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Synthesis of compounds of hetero (Atoms, cycles) via anil compounds

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ABSTRACT - In this paper, synthesis of a series ofcompounds of hetero(Atoms, cycles) from (5,6,7,8-membered) ring via cyclo addition reaction of anil compound to produce compound [1-13]. The structure of the newly synthesized compounds [1-13] were confirmed with (C.H.N)- analysis and substantiated with (FT.IR, H.NMR) data and melting points.

Key words - heterocyclic, Eightmemberd ring, Cyclo addition, Anil

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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, and are known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis[5-8].

The utility of anil compounds lay in their usefulness as synthonsin the synthesis of bio active molecules, it has ben found that the activity of hetero cycles increases on the incorporation of anil groups [9-14].

EXPERIMENTAL METHODOLOGY

– All chemicals used were supplied from BDH and Fluka- company, purity 99.5 per cent.

– All measurements were carried out by :

Melting points :

Electro thermal 9300, melting point engineering LTD, U.K

FT. IR spectra :

Fourrier transform infrared shimadzu 8300 – (FT. IR), KBr disc was performed by CO.S.Q.C. Iraq

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 equimolaramounts (0.1 mole,12.0 g) of p-methyl benzaldehyde and (0.1 mole,9.7 g) of 2-amino thiophene were react for (2hrs), the precipitate was filtered and recrystallized from ethanol to produce 83 per cent of anil compounds [1].

Synthesis of compounds [2-5]:

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

Synthesis of compounds [6-9]:

A mixture of compound [5] (0.01 mole, 2.58g)was reacted with one of {(0.01 mole,1.18 g)of succinic acid), (0.01 mole, 1.04 g of malonic acid), (0.01 mole, 0.78gm of acetyl chloride), (0.01 mole, 1.06g of benzaldehyde)}, respectively, with reflux for (6hrs) in presence of absolute ethanol (100) ml with drops of sodium ethoxide. The precipitate was filtered, dried, and crystallized from absolute ethanol to give per cent (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 g)was reacted with one of {(0.01 mole, 1.04 g)of malonic acid), (0.01mole, 1.18 g 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, and crystallized from absolute ethanol to produce per cent (87, 85), respectively, from compounds [10, 11].

Synthesis of compounds [12, 13]:

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

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

EXPERIMENTAL FINDINGS AND ANALYSIS

In this study, we wish to report on anew approach for preparation of hetero atoms cycles (S,N,O) and 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 and other bands are appear at {(1685-1698) cm^{-1} for amide[15] group (—C(=O)—N—) (1530-1545) cm^{-1} for (C-N) endocycle and 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], and other bands are summarized in Table 1 and Fig. 1-4.

Their H.NMR-Spectra showed signal at 8.89□ for proton of azomethine group (CH=N) in compound [1] which disappear and 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 (HN - C(=O)–) in compound [12] as result of formed cycles, and other data of functional groups show in the following Table 2 and Fig. 5-8.

Their (C.H.N)- analysis and melting points, it was found from compared the calculated data with experimentally data of

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

Com P. 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 ,(—C(=O)—) ketone: 1725, (CH) aliphatic :2950 .
[7]	(O=C-N) amide:1680,(C-N) endocyclic :1498 ,(—C(=O)—) 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 ,(—C(=O)—) ketone: 1720, (CH) aliphatic :2920 .
[11]	(O=C-N) amide:1690,(C-N) endocyclic :1540 ,(—C(=O)—) 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]

Comp. No.	$H.NMR_{(DMF)}$ (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 (CH_2—C(=O)—N) .
[6]	3.1 (1H ,CH-N), 12.2 (O=C-CH_2-) ,10.2 (CH_2—C(=O)—N) .
[7]	3.19 (1H ,CH-N) , 12.79 (2H , O=C-CH_2).
[8]	3.1 (1H , CH-N), 10.1 (CH_2—C(=O)—N), 10.5 (CH_3—C(=O)—N) .
[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 (CH_2—C(=O)—C), 12.72(O=C-CH_2-C=O) .
[12]	9.72 (—C(=O)—NH), 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 3 : Physical properties and (C-H-N)- analysis of compounds [1-13]

Comp. no	M.F	M.P (C°)	Name of compounds	Calc. /Found		
				C%	H%	N%
[1]	$C_{12}H_{11}N_1S_1$	161	2-(4¯Toluine)-thiophenidine .	71.641	5.472	6.965
				71.342	5.211	6.654
[2]	$C_{19}H_{15}NOS_2$	242	2-(4¯Toluine)- 3-thiophenidine-5,6- benzo-1,3-	67.655	4.451	4.154
			Thiazane-4-one.	67.462	4.318	4.310
[3]	$C_{19}H_{16}N_2OS$	218	2-(4¯Toluine)- 3-thiophenidine-5,6- benzo-	71.25	5.00	8.750
			pipyrimidine-4-one.	71.012	5.021	8.592
[4]	$C_{19}H_{15}NO_2S$	235	2-(4¯Toluine)- 3-thiophene-1-oxo-5,6- benzo-	71.028	4.672	4.361
			pipyrimidine-4-one.	71.320	4.711	4.451
[5]	$C_{14}H_{14}N_2OS$	195	2-(4¯-Toluine)- 3-thiophene Imidazoline-4-one.	65.116	5.426	10.852
				65.014	5.201	10.312
[6]	$C_{18}H_{16}N_2O_3S$	238	3-(2¯- Thiophene) -2-(4¯-Toluine)-1,5-(2¯,5¯ - di	63.529	4.705	8.235
			one –azane) – imadazol-4-one.	63.342	4.611	8.301
[7]	$C_{17}H_{14}N_2O_3S$	222	3-(2¯- Thiophene) -2-(4¯-Toluine)-1,5-(2¯,4¯-di one	62.576	4.294	8.588
			–azolidine) – imadazol-4-one.	62.328	4.271	8.401
[8]	$C_{16}H_{16}N_2O_2S$	200	2-(4¯-Toluine)- 3-thiophene-1-aceto- Imidazoline-	64.00	5.333	9.333
			4-one.	64.018	5.350	9.114
[9]	$C_{21}H_{18}N_2OS$	210	3-(2¯- Thiophene) -2-(4¯-Toluine)-1,5-(2¯,4¯ ,6¯ -Tri	72.832	5.202	8.092
			one –azecane) – imadazol-4-one.	72.672	5.151	8.001
[10]	$C_{19}H_{16}N_2O_4S$	240	3-(2¯- Thiophene) -2-(4¯-Toluine)-1,5-(2¯,4¯ ,6¯ -Tri	61.956	4.347	7.608
			one –azepane) – imadazol-4-one.	61.813	4.238	7.516
[11]	$C_{20}H_{18}N_2O_4S$	229	2-(4¯-Toluine)- 3-thiophene-5-styrene-	62.827	4.712	7.329
			Imidazoline-4-one.	62.719	4.623	7.113
[12]	$C_{16}H_{14}N_1O_1Cl$	165	N-(4-Chloro phenyl)-3-Toluine acrylamide.	70.718	5.156	5.156
				70.651	5.08	5.201
[13]	$C_{16}H_{16}N_3Cl$	176	4-[(5¯ -Toluine-4¯,5¯ -dihydro pyrazol-3¯ -yl)amino]	67.250	5.604	14.711
			chloro benzene.	67.161	5.587	14.511

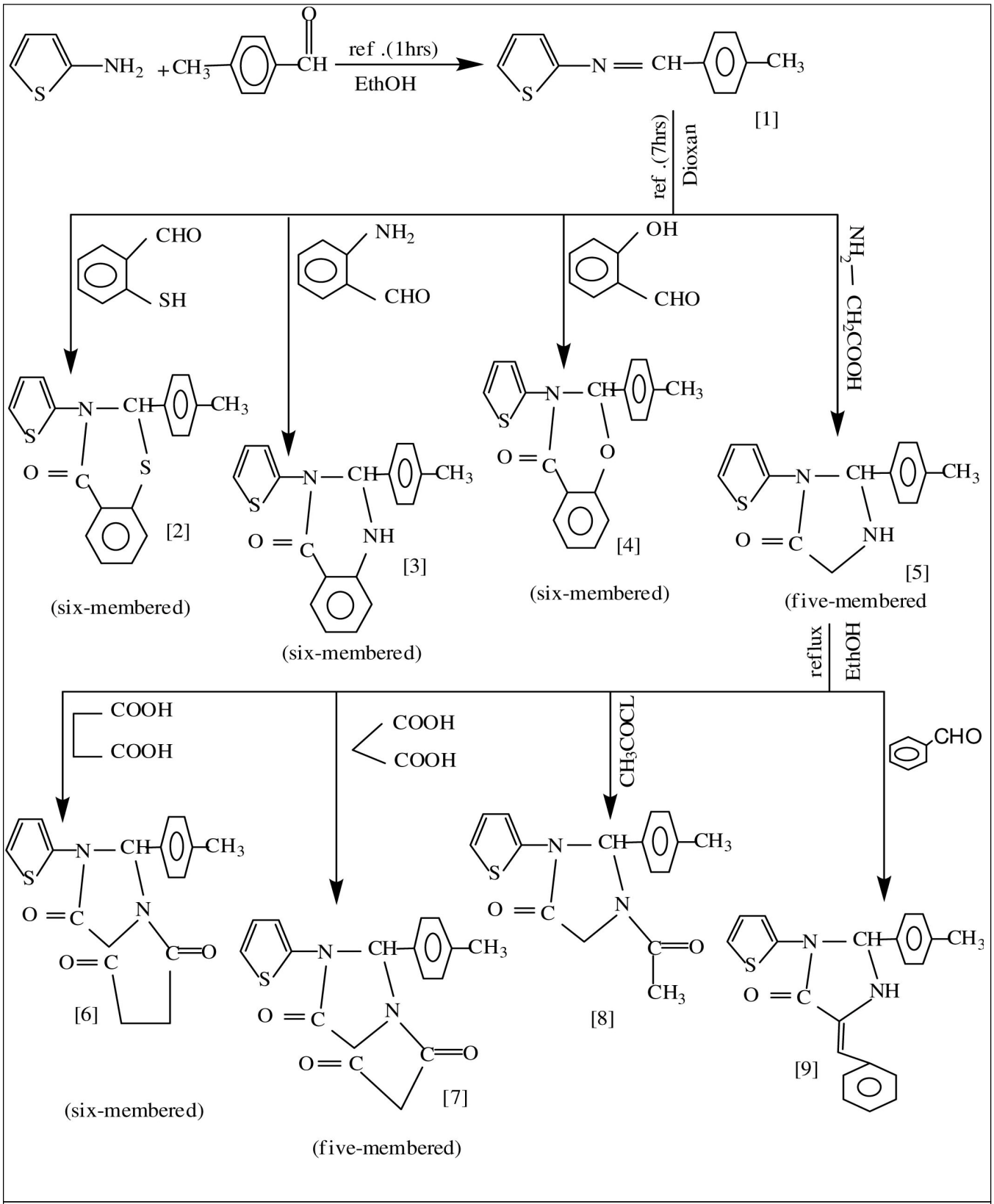

Fig. 1 to 9 : Scheme reaction

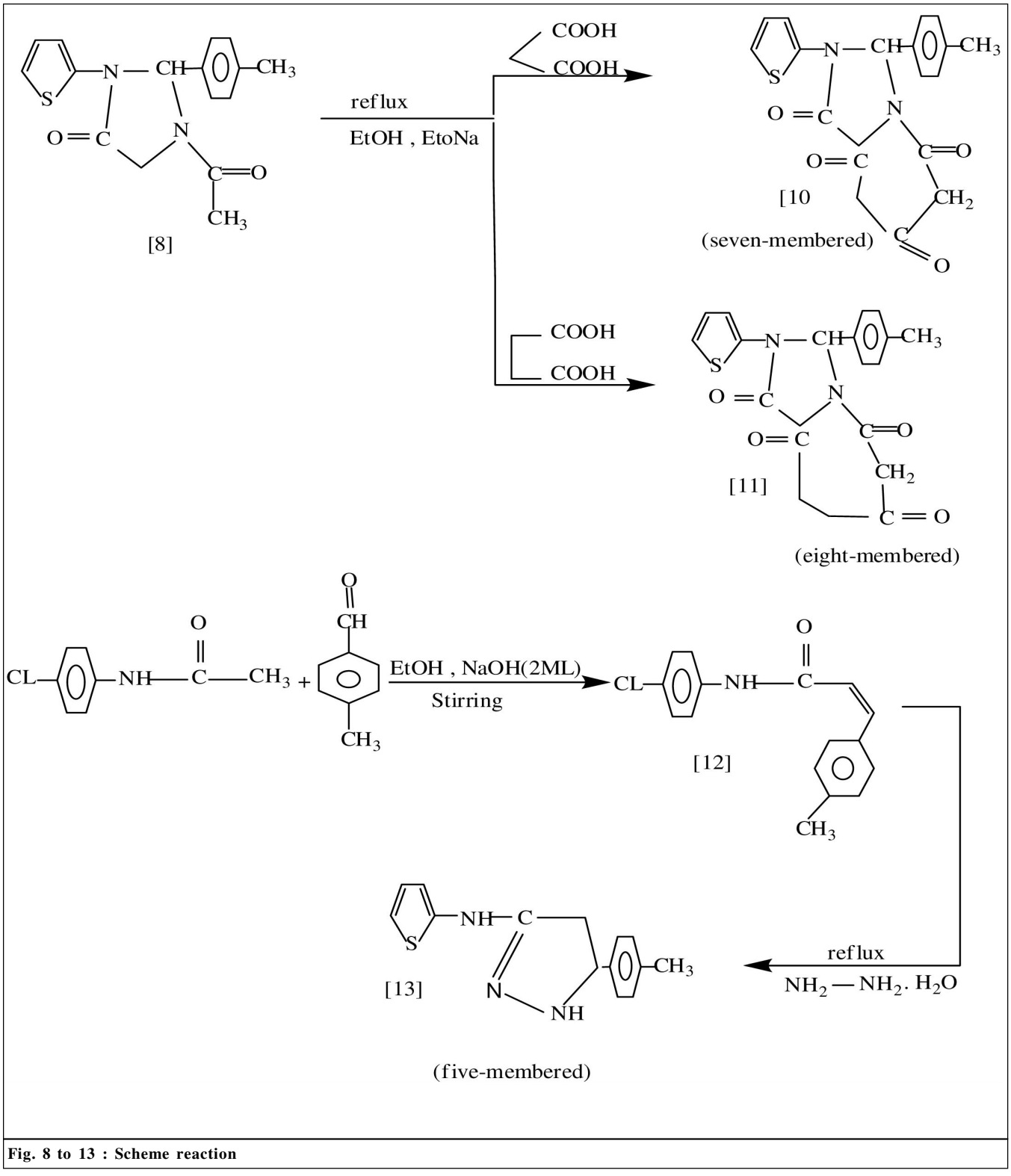

Fig. 8 to 13 : Scheme reaction

these compounds, the results were compactable, the data of analysis, M.F and melting points are listed in Table 3.

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