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Research Article

# SYNTHESIS AND INVESTIGATION OF NEW CYCLIC MANNICH BASES

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**ABSTRACT**

The aim of this paper , cyclic compounds of mannich bases were synthesized through condensation of diketone compounds with ammonia or amine derivatives to give enamino ketone as intermediate , which reacts with aldehyde compounds to yield compounds [1-4] .
All structures of formated compounds were characterized by (C.H.N)elementary analysis , $^1$HNMRspectra and FT-IRspectra.The data obtained gave good support for synthesized compounds [1-4] .

**Keywords:** CyclicMannich Bases ,intermediate.

## INTRODUCTION

Mannich bases are class of compounds well known for a long time and still continue the object of considerable interest , mainly due to their pharmacological activities[1-6] , technological applications in polymer industry specially as paints and surface active reagents and other applications in different fields[7-11] .

In recent literature is enriched with progressive findings about the synthesis and biological significance of fused heterocyclic from mannich bases [1-4]which are reported to show biological properties such as antimicrobial ,anti tubercular , anti convuslant, herbicidal pesticidal, anti inflammatory and insecticidal properties[12-16] .The activating mathylene group of these intermediates (mannich bases) are react with aldehyde compounds to yield final products of compounds [1-4], this reaction is highly regiospesific and highly product[17].

## Experimental

-All chemicals used were supplied from Fluka and Merck- chemical companies.
-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 Qualtitative-Iraq .
-$^1$HNMR-Spectra and( C.H.N) Analysis : in DMSO as solvent ,Erk, 3380 ,Germany ,carried out in center lab in Jordan.

Synthesis of1,4-dihydro-{4-(N,N-dimethylbenzene)-2,3,5,6-bis (dimethyl cyclohexanone)}-pyridine[1]

A mixture of 5,5–dimethycyclohexyl–1,3–dione (0.01mole ,5.5 ml) was condensed with *p*-N,N-dimethylbenzaldehyde (0.01mole, 2.8 g) and ammonia (7ml), the precipitate was filtered and recrystallized from absolute ethanol to yield 79% of compound [1] .

Synthesis of 1,4,5,6-Tetra hydro –{5-(methyl phenyl sulphide )-2,8-dimethyl -4,6-di acetoazine[2]

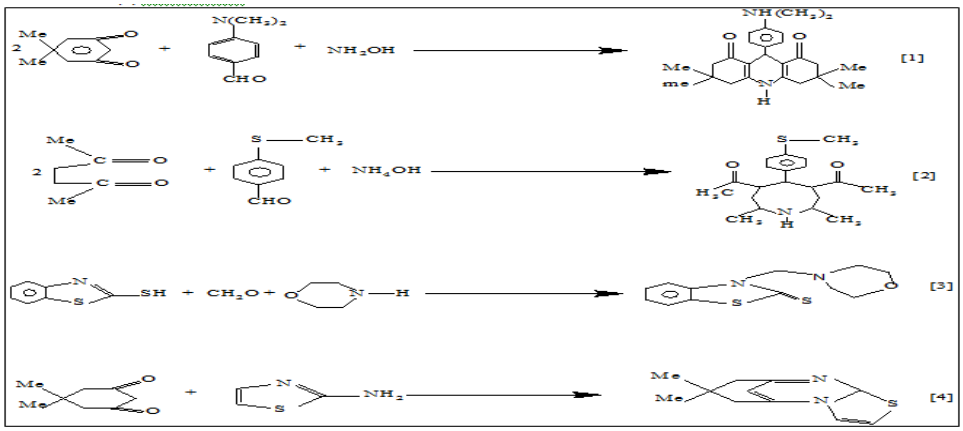
A solution of 2,5–hexane–dione (0.01mole, 5 ml) and *p*-thiomethylbenzaldehyde(0.01mole, 3.4 g) with ammonia (7 ml)was refluxed for (5h) , after cooling, the precipitate was filtered and recrystallized from absolute ethanol to yield 81% of compound [2] .

Synthesis of 3-methylene Morpolone -2-thione –benzothiazole[3]

A solution of 2-mercaptobenzothiazole (0.01mole, 3.4 g) with morpholene (0.01mole ,5 ml) and formaldehyde (0.01mole ,6ml) was refluxed for (4h) in absolute ethanol , the precipitate was filtered and recrystallized from absolute ethanol to yield 85% of compound [3].

Synthesis 1,2-(thiazolino)-4,6-(5,5-dimethyl cyclohexane)-2-hydropyrimidine[4]

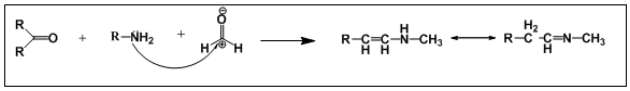
A mixture of 5,5 – dimethyl cyclohexyl -1,3-dione (0.01mole ,6.5ml) was reacted with 2-amino thiazole (0.01mole , 2.3 g) in absolute of ethanol , the precipitate was filtered and recrystallized from absolute ethanol to give 78%of compound[4].



**Scheme1: Reactions scheme**

**RESULTS AND DISCUSSION**

The mechanism of synthesis of mannich compounds [1-4] proceed through reaction between amine compound and carbonyl of aldehyde compound with ketone, the general mechanism of this reaction was shown in scheme (2)



**Scheme2: Mannich reaction mechanism**

All synthesized compounds [1-4] have been characterized by (C.H.N) analysis and the spectroscopic methods(FT-IR spectra and$^{1}$HNMR spectra):

**FT-IR Spectra**

In FT-IR spectra ,the formation of mannichcomppounds is followed by appearance of absorption band at (3440) $cm^{-1}$ due to (N-H) endo cycle of pyridine , band at(1718) $cm^{-1}$ due to carbonyl of keton (CO) , bands at (1538,1569)$cm^{-1}$ is due to (C-N) endocycle and band at (1373) $cm^{-1}$ is due to

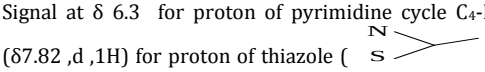
(4-N$(CH_3)_2$) in compound[1] , while compound[2] is appeare absorption band at (3338)$cm^{-1}$ is due to (N-H) endocycle of pyridine , band at (1735) $cm^{-1}$ is due to carbonyl of ketone (CO) ,band at (1587)$cm^{-1}$ is due to (C-N) endocycle[19] ,and band at (1411)$cm^{-1}$ is due to (S-$CH_3$)group , where as compound [3] appears absorption band at (1537)$cm^{-1}$ is due to (C-N) endo cycle[19] , band at (1230)$cm^{-1}$ is due to (C-O-C) of morfholene cycle & band at ( 729)$cm^{-1}$ is due to (C-S) endo cycle of thiazole[18] , while compound [4] is appear absorption band at (1577)$cm^{-1}$ is due to (C=N) endocycle[19] of pyrimidine & band at (740)$cm^{-1}$ is due to[18] (C-S) endo cycle of thiazole . And other data of functional groups show in the following , table (1) and figures(1-4) .]

$^{1}$HNMR Spectra

$^{1}$HNMR Spectrum of compounds in DMSO as solvent showed : singlet signal at (δ8.87 ,S ,1H) for proton of (N-H) group , signal at (δ 7.26 , for proton of pyridine cycle & signal at (δ 3.99 ,S ,6H) for six proton of dimethyl group (N$(CH_3)_2$) in compounds [1] .

Singlet signal at (δ4.63 ,S, 3H) for protons of methy group[19] (S-$CH_3$) , doublet Signal at (δ 7.78 ,d ,2H-2H) for 1,4-disubstitute of phenyl ( -ph-S- ) [18] , and signal at (δ8.69 ,S ,1H) for proton of (N-H) in compound [2] .

Signal at (δ 4.84 ,t ,2H) for protons of (` O-$CH_2$-$CH_2$-N ) of morpholene cycle and signal at (δ 4.28 ,S ,2H) for protons of methylene group of (N-$CH_2$-N)[18,19] in compound [3] .

Signal at δ 6.3 for proton of pyrimidine cycle $C_4$-H and signal at (δ7.82 ,d ,1H) for proton of thiazole (  ) in compound [4] , and other peaks shown in the following , figures (5-8) .

(C.H.N)–Analysis

(C.H.N) analysis , from comparison the calculated data with found data of these compounds , the results were comparable , the data of analysis , M.F and melting points are listed in table (2) .Appearance of ($^{1}$HNMR , FT-IR , C.H.N) spectra results are strong evidences to synthesized compounds [1-4]

**ACKNOWLEDGEMENTS**

The anther is thankful to ((khaled company )) and ((united Arabic company )) in Jordan for supplied some materials .And express thank to Mr .Audai in Jordan for providing (C.H.N) element analytical , $^{1}$HNMR spectra and melting points.

**Table1: FT.IR data (cm-1) of compounds [1-4]**

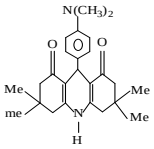
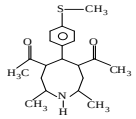
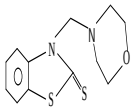
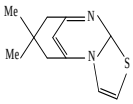
| Comp. No. | Structural formula | Name of compounds | Functional groups (Importance groups) |
|---|---|---|---|
| [1] |  | 1,4-dihydro-{4-(N,N-dimethyl phenyl)-2,3,5,6-bis(dimethyl cyclohexanone)}-pyridine. | υ (N-H):3440 m , ( -CO- ) of ketone : 1718S ,(C-N)endocycle of-pyridine :1538,1569S ,4-N$(Me)_2$:Aromatic :1373 |
| [2] |  | 1,4,5,6-Tetra hydro –{5-(methyl phenyl sulphide )-2,8-dimethyl-4,6-di acetoazine . | υ(N-H):3338M , (-CO-)of ketone :1735S, (S-$CH_3$): 1411S, (C-N)endocycle:1537 |
| [3] |  | 3-methylene Morpolone -2-thione –benzothiazole . | (C-N)endo cycle:1537 (C-S)endocycle of thiazole: 729 ,(C-O-C) of morpholene :1230 |
| [4] |  | 1,2-(thiazolino)-4,6-(5,5-dimethyl cyclo hexane )-2-hydropyrimidine | (C=N) endocycle of pyrimidine : 1577 S, (C-S)endocycle of thiazole : 740 S |

**Table2: Melting points ,M.F & Elemental Analysis of compounds [1-4]**

| Comp. No. | M.F | M.P (°C) | Calc. /Found. C% | H% | N% |
|---|---|---|---|---|---|
| [1] | $C_{25}H_{32}N_2O_2$ | 178 | 76.530 | 8.163 | 7.142 |
| | | | 76.428 | 8.113 | 7.029 |
| [2] | $C_{20}H_{25}NO_2S$ | 171 | 69.970 | 7.288 | 4.081 |
| | | | 69.804 | 7.113 | 4.006 |
| [3] | $C_{12}H_{14}N_2OS_2$ | 165 | 54.135 | 5.263 | 10.526 |
| | | | 54.037 | 5.123 | 10.417 |
| [4] | $C_{11}H_{14}N_2S$ | 157 | 64.077 | 6.796 | 13.592 |
| | | | 63.968 | 6.637 | 13.387 |

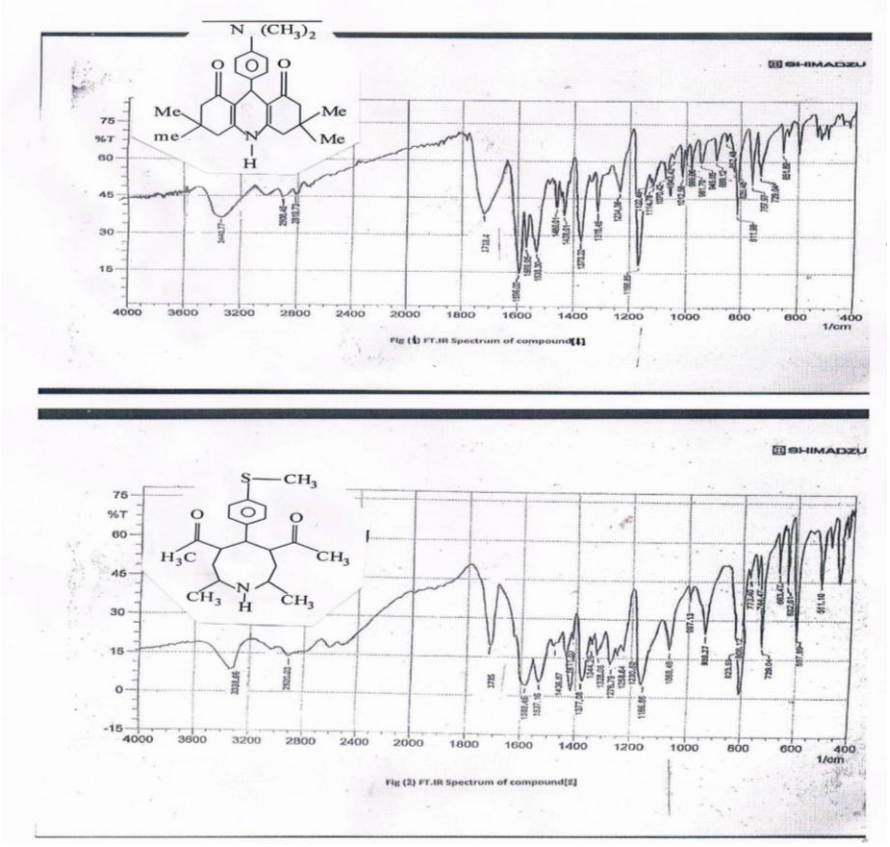



**Fig1: FT.IR spectrum of Compound[1,2]**

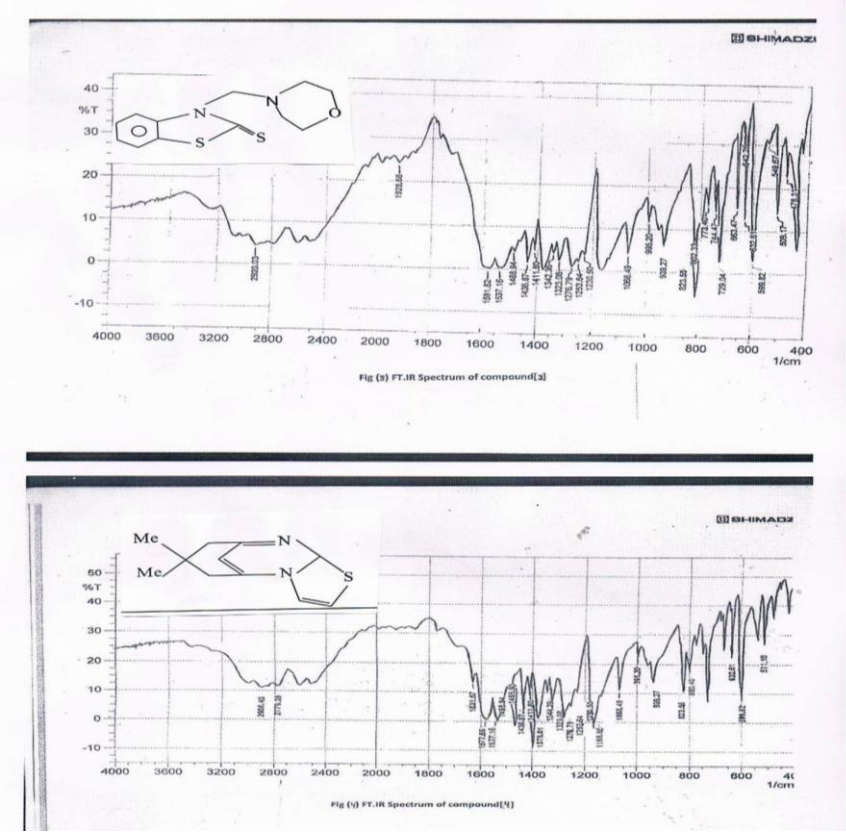



**Fig2:FT.IR spectrum of Compound[3 ,4]**

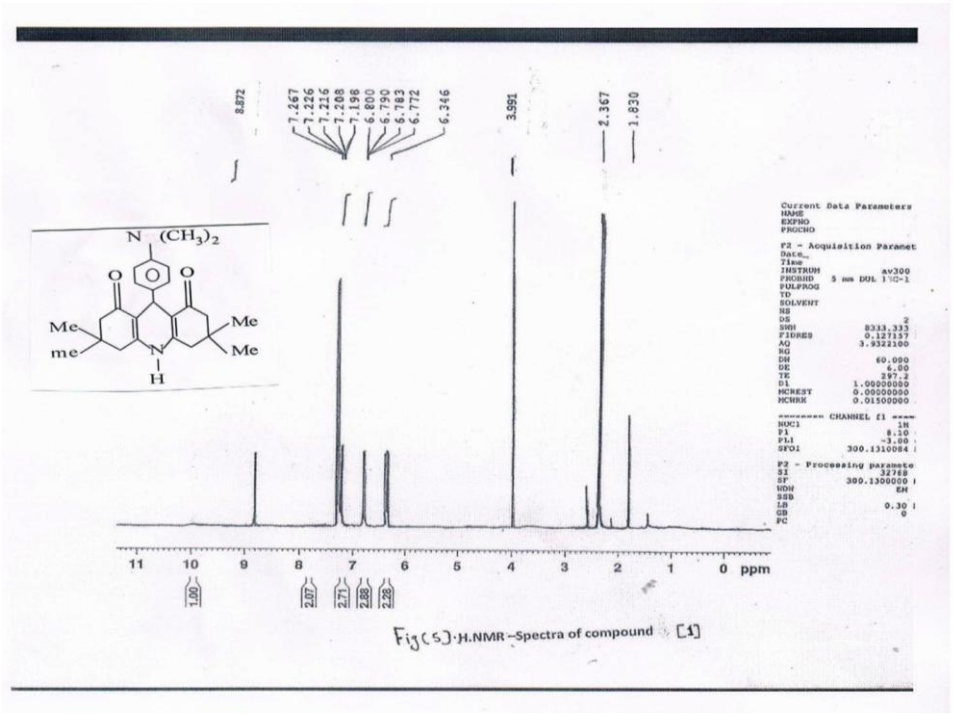



**Fig3:1HNMR spectrum of Compound[1]**

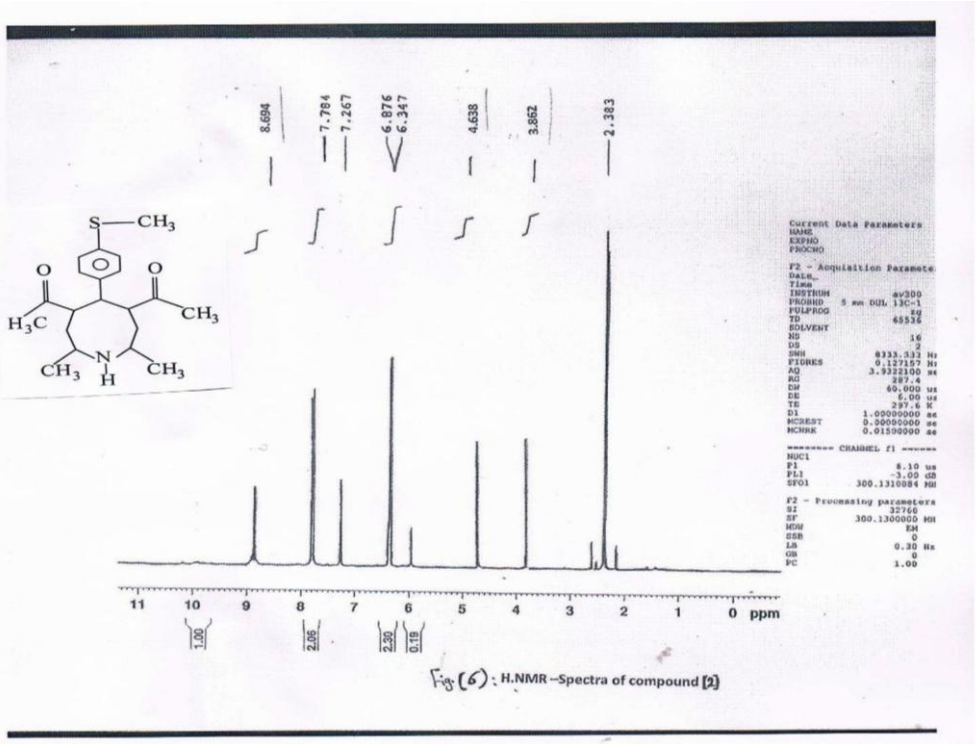



**Fig4:1HNMR spectrum of Compound [2]**

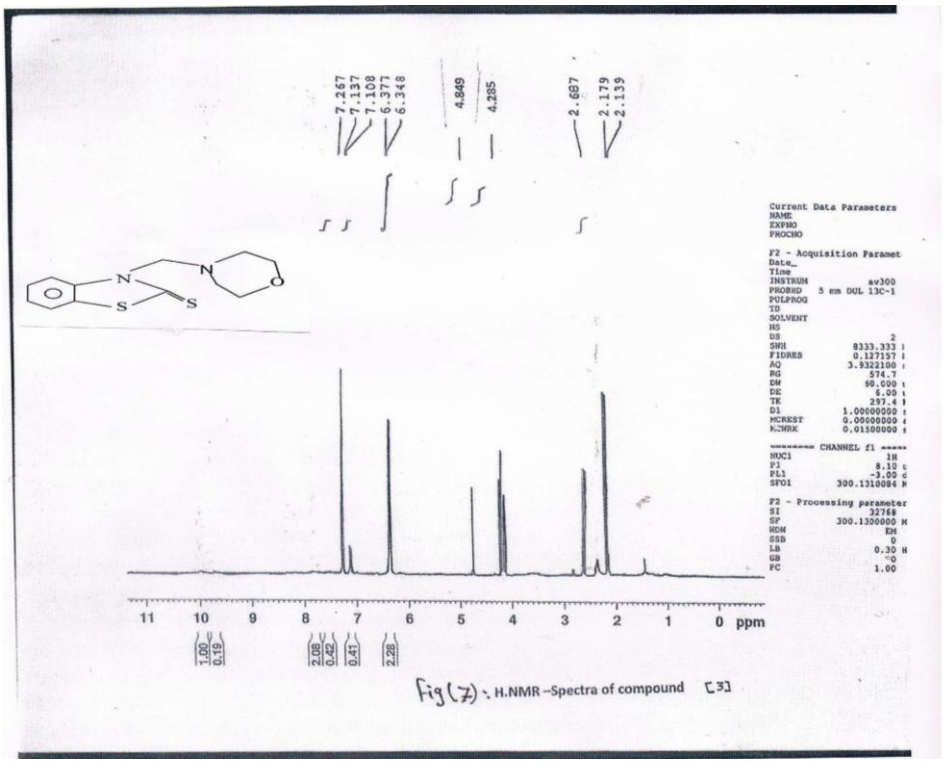



**Fig5:1HNMR spectrum of Compound[3]**

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