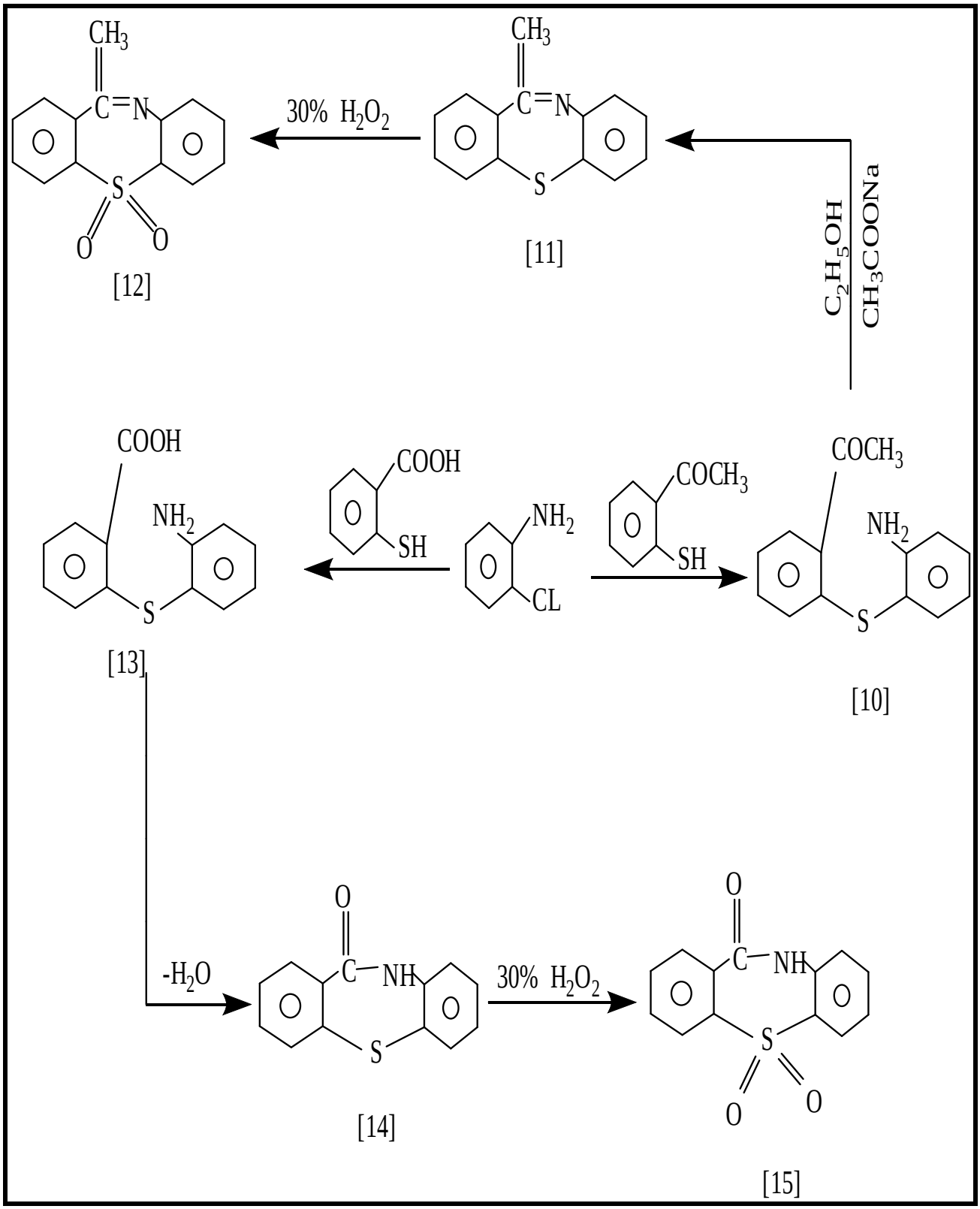
Synthesis of Compounds [13-15]

A refluxing mixture of 2-mercapto benzoic acid (0.1mole , 15.4 g)with 2-chloro aniline (0.1mole , 12.7 g) were reacted in presence of ethanol to give compound [13] ,which cyclized by reflux in presence of ethanol to yield compound [14] , which oxidized by hydrogen peroxide to yield 81% of compound [15] .

Scheme (1) :synthesis of compounds [1-9].



Scheme (2) :synthesis of compounds [11-15].



Results and Discussion

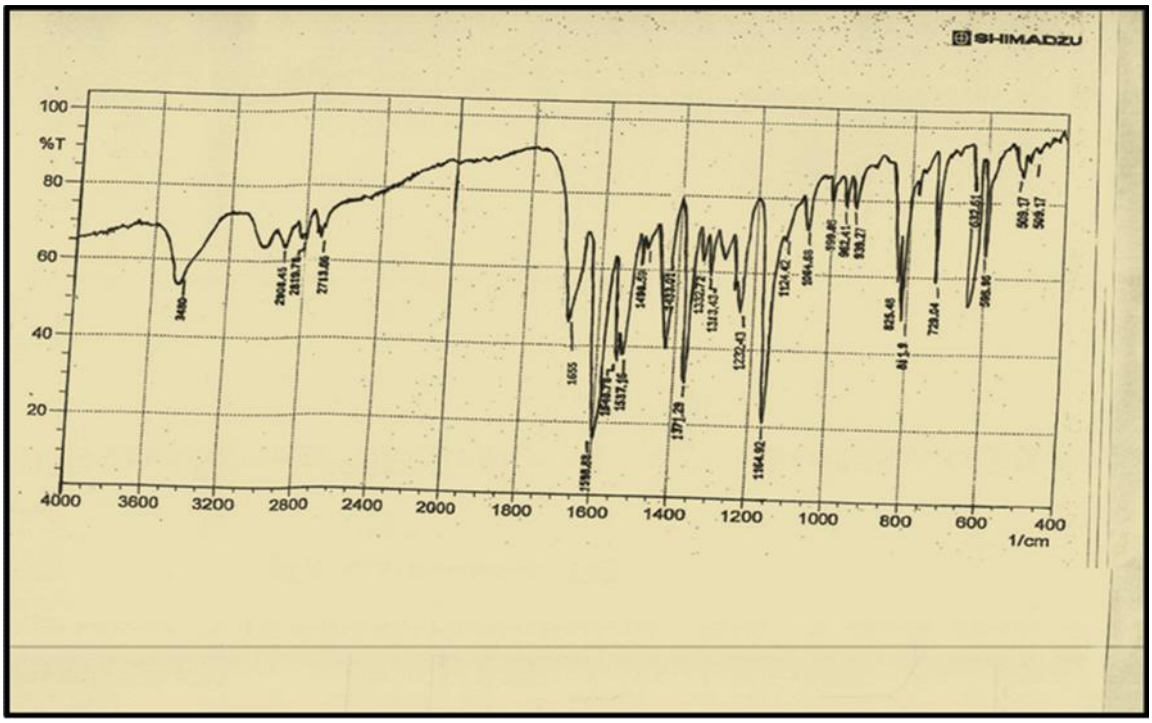
All the synthesized compounds [1-15] have been characterized their meting points and spectroscopic methods (FT.IR- spectra , H.NMR –spectra ,(C.H.N) - analysis .

Their FT.IR –spectrum showed an absorption band at (875) cm^{-1} in compound [1]due to the (C-Br) ,which disappear and other bands are appear at (1410-1334)cm^{-1} in compounds [2-9] due to [11,12] (CH_2-S) sulfid group , bands at (1614-1655)cm^{-1} in compounds [3-5] and [7-9] due to (C=N) imine group , bands at (1350-1360) cm^{-1} in compounds [5-9] due to (-CH_2-SO_2) sulphonegroup[12] .

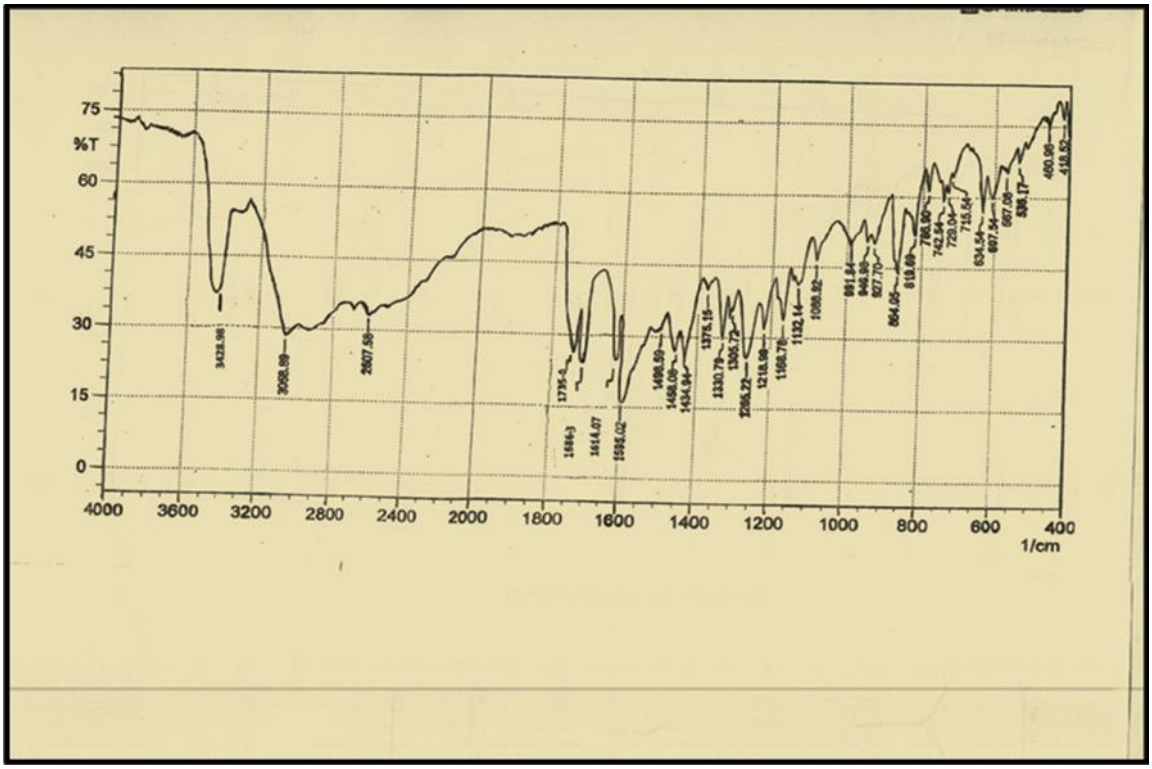
While compound [10] appeared bands at (3360) cm^{-1} due to (- NH_2) amine group and (1720) cm^{-1} due to (-CO –CH_3) carbonyl of ketone , which disappear and other bands are appear at (1630-1640) cm^{-1} due to (C=N) imine group (11-13) in compounds [11,12] and bands at (1690-1695)cm^{-1} due to (CO–NH_2) amide group in compounds [14,15] , bands at (1370-1385) cm^{-1} due to (-SO_2-) sulphone group[12] in compounds [12,15] .And other bands[11-13] are summarized in table (1) and figures (1-4) .

Table (1) : FT.IR –data (cm^{-1}) of compounds [1-15] .

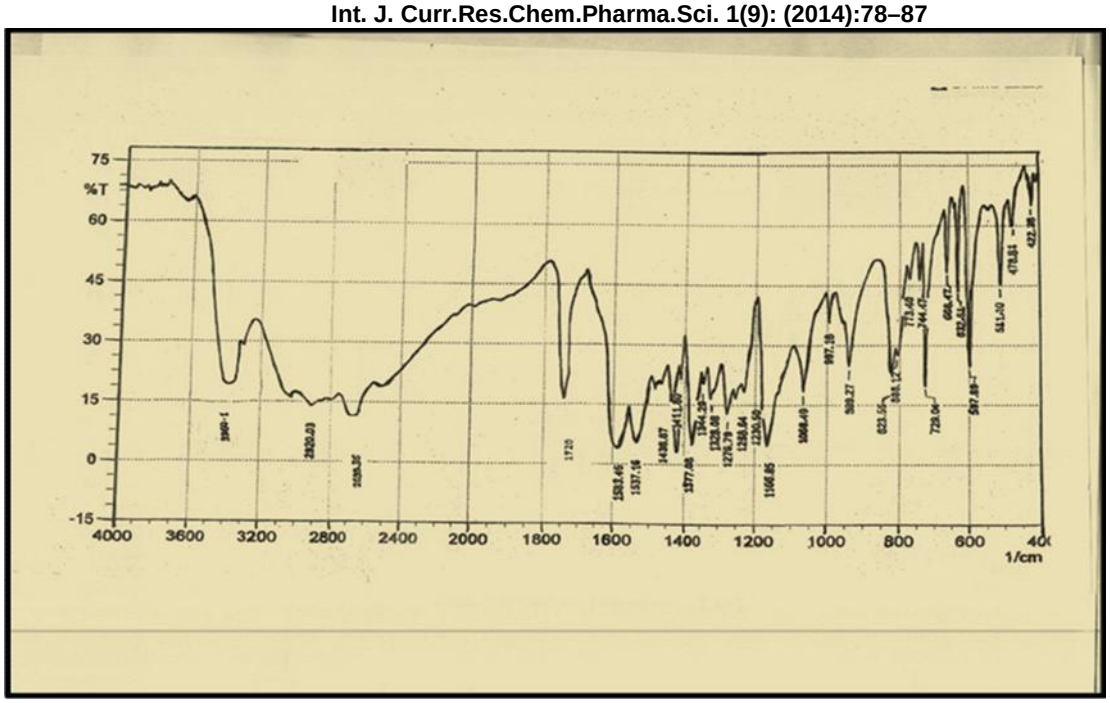
Comp. No.	$IR_{(KBR)}$ (Importance Groups)
[1]	(C-Br) :875 .
[2]	(CH_2-S):1410 , (C-S): 670 , (CH) aliphatic : 2930 .
[3]	(C=N) Imine group :1655 , (NH): 3480 , (CH_2-S): 1433, (CH) aliphatic :2908 .
[4]	(C=N) imine group : 1630 , (NH) : 3330 , (CH) aliphatic : 2925 .
[5]	(C=N) imine group : 1620 , (NH) 3350 , (CH) aliphatic : 2920 (CH_2- SO_2) sulfone group : 1350 .
[6]	(CH_2-S) :1390 , (C-S): 680 , (-COO-) carbonyl of carboxyl group : 1760 .
[7]	(C=N) imine group : 1614 , (NH-CO-) carbonyl of amide group : 1686 , (CH_2-S):1434 , (C-S) :634 , (-COO-)carbonyl of carboxyl group :1735 .
[8]	(C=N) imine group :1625 ,(NH-CO-) carbonyl of amide : 1995 , (COO-)carbonyl of carboxyl group : 1740 .
[9]	(C=N) imine group :1620 , (NH-CO-)carbonyl of amide :1998 , (COO-) carbonyl of carboxyl : 1745 ,(CH_2-SO_2-) sulfonyl group : 1360 .
[10]	(C-S) :668 , (CH_3-CO-) carbonyl of ketone : 1720 , (NH_2): 3360 .
[11]	(C=N) endo : 1505 , (C-S) :651 , (CH) aliphatic : 2908 , (C-N) endo cyclic : 1299 .
[12]	(C=N) endo :1510 , (-SO_2-) sulphonyl group : 1370 , (CH) aliphatic : 2955 .
[13]	(C-S) :675 ,(NH_2): 3340 , (COO-) carbonyl of carboxyl group : 1755 .
[14]	(C-S) : 670 , (NH-CO-) carbonyl of amide : 1690 .
[15]	(N-CO-) carbonyl of amide : 1695 , (SO_2) sulphonyl group : 1385 .



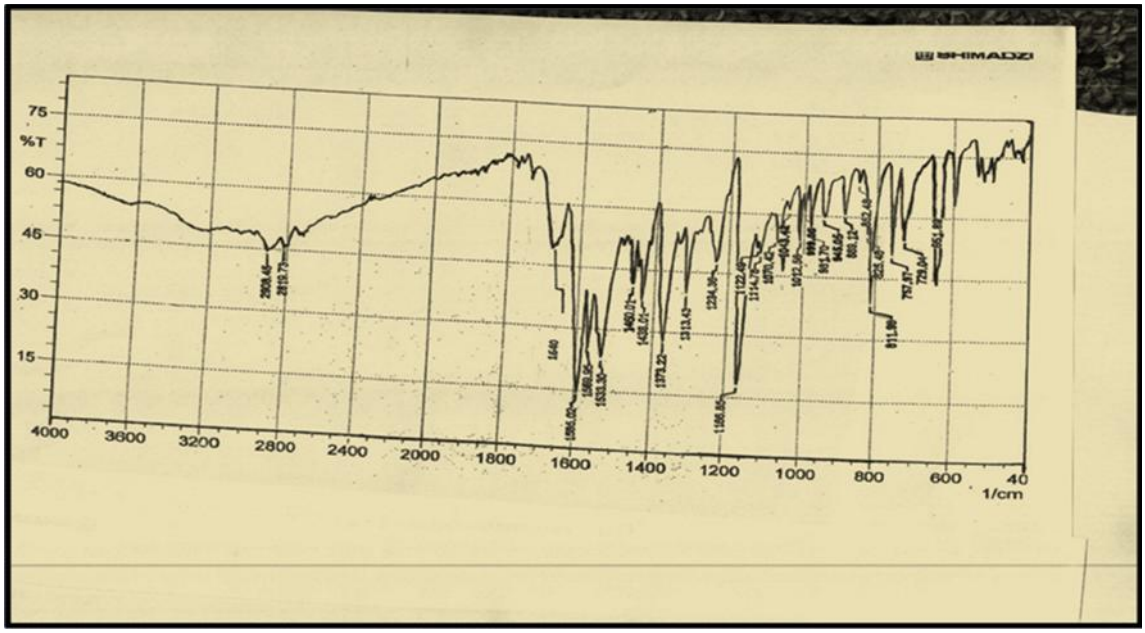
Fig(1): FT.IR of Compound [3]



Fig(2): FT.IR of Compound [7]



Fig(3): FT.IR of Compound [10]



Fig(4): FT.IR of Compound [11]

Their H.NMR –spectra showed signal due to ketone in compound [2] , which converted to (C=N) imine group and (NH) imine of hydrazine in compounds [3-5] , appearance signals such as :(NH-CO-) amide in compounds [7-9] , signals due to proton of carboxyl group (COOH) in compounds [6-9] .

While signals in compound[10] such as ƃ(3.54 ,2.2)which due to(NH_2,CO-CH_3) disappeared and other signals appeared such as ƃ(2.02,2.81) due to (CH_3-C=N) in compound [11,12] , ƃ(10.4 ,10.63) due to (CO-NH) amide group in compound [14,15].And other signals of functional groups[12,13] show in the following , table (2) and figures (5-7) .

Table (2) :H.NMR –data (δ_{PPM}) of compounds [1-15] .

Comp. No.	H.NMR (Important peaks)
[1]	2.7 (2H , CH_2-CO-) proton of ketone .
[2]	0.82 (3H , CH_3) , 3.03 (2H , CH_2-S) .
[3]	4.54 (1H , NH), 3.37 (2H , CH_2-S), 1.02 (3H , CH_3) .
[4]	4.74 (1H , NH) , 3.43 (2H , CH_2-SO) , 0.713 (3H , CH_3) .
[5]	4.81 (1H , NH) , 0.831 (3H , CH_3) , 3.9 (CH_2SO_2) .
[6]	2.7 (CH_2-CO-) proton of ketone , 13.41 (1H ,COOH) proton of carboxyl group .
[7]	4.12 (2H , CH_2 –S) , 13.42 (1H ,COOH) proton of carboxyl group , 10.24 (NH-CO-)of amide.
[8]	13.48 (1H ,COOH) , 10.43 (NH-CO-) amide .
[9]	13.93 (1H , COOH) , 10.5 (NH-CO-) amide .
[10]	3.54 (2H , NH_2) , 2.9 (3H , CH_3-CO)ketone .
[11]	2.02 (3H , CH_3-C=) .
[12]	2.81 (3H , CH_3-C=) .
[13]	5.51 (2H , NH_2) , 13.46 (1H , COOH) .
[14]	10.4 (1H , NH-CO-) amide .
[15]	10.63 (1H, NH-CO-) amide .

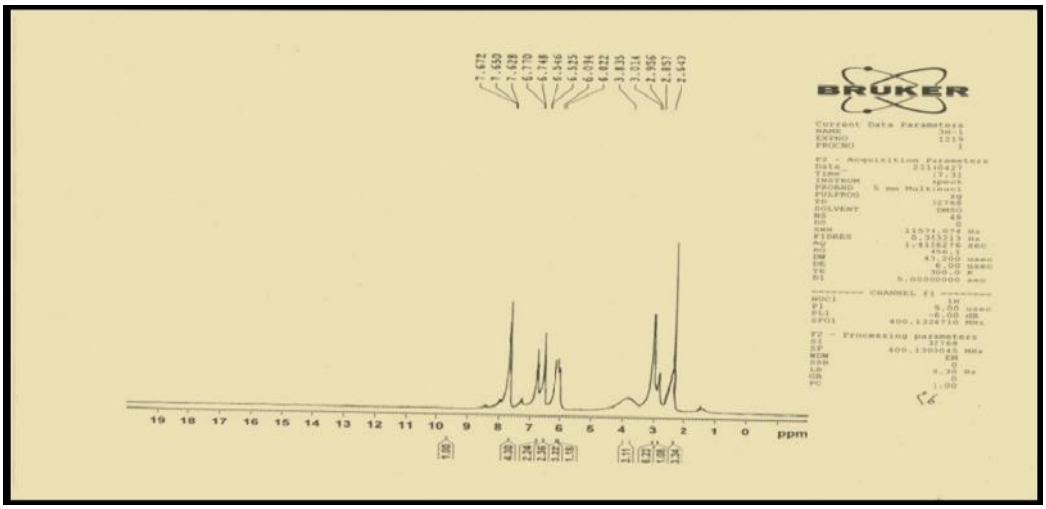


Fig (5): H.NMR of Compound [2]

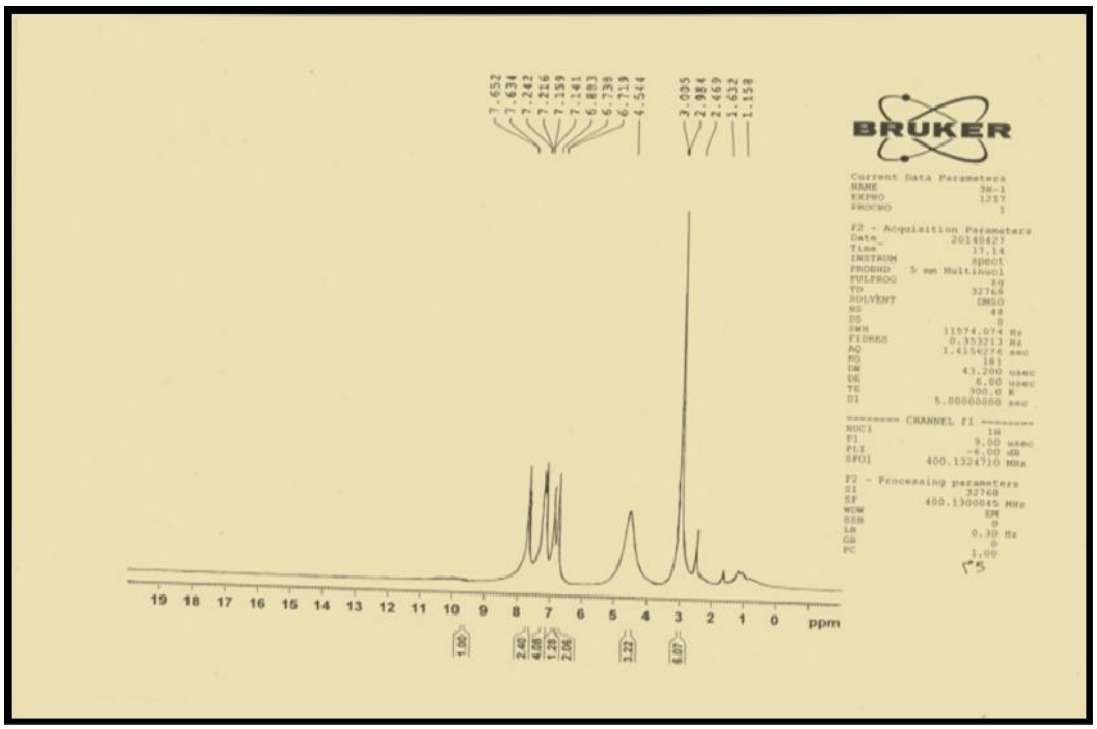


Fig (6): H.NMR of Compound [5]

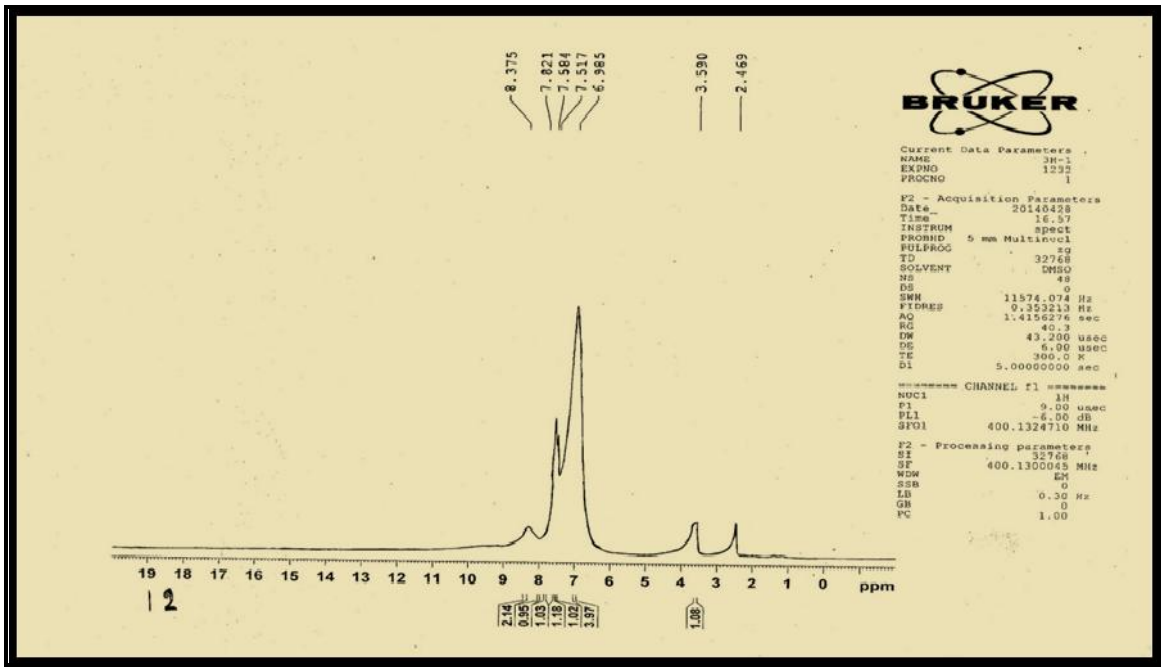


Fig (7): H.NMR of Compound [10]

Their (C.H.N)–analysis ,it was found from compared the calculated data with experimentally data of these compounds , the results were compactable . the data of analysis , M.F and melting points are listed in table (3).

Table (3) : physical properties & (C.H.N)-analysis of compounds [1-15].

Comp No.	M.F	M.P (C°)	Name of compounds	Calc./found.		
				C%	H%	N%
[1]	C_8H_7OBr	142	2-Phenyl –acetyl bromide	48.362 48.221	3.526 3.411	--- ---
[2]	$C_{15}H_{14}OS$	165	2-phenyl -1-(4- -methyl benzene)-aceto sulfide	65.934 65.842	7.692 7.55	--- ---
[3]	$C_{21}H_{20}N_2S$	189	2-phenyl-2-(aniline imine)-1-(4-methyl benzene)ethyl sulfide	75.903 75.842	6.024 6.00	8.433 8.401
[4]	$C_{21}H_{20}N_2OS$	197	2-phenyl-2-(aniline imine)-1-(4- -methyl benzene) ethyl sulfoxide	72.413 72.361	5.747 5.656	8.045 8.012
[5]	$C_{21}H_{20}N_2O_2S$	210	2-phenyl -2-(anilinoimine) -1-(4- -methyl benzene) ethyl sulfide	69.230 69.113	5.494 5.381	7.692 7.57
[6]	$C_{15}H_{12}O_3S$	181	2-phenyl -1-(4-carboxyl phenyl)- aceto sulfide	66.176 66.092	4.411 4.351	--- ---
[7]	$C_{23}H_{20}N_2O_3S$	200	2-(phenyl)-2-(4-acetanilide imine)-1-(4-carboxy phenyl) ethyl sulfide	68.316 68.25	4.95 4.88	6.930 6.900
[8]	$C_{23}H_{20}N_2O_4S$	215	2-(phenyl)-2-(4-acetanilide imine)-1-(4-carboxyphenyl)ethyl sulfoxide	65.714 65.675	4.761 4.71	6.666 6.61
[9]	$C_{23}H_{20}N_2O_5S$	222	2-(phenyl)-2-(4-acetanilide imine)-1-(4-carboxy phenyl) ethyl sulfone	63.302 63.21	4.587 4.501	6.422 6.371
[10]	$C_{14}H_{13}NOS$	187	2-amino-2-acetodiphenylsulfide	69.135 69.101	5.349 5.541	5.761 5.80
[11]	$C_{14}H_{11}NS$	205	5-methyl-2,3,6,7-dibenzo thiazepine	74.666 74.59	4.888 4.801	6.222 6.191
[12]	$C_{14}H_{11}NO_2S$	220	5-methyl -2,3,6,7-di benzothiazepinesulfone	65.369 65.241	4.280 4.201	5.447 5.39
[13]	$C_{13}H_{11}NO_2S$	210	2-amino-2-carboxyl diphenyl sulfide	63.673 63.611	4.489 4.381	5.714 5.62
[14]	$C_{13}H_9NOS$	230	2,3,6,7-dibenzothiazepine-5-one	68.722 68.693	3.964 3.872	6.167 6.08
[15]	$C_{13}H_9NO_3S$	245	2,3,6,7-dibenzo thiazepine-5-one–sulfone	60.231 60.187	3.474 3.491	5.405 5.34

Acknowledgement :

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