SOUTHERN BRAZILIAN, JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 20, No. 20, 2012

SYNTHESIS OF NEW SPIRO- HETEROCYCLES CONTAINING DIHYDROTETRAZINE MOIETY

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ABSTRACT

The reaction of nitrilimines with hydrazones of alkanones and cycloalkanones led to the formation of acyclic electrophilic addition products, which upon treatment with C/S/Zn cyclized to 1,6-dihydro-1,2,4,5-tetrazine derivatives. The structures of the synthesized compounds have been established by their elemental analyses and spectroscopical data.

KEYWORDS

Nitrilimines, Hydrazones, Cyclization, Synthesis, 1,6-dihydro-1,2,4,5-tetrazine

RESUMO

A reação de nitriliminas com hidrazonas de alcanonas e cicloalcanonas levou à formação de produtos acíclicos de adição eletrofílica. Depóis de tratamento com C/S/Zn eles levaram a derivados cíclicos de 1,6-dihidro-1,2,4,5-tetrazinas.As estruturas dos compostos sintetizados foram comprovadas com análise elementar e dados especroscópicos.

PALAVRAS CHAVE

Nitriliminas, Hidrazonas, Ciclização, Síntese de 1,6-dihidro-1,2.4,5-tetrazina

DOI: 10.48141/SBJCHEM.v20.n20.2012.54_Revista_2012a.pdf

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GRAPHICAL ABSTRACT

Synthesis of New Spiro-Heterocycles Containing Dihydrotetrazine moiety

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III V-IX

V, Ar = Ph; VI, Ar = PhNH; VII, Ar = 2-Furyl;
VIII, Ar = 2-Tienyl; IX, Ar = 2-Naphthyl

1. INTRODUCTION

Previous publications, showed that the simple hydrazones derived from aliphatic aldehydes and ketones react with nitrilimines at ambient temperature to give acyclic addition products, which undergo oxidative cyclization upon refluxing with active charcoal to yield the corresponding 1,6-dihydro-s-tetrazines [1] or amidrazones [2,3]. On the other hand, methyl hydrazones of alkanals and alkanones furnish 1,2,3,4-tetrahydro-s-tetrazines [3,4].

Recently, we found that nitrilimines react with 1-methyl, 1-phenyl, 1-acetyl, 1-formyl and 1-ethoxycarbonyl-1-methylhydrazines at room temperature afforded acyclic electrophilic addition products, which cyclized intramolecularly to the corresponding 1,2,3,4-tetrahydro-1,2,4,5-tetrazines by heating them with activated charcoal or lithium hydride in refluxing benzene or toluene [5.]

Quite recently, we described the synthesis of 1,2,3,4-tetrahydro-1,2,4,5-tetrazin-3-ones by the reaction of acetylhydrazone pyridinium chloride (Girard-reagent P) with different nitrilimines [6]. Several methods have been reported for the synthesis of tetrazine derivatives, and the most frequently used method for the preparation of 1,2,3,4-tetrahydro-1,2,4,5-tetrazines is the cyclization of alkylformazanes by heating or base treatment [7].

In the present study, the synthesis of a series of new substituted 1,2,4,5-tetrazines **5-9** were performed (Scheme 1) and their structures were characterized by ^{1}H NMR ^{13}C NMR, IR spectroscopy and elemental analysis.

2. RESULTS AND DISCUSSION

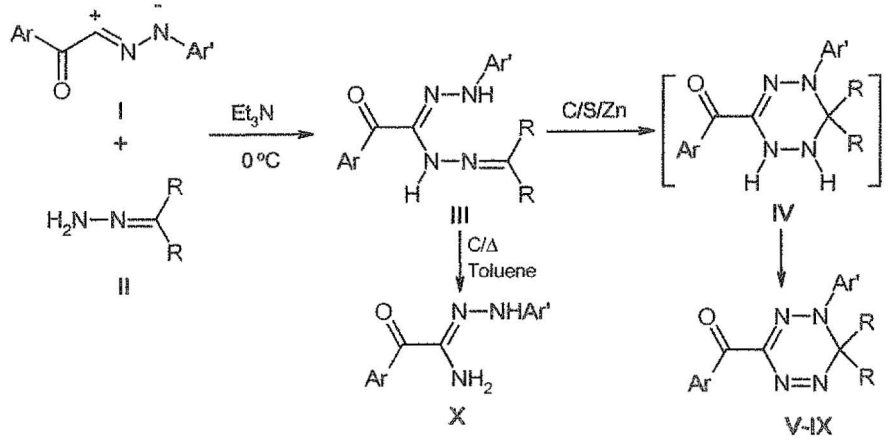
The formazans (acyclic adducts) **III** were synthesized via reaction of nitrilimines **I** with alkanones and cycloalkanone hydrazones **II** as shown in Scheme 1. Attempts to cyclize the acyclic adducts **III** (Ar = Me or OMe) by heating in tetrahydrofuran or ethanol were unsuccessful. However, treatment of solution of later adducts **III** (Ar = Me or OMe) with palladium-carbon brought about oxidative cyclization to the 1,6-dihydro-1,2,4,5-tetrazines [1].

On the other hand, cyclization of acyclic compounds **III** (Ar = Ph, PhNH, 2-furyl, 2-theinyl, 2-naphthyl) using active charcoal in refluxing toluene give complicated mixture of products as indicated by TLC, among which amidrazones **X** were separated, rather than the expected 1,6-dihydro-1,2,4,5-tetrazines [2,3] (Figure 1).

Treatment of solution of formazans **III** (Ar = Ph, PhNH, 2-furyl, 2-theinyl, 2-naphthyl) with new catalyst containing (C/S/Zn), developed in our laboratory by our colleague of physical chemistry, at room temperature in benzene or toluene give directly 1,6-dihydro-1,2,4,5-tetrazines **V-IX** (Figure 1) in excellent yields. (Table 1). It is suggested that the conversion of acyclic compounds **III** into s-tetrazines **V-IX** involves the non isolable intermediate formation of the tetrahydro-s-tetrazines **IV** (Figure 1).

2.1 Spectral data analysis

The assignment of structures of compounds **V-IX** is based on their analytical and spectroscopic data. Physical properties and microanalysis are presented in Table 1. These compounds gave satisfactory combustion analysis for the proposed structures which are confirmed on the basis of their spectroscopic data.



V, Ar = Ph; VI, Ar = PhNH; VII, Ar = 2-Furyl;
VIII, Ar = 2-Tienyl; IX, Ar = 2-Naphthyl

Ar' = 4-X-C_6H_4-

Entery	a	b	c	d	e	f	g	h	i	j	k	l
X	Cl	Cl	Cl	Cl	Cl	H	H	H	H	H	H	H
R R	Me Me					Me Me						

Figure 1. Synthetic pathway for the preparation of compounds **V-IX**.

In the IR spectra of compounds **V-IX**, showed the disappearance of NH signals and the C=O bond stretching of the carbonyl group at C-3 occurs at higher frequency (1665-1655 cm^{-1}) than it dose in the acyclic precursors **III** (1650-1635 cm^{-1}). This implies that conjugation of this exocyclic group with the hetero-ring π–system is decreased as a consequence of homoaromaticity and the slightly non-planar arrangement of the N-2, N-4 and C-3 plane with the substituents at C-3 [8-9] Compounds **V-IX** revealed strong absorption at about 1620-1600 cm^{-1} assigned to C=N bond stretching.

^{1}H and ^{13}C NMR spectra of obtained compounds **V-IX** provide strong evidence in support of the proposed structures. Their ^{1}H NMR spectra showed the disappearance of 2NH signals, in addition to aromatic protons signals, a characteristic signal due to amide NH proton for compounds **VI** resonating as singlet at 9.10-8.80 ppm. For compounds **Va,VIa,VIf,IXa** tow signals for the

methyl groups ($2CH_3$) protons appeared as singlet at 1.41-1.34 ppm and the signals of the cycloalkane protons in other compounds appeared in the range of 2.53-1.51 ppm.

The dihydrotetrazines **V-IX** exhibited a characteristic ^{13}C NMR signal at 68-87 ppm assigned to the C-6. This is similar to reported values of quaternary or spiro carbon flanked by tow nitrogens in six-membered heterocycles [2,3]. In the acyclic analogues **III**, this carbon resonates at 140-155 ppm [2,3]. This provides a strong evidence in support of cyclic structure of compounds **V-IX**. The ^1H and ^{13}C NMR spectral data of the synthesized compounds are presented in the experimental part.

3. EXPERIMENTAL SECTION

3.1. Reagents and Instrumentation

Triethylamine (TEA), tetrahydrofuran (THF), acetone, cyclohexanone, 4-methylcyclohexanone, 4-t-butylcyclohexanone, cyclopentanone, cycloheptanone, cyclooctanone and toluene were purchased from Avocado Chemical Company, England, and used as purchased. All melting points were determined on a Stuart Electrothermal Apparatus and are uncorrected.

The IR spectra were obtained by using Perkin-Elmer 737 infrared spectrophotometer in potassium bromide pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer (400.13 MHz) at room temperature in $CDCl_3$ and DMSO-d_6, using tetramethylsilane (TMS) as an internal reference. All chemical shifts were reported as δ values in parts per million (ppm) downfield from internal TMS.

Electron impact (EI) mass spectra were measured on Shimadzu GCMS-QP1000 EX Mass spectrometers at 70 eV. Elemental analysis are performed at Cairo University, Egypt, and the results agreed with the calculated values within experimental errors. Nitrilimines **1** and hydrazones **2** used in this study, were prepared according to described procedures [1,10,11].

3.2. Synthesis of 1,6-dihydro-s-tetrazines V-IX

3.2.1 Reaction of nitrilimines I with hydrazones II

To a stirred mixture of the appropriate hydrazonoyl halide [nitrilimines **I** precursors] (0.01 mol) and hydrazones **II** (0.02 mol) in dry THF (100 mL), triethylamine (5 mL, 0.05 mol) in THF (20 mL) was dropwise added at -5 to 0 °C and the reaction mixture was controlled by TLC. The reaction temperature was allowed to rise slowly to room temperature and stirring was continued until the starting substrates were completely consumed (4-6 hours). The precipitated triethylammonium chloride salt was filtered off, the solvent was removed under reduced pressure. The residue was washed with water (3x50 mL), then triturated with ethanol (10 mL), the crude solid product was collected and recrystallized from aqueous ethanol to give the desired compounds **III**.

Table 1. Physical data and elemental analysis for compounds (V-IX).

Comp.	Molecular Formula (MW)	Yield (%)	mp (°C)	Analysis (%) Calculated / (Found)		
				C	H	N
Va	$C_{17}H_{15}ClN_4O$ (326.79)	82	173-5	62.48 (62.70)	4.63 (4.50)	17.14 (17.25)
Vb	$C_{19}H_{17}ClN_4O$ (352.83)	86	166-8	64.68 (64.45)	4.86 (4.75)	15.88 (16.05)
Vc	$C_{20}H_{19}ClN_4O$ (366.85)	89	184-6	65.48 (65.75)	5.22 (5.35)	15.27 (15.10)
Vd	$C_{21}H_{21}ClN_4O$ (380.88)	91	167-9	66.22 (61.95)	5.56 (5.70)	14.71 (14.60)
Ve	$C_{22}H_{23}ClN_4O$ (394.91)	87	175-7	66.91 (67.10)	5.87 (5.00)	14.19 (14.30)
VIa	$C_{17}H_{16}ClN_5O$ (341.80)	81	182-4	59.74 (60.00)	4.72 (7.65)	20.49 20.30)
VIc	$C_{20}H_{20}ClN_5O$ (381.87)	86	191-3	62.91 (63.15)	5.28 (5.35)	18.43 (18.60)
VIe	$C_{22}H_{24}ClN_5O$ (409.92)	84	187-9	64.46 (64.20)	5.90 (6.05)	17.08 (16.95)
VIf	$C_{17}H_{17}N_5O$ (307.36)	88	194-6	66.43 (66.65)	5.58 (5.40)	22.79 (22.90)
VIg	$C_{19}H_{19}N_5O$ (333.40)	92	201-3	68.45 (68.25)	5.74 (5.90)	21.01 (20.85)
VIh	$C_{20}H_{21}N_5O$ (347.42)	90	181-3	69.14 (68.90)	6.09 (5.95)	20.16 (20.30)
VIi	$C_{21}H_{32}N_5O$ (361.45)	87	196-8	69.78 (69.55)	6.41 (6.25)	19.38 (19.55)
VIj	$C_{24}H_{29}N_5O$ (403.53)	83	167-9	71.44 (71.15)	7.24 (7.35)	17.36 (17.20)
VIk	$C_{21}H_{23}N_5O$ (361.45)	94	177-9	69.78 (69.95)	6.41 (6.55)	19.38 (19.25)
VIl	$C_{22}H_{25}N_5O$ (375.48)	91	183-5	70.38 (70.10)	6.71 (6.55)	18.65 (18.80)
VIIb	$C_{17}H_{15}ClN_4O_2$ (342.74)	93	153-5	59.57 (59.80)	4.41 (4.30)	16.34 (16.20)
VIIc	$C_{18}H_{17}ClN_4O_2$ (356.81)	90	148-50	60.59 (60.35)	4.80 (4.95)	15.70 (15.85)
VIIIb	$C_{17}H_{15}ClN_4O_2S$ (358.85)	85	163-5	56.90 (57.15)	4.21 (4.40)	15.61 (15.50)
VIIId	$C_{19}H_{19}ClN_4O_2S$ (386.91)	89	146-8	58.98 (59.25)	4.95 (5.10)	14.48 (14.35)
IXa	$C_{21}H_{17}ClN_4O$ (376.85)	83	190-2	66.93 (67.20)	4.55 (4.40)	14.87 (15.00)
IXb	$C_{23}H_{19}ClN_4O$ (402.89)	91	176-8	68.57 (68.80)	4.75 (4.65)	13.91 (14.05)
IXc	$C_{24}H_{21}ClN_4O$ (416.91)	87	189-91	69.14 (68.90)	5.08 (4.95)	13.44 (13.60)
IXd	$C_{25}H_{23}ClN_4O$ (430.94)	84	168-70	69.68 (69.90)	5.38 (5.50)	13.00 (12.85)
IXe	$C_{26}H_{25}ClN_4O$ (444.97)	89	184-6	70.18 (69.95)	5.66 (5.80)	12.59 (12.45)

3.2.2 Cyclization of compounds (III):

Acyclic compounds III (0.005 mol) and C/S/Zn (0.1 w/w%) in benzene or toluene were stirred at room temperature for 1-2 hours and monitored by TLC. The reaction mixture was cooled, then filtered and the solvent was minimized and petroleum ether (bp. 40-60 °C) was slowly added to effect complete crystallization of the desired cyclic compounds V.
The following compounds were prepared using this method:

3-Benzoyl-1-(4-chlorophenyl)-6,6-dimethyl-1,6-dihydro-1,2,4,5-tetrazine (Va): ^{1}H NMR ($CDCl_3$) δ: 7.92-7.03 (m, 9H, Ar-CH), 1.39 (s, 3H, CH_3), 1.37 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 187.4 (C=O), 171.6 (COOH), 143.7 (C=N), 144.3-126.6 (Ar-C), 68.6 (quaternary carbon), 22.5 (CH_3). IR (KBr) *v*/cm^{-1}: 1660 (C=O), 159.2 (C=N).

8-Benzoyl-6-(4-chlorophenyl)-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (Vb): ^{1}H NMR ($CDCl_3$) δ: 8.02-7.11 (m, 9H, Ar-CH), 1.90-1.68 (m, 8H, cyclopentane protons). ^{13}C NMR ($CDCl_3$) δ: 185.7 (C=O), 143.9 (C=N), 144.9-126.1 (Ar-C), 86.7 (spiro carbon), 32.1, 23.7 (cyclopentane carbons). IR (KBr) *v*/cm^{-1}: 1655 (C=O), 1594 (C=N).

3-Benzoyl-1-(4-chlorophenyl)-1,2,4,5-tetraazaspiro[5.5]undec-2,4-diene (Vc): ^{1}H NMR (DMSO-d_6) δ: 7.97-7.06 (m, 9H, Ar-CH), 1.86-1.66 (m, 10H, cyclohexane protons). ^{13}C NMR (DMSO-d_6) δ: 185.5 (C=O), 143.9 (C=N), 144.4-126.2 (Ar-C), 84.3 (spiro carbon), 32.1, 24.7, 23.4 (cyclohexane carbons). IR (KBr) *v*/cm^{-1}: 1655 (C=O), 1593 (C=N).

3-Benzoyl-1-(4-chlorophenyl)-1,2,4,5-tetraazaspiro[5.6]dodec-2,4-diene (Vd): ^{1}H NMR ($CDCl_3$) δ: 8.27-7.00 (m, 9H, Ar-CH), 2.53-1.56 (m, 12H, cycloheptane protons). ^{13}C NMR ($CDCl_3$) δ: 185.6 (C=O), 143.4 (C=N), 142.7-119.6 (Ar-C), 87.5 (spiro carbon), 39.5, 28.7, 22.3 (cycloheptane carbons). IR (KBr) *v*/cm^{-1}: 1660 (C=O), 1597 (C=N).

3-Benzoyl-1-(4-chlorophenyl)-1,2,4,5-tetraazaspiro[5.7]tridec-2,4-diene (Ve): ^{1}H NMR ($CDCl_3$) δ: 7.99-6.96 (m, 9H, Ar-CH), 2.46-1.36 (m, 14H, cyclooctane protons). ^{13}C NMR ($CDCl_3$) δ: 185.6 (C=O), 143.9 (C=N), 145.0-114.8 (Ar-C), 86.6 (spiro carbon), 34.4, 27.2, 25.2, 23.1 (cyclooctane carbons). IR (KBr) *v*/cm^{-1}: 1650 (C=O), 1594 (C=N).

1-(4-Chlorophenyl)-3-phenylaminocarbonyl-6,6-dimethyl-1,6-dihydro-1,2,4,5-tetrazine (VIa): ^{1}H NMR (DMSO-d_6) δ: 9.12 (s, 1H, NH), 7.61-7.18 (m, 10H, Ar-CH), 1.41 (s, 3H, CH_3), 1.38 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ: 159.2 (C=O amide), 136.7 (C=N), 142.4-126.6 (Ar-C), 68.7 (spiro carbon), 22.5 (CH_3). IR (KBr) *v*/cm^{-1}: 1650 (C=O), 1594 (C=N).

1-(4-Chlorophenyl)-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.5]-undec-2,4-diene (VIc): ^{1}H NMR (DMSO-d_6) δ: 9.10 (s, 1H, NH), 7.63-7.20 (m, 10H, Ar-CH), 1.86-1.60 (m, 10H, cyclohexane protons). ^{13}C NMR (DMSO-d_6) δ: 159.3 (C=O amide), 136.9 (C=N), 141.9-125.8 (Ar-C), 84.8 (spiro carbon), 31.4, 25.7, 22.6 (cyclohexane carbons). IR (KBr) *v*/cm^{-1}: 1655 (C=O), 1598 (C=N).

1-(4-Chlorophenyl)-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.7]-tridec-2,4-diene (VIe): ^{1}H NMR (DMSO-d_6) δ: 9.12 (s, 1H, NH), 7.60-7.20 (m, 14H, Ar-CH), 2.53-1.44 (m, 10H, cyclooctane protons). ^{13}C NMR (DMSO-d_6) δ: 159.4 (C=O amide), 136.8 (C=N), 141.7-126.0 (Ar-C), 86.5 (spiro carbon), 34.5,

30.7, 28.4, 23.2 (cyclooctane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1596 (C=N).

1-Phenyl-3-phenylaminocarbonyl-6,6-dimethyl-1,6-dihydro-1,2,4,5-tetrazine (VIf): ^{1}H NMR (DMSO-d_6) δ: 9.00 (s, 1H, NH), 7.63-7.23 (m, 10H, Ar-CH), 1.37 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ: 158.9 (C=O amide), 136.7 (C=N), 143.7-124.4 (Ar-C), 68.7 (spiro carbon), 22.7 (CH_3). IR (KBr) ν/cm^{-1}: 1650 (C=O), 1598 (C=N).

6-Phenyl-8-phenylaminocarbonyl-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (VIg): ^{1}H NMR (DMSO-d_6) δ: 9.10 (s, 1H, NH), 7.60-7.19 (m, 10H, Ar-CH), 1.95-1.70 (m, 8H, cyclopentane protons). ^{13}C NMR (DMSO-d_6) δ: 158.8 (C=O), 136.4 (C=N), 142.3-126.2 (Ar-C), 86.6 (spiro carbon), 32.3, 23.4 (cyclopentane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1596 (C=N).

1-Phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.5]undec-2,4-diene (VIh): ^{1}H NMR (DMSO-d_6) δ: 9.00 (s, 1H, NH), 7.58-7.16 (m, 10H, Ar-CH), 1.85-1.63 (m, 10H, cyclohexane protons). ^{13}C NMR (DMSO-d_6) δ: 158.5 (C=O amide), 136.7 (C=N), 141.7-124.6 (Ar-C), 80.6 (spiro carbon), 32.0, 24.8, 23.1 (cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1595 (C=N).

9-Methyl-1-phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.5]-undec-2,4-diene (VIi): ^{1}H NMR (DMSO-d_6) δ: 9.05 (s, 1H, NH), 7.62-7.17 (m, 10H, Ar-CH), 2.05-1.22 (m, 9H, cyclohexane protons), 0.94 (s, 3H, CH_3 at cyclohexane). ^{13}C NMR (DMSO-d_6) δ: 158.6 (C=O amide), 136.6 (C=N), 141.5-125.0 (Ar-C), 84.5 (spiro carbon), 33.8, 31.4, 28.4, 22.7 (methyl-cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1598 (C=N).

9-tert-Butyl-1-phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro-[5.5]undec-2,4-diene (VIj): ^{1}H NMR (DMSO-d_6) δ: 9.10 (s, 1H, NH), 7.66-7.21 (m, 10H, Ar-CH), 2.05-1.10 (m, 9H, cyclohexane protons), 0.88 (s, 9H, tert-butyl group) . ^{13}C NMR (DMSO-d_6) δ: 158.7 (C=O amide), 136.5 (C=N), 141.6-124.3 (Ar-C), 84.9 (spiro carbon), 47.1, 35.8, 32.4, 27.6, 24.1 (tert-butyl-cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1650 (C=O), 1594 (C=N).

1-Phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.6]dodec-2,4-diene (VIk): ^{1}H NMR (DMSO-d_6) δ: 8.95 (s, 1H, NH), 7.65-7.20 (m, 10H, Ar-CH), 2.45-1.62 (m, 12H, cycloheptane protons). ^{13}C NMR (DMSO-d_6) δ: 158.5 (C=O amide), 136.7 (C=N), 141.7-124.6 (Ar-C), 87.7 (spiro carbon), 39.6, 28.4, 22.3 (cycloheptane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1596 (C=N).

1-Phenyl-3-phenylaminocarbonyl-1,2,4,5-tetraazaspiro[5.7]tridec-2,4-diene (VIl): ^{1}H NMR (DMSO-d_6) δ: 9.10 (s, 1H, NH), 7.60-7.20 (m, 10H, Ar-CH), 2.52-1.43 (m, 14H, cyclooctane protons). ^{13}C NMR (DMSO-d_6) δ: 158.4 (C=O amide), 136.5 (C=N), 139.7-126.6 (Ar-C), 86.9 (spiro carbon), 34.8, 31.1, 28.7, 23.2 (cyclooctane carbons). IR (KBr) ν/cm^{-1}: 1655 (C=O), 1593 (C=N).

6-(4-Chlorophenyl)-8-(2-furoyl)-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (VIIb): ^{1}H NMR ($CDCl_3$) δ: 7.87-7.26 (m, 7H, Ar-CH), 1.95-1.70 (m, 8H, cyclopentane protons). ^{13}C NMR (DMSO-d_6) δ: 174.7 (C=O), 143.3 (C=N), 136.8-115.9 (Ar-C), 86.6 (spiro carbon), 34.5 32.2, 23.2 (cyclopentane carbons). IR (KBr) ν/cm^{-1}: 1665 (C=O), 1594 (C=N).

1-(4-Chlorophenyl)-3-(2-furoyl)-1,2,4,5-tetraazaspiro[5.5]undec-2,4-diene (VIIc): ^{1}H NMR ($CDCl_3$) δ: 8.26-7.21 (m, 7H, Ar-CH), 1.84-1.61 (m, 10H, cyclohexane protons). ^{13}C NMR (DMSO-d_6) δ: 174.6 (C=O), 143.1 (C=N), 136.7-

116.1 (Ar-C), 80.6 (spiro carbon), 32.6, 24.8, 23.3 (cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1660 (C=O), 1595 (C=N).

6-(4-Chlorophenyl)-8-(2-thenoyl)-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (VIIIb): ^{1}H NMR ($CDCl_3$) δ: 8.23-7.18 (m, 7H, Ar-CH), 1.92-1.67 (m, 8H, cyclopentane protons). ^{13}C NMR (DMSO-d_6) δ: 174.6 (C=O), 143.4 (C=N), 136.7-115.0 (Ar-C), 86.8 (spiro carbon), 32.4 23.7 (cyclopentane carbons). IR (KBr) ν/cm^{-1}: 1665 (C=O), 1598 (C=N).

1-(4-Chlorophenyl)-3-(2-thenoyl)-1,2,4,5-tetraazaspiro[5.6]dodec-2,4-diene (VIIId): ^{1}H NMR ($CDCl_3$) δ: 8.21-7.16 (m, 7H, Ar-CH), 2.42-1.60 (m, 12H, cycloheptane protons). ^{13}C NMR (DMSO-d_6) δ: 174.6 (C=O), 143.2 (C=N), 136.6-114.6 (Ar-C), 87.5 (spiro carbon), 39.5 28.2, 22.5 (cycloheptane carbons). IR (KBr) ν/cm^{-1}: 1665 (C=O), 1596 (C=N).

1-(4-Chlorophenyl)-6,6-dimethyl-3-(2-naphthoyl)-1,6-dihydro-1,2,4,5-tetrazine (IXa): ^{1}H NMR ($CDCl_3$) δ: 8.59-7.16 (m, 11H, Ar-CH), 1.41 (s, 3H, CH_3), 1.39 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ: 187.5 (C=O), 135.5 (C=N), 144.2-125.9 (Ar-C), 68.6 (spiro carbon), 22.6 (CH_3). IR (KBr) ν/cm^{-1}: 1645 (C=O), 1595 (C=N).

6-(4-Chlorophenyl)-8-(2-napthoyl)-6,7,9,10-tetraazaspiro[4.5]dec-7,9-diene (IXb): ^{1}H NMR ($CDCl_3$) δ: 8.57-7.12 (m, 11H, Ar-CH), 2.10-1.67 (m, 8H, cyclopentane protons). ^{13}C NMR (DMSO-d_6) δ: 187.4 (C=O), 135.4 (C=N), 144.0-115.3 (Ar-C), 80.7 (spiro carbon), 31.9, 23.5 (cyclopentane carbons). IR (KBr) ν/cm^{-1}: 1646 (C=O), 1598 (C=N).

1-(4-Chlorophenyl)-3-(2-naphthoyl)-1,2,4,5-tetraazaspiro[5.5]undec-2,4-diene (IXc): ^{1}H NMR ($CDCl_3$) δ: 8.56-7.13 (m, 11H, Ar-CH), 2.15-1.58 (m, 10H, cyclohexane protons). ^{13}C NMR ($CDCl_3$) δ: 187.5 (C=O), 135.5 (C=N), 143.9-126.0 (Ar-C), 70.9 (spiro carbon), 30.8, 25.8, 22.6 (cyclohexane carbons). IR (KBr) ν/cm^{-1}: 1648 (C=O), 1597 (C=N).

1-(4-Chlorophenyl)-3-(2-naphthoyl)-1,2,4,5-tetraazaspiro[5.6]dodec-2,4-diene (IXd): ^{1}H NMR ($CDCl_3$) δ: 8.58-7.24 (m, 11H, Ar-CH), 2.35-1.65 (m, 12H, cycloheptane protons). ^{13}C NMR ($CDCl_3$) δ: 187.1 (C=O), 135.6 (C=N), 144.5-119.6 (Ar-C), 85.3 (spiro carbon), 39.4, 31.2, 28.3, 22.6 (cycloheptane carbons). IR (KBr) ν/cm^{-1}: 1645 (C=O), 1593 (C=N).

1-(4-Chlorophenyl)-3-(2-naphthoyl)-1,2,4,5-tetraazaspiro[5.7]tridec-2,4-diene (IXe): ^{1}H NMR ($CDCl_3$) δ: 8.56-6.98 (m, 11H, Ar-CH), 2.48-1.37 (m, 14H, cyclooctane protons). ^{13}C NMR ($CDCl_3$) δ: 187.2 (C=O), 135.7 (C=N), 142.1-114.7 (Ar-C), 84.9 (spiro carbon), 34.6, 30.8, 28.7, 23.4 (cyclooctane carbons). IR (KBr) ν/cm^{-1}: 1645 (C=O), 1594 (C=N).

4. CONCLUSION

In conclusion, the results demonstrate that the nitrilimines react with hydrazone of aliphatic alkanones and cycloalkanone to give an acyclic addition product, which upon treatment with new catalyst (C/S/Zn) yielded the spiro heterocyclic compounds containing tetrazine moiety.

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http://www.sbjchem.com.
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