

Preparation and identification of new hetero bicycle compound via cyclization reaction

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ABSTRACT - In this paper, synthesis of new bicycles of (five, six, seven)- member hetero cyclic compounds[4-8] via cyclization reactions. The synthesized compounds [1-8] have been characterized using several chemical techniques (H.NMR-spectra, (C.H.N)-analysis, FT.IR-spectra) and melting points.

Key words - Cyclization, Hetero bicycle

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In this work, the compounds have been synthesized from combination of two compounds by cyclocondensation or cyclization of same compound to produce hetero cycles including heteroatom from nitrogen and sulphur atoms, for this reason their biological activity highly efficient and low poisonous.

Since the discovery of the biological importance^(1,2) of these compounds, the aim of many researches product was to synthesize many different substituted and various uses were a subject of many studies⁽³⁻¹²⁾.

EXPERIMENTAL METHODOLOGY

- All chemicals used were supplied from Merck and BDH-chemical company .

- 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 4-Ptopanoat -6-methyl-hydro pyridazinone [4]:

The compound [4] was synthesized by reaction between

(0.01 mole, 1.6 g) diethylmalonate and acetyl methyl chloride in refluxed for (2hrs) until the precipitate formed, after cooling, the precipitate was filtered off, then (0.01 mole, 2.1 g) of this precipitate was condensed with (0.01 mole, 0.32 g) of hydrazine in presence of absolute ethanol with reflux for (2hrs), after cooling, the precipitate was filtered off and recrystallized to yield 86 per cent from compound [4].

Synthesis of : 3,4-pyrazolone-6-methyl hydro pyridazine [5]: and : 3,4-thiazepanone -6-methyl –hydro pyridazine [6]:

Condensation reaction by refluxing mixture of (0.01 mole, 1.8 g) of compound [4] with one of [(0.01 mole, 0.32 g) of hydrazine, (0.01 mole, 0.7 g) of mercapto amino ethylene)], respectively, were react for (4hrs), after cooling, the precipitate was filtered off and recrystallized to give 84 per cent, 87 per cent of compounds [5, 6], respectively.

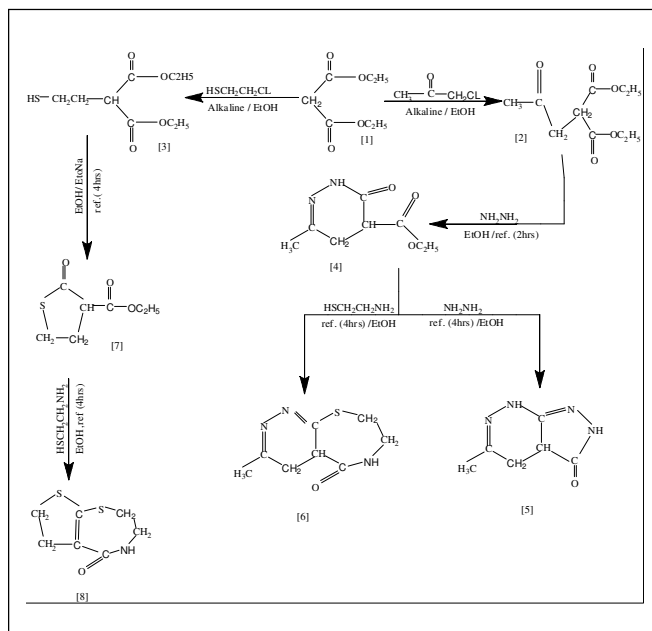
Synthesis of 3-propanoate –hydro thiophen -2-one [7] : and 2,3-thiazepinone –dihydrothiophen [8]:

(0.01 mole, 1.6 g) of diethyl malonate was condensed with (0.01 mole, 0.9 g) of mercapto ethylene chloride in presence of ethanol with refluxing for (2hrs), the precipitate was filtered off, then (0.01 mole, 2.2 g) of this precipitate was cyclized upon heating in refluxing for (4hrs), after cooling, the

precipitate was filtered off and recrystallized to yield 85 per cent of compound [7].

The compound [8] was synthesized by refluxing between (0.01 mole 1.7 g) of compound[4] and (0.01 mole, 0.7 g) of mercapto amino ethylene for (4hrs), after cooling, the precipitate was filtered and recrystallized to yield 87 per cent.

Reaction scheme:



EXPERIMENTAL FINDINGS AND ANALYSIS

All synthesized compounds [1-8] have been characterized by their melting points and spectroscopic techniques (FT-IR-spectra, (C.H.N)-analysis, and H-NMR-spectra) :

FT-IR-Spectra:

FT-IR-spectra of compounds [1-8] showed :

-Compound [4]: absorption band appeared at (1678)cm⁻¹ due to carbonyl of amide ($\text{—}\overset{\text{O}}{\parallel}\text{—NH}$), other band appeared at (1588)cm⁻¹ due to (C=N) endocyclic .

-Compound [5] :absorption band appeared at (1681)cm⁻¹ due to carbonyl group of amide ($\text{—}\overset{\text{O}}{\parallel}\text{—NH}$), two bands appeared at (1577, 1488) cm⁻¹ due to (C=N) endocyclic, other bands appeared at (3345)⁽¹³⁻¹⁵⁾ cm⁻¹ due to (-NH) of amide .in cycle.

-Compound [6] :absorption band appeared at (1686)⁽¹⁶⁾ cm⁻¹ due to carbonyl group of amide ($\text{—}\overset{\text{O}}{\parallel}\text{—NH}$), two bands appeared at (651, 1438) cm⁻¹ due to (C-S) and (S-CH₂),

respectively of endocyclic ,other bands appeared at (1595 , 1460) cm⁻¹ due to (C=N)endocyclic .

Compound [7] :absorption band appeared at (1730)cm⁻¹ due to carbonyl group of ester ($\text{—}\overset{\text{O}}{\parallel}\text{—OC}_2\text{H}_5$), two bands appeared at (1436 , 1629)cm⁻¹ due to (S-CH₂) , ($\text{—}\overset{\text{O}}{\parallel}\text{—}$), endocyclic, respectively .

Compound [8] :absorption band appeared at (1660)cm⁻¹ due to carbonyl group of amide ($\text{—}\overset{\text{O}}{\parallel}\text{—NH}$), and two bands appeared at (663, 1486)cm⁻¹ due to (C-S) and (S-CH₂) endocyclic, respectively, and other data of functional groups shown in the following in Table 1 , Fig. 1-5.

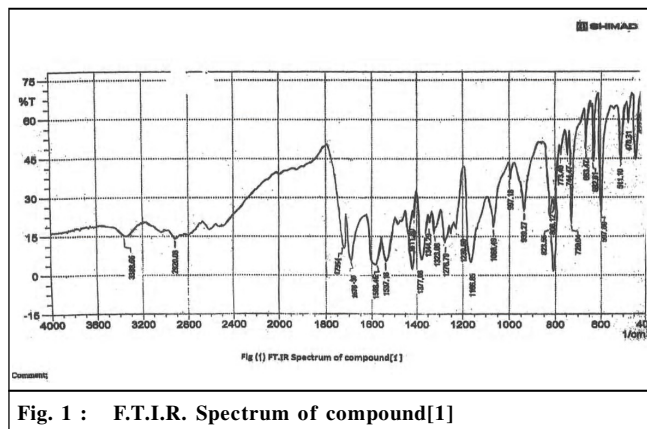


Fig. 1 : F.T.I.R. Spectrum of compound[1]

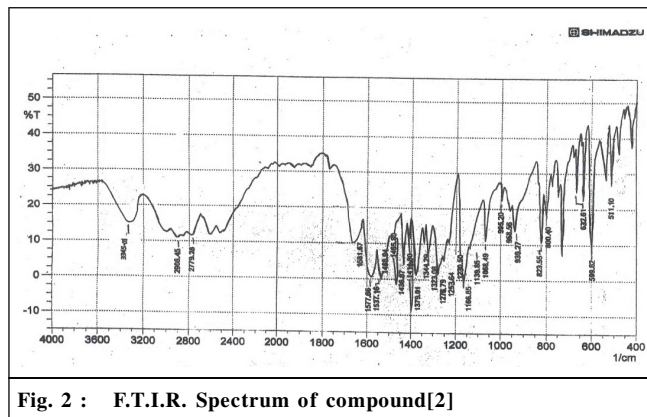


Fig. 2 : F.T.I.R. Spectrum of compound[2]

H-NMR-Spectrum :

H-NMR-spectrum of compounds [1-8]showed :

-Compound[4]: singlet signal at 0 9.8 for one proton of amide ($\text{—}\overset{\text{O}}{\parallel}\text{—NH}$) signals at 0 10.43 for protons of ethyl group of ester ($\text{—}\overset{\text{O}}{\parallel}\text{—OC}_2\text{H}_5$), singlet signal at 0 2.38 for three protons

Table 1: FT.IR data (cm⁻¹) of compounds[4-8]

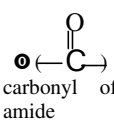
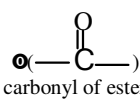
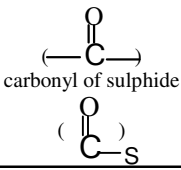
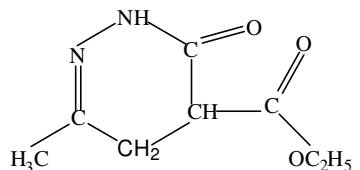
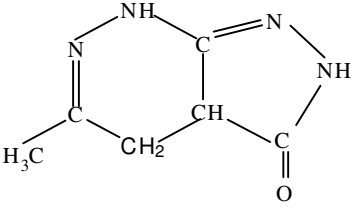
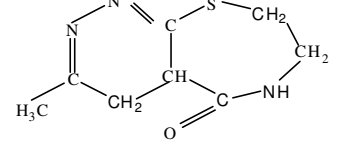
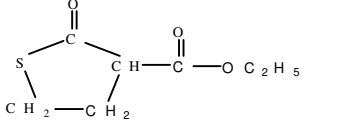
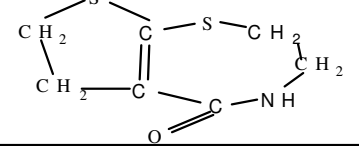

Comp. No.	Structural formula	 carbonyl of amide	$\nu(\text{NH})$ str. (NH) bend	(C-S) (S-CH ₂) Endo cyclic	(C=N) Endo cyclic	 carbonyl of ester	 carbonyl of sulphide
[4]		1678	3388 1537	---	1588	1735	---
[5]		1681	3345 1537	---	1577 , 1488	---	---
[6]		1686	3340 1569	651 1438	1595 , 1460	---	---
[7]		---	---	---	---	1730	1629
[8]		1660	3365 1580	663 1486	---	---	---

Table 2 : Melting points, M.F. and elemental analysis of compounds [4-8]

Comp. No.	M.F	M.P. C%	Calc /Found. C%	H%	N%
[4]	C ₈ H ₁₂ N ₂ O ₃	169	52.173 52.058	6.521 6.387	15.217 15.106
[5]	C ₆ H ₈ N ₄ O	182	47.368 47.205	5.263 5.094	36.842 36.617
[6]	C ₈ H ₁₁ N ₃ OS	218	48.730 48.583	5.583 5.402	21.319 21.182
[7]	C ₇ H ₁₀ O ₃ S	197	48.173 48.045	5.747 5.614	-----
[8]	C ₇ H ₉ NOS ₂	236	44.919 44.778	4.812 4.653	7.486 7.317

of methyl group (-CH₃), signals at 0 2.9 for protons of (CH₂-CH₂-) in cycle .

-Compound[5]: singlet signal at 0 9.8 for one proton of

amide () singlet signal at 0 7.82 for one proton of (NH-N=) in cycle , signals at 0 3.45, 0 2.9 for protons of (CH₂-

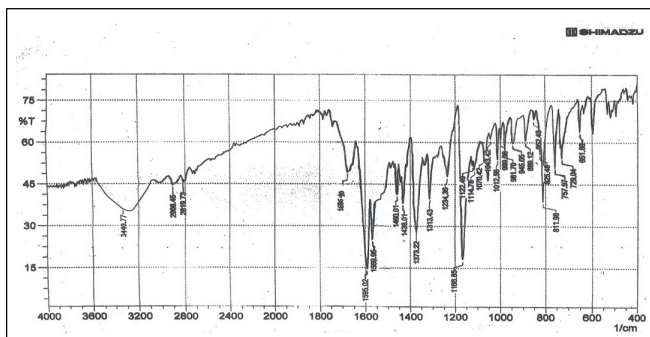


Fig. 3 : F.T.I.R. Spectrum of compound[3]

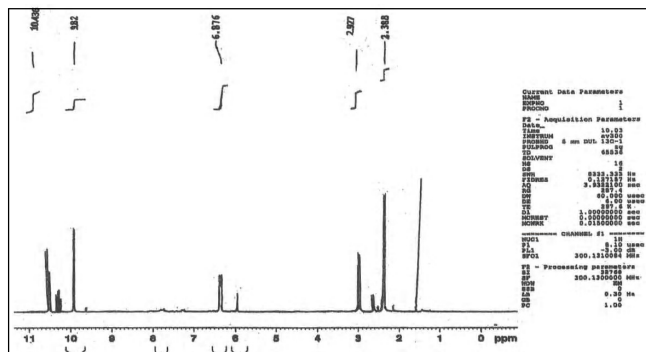


Fig. 6: H.NMR Spectrum of compound[1]

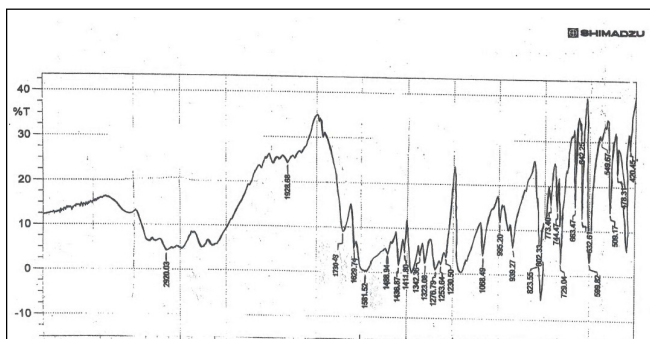


Fig. 4 : F.T.I.R. Spectrum of compound[4]

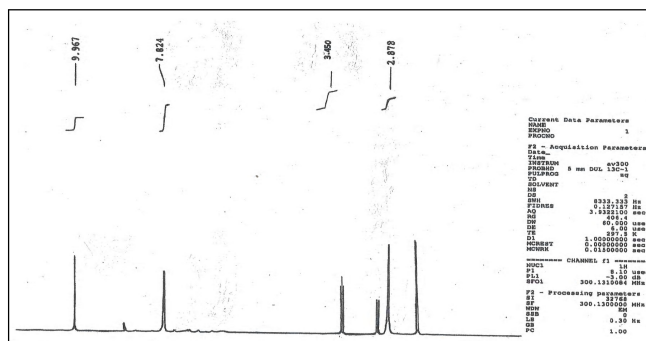


Fig. 7 : H.NMR Spectrum of compound[2]

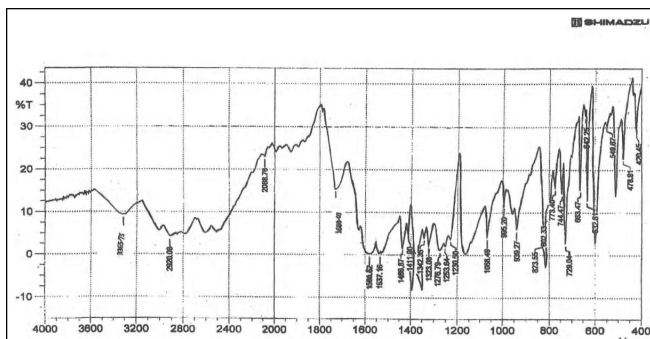


Fig. 5 : F.T.I.R. Spectrum of compound[5]

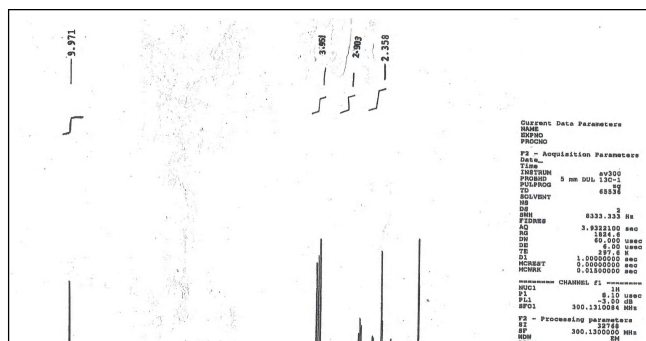


Fig. 8 : H.NMR Spectrum of compound[3]

CH-) in cycle and singlet signal at 0 2.87 for three protons of methyl group (-CH₃).

-Compound [6]: singlet signal at 0 9.9 for one proton of amide ($\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}$), signal at 0 3.95 for for protons of (CH₂-CH-) in cycle.

Compound [7]:signals at 0 3.98 for protonsof (S-CH₂CH₂-), signals at 0 10.36 for protons of ethyl group of ester ($\text{C}-\overset{\text{O}}{\parallel}{\text{O}}-\text{C}_2\text{H}_5$).

-Compound[8]: singlet signal at ? 9.72 for proton of amide ($\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}$), signal at 0 3.80 for protons of (S-CH₂CH₂-N) in first cycle and signal at 0 3.10 for protons of (SCH₂CH₂-) in second cycle .

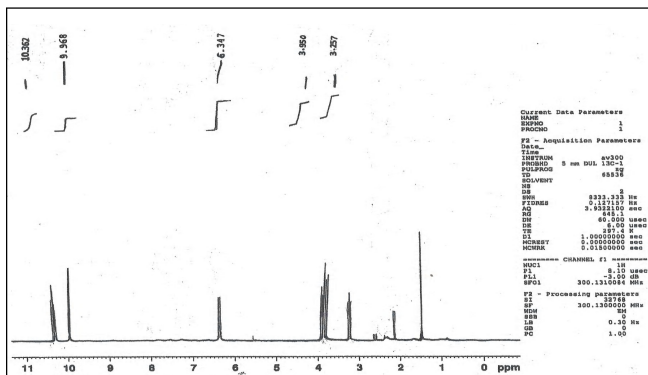


Fig. 9 : H-NMR Spectrum of compound[4]

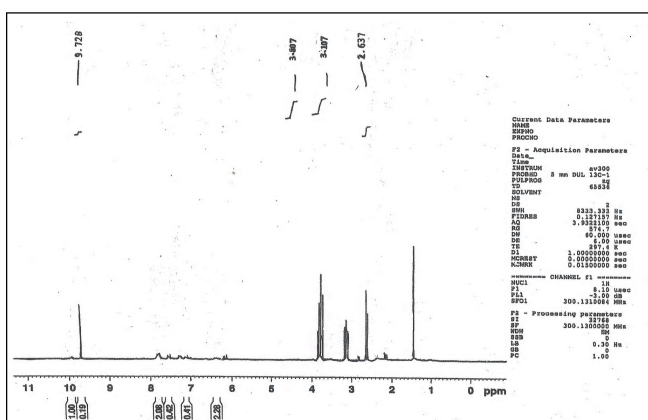


Fig. 10 : H-NMR Spectrum of compound[5]

And other peaks shown in the following Fig. (6-10).

(C.H.N) – analysis :

It was found that the calculated data with found data of these compounds , the results were compactable, the data of analysis, M.F. and melting points are listed in Table (2) .

Acknowledgement :

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