Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.6 No.9, 2014
www.iiste.org

Synthesis of (5,6,7,8)-Membered Rings of (Sulfur ,Nitrogen) via Cyclization of Imine Compounds

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Abstract
In this paper , synthesis of a series of compounds from hetero (Atoms, cycles) like (5,6,7,8-membered)ring via cyclo addition reaction of anil compound to produce compound [1-13], this reactions involved addition of carbonyl compounds like ((succinic acid , malonic acid , any compounds have two terminal from amine and thiol or carboxyl group)) to anil compounds to produce various membered rings. The structure of the newly synthesized compounds [1-13] were confirmed with (C.H.N)- analysis & substantiated with (FT.IR ,H.NMR) data & melting points.
Keywords : eight membered , sulphur ,macrocycle , Imine ,heterocycle, five membered.

Introduction :
Hetromacrocycles by far are the largest classical division of organic chemistry .
Hetero cycles bearing nitrogen ,sulphur ,oxygen, constitute the core structure of a number of biologically interesting compounds ,some of them are pyrazoles , imidazoles ,which are structural subunits of several biologically active compounds[1-4] .

Heterocycles have been used a scaffold to synthesize numerous therapeutic molecules , which are known for their medicinal importance as anticancer antibacterial ,antiseptics, & are known to be involved in a number of biological reactions such as inhibition of DNA ,RNA & protein synthesis[5-8].
The utility of anil compounds lay in their usefulness as synthons in the synthesis of bio active molecules , it has ben found that the activity of hetero cycles increases on the incorporation of anil groups [9-13] .

Experimental:
- All chemicals used were supplied from BDH & Fluka- company , purity 99.5 % .
- 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 was performed by CO.S.Q.C. Iraq
3 – H.NMR-spectra and (C.H.N) – analysis : in center lab – institute of earth and environmental science , al – byat university , Jordan .

Synthesis of compound [1].
Condensation reaction by refluxing ethanolic mixture of equimolar amounts (0.1 mole ,12.0 gm) of p-methyl benzaldehyde & (0.1 mole ,9.7 gm) of 2-amino thiophene were react for (2hrs), the precipitate was filtered & recrystallized from ethanol to produce 83% of anil compounds [1].

Synthesis of compounds [2-5]:
A mixture of compound [1] (0.01 mole , 2.01 gm)was reacted with one of {(0.01 mole,1.38 gm)of 2-mercapto benzaldehyde), (0.01mole, 1.19 gm of 2-amino benzaldehyde), (0.01 mole , 1.20 gm of salicyldehyde) ,(0.01mole , 0.75 gm of alanine)}, respectively , under reflux for (10hrs) in presence of anhydrous 1,5-dioxan (100) ml , the precipitate was filtered , dried ,& crystallized from absolute ethanol to produce % (86,84,82,86) respectively from compounds [2,3,4,5].

Synthesis of compounds [6-9]:
A mixture of compound [5] (0.01 mole , 2.58 gm)was reacted with one of {(0.01 mole,1.18 gm)of succinic acid), (0.01mole,1.04 gm of malonic acid), (0.01 mole , 0.78 gm of acetyl chloride) ,(0.01mole , 1.06 gm of benzaldehyde)}, respectively , with reflux for (6hrs) in presence of absolute ethanol (100) ml with drops of sodium ethoxide.
the precipitate was filtered , dried ,& crystallized from absolute ethanol to give % (82,85,87,86) respectively, from compounds [6,7,8,9].

Synthesis of compounds [10,11]:

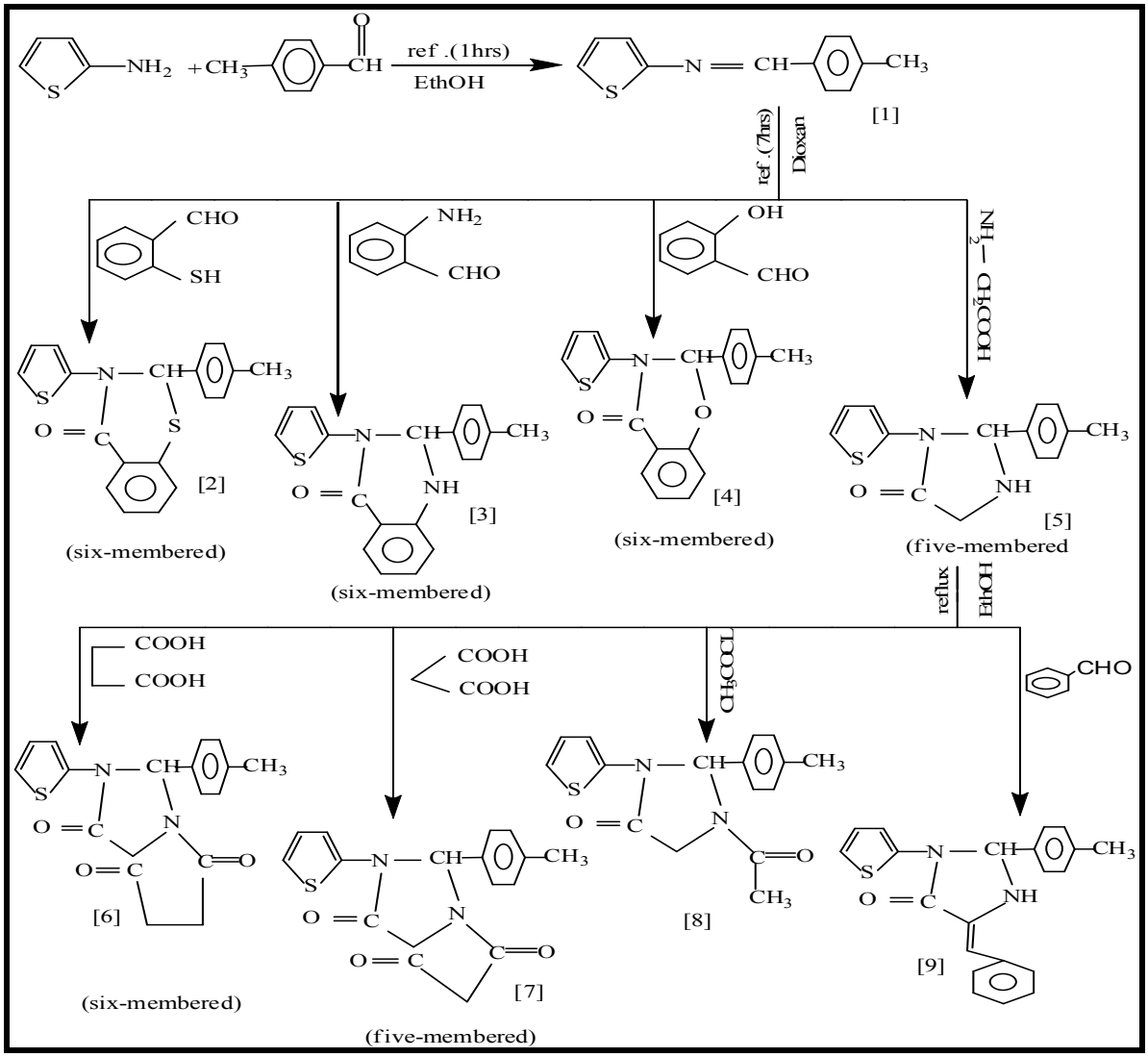
A mixture of compound [8] (0.01 mole , 3 gm)was reacted with one of {(0.01 mole,1.04 gm)of malonic acid), (0.01mole,1.18 gm of succinic acid)} respectively under reflux for (6hrs) in presence of absolute ethanol (100) ml with drops of sodium ethoxide, the precipitate was filtered , dried ,& crystallized from absolute ethanol to produce % (87,85) respectively, from compounds [10,11].

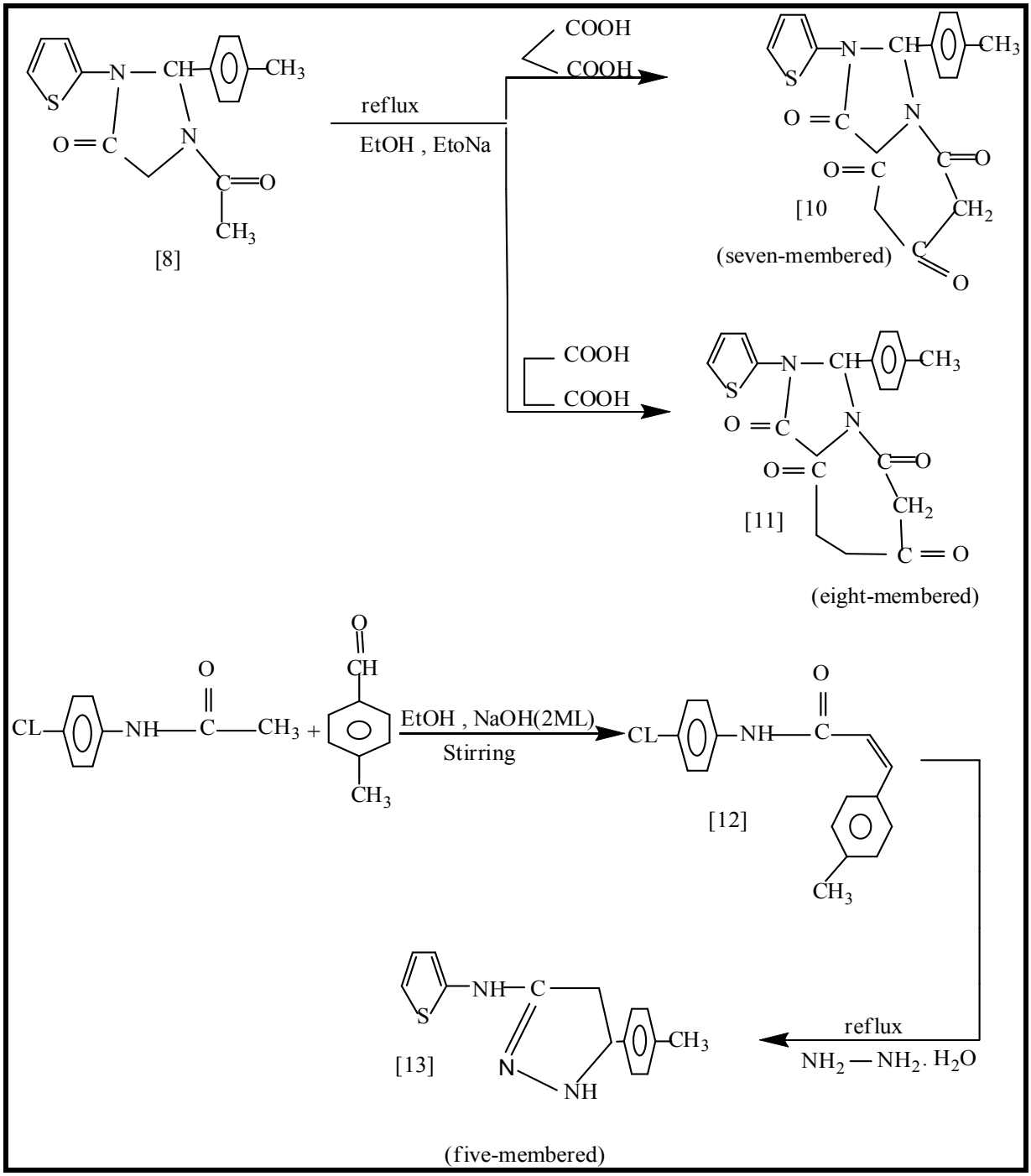
Synthesis of compounds [12,13]:

A mixture of p-methyl benzal dehyde (0.1mole ,1.2 gm)with P-chloro acetanilide(0.1 mole , 1.69gm) in ethanol (100) ml& 2ml of (3% sodium hydroxide solution)with stirring for (5hrs) at room temperature ,then refluxed for (8hrs), , the precipitate was filtered , dried ,& crystallized from ethanol to produce 88 % of compounds [12].

To prepare compound [13], mixture of compound [12] (0.01 mole , 2.71 gm) & hydrazine(0.01 mole , 0.50 gm) under reflux for (7hrs) in presence of absolute ethanol (100) ml, the precipitate was filtered , dried ,& crystallized from ethanol to produce % 86 of compound [13].

Scheme Reaction :



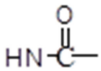


Results & Discussion :

In this study , we wish to report on anew approach for preparation of hetero atoms cycles (S,N,O) & hetero cycles (5,6,7,8-membered) ring from compounds [1-13].

Their FT.IR-Spectrum showed an absorption band at (1620) cm^{-1} in compound [1] due to the (CH=N) anil group ,which disappear & other bands are appear at {(1685-1698) cm^{-1} for amide[15] group (—C(=O)—N—),(1530-1545) cm^{-1} for (C-N) endocycle & bands due to(C-S , C-NH , C-O , CH-NH)} in formed compounds [2-13] also new bands appeared such as (C=CH) due to alkene in compounds [9,12] ,bands at (1710-1725)cm^{-1} due to carbonyl of ketone in forned cycles in compounds [6-11] , & other bands are summarized in table (1) & figure (1-4).

Their H.NMR-Spectra showed signal at 8.89 ∫ for proton of azomethine group (CH=N) in compound [1] which disappear & new signals appear at (5.96 ∫ for CH-S)[16] in compound [2] , (3.9 ∫ for CH-O) in

compound[4] ,(3.09 ∫ - 3.19 ∫ for CH-NH in cyclic compounds[3,5-11,13] , (9.72 ∫ for proton of amide ) in compound [12] as result of formed cycles ,& other data of functional groups show in the following , Table (2) & figure (5-8) .

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

Acknowledgment :
I would like to express my thanks to Mr.Samer in Jordan for providing (C.H.N) element analytical , and H.NMR –spectra & melting points And express my thanks to(United Arabic Company) & ((Zaidan Company of Chemical)) for supplied some materials .

Table (1): (FT.IR)-data (cm^{-1}) of compounds [1-13].

ComP. no.	$I.R_{(KBR)}$ (Important Groups)
[1]	(CH=N) azomethine group : 1620
[2]	(O=C-N) amide of endocyclic :1698,(C-N) endocyclic :1537 ,(C-S) endocyclic :675 ,1404, (C=C) aromatic:1581 .
[3]	(O=C-N) amide of endocyclic :1690,(C-N) endocyclic :1540 ,(NH): 3320 .
[4]	(O=C-N) amide:1698,(C-N) endocyclic :1540 ,(C-O-C): 1050 .
[5]	(O=C-N) amide:1685,(C-N) endocyclic :1535 ,(NH): 3330, (CH) aliphatic :2930 .
[6]	(O=C-N) amide:1690,(C-N) endocyclic :1530 ,() ketone: 1725, (CH) aliphatic :2950 .
[7]	(O=C-N) amide:1680,(C-N) endocyclic :1498 ,() ketone: 1717, (CH) aliphatic :2925 .
[8]	(O=C-N) amide:1690,(C-N) endocyclic :1544 ,(CH) aliphatic :2930.
[9]	(O=C-N) amide:1695,(C-N) endocyclic :1545 ,(NH):3320,(=CH) alkene:3080 .
[10]	(O=C-N) amide:1686,(C-N) endocyclic :1537 ,() ketone: 1720, (CH) aliphatic :2920 .
[11]	(O=C-N) amide:1690,(C-N) endocyclic :1540 ,() ketone: 1725, (CH) aliphatic :2940 .
[12]	(O=C-N) amide:1695,(=CH) alkene: 3050 .
[13]	(C=N) azomethine:1620,(N-N) endocyclic :1400 ,(NH) : 3330, (CH) aliphatic :2940 .

Table (2): H.NMR-data(δ_{ppm}) of compounds [1-13] .

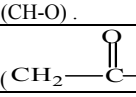
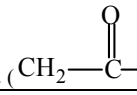
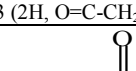
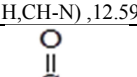
Comps	$H.NMR_{(DMF)}$ (Important peaks)
[1]	8.89 {1H ,(CH=N)} proton of azomethine group.
[2]	6.34-7.8 (Ar-H) , 5.96 (CH-S).
[3]	6.6-7.8 (Ar-H) ,3.11 (CH-NH) .
[4]	6.36-7.3 (Ar-H) , 3.9 (CH-O) .
[5]	3.09 (CH-NH) , 9.96 () .
[6]	3.1 (1H ,CH-N), 12.2 (O=C-CH_2-) ,10.2 () .
[7]	3.19 (1H ,CH-N) , 12.79 (2H , O=C-CH_2).
[8]	3.1 (1H , CH-N), 10.1 (), 10.5 () .
[9]	2.3 (1H ,CH=C), 3.4 (CH-NH), 6.4-7.2 (Ar-H).
[10]	3.12 (1H,CH-N), 12.3 (2H, O=C-CH_2-C=O) .
[11]	3.3(1H,CH-N) ,12.59 (), 12.72(O=C-CH_2-C=O) .
[12]	9.72 (), 2.63 (CH=CH), 6.34-7.56 (Ar -H) , 1.01 (CH_3) .
[13]	1.2 (2H,CH_2 –C) , 3.2 (CH-NH) , 6.4- 7.2 (Ar- H) , 1.2 (CH_3) .

Table (2): physical properties & (C.H.N)- analysis of compounds [1-13].

Comps	M.F	M.P (C°)	Name of compounds	Calculation/Found		
				C%	H%	N%
[1]	$C_{12}H_{11}N_1S_1$	161	2-(4¯Toluine)- thiophenidine .	71.641 71.342	5.472 5.211	6.965 6.654
[2]	$C_{19}H_{15}NOS_2$	242	2-(4¯Toluine)- 3-thiophenidine-5,6- benzo-1,3-Thiazane-4-one.	67.655 67.462	4.451 4.318	4.154 4.310
[3]	$C_{19}H_{16}N_2OS$	218	2-(4¯Toluine)- 3-thiophenidine-5,6- benzo-pipyrimidine-4-one.	71.25 71.012	5.00 5.021	8.750 8.592
[4]	$C_{19}H_{15}NO_2S$	235	2-(4¯Toluine)- 3-thiophene-1-oxo-5,6- benzo-pipyrimidine-4-one.	71.028 71.320	4.672 4.711	4.361 4.451
[5]	$C_{14}H_{14}N_2OS$	195	2-(4ˉ- Toluine)- 3-thiophene Imidazoline-4-one.	65.116 65.014	5.426 5.201	10.852 10.312
[6]	$C_{18}H_{16}N_2O_3S$	238	3-(2ˉ- Thiophene) -2-(4ˉ-Toluine)-1,5-(2ˉ,5ˉ- dione–azane)–imadazol-4-one.	63.529 63.342	4.705 4.611	8.235 8.301
[7]	$C_{17}H_{14}N_2O_3S$	222	3-(2ˉ- Thiophene)-2-(4ˉ-Toluine)-1,5-(2ˉ,4ˉ-di one –azolidine)–imadazol-4-one.	62.576 62.328	4.294 4.271	8.588 8.401
[8]	$C_{16}H_{16}N_2O_2S$	200	2-(4ˉ- Toluine)-3-thiophene-1-aceto- Imidazoline-4-one.	64.00 64.018	5.333 5.350	9.333 9.114
[9]	$C_{21}H_{18}N_2OS$	210	3-(2ˉ- Thiophene) -2-(4ˉ-Toluine)-1,5-(2ˉ,4ˉ ,6ˉ-Tri one –azecane)–imadazol-4-one.	72.832 72.672	5.202 5.151	8.092 8.001
[10]	$C_{19}H_{16}N_2O_4S$	240	3-(2ˉ- Thiophene)-2-(4ˉ-Toluine)-1,5-(2ˉ,4ˉ ,6ˉ -Tri one –azepane)–imadazol-4-one.	61.956 61.813	4.347 4.238	7.608 7.516
[11]	$C_{20}H_{18}N_2O_4S$	229	2-(4ˉ- Toluine)- 3-thiophene-5-styrene- Imidazoline-4-one.	62.827 62.719	4.712 4.623	7.329 7.113
[12]	$C_{16}H_{14}N_1O_1Cl$	165	N-(4-Chloro phenyl)-3-Toluine acrylamide.	70.718 70.651	5.156 5.08	5.156 5.201
[13]	$C_{16}H_{16}N_3Cl$	176	4-[(5ˉ -Toluine-4ˉ,5ˉ -dihydro pyrazol-3ˉ -yl)amino] chloro benzene.	67.250 67.161	5.604 5.587	14.711 14.511

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