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# REACTION OF NITRILIMINES WITH SUBSTITUTED HYDRAZINES: SYNTHESIS OF 1,2,4,5-TETRAAZA-3-PENTENES AND FORMAZANS



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## ABSTRACT

*A series of 1,2,4,5-tetraaza-3-pentenes **4a-j** were synthesized by the reaction of appropriate nitrilimines **2** with substituted hydrazines ($H_2NNHCOR$, R=Ph, OMe) **3**. Heating the compounds **4a-j** with activated charcoal in refluxing benzene oxidized to formazans **5a-j** and some formazans **5f,j** (R = OMe) gave s-tetrazinones **6f,j** in presence of lithium hydride. The microanalysis and spectral data of the synthesized compounds are in full agreement with their molecular structure.*

## KEYWORDS
Nitrilimines, 1,2,4,5-tetraaza-3-pentenes, formazans, s-tetrazinones

## RESUMO

*Uma série de 1,2,4,5-tetraazo -3-pentenos **4a-j** foram sintetizados pela reação das nitriliminas apropriadas **2** com hidrazinas substituídas ($H_2NNHCOR$, R=Ph, OMe) **3**. O aquecimento dos compostos **4a-j** com carvão ativado em benzeno quente levou á oxidação para formazanaos **5aj** e alguns formazanos **5f,j** (R=OMe) e na presença de LiH formaram s-tetrazinonas **6f,j** . As microanalises o os dados espectrais concordam com as estruturas moleculares dos compostos.*

## PALAVRAS CHAVE:

Nitriliminas, 1,2,4,5 tetraazo -3-pentenos, formazanas, s-tetrazinonas



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## GRAPHICAL ABSTRACT

**Reaction of Nitrilimines with Substituted Hydrazines: Synthesis of 1,2,4,5-Tetraaza-3-pentenes and Formazans**

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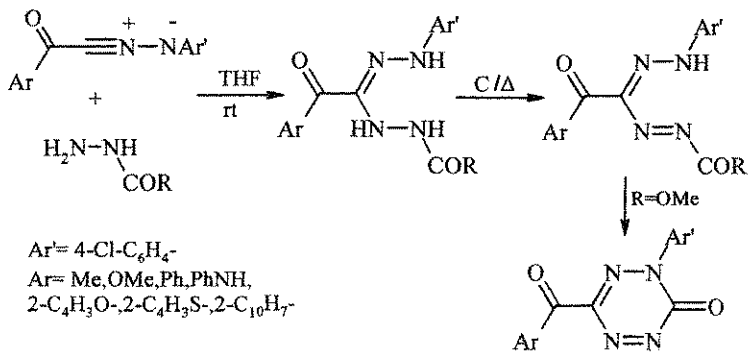


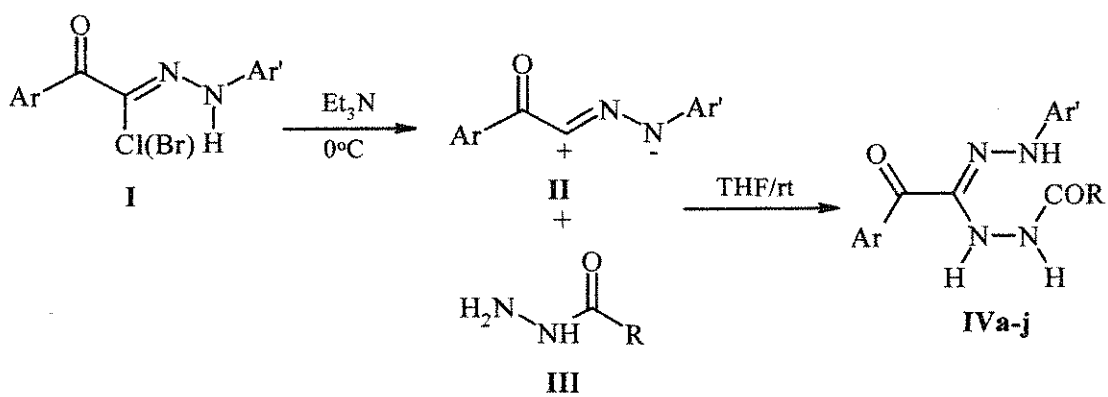
## 1. INTRODUCTION

The preparation of hydrazonoyl halides is well known because of their extensive use in 1,3-dipolar cycloaddition and cyclocondensation reactions. El-Haddad *et al.* [1] was reported the synthesis of 1-methoxycarbonyl-2-[1-(4-chlorophenyl)hydrazono-propan-2-one]hydrazine, which oxidized upon heating with charcoal in refluxing toluene to 3-acetyl-1-methoxy-carbonyl-5-(4-chlorophenyl)formazan.

The reactions nitrilimines and nitrile oxides were recently reviewed by Ferwanah *et al.* [2]. In a continuation of our work concerning the utility of nitrilimines in the synthesis of aza compounds, we investigated the reaction of different C-substituted-N-arylnitrilimines with benzoyl- and methoxycarbonyl hydrazines.

## 2. RESULTS AND DISCUSSION

The precursors of nitrilimines hydrazonoyl chlorides **I** employed in this study were prepared according to reported literature procedures [3-7]. The non isolable nitrilimines **II** immediately reacted with benzoyl and methoxycarbonyl hydrazines **III** affording the corresponding acyclic adducts, 1,2,4,5-tetraaza-3-pentenes **IVa-j** (Scheme 1) in good yields. Structural assignment of **IVa-j** was based on elemental analysis and spectral data. IR spectra of these compounds revealed the presence of the characteristic functional groups. The signals of the $OCH_3$ in both $^1H$- and $^{13}C$ NMR spectra is of particular importance in support of the suggested acyclic structure. The spectral data of the obtained compounds **IVa-j** are presented in the experimental section.

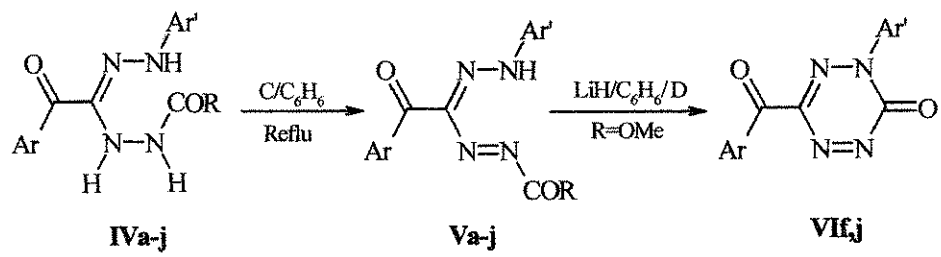



Ar' = 4-Cl-$C_6H_4$-

Ar/R = **a** Me/Ph; **b** Me/OMe; **c** MeO/Ph; **d** Ph/Ph; **e** PhNH/Ph; **f** PhNH/OMe; **g** 2-$C_4H_3O$/Ph; **h** 2-$C_4H_3S$/Ph; **i** 2-$C_{10}H_7$/Ph; **j** 2-$C_{10}H_7$/OMe

**Figure 1.** Synthetic pathway for the preparation of compounds **IVa-j.**

The acyclic adducts **Va-j** were oxidized to the corresponding formazans **Va-j** by heating them with activated charcoal in refluxing benzene or toluene for 6 hours (Scheme 2). No other cyclic products were observed using TLC. Structure elucidation of the obtained formazans **Va-j** was achieved by analytical and spectral data summarized in the experimental section. Their IR spectra revealed the absence of two NH absorption bands. Both and $^{1}$H- and $^{13}$C NMR spectra of compounds **Va-j** showed all the signals of the proposed structures, indicating the disappearance of HN-NH protons, however, the $OCH_3$ signal in compounds **Vb,f,j** does not disappeared which indicated that those compounds are oxidized to the formazans without further cyclization to the expected tetrazinones.




Ar' = 4-Cl-$C_6H_4$-; R = Ph, OMe
Ar = **a** Me; **b** Me; **c** MeO; **d** Ph; **e** PhNH; **f** PhNH; **g** 2-$C_4H_3O$; **h** 2-$C_4H_3S$; **i** 2-$C_{10}H_7$; **j** 2-$C_{10}H_7$

**Figure 2.** Synthetic pathway for the preparation of compounds **Va-j** and **VIf,j.**

The thermal cyclization of formazans **Vf,j** was performed by heating them with lithium hydride in benzene for 4 hours. New products were formed as indicated by TLC and found to be s-tetrazinones **VIf,j** (Figure 2). Structural assignment of compounds **VIf,j** is based on elemental analysis, mass spectra and NMR results. Elemental analysis and mass spectra showed a loss of methanol molecule. Further evidence was obtained from NMR measurements. The $^{1}$H NMR indicate that the NH ($\delta$ = 11.40 ppm) and methoxy protons ($\delta$ = 3.90 ppm) are disappeared. Also the $^{13}$C NMR data illustrated that compounds **VIf,j** have the assigned cyclic structure by the absence of signal for methoxy carbon ($\delta$ = 53.80 ppm) and the presence of the signal at $\delta$ = 159 ppm for the carbonyl carbon of tetrazinone ring.

## 3. EXPERIMENTAL SECTION

### 3.1. Reagents and Instrumentation

Melting points were determined on an A. Krüss Melting Point Meter equipped with a thermometer and are uncorrected. The IR spectra were measured as potassium bromide pellets using a Satellite 3000 Mid infrared spectrophotometer. The $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker AM 300 MHz spectrometer at room temperature in DMSO-$d_6$ solution using tetramethylsilane (TMS) as internal reference. Chemical shifts were recorded as $\delta$ values in parts per millions (ppm) downfield from internal TMS. Electron impact (EI) mass spectra were run on a Shimadzu GCMS-QP1000 EX spectrometer at 70 eV. All compounds were analyzed satisfactorily for C, H and N. The hydrazonoyl halides **Ia-j** [3-7] were prepared according to literature procedures. Tetrahydrofuran (THF) and triethylamine were obtained from Across Company, Belgium. Benzoic acid hydrazide and methyl hydrazinocarboxylate were purchased from Avocado Research Chemicals, England, and used without further purification.

### 3.2. Synthesis of Compounds IVa-j

To a stirred solution of the appropriate hydrazonoyl halide **I** (10 mmol) and hydrazine **III** (20 mmol) in THF (70 mL), triethylamine (4mL, 30 mmol) in THF (10 mL) was dropwise added at 0 °C. The temperature of the reaction mixture was then allowed to rise slowly to room temperature, and stirring was continued overnight. The solvent was then evaporated *in vacuo*, and the residue washed with water (100 mL). The resulting crude solid product was collected and recrystallized from ethanol. The following compounds were prepared using this method:

**3-Acetyl-1-benzoyl-5-(4-chlorophenyl)-1,2,4,5-tetraaza-3-pentene (IVa);** Yield: 75%; m.p.: 177-179 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3432, 3342, 3315 (NH), 1693 ($CH_3$-C=O) 1675 ( Ph-C=O), 1592 (C=N); $^{1}H$ NMR ($CDCl_3$): $\delta$ 9.50 (*s*, 1H, NH), 8.90 (*s*, 1H, NH), 8.27-7.26 (*m*, 9H, Ar-H), 7.31 (*s*, 1H, NH), 2.45 (*s*, 3H, $COCH_3$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 192.3, 169.1, 141.0, 139.6, 135.6, 133.2, 130.8, 130.4, 129.3, 128.5, 120.4, 24.5; MS: *m/z* 330/332 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{16}H_{15}N_4O_2$ (330.78): C, 58.10; H, 4.57; N, 16.94; Found: C, 57.85; H, 4.45; N, 17.10.

**3-Acetyl-5-(4-chlorophenyl)-1-methoxycarboyl-1,2,4,5-tetraaza-3-pentene (IVb):** Yield: 78%; m.p.: 146-148 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3434, 3340, 3319 (NH), 1693 ($CH_3$-C=O) 1710 (O-C=O), 1596 (C=N); $^{1}H$ NMR ($CDCl_3$): $\delta$ 9.54 (*s*, 1H, NH), 8.86 (*s*, 1H, NH), 7.45-6.86 (*m*, 4H, Ar-H), 7.36 (*s*, 1H, NH), 3.61 (*s*, 3H, $OCH_3$), 2.42 (*s*, 3H, $COCH_3$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 192.1, 156.9, 141.0, 139.1, 129.0, 128.2, 120.6, 52.3, 24.6; MS: *m/z* 284/286 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{11}H_{13}N_4O_3$ (284.70): C, 46.41; H, 4.60; N, 19.68; Found: C, 46.20; H, 4.72; N, 19.55.

**1-Benzoyl-5-(4-chlorophenyl)-3-methoxycarbonyl-1,2,4,5-tetraaza-3-pentene (IVc):** Yield: 76%; m.p.: 169-171 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3429, 3337, 3320 (NH), 1715 (O-C=O) 1675 ( Ph-C=O), 1594 (C=N); $^1H$ NMR ($CDCl_3$): δ 9.56 (*s*, 1H, NH), 8.89 (*s*, 1H, NH), 8.22-7.21 (*m*, 9H, Ar-H), 7.38 (*s*, 1H, NH), 3.59 (*s*, 3H, $OCH_3$); $^{13}C$ NMR ($CDCl_3$): *δ* 169.3, 157.1, 141.3, 139.7, 135.3, 133.0, 130.9, 130.2, 129.1, 128.7, 120.7, 52.6; MS: *m/z* 346/348 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{16}H_{15}N_4O_3$ (346.78): C, 55.42; H, 4.36; N, 16.16; Found: C, 55.70; H, 4.21; N, 15.05.

**5-(4-Chlorophenyl)-1,3-dibenzoyl-1,2,4,5-tetraaza-3-pentene (IVd):** Yield: 75%; m.p.: 182-184 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3427, 3337, 3322 (NH), 1677 ( N-C=O), 1640 (Ph-C=O), 1598 (C=N); $^1H$ NMR ($CDCl_3$): δ 10.31 (*s*, 1H, NH), 8.31 (*s*, 1H, NH), 8.17-7.10 (*m*, 14H, Ar-H), 7.37 (*s*, 1H, NH); $^{13}C$ NMR ($CDCl_3$): *δ* 187.5, 169.1, 141.7, 139.5, 136.4, 135.6, 133.2, 132.2, 130.7, 130.1, 129.3, 128.5, 127.9, 127.1, 115.8; MS: *m/z* 392/394 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{21}H_{17}ClN_4O_2$ (392.85): C, 64.21; H, 4.36; N, 14.26; Found: C, 63.98; H, 4.50; N, 14.37.

**1-Benzoyl-5-(4-chlorophenyl)-3-phenylaminocarbonyl-1,2,4,5-tetraaza-3-pentene (IVe):** Yield: 77%; m.p.: 178-180 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3435, 3340, 3328, 3275 (NH), 1675 ( Ph-C=O), 1655 (amide C=O), 1605 (C=N); $^1H$ NMR ($CDCl_3$): δ 10.36, (s, 1H, NH), 9.50 (*s*, 1H, NH), 8.92 (*s*, 1H, NH), 8.83 (*s*, 1H, NH), 8.27-7.26 (*m*, 14H, Ar-H), 7.31 (*s*, 1H, NH); $^{13}C$ NMR ($CDCl_3$): *δ* 169.3, 160.3, 142.5, 138.6, 135.6, 133.2, 130.8, 130.4, 129.4, 128.7, 128.5, 125.0, 123.6, 120.5, 116.2; MS: *m/z* 407/409 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{21}H_{18}ClN_5O_2$ (407.86): C, 61.84; H, 4.45; N, 17.17; Found: C, 62.05; H, 4.30; N, 17.00.

**5-(4-Chlorophenyl)-1-methoxycarboyl-3-phenylaminocarbonyl-1,2,4,5-tetra-aza-3-pentene(IVf):** Yield: 74%; m.p.: 158-160 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3433, 3335, 3325, 3270 (NH), 1725 ( O-C=O), 1653 (amide C=O), 1600 (C=N); $^1H$ NMR ($CDCl_3$): δ 9.49 (*s*, 1H, NH), 8.91 (*s*, 1H, NH), 8.82 (*s*, 1H, NH), 7.45-6.86 (*m*, 9H, Ar-H), 7.36 (*s*, 1H, NH), 3.61 (*s*, 3H, $OCH_3$); $^{13}C$ NMR ($CDCl_3$): *δ* 160.2, 157.6, 142.0, 138.1, 135.2, 129.7, 129.0, 128.2, 127.3, 125.1, 119.8, 52.3; MS: *m/z* 361/363 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{16}H_{16}ClN_5O_3$ (361.79): C, 53.12; H, 4.46; N, 19.36; Found: C, 52.86; H, 4.35; N, 19.45.

**1-Benzoyl-5-(4-chlorophenyl)-3-(2-furoyl)-1,2,4,5-tetraaza-3-pentene (IVg):** Yield: 73%; m.p.: 166-168 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3433, 3341, 3321 (NH), 1676 ( Ph-C=O), 1665 (C=O), 1597 (C=N); $^1H$ NMR ($CDCl_3$): δ 9.49 (*s*, 1H, NH), 8.89 (*s*, 1H, NH), 8.21-7.13 (*m*, 12H, Ar-H), 7.33 (*s*, 1H, NH); $^{13}C$ NMR ($CDCl_3$): *δ* 174.2, 169.2, 141.6, 140.1, 139.1, 135.6, 135.1, 133.2, 130.8, 130.6, 129.0, 128.1, 127.9, 125.4, 120.6; MS: *m/z* 382/384 [$M^+$]; Anal. Calcd. for $C_{19}H_{15}ClN_4O_3$ (382.81): C, 59.62; H, 3.95; N, 14.64; Found: C, 59.40; H, 4.10; N, 14.55.

**1-Benzoyl-5-(4-chlorophenyl)-3-(2-thenoyl)-1,2,4,5-tetraaza-3-pentene (IVh):** Yield: 75%; m.p.: 159-161 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3436, 3340, 3325 (NH), 1678 ( Ph-C=O), 1660 (C=O), 1596 (C=N); $^1H$ NMR ($CDCl_3$): δ 9.46 (*s*, 1H, NH), 8.87 (*s*, 1H, NH), 8.30-7.10 (*m*, 12H, Ar-H), 7.31 (*s*, 1H, NH); $^{13}C$ NMR ($CDCl_3$): *δ* 174.6, 169.3, 141.3, 140.2, 139.3, 135.1, 134.9, 133.2, 130.8, 130.4, 129.3, 128.3, 128.0, 125.3, 120.4; MS: *m/z* 398/400 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{19}H_{15}ClN_4O_2S$ (334.38): C, 57.21; H, 3.79; N, 14.05; Found: C, 57.45; H, 3.90; N, 13.95.

**1-Benzoyl-5-(4-chlorophenyl)-3-(2-naphthoyl)-1,2,4,5-tetraaza-3-pentene (IVi):** Yield: 71%; m.p.: 171-173 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3424, 3331, 3309 (NH), 1693 ($CH_3$-C=O) 1675 ( Ph-C=O), 1592 (C=N); $^1H$ NMR ($CDCl_3$): δ 9.50 (*s*, 1H, NH), 8.90 (*s*, 1H, NH), 8.77-7.26 (*m*, 16H, Ar-H), 7.36 (*s*, 1H, NH); $^{13}C$ NMR ($CDCl_3$): *δ* 183.3, 169.2, 141.4, 139.6, 135.9, 133.8, 133.1, 132.4, 132.2, 130.3, 129.9, 129.1, 128.7, 128.6, 127.9, 127.8, 127.7, 127.4, 126.6, 125.5, 124.3; MS: *m/z* 442/444 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{25}H_{19}ClN_4O_2$ (442.91): C, 67.80; H, 4.32; N, 12.65; Found: C, 68.05; H, 4.20; N, 12.50.

**5-(4-Chlorophenyl)-1-methoxycarbonyl-3-(2-naphthoyl)-1,2,4,5-tetraaza-3-pentene (IVj)**: Yield: 74%; m.p.: 179-181 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3430, 3333, 3311 (NH), 1693 ($CH_3$-C=O) 1675 ( O-C=O), 1592 (C=N); $^1H$ NMR ($CDCl_3$): δ 9.49 (*s*, 1H, NH), 8.86 (*s*, 1H, NH), 8.75-7.24 (*m*, 11H, Ar-H), 7.32 (*s*, 1H, NH), 3.57 (*s*, 3H, $OCH_3$); $^{13}C$ NMR ($CDCl_3$): *δ* 183.6, 157.8, 141.4, 139.1, 135.6, 134.1, 132.5, 132.3, 130.5, 129.9, 129.2, 128.4, 127.8, 127.7, 126.5, 125.6, 124.4, 53.1; MS: *m/z* 396/398 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{20}H_{19}ClN_4O_3$ (396.84): C, 60.53; H, 4.32; N, 14.12; Found: C, 60.35; H, 4.40; N, 14.05.

### 3.3. Synthesis of formazans Va-j

Compounds **IVa-j** (5 mml) were refluxed in benzene or toluene (50 mL) and activated charcoal (1.0 g) for 6 hours. After cooling the reaction was then filtered and the solvent was removed under reduced pressure and the residual solid was collected and recrystallized from chloroform/petroleum ether (b.p. 40-60 oC) to give formazans **Va-j**. The following compounds were prepared using this method:

**3-Acetyl-1-benzoyl-5-(4-chlorophenyl)formazan (Va)**: Yield: 76%; m.p.: 149-151 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3348 (NH), 1685 ($CH_3$-C=O) 1679 ( Ph-C=O), 1590 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.49 (*s*, 1H, NH), 7.40-7.29 (*m*, 11H, Ar-H), 2.60 (*s*, 3H, $COCH_3$); $^{13}C$ NMR ($CDCl_3$): *δ* 193.9 ($CH_3$-C=O), 169.1 (N-C=O), 150.5 (C=N), 26.6 ($COCH_3$); MS: *m/z* 328/330 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{16}H_{13}ClN_4O_2$ (328.76): C, 58.46; H, 3.99; N, 17.04; Found: C, 58.25; H, 4.10; N, 16.90.

**3-Acetyl-5-(4-chlorophenyl)-1-methoxycarboylformazan (Vb):** Yield: 79%; m.p.: 136-138 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3347 (NH), 1720 ( O-C=O), 1686 ($CH_3$-C=O), 1590 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.51 (*s*, 1H, NH), 7.42-7.31 (*m*, 11H, Ar-H), 3.91 (*s*, 3H, $OCH_3$), 2.61 (*s*, 3H, $COCH_3$); $^{13}C$ NMR ($CDCl_3$): *δ* 193.9 ($CH_3$-C=O), 153.8 (N-C=O), 150.4 (C=N), 53.9 ($OCH_3$), 26.6 ($COCH_3$); MS: *m/z* 282/284 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{11}H_{11}ClN_4O_3$ (282.69): C, 46.74; H, 3.92; N, 19.82; Found: C, 46.60; H, 4.05; N, 19.70.

**1-Benzoyl-5-(4-chlorophenyl)-3-methoxycarbonylformazan (Vc):** Yield: 80%; m.p.: 127-129 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3325 (NH), 1725 ( O-C=O), 1673 (Ph-C=O), 1586 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.43 (*s*, 1H, NH), 7.45-7.21 (*m*, 11H, Ar-H), 3.92 (*s*, 3H, $OCH_3$), 2.61 (*s*, 3H, $COCH_3$); $^{13}C$ NMR ($CDCl_3$): *δ* 168.8 (N-C=O), 158.4 (O-C=O), 149.7 (C=N), 53.9 ($OCH_3$); MS: *m/z* 344/346 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{16}H_{13}ClN_4O_3$ (344.76): C, 55.74; H, 3.80; N, 16.25; Found: C, 55.90; H, 3.72; N, 16.33.

**5-(4-Chlorophenyl)-1,3-dibenzoylformazan (Vd)**: Yield: 81%; m.p.: 176-178 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3322 (NH), 1673 (Ph-C=O), 1645 ( Ar-C=O), 1585 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.43 (*s*, 1H, NH), 7.75-7.20 (*m*, 11H, Ar-H); $^{13}C$ NMR ($CDCl_3$): *δ* 185.5 (Ph-C=O), 168.7 (N-C=O) 149.2 (C=N); MS: *m/z* 390/392 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{21}H_{15}ClN_4O_2$ (390.83): C, 64.54; H, 3.87; N, 14.34; Found: C, 64.40; H, 3.75; N, 14.50.

**1-Benzoyl-5-(4-chlorophenyl)-3-phenylaminocarbonyl formazan (Ve):** Yield: 76%; m.p.: 198-200 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3328, 3245 (NH), 1675 ( Ph-C=O), 1655 (Ar- C=O), 1592 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.36, (s, 1H, NH), 8.92 (*s*, 1H, NH), 8.31-7.26 (*m*, 14H, Ar-H); $^{13}C$ NMR ($CDCl_3$): *δ* 168.3 (N-C=O), 161.4 (Ar-C=O), 150.3 (C=N); MS: *m/z* 405/407 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{21}H_{16}ClN_5O_2$ (405.85): C, 62.15; H, 3.97; N, 17.26; Found: C, 61.95; H, 4.10; N, 17.35.

**5-(4-Chlorophenyl)-1-methoxycarboyl-3-phenylaminocarbonylformazan (Vf):** Yield: 79%; m.p.: 188-190 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3325, 3236 (NH), 1722 ( O-C=O), 1650 (Ar-C=O), 1590 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.39 (*s*, 1H, NH), 8.96 (*s*, 1H, NH), 7.45-7.18 (*m*, 9H, Ar-H), 3.90 (*s*, 3H, $OCH_3$); $^{13}C$ NMR ($CDCl_3$): *δ* 161.2 (Ar-C=O), 158.6 (O-C=O), 150.1 (C=N), 53.8 ($OCH_3$); MS: *m/z* 359/361 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{16}H_{14}ClN_5O_3$ (359.77): C, 53.42; H, 3.92; N, 19.47; Found: C, 53.60; H, 4.05; N, 19.35.

**1-Benzoyl-5-(4-chlorophenyl)-3-(2-furoyl) formazan (Vg):** Yield: 81%; m.p.: 172-173 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3329 (NH), 1673 (Ph-C=O), 1660 ( Ar-C=O), 1591 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.36 (*s*, 1H, NH), 7.45-6.71 (*m*, 11H, Ar-H); $^{13}C$ NMR ($CDCl_3$): *δ* 173.4 (Ar-C=O), 168.9 (N-C=O), 150.2 (C=N); MS: *m/z* 380/382 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{19}H_{13}ClN_4O_3$ (380.79): C, 59.93; H, 3.44; N, 14.71; Found: C, 60.15; H, 3.30; N, 14.60.

**1-Benzoyl-5-(4-chlorophenyl)-3-(2-thenoyl) formazan (Vh):** Yield: 82%; m.p.: 165-167 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3325 (NH), 1673 (Ph-C=O), 1665 ( Ar-C=O), 1593 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.37 (*s*, 1H, NH), 7.45-6.71 (*m*, 11H, Ar-H); $^{13}C$ NMR ($CDCl_3$): *δ* 174.6 (Ar-C=O), 168.7 (N-C=O), 150.7 (C=N); MS: *m/z* 396/398 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{19}H_{13}ClN_4O_2S$ (334.38): C, 57.50; H, 3.30; N, 14.12; Found: C, 57.32; H, 3.42; N, 13.98.

**1-Benzoyl-5-(4-chlorophenyl)-3-(2-naphthoyl)formazan (Vi):** Yield: 76%; m.p.: 189-191 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3326 (NH), 1672 (Ph-C=O), 1645 ( Ar-C=O), 1591 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.40 (*s*, 1H, NH), 8.63-7.49 (*m*, 11H, Ar-H); $^{13}C$ NMR ($CDCl_3$): *δ* 183.7 (Ar-C=O), 168.5 (N-C=O), 149.9 (C=N); MS: *m/z* 440/442 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{25}H_{17}ClN_4O_2$ (440.89): C, 68.11; H, 3.89; N, 12.71; Found: C, 67.95; H, 4.00; N, 12.60.

**5-(4-Chlorophenyl)-1-methoxycarbonyl-3-(2-naphthoyl)formazan (Vj):** Yield: 78%; m.p.: 176-178 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3326 (NH), 1671 (Ph-C=O), 1645 ( Ar-C=O), 1591 (C=N); $^1H$ NMR ($CDCl_3$): δ 11.43 (*s*, 1H, NH), 8.65-7.51 (*m*, 11H, Ar-H), 3.90 (*s*, 3H, $OCH_3$);; $^{13}C$ NMR ($CDCl_3$): *δ* 183.7 (Ar-C=O), 153.9 (N-C=O), 149.8 (C=N), 53.8 ($OCH_3$); MS: *m/z* 394/396 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{20}H_{15}ClN_4O_3$ (394.82): C, 60.84; H, 3.83; N, 14.19; Found: C, 60.65; H, 3.72; N, 14.10.

### 3.4. Thermal cyclization of compounds V(f,j) to s-tetrazinones VI(f,j)

To a stirred solution of compounds **Vf,j** (5 mmol) in benzene (50 mL) was carefully added lithium hydride (0.08 g, 10 mmol) at r. t. The resulting reaction mixture was refluxed for 4 hours. After cooling excess lithium hydride was destroyed with some drops of glacial acetic acid . The solvent was evaporated under reduced pressure and the residue was washed with water and then triturated with ethanol (10 mL). The resulting solid product was collected and recrystallized from diethyl ether/petroleum ether (b.p. 40-60 oC) to give s-tetrazinones **VIf,j**. The following compounds were synthesized using this method:

**1-(4-Chlorophenyl)-3-phenylaminocarbonyl-s-tetrazinone (VIf):** Yield: 84%; m.p.: 158-160 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 3276 (NH), 1655 (Ar-C=O), 1598 (C=N); $^1H$ NMR (DMSO-$d_6$): δ 8.86 (*s*, 1H, NH), 7.45-7.18 (*m*, 9H, Ar-H); $^{13}C$ NMR (DMSO-$d_6$): *δ* 159.8 (C=O), 157.8 (PhNH-C=O), 139.8 (C=N); MS: *m/z* 327/329 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{15}H_{10}ClN_5O_2$ (327.73): C, 54.97; H, 3.08; N, 21.37; Found: C, 55.15; H, 2.95; N, 21.45.

**1-(4-Chlorophenyl)-3-(2-naphthoyl)-s-tetrazinone (VIj):** Yield: 82%; m.p.: 168-170 °C; IR (KBr) $\nu_{max}$: $cm^{-1}$ 1645 ( Ar-C=O), 1599 (C=N); $^1H$ NMR (DMSO-$d_6$): δ 8.60-7.48 (*m*, 11H, Ar-H); $^{13}C$ NMR (DMSO-$d_6$): *δ* 184.3 (Ar-C=O), 159.7 (C=O), 140.3 (C=N); MS: *m/z* 362/364 [$M^+$, Chlorine isotopes]; Anal. Calcd. for $C_{19}H_{11}ClN_4O_2$ (362.78): C, 62.91; H, 3.06; N, 15.44; Found: C, 63.10; H, 2.98; N, 15.53.

## 4. CONCLUSION

The nitrilimines **IIa-j** reacted with benzoyl and methoxycarbonyl hydrazines **III** affording the 1,2,4,5-tetraaza-3-pentenes **IVa-j**, which underwent thermal oxidation to the corresponding formazans **Va-j**. The treatment of formazans **Vf,j** with lithium hydride in refluxing benzene gave s-tetrazinones **VIf,j**.

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