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Synthesis of *N*-Aryl-1,5,3-dithiazepanes and *N*-Aryl-1,5,3-dithiazocanes in the Presence of Samarium- and Cobalt-Containing Catalysts

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Abstract—Efficient procedures were developed for the synthesis of *N*-aryl-1,5,3-dithiazepanes and *N*-aryl-1,5,3-dithiazocanes by cyclocondensation of anilines with formaldehyde and α,ω-dithiols (etane-1,2-dithiol and propane-1,3-dithiol), as well as by transamination of *N*-*tert*-butyl-1,5,3-dithiazepane or *N*-*tert*-butyl-1,5,3-dithiazocane with aromatic amines in the presence of samarium and cobalt complexes.

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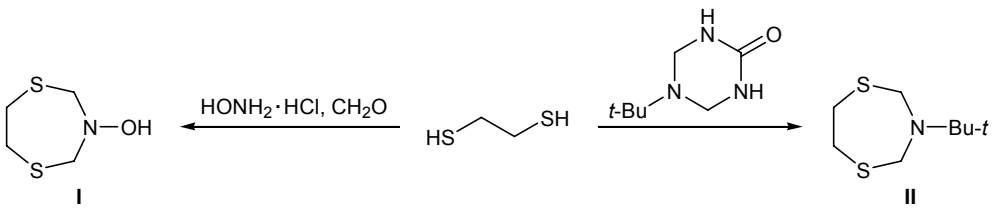
One of the most widely known and simplest procedures for the synthesis of practically important [1–3] heterocycles of the dithiazinane series is based on classical [4] cyclocondensation of primary amines with hydrogen sulfide and formaldehyde [5–10]. Published data on the synthesis of bicyclic [11–15] and N-substituted dithiazepanes [16, 17] are considerably scantier. Ito and Sekiya [16] reported on the synthesis of *N*-hydroxy-1,5,3-dithiazepane (**I**) by cyclocondensation of hydroxylamine hydrochloride with ethane-1,2-dithiol and formaldehyde. Another approach to the synthesis of dithiazepane **II** is based on recyclization of 5-*tert*-butylhexahydro-1,3,5-triazin-2-one with ethane-1,2-dithiol in the presence of $BF_3 \cdot 2HOAc$ [17] (Scheme 1). There are almost no data on preparative procedures for the synthesis of *N*-aryl-1,5,3-dithiazepanes and *N*-aryl-1,5,3-dithiazocanes.

Taking into account the data of [16, 17], we tried to synthesize *N*-aryl-1,5,3-dithiazepanes and *N*-aryl-1,5,3-dithiazocanes by cyclocondensation of primary aromatic amines with formaldehyde and α,ω-dithiols (ethane-1,2-dithiol and propane-1,3-dithiol). We examined in detail the effects of the solvent nature, reactant ratio, temperature, and reaction time on the yield of cyclocondensation products from aniline, formaldehyde, and ethane-1,2-dithiol. Aniline reacted with CH_2O and ethane1,2-dithiol at a molar ratio of 1 : 2 : 1 in chloroform at 20°C to give ~65% of *N*-phenyl-1,5,3-dithiazepane (**IIIa**) in 6 h (Scheme 2). With a view to improve the yield of **IIIa**, the reaction was carried out in the presence of Cu, Co, Mn, Ti, Hf, V, Fe, Sm, and Ni salts and complexes, which were used by us previously [18] to catalyze the synthesis of N-substituted 1,3,5-dithiazinanes. Among the examined catalysts, only $Sm(NO_3)_3 \cdot 6H_2O$ ensured formation of heterocycle **IIIa** in 88% yield in 0.5 h (see table). Therefore, all subsequent heterocyclizations of anilines with formaldehyde and ethane-1,2-dithiol were carried out in the presence of 5 mol % of $Sm(NO_3)_3 \cdot 6H_2O$ as catalyst.

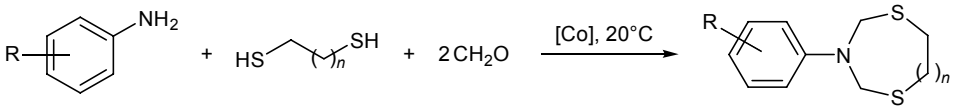
Under analogous conditions [5 mol % of $Sm(NO_3)_3 \cdot 6H_2O$, 20°C, 0.5 h, $CHCl_3$ as solvent] heterocycliza-

Scheme 1.



I II

Scheme 2.



IIIa–IIIi, n = 1; **IVa–IVi**, n = 2

R = H (**a**), 3-Me (**b**), 4-Me (**c**), 2-MeO (**d**), 3-MeO (**e**), 4-MeO (**f**), 2-O_2N (**g**), 3-O_2N (**h**), 4-O_2N (**i**).

tion of *m*- and *p*-toluidines with formaldehyde and ethane-1,2-dithiol gave 3-(3- and 4-methylphenyl)-1,5,3-dithiazepanes **IIIb** and **IIIc** in 73 and 79% yield, respectively. Likewise, from *o*-, *m*-, and *p*-methoxyanilines we obtained 59–87% of the corresponding 3-(methoxyphenyl)-1,5,3-dithiazepanes **IIId**–**IIIf**. The cyclocondensation with isomeric nitroanilines afforded 68–79% of *N*-(nitrophenyl) derivatives **IIIg**–**IIIi**.

In the ^{1}H NMR spectrum of **IIIa**, signals from protons on C^2 and C^4 appeared as sharp singlets at δ 4.80 ppm, while the 6-H and 7-H protons resonated at δ 3.08 ppm, indicating fast ring inversion on the NMR time scale. The ^{13}C NMR spectrum contained signals at δ_C 54.92 and 35.78 ppm due to carbon atoms in the dithiazepane ring.

We presumed that *N*-aryl-1,5,3-dithiazepanes **III** are obtained in the cyclocondensation with ethane-1,2-dithiol and formaldehyde via initial formation of 1,3,6-oxadithiepane which then undergoes recyclization by the action of aromatic amine in the presence of the selected catalyst. This assumption was verified by reacting 1,3,6-oxadithiepane with aniline, *m*-toluidine, *o*-methoxyaniline, and *p*-nitroaniline in the presence of $Sm(NO_3)_3\cdot 6H_2O$ (reactant molar ratio 10 : 10 : 0.5, 20°C, $CHCl_3$, 3 h). In all cases, the corresponding *N*-aryl-1,5,3-dithiazepanes **IIIa**, **IIIb**, **IIId**, and **IIIi** were formed in 74, 76, 70, and 82% yield, respectively, which was confirmed by NMR data. In the ^{13}C NMR spectrum of 1,3,6-oxadithiepane carbon atoms in the SCH_2CH_2S fragment resonated at δ_C 31.90 ppm, and the SCH_2O carbon signal appeared at δ_C 66.17 ppm. After addition of an equimolar amount of aniline containing 5 mol % of $Sm(NO_3)_3\cdot 6H_2O$, signals assigned to 1,3,6-oxadithiepane disappeared from the ^{13}C NMR spectrum, and those typical of 1,5,3-dithiazepanes appeared instead at δ_C 35.27 and 54.52 ppm. Presumably, catalytic opening of the oxadithiepane ring under the conditions given in [17–19] is followed by nucleophilic addition of aromatic amine to the carbenium ion thus generated, leading to complex **B** through intermediate **A**. In the final step, intramolecular cyclization yields *N*-aryl-1,5,3-dithiazepane (Scheme 3).

We also tried to elucidate the possibility for selective synthesis of 1,5,3-dithiazocane derivatives by analogous reaction. For this purpose, propane-1,3-dithiol was involved in catalytic heterocyclization with aromatic amines and formaldehyde. The reaction of aniline with CH_2O and propane-1,3-dithiol (1 : 2 : 1) at room temperature in the absence of a catalyst gave 10% of a product which was identified as 3-phenyl-1,5,3-dithiazocane (**IVa**). The yield of **IVa** was improved to 48% using 5 mol % of $Sm(NO_3)_3\cdot 6H_2O$ as catalyst ($CHCl_3$, 3 h, 20°C). The best results were obtained with the use of $Co(acac)_2$ which ensured formation of 66% of compound **IVa** in 3 h at 20°C. Under analogous conditions, heterocyclizations of *m*- and *p*-toluidines, *o*-, *m*-, and *p*-methoxyanilines, and *o*-, *m*-, and *p*-nitroanilines with formaldehyde and propane-1,3-dithiol selectively produced the corresponding *N*-aryl-1,5,3-dithiazocanes **IVb**–**IVi** in 69–95% yield (Scheme 2).

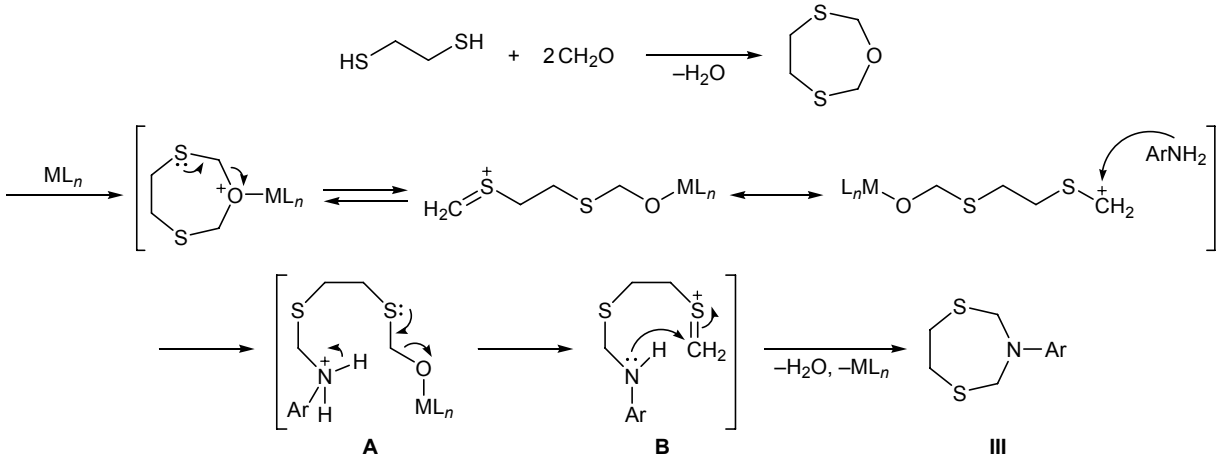
The ^{1}H NMR spectrum of compound **IVa** contained a triplet at δ 2.74 ppm due to protons on C^6 and C^8, methylene protons on C^2 and C^4 gave a sharp singlet at δ 4.78 ppm, and protons on C^7 resonated as a multiplet at δ 1.79 ppm.

In continuation of our previous study on the synthesis of *N*-aryl-1,3,5-dithiazinanes by catalytic transamination of *N*-methyl-1,3,5-dithiazinane with aromatic amines [18], we examined analogous transamination of *N*-*tert*-butyl-1,5,3-dithiazepane with anilines in the presence of catalysts based on transition and rare-earth

Yields of *N*-phenyl-1,5,3-dithiazepane (**IIIa**) in the reaction of aniline with formaldehyde and ethane-1,2-dithiol (reactant ratio 1 : 2 : 1) in the presence of different catalysts (5 mol %; 20°C, 0.5 h, $CHCl_3$)

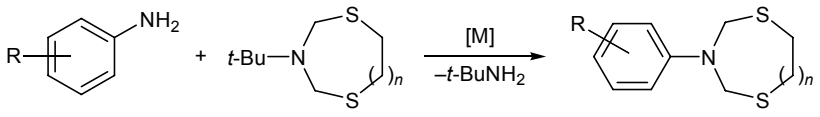
Catalyst	**IIIa**, %	Catalyst	**IIIa**, %
$Sm(NO_3)_3\cdot 6H_2O$	88	$MnCl_2$	59
Cp_2TiCl_2	75	Cp_2HfCl_2	52
$CuCl_2$	72	$VO(acac)_2$	49
$FeCl_3\cdot 6H_2O$	70	$NiCl_2$	45
$CoCl_2$	66	No catalyst	7

Scheme 3.



M = Sm, Ti, Cu, Co, Mn, Hf, V, Ni.

Scheme 4.



IIIa, **IIIb**, **IIIe**, **IIIh**, *n* = 1
IVa, **IVb**, **IVe**, **IVh**, *n* = 2

R = H (**a**), 3-Me (**b**), 3-MeO (**e**), 3-O_2N (**h**).

metals with a view to develop a new selective procedure for the synthesis of *N*-aryl-1,5,3-dithiazepanes (Scheme 4).

Preliminary experiments showed that the reaction of aniline with an equimolar amount of *N*-*tert*-butyl-1,5,3-dithiazepane without a catalyst ($CHCl_3$, 20°C, 3 h) leads to the formation of *N*-phenyl-1,5,3-dithiazepane (**IIIa**) in a poor yield (~8%). To raise the yield of compound **IIIa**, the reaction was carried out in the presence of Cu, Pd, Co, Zr, Ti, Hf, V, Fe, and Sm salts and complexes [18]. Among the examined catalysts, $Sm(NO_3)_3 \cdot 6H_2O$ (5 mol %) revealed the highest catalytic activity, and *N*-phenyl-1,5,3-dithiazepane (**IIIa**) was obtained in 78% yield. Under the developed conditions [5 mol % of $Sm(NO_3)_3 \cdot 6H_2O$, 20°C, 3 h, $CHCl_3$], *m*-toluidine and *m*-methoxyaniline reacted with *N*-*tert*-butyl-1,5,3-dithiazepane to produce *N*-(3-methylphenyl)- and *N*-(3-methoxyphenyl)-1,5,3-dithiazepanes **IIIb** and **IIIe** in 70 and 73% yield, respectively. Likewise, the transamination of *N*-*tert*-butyl-1,5,3-dithiazepane with *m*-nitroaniline selectively afforded 64% of *N*-(3-nitrophenyl)-1,5,3-dithiazepane (**IIIh**). The same procedure was successfully used to synthesize difficultly accessible *N*-aryl-1,5,3-dithiazocanes **IV** (yield 63–86%) by transamination of *N*-*tert*-butyl-1,5,3-dithiazocane with aniline, *m*-toluidine, *m*-methoxyaniline, and *m*-nitroaniline in the presence of $Sm(NO_3)_3 \cdot 6H_2O$ (20°C, 3 h, $CHCl_3$).

EXPERIMENTAL

The progress of reactions was monitored by TLC on Silufol UV-254 plates; spots were developed with iodine vapor. The products were analyzed by HPLC on an Altex-330 chromatograph (USA) equipped with a UV detector (λ 340 nm). The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400.13 and 100.62 MHz, respectively, from solutions in $CDCl_3$ using standard Bruker procedures. GC–MS analysis was performed on Finnigan-4021 (HP-5 glass capillary column, 50 m×0.25 mm; carrier gas helium; oven temperature programming from 50 to 300°C at a rate of 5 deg/min, injector temperature 280°C; ion source temperature 250°C; electron impact, 70 eV) and Shimadzu QP-2010Plus instruments (Supelco PTE-5 capillary column, 30 m×0.25 mm). Silica gel KSK (100–200 μm) was used for column chromatography; eluent hexane–chloroform–ethyl acetate (5:1:1).

***N*-Aryl-1,5,3-dithiazepanes and *N*-aryl-1,5,3-dithiazocanes (*general procedures*).** *a. Cyclocondensa-*

tion of aromatic amines with formaldehyde and ethane-1,2-dithiol or propane-1,3-dithiol. A Schlenk flask equipped with a magnetic stirrer was charged at 20°C under argon with 20 mmol of formaldehyde and 10 mmol of ethane-1,2-dithiol or propane-1,3-dithiol, the mixture was stirred for 30 min, 5 ml of chloroform, 0.5 mmol of $Sm(NO_3)_3 \cdot 6H_2O$, and 10 mmol of the corresponding aromatic amine were added, and the mixture was stirred for 30 min at 20°C.

b. Transamination of N-tert-butyl-1,5,3-dithiazepane or N-tert-butyl-1,5,3-dithiazocane with aromatic amines. A Schlenk flask equipped with a magnetic stirrer was charged under argon with 10 mmol of *N-tert*-butyl-1,5,3-dithiazepane or *N-tert*-butyl-1,5,3-dithiazocane, 5 ml of chloroform, 0.5 mmol of $Sm(NO_3)_3 \cdot 6H_2O$, and 10 mmol of the corresponding amine were added, and the mixture was stirred for 3 h at 20°C.

3-Phenyl-1,5,3-dithiazepane (IIIa). Yield 88%, R_f 0.44, mp 99–100°C. ^{1}H NMR spectrum, δ, ppm: 3.08 s (4H, CH_2), 4.80 s (4H, CH_2), 6.91–7.35 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 35.78 (C^6, C^7), 54.92 (C^2, C^4), 115.93 (C^9, C^{13}), 119.95 (C^{11}), 129.30 (C^{10}, C^{12}), 145.83 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 211 (12) $[M]^+$, 77 (10) $[C_6H_5]^+$, 91 (15) $[C_6H_5N]^+$, 137 (100) $[C_7H_7NS]^+$, 165 (95) $[C_9H_{12}NS]^+$. Found, %: C 56.46; H 6.10; N 6.24; S 30.15. $C_{10}H_{13}NS_2$. Calculated, %: C 56.83; H 6.20; N 6.63; S 30.34. *M* 211.35.

3-(3-Methylphenyl)-1,5,3-dithiazepane (IIIb). Yield 72%, R_f 0.64, mp 121–123°C. ^{1}H NMR spectrum, δ, ppm: 2.38 s (3H, CH_3), 3.10 s (4H, CH_2), 4.81 s (4H, CH_2), 6.79–7.23 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 21.83 (CH_3), 35.91 (C^6, C^7), 55.06 (C^2, C^4), 112.29 (C^{13}), 116.69 (C^9), 120.93 (C^{11}), 129.08 (C^{10}), 138.90 (C^{12}), 145.95 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 225 (12) $[M]^+$, 91 (70) $[C_7H_7]^+$, 106 (100) $[C_7H_8N]^+$, 119 (100) $[C_8H_9N]^+$, 165 (40) $[C_{11}H_{14}NS]^+$. Calculated: *M* 225.38.

3-(4-Methylphenyl)-1,5,3-dithiazepane (IIIc). Yield 70%, R_f 0.75, mp 120–122°C. ^{1}H NMR spectrum, δ, ppm: 2.33 s (3H, CH_3), 3.91 s (4H, CH_2), 4.89 s (4H, CH_2), 6.53–6.67 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 21.77 (C^{14}), 35.83 (C^6, C^7), 54.95 (C^2, C^4), 114.76 (C^9, C^{13}), 119.43 (C^{10}, C^{12}), 139.04 (C^{11}), 148.74 (C^8). Found, %: C 58.40; H 6.23; N 6.07; S 28.19. $C_{11}H_{15}NS_2$. Calculated, %: C 58.62; H 6.71; N 6.21; S 28.46.

3-(2-Methoxyphenyl)-1,5,3-dithiazepane (IIId). Yield 65%, R_f 0.71, mp 112–114°C. ^{1}H NMR spectrum, δ, ppm: 2.71–2.95 m (4H, CH_2), 3.35 s (3H, CH_3), 4.53 s (4H, CH_2), 6.67–7.87 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 33.48 (C^6, C^7), 53.66 (C^{15}), 58.93 (C^2, C^4), 111.35 (C^{11}), 115.76 (C^{13}), 123.05 (C^{10}), 128.96 (C^{12}), 144.78 (C^9), 147.20 (C^8). Found, %: C 54.13; H 6.09; N 5.59; S 26.05. $C_{11}H_{15}NOS_2$. Calculated, %: C 54.74; H 6.26; N 5.80; S 26.57.

3-(3-Methoxyphenyl)-1,5,3-dithiazepane (IIIe). Yield 89%, R_f 0.77, mp 109–110°C. ^{1}H NMR spectrum, δ, ppm: 2.61–2.73 m (4H, CH_2), 3.42 s (3H, CH_3), 4.47 s (4H, CH_2), 6.71–7.53 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 33.95 (C^6, C^7), 52.00 (C^{15}), 60.97 (C^2, C^4), 109.89 (C^{11}), 112.43 (C^{12}), 119.97 (C^{13}), 124.77 (C^9), 144.55 (C^{10}), 147.32 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 241 (20) $[M]^+$, 77 (70) $[C_6H_5]^+$, 106 (40) $[C_7H_6O]^+$, 120 (100) $[C_7H_6ON]^+$, 135 (60) $[C_8H_9NO]^+$, 180 (10) $[C_9H_{11}NOS]^+$, 208 (80) $[C_{11}H_{15}NOS]^+$. Calculated: *M* 241.37.

3-(4-Methoxyphenyl)-1,5,3-dithiazepane (IIIf). Yield 79%, R_f 0.62, mp 118–120°C. ^{1}H NMR spectrum, δ, ppm: 2.64–2.81 m (4H, CH_2), 3.51 s (3H, CH_3), 4.39 s (4H, CH_2), 6.59–7.12 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 34.28 (C^6, C^7), 51.93 (C^{15}), 59.99 (C^2, C^4), 113.33 (C^9, C^{13}), 125.07 (C^{10}, C^{12}), 143.98 (C^{11}), 148.01 (C^8). Found, %: C 54.33; H 6.18; N 5.47; S 26.38. $C_{11}H_{15}NOS_2$. Calculated, %: C 54.74; H 6.26; N 5.80; S 26.57.

3-(2-Nitrophenyl)-1,5,3-dithiazepane (IIIg). Yield 67%, R_f 0.65, mp 81–83°C. ^{1}H NMR spectrum, δ, ppm: 2.66–2.99 m (4H, CH_2), 4.46 s (4H, CH_2), 6.67–7.87 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 34.51 (C^6, C^7), 59.65 (C^2, C^4), 110.55 (C^{11}), 114.71 (C^{13}), 122.45 (C^{10}), 129.01 (C^{12}), 145.92 (C^9), 147.20 (C^8). Mass spectrum, *m*/*z* (I_{rel}, %): 256 (20) $[M]^+$, 122 (70) $[C_6H_4NO_2]^+$, 136 (40) $[C_6H_4N_2O_2]^+$, 181 (100) $[C_7H_8N_2O_2S]^+$, 210 (100) $[C_9H_{10}N_2O_2S]^+$. Calculated: *M* 256.35.

3-(3-Nitrophenyl)-1,5,3-dithiazepane (IIIh). Yield 79%, R_f 0.68, mp 76–78°C. ^{1}H NMR spectrum, δ, ppm: 2.74–2.79 m (4H, CH_2), 4.14 s (4H, CH_2), 7.12–7.74 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 35.45 (C^6, C^7), 61.59 (C^2, C^4), 109.43 (C^{11}), 113.55 (C^{13}), 121.13 (C^9), 128.73 (C^{12}), 143.67 (C^{10}), 147.01 (C^8). Found, %: C 46.63; H 4.72; N 10.57; S 25.00. $C_{10}H_{12}N_2O_2S_2$. Calculated, %: C 46.85; H 4.72; N 10.93; S 25.02.

3-(4-Nitrophenyl)-1,5,3-dithiazepane (IIIi). Yield 73%, R_f 0.55, mp 91–92°C. ^{1}H NMR spectrum, δ, ppm: 2.79–2.90 m (4H, CH_2), 4.30 s (4H, CH_2), 6.91–7.85 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 36.41 (C^6, C^7), 59.75 (C^2, C^4), 111.92 (C^9, C^{13}), 124.25

(C^{10}, C^{12}), 138.90 (C^{11}), 149.52 (C^{8}). Found, %: C 46.33; H 4.41; N 10.52; S 24.99. $C_{10}H_{12}N_2O_2S_2$. Calculated, %: C 46.85; H 4.72; N 10.93; S 25.02.

3-Phenyl-1,5,3-dithiazocane (IVa). Yield 95%, R_f 0.77, mp 96–98°C. ^{1}H NMR spectrum, δ, ppm: 1.79–1.84 m (2H, CH_2), 2.74 t (4H, CH_2, J = 5.6 Hz), 4.78 s (4H, CH_2), 6.88–7.37 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 29.00 (C^7), 29.16 (C^6, C^8), 55.16 (C^2, C^4), 114.66 (C^{12}), 119.58 (C^{14}), 120.94 (C^{11}), 128.78 (C^{13}), 143.31 (C^{10}), 144.38 (C^9). Mass spectrum, m/z (I_{rel}, %): 225 (10) $[M]^+$, 77 (20) $[C_6H_5]^+$, 91 (80) $[C_6H_5N]^+$, 107 (20) $[C_5H_7N]^+$, 120 (100) $[C_8H_{10}N]^+$. Calculated: M 225.38.

3-(3-Methylphenyl)-1,5,3-dithiazocane (IVb). Yield 88%, R_f 0.90, mp 77–79°C. ^{1}H NMR spectrum, δ, ppm: 1.79 m (2H, CH_2), 2.43 s (3H, CH_3), 2.76 t (4H, CH_2, J = 5.6 Hz), 4.78 s (4H, CH_2), 6.76–7.28 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 22.21 (C^{15}), 29.05 (C^7), 32.29 (C^6, C^8), 56.70 (C^2, C^4), 111.01 (C^{14}), 113.25 (C^{12}), 119.66 (C^{13}), 129.23 (C^{11}), 139.04 (C^{10}), 143.47 (C^9). Mass spectrum, m/z (I_{rel}, %): 239 (20) $[M]^+$, 91 (80) $[C_7H_7]^+$, 105 (100) $[C_7H_7N]^+$, 150 (50) $[C_8H_9NS]^+$, 180 (100) $[C_{10}H_{16}NS]^+$. Calculated: M 239.40.

3-(4-Methylphenyl)-1,5,3-dithiazocane (IVc). Yield 81%, R_f 0.88, mp 70–72°C. ^{1}H NMR spectrum, δ, ppm: 1.83 m (2H, CH_2), 2.36 s (3H, CH_3), 2.71 t (4H, CH_2, J = 5.6 Hz), 4.72 s (4H, CH_2), 6.80–7.29 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 22.04 (C^{15}), 30.42 (C^7), 32.92 (C^6, C^8), 56.77 (C^2, C^4), 114.30 (C^{14}, C^{16}), 126.51 (C^{11}, C^{13}), 138.98 (C^{12}), 142.90 (C^9). Found, %: C 60.13; H 7.08; N 5.43; S 26.62. $C_{12}H_{17}NS_2$. Calculated, %: C 60.20; H 7.16; N 5.85; S 26.79.

3-(2-Methoxyphenyl)-1,5,3-dithiazocane (IVd). Yield 66%, R_f 0.56, mp 83–85°C. ^{1}H NMR spectrum, δ, ppm: 1.82 m (2H, CH_2), 2.66 m (4H, CH_2), 3.77 s (3H, CH_3), 4.72 s (4H, CH_2), 6.77–7.74 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 29.17 (C^7), 30.36 (C^6, C^8), 53.79 (C^{16}), 55.16 (C^2, C^4), 106.33 (C^{11}), 127.61 (C^{14}), 129.93 (C^{13}), 131.57 (C^{12}), 144.81 (C^9), 160.42 (C^{10}). Mass spectrum, m/z (I_{rel}, %): 255 (20) $[M]^+$, 107 (10) $[C_7H_7O]^+$, 121 (70) $[C_7H_7NO]^+$, 135 (25) $[C_8H_9NO]^+$, 149 (100) $[C_9H_{11}NO]^+$. Calculated: M 255.40.

3-(3-Methoxyphenyl)-1,5,3-dithiazocane (IVe). Yield 83%, R_f 0.71, mp 94–95°C. ^{1}H NMR spectrum, δ, ppm: 1.78 m (2H, CH_2), 2.83 t (4H, CH_2, J = 5.6 Hz), 3.83 s (3H, CH_3), 4.74 s (4H, CH_2), 6.55–7.28 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 29.00 (C^7), 32.14 (C^6, C^8), 55.24 (C^{16}), 55.59 (C^2, C^4), 100.32 (C^{10}), 103.91 (C^{12}), 107.91 (C^{14}), 130.07 (C^{13}), 147.20 (C^9), 160.74 (C^{11}). Found, %: C 56.21; H 6.50; N 5.13; S 25.08. $C_{12}H_{17}N_2OS_2$. Calculated, %: C 56.44; H 6.71; N 5.48; S 25.11.

3-(4-Methoxyphenyl)-1,5,3-dithiazocane (IVf). Yield 80%, R_f 0.79, mp 97–98°C. ^{1}H NMR spectrum, δ, ppm: 1.81 m (2H, CH_2), 2.73 t (4H, CH_2, J = 5.6 Hz), 3.80 s (3H, CH_3), 4.76 s (4H, CH_2), 6.81–7.27 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 29.99 (C^7), 32.26 (C^6, C^8), 55.65 (C^{16}), 57.04 (C^2, C^4), 114.36 (C^{11}, C^{13}), 114.89 (C^{10}, C^{14}), 137.34 (C^9), 152.85 (C^{12}). Found, %: C 56.41; H 6.38; N 5.24; S 25.03. $C_{12}H_{17}N_2OS_2$. Calculated, %: C 56.44; H 6.71; N 5.48; S 25.11.

3-(2-Nitrophenyl)-1,5,3-dithiazocane (IVg). Yield 69%, R_f 0.55, mp 91–92°C. ^{1}H NMR spectrum, δ, ppm: 1.57 m (2H, CH_2), 2.63 m (4H, CH), 4.52 s (4H, CH_2), 6.77–7.74 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 38.67 (C^7), 29.47 (C^6, C^8), 55.46 (C^2, C^4), 114.81 (C^{10}, C^{14}), 116.85 (C^{12}), 126.92 (C^{11}, C^{13}), 136.02 (C^9). Mass spectrum, m/z (I_{rel}, %): 270 (20) $[M]^+$, 122 (80) $[C_6H_4NO_2]^+$, 136 (100) $[C_6H_4N_2O_2]^+$, 150 (40) $[C_7H_6N_2O_2]^+$, 196 (20) $[C_8H_8N_2O_2S]^+$. Calculated: M 270.37.

3-(3-Nitrophenyl)-1,5,3-dithiazocane (IVh). Yield 75%, R_f 0.60, mp 63–64°C. ^{1}H NMR spectrum, δ, ppm: 1.92 m (2H, CH_2), 2.28 m (4H, CH_2), 4.51 s (4H, CH_2), 7.01–8.23 m (5H, CH). ^{13}C NMR spectrum, δ_C, ppm: 27.99 (C^7), 32.00 (C^6, C^8), 53.98 (C^2, C^4), 111.33 (C^{14}), 118.85 (C^{12}), 121.27 (C^{10}), 129.80 (C^{11}), 138.90 (C^9), 141.60 (C^{13}). Found, %: C 48.50; H 5.15; N 10.21; S 23.52. $C_{11}H_{17}N_2O_2S_2$. Calculated, %: C 48.86; H 5.22; N 10.36; S 23.72.

3-(4-Nitrophenyl)-1,5,3-dithiazocane (IVi). Yield 86%, R_f 0.53, mp 81–83°C. ^{1}H NMR spectrum, δ, ppm: 1.84 m (2H, CH_2), 2.72 t (4H, CH_2, J = 6, 5.6 Hz), 4.78 s (4H, CH_2), 7.93–8.22 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 29.17 (C^7), 31.77 (C^6, C^8), 56.56 (C^2, C^4), 112.87 (C^{10}, C^{14}), 125.72 (C^{11}, C^{13}), 139.63 (C^{12}), 148.70 (C^9). Found, %: C 48.31; H 5.18; N 10.10; S 23.29. $C_{11}H_{17}N_2O_2S_2$. Calculated, %: C 48.86; H 5.22; N 10.36; S 23.72.

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