Novel 1,5,3-dithiazepanes: three-component synthesis, stereochemistry, and fungicidal activity

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Three-component heterocyclization of hydrazine with formaldehyde and ethane-1,2-dithiol gave previously unknown 3,3′-bi(1,5,3-dithiazepane). Its stereochemistry was determined by X-ray diffraction. The reaction with higher aliphatic aldehydes RCHO (R = Me, Et, Pr^n, and Bu^n) yielded 2,4-dialkyl-3-alkylideneamino-1,5,3-dithiazepanes. The stereochemistry of the latter was determined by ^1H and ^{13}C NMR spectroscopy and confirmed by quantum chemical calculations. Heterocyclizations of phenylhydrazine and benzylhydrazine with ethane-1,2-dithiol gave 3-amino-1,5,3-dithiazepanes only with CH_2O and MeCHO as the aldehyde component. 3,3′-Bi(1,5,3-dithiazepane) and its N-adduct with MeI were found to exhibit fungicidal activity against microscopic fungi.

Key words: heterocyclization, hydrazines, aldehydes, ethane-1,2-dithiol, 1,5,3-dithiazepanes, stereochemistry, X-ray diffraction analysis, fungicides.

In the last few years, multicomponent and domino reactions have given strong impetus to the development of "one pot" methods for the regiocontrolled synthesis of heterocycles. In particular, three-component reactions of hydrazines with formaldehyde and H_2S are used to obtain 1,3,4-thiadiazolidines,[1,2] which are valuable bactericides, fungicides, and drugs.[3—5]

We assumed that the use of ethane-1,2-dithiol in the thiomethylation of hydrazine would extend the synthetic scope of this reaction and afford novel biologically active heterocyclic systems containing the methylenethioethylene fragments $—CH_2SCH_2CH_2—$.

The literature data on three-component condensation of ethane-1,2-dithiol with aldehydes and hydrazine are lacking. However, it has been reported[6] that base-catalyzed three-component heterocyclization between ethane-1,2-dithiol, CH_2O, and ketones produces 6-acyl-1,4-dithiepanes as mixtures with polymeric γ-oxo bissulfides.

The present work was intended to develop methods for the synthesis of dialkyldithiazepanes. For this purpose, we studied three-component condensation between hydrazines, ethane-1,2-dithiol, and aliphatic aldehydes RCHO (R = H, Me, Et, Pr^n, and Bu^n). The stereochemistry of the compounds obtained was examined both theoretically and experimentally. In addition, they were tested for fungicidal activity against the microscopic fungi *Bipolaris sorokiniana*, *Fusarium oxysporium*, *Aspergillus fumigatus*, *Aspergillus niger*, and *Paecilomyces variotii*.

Results and Discussion

Recently,[7] we have demonstrated that the regiospecificity of three-component heterocyclization between hydrazine, H_2S, and acetaldehyde substantially depends on the reaction conditions. By optimizing the reaction conditions, we succeeded in the selective synthesis of 2,4,6,8-tetramethyl-1,3,4-thiadiazolo[3,4-*c*]-1,3,4-thiadiazole or 5-amino-2,4,6-trimethyl-1,3,5-dithiazinane.[8]

Here, we carried out a reaction between hydrazine (**1**), CH_2O (**2**), and ethane-1,2-dithiol (**3**) by varying several

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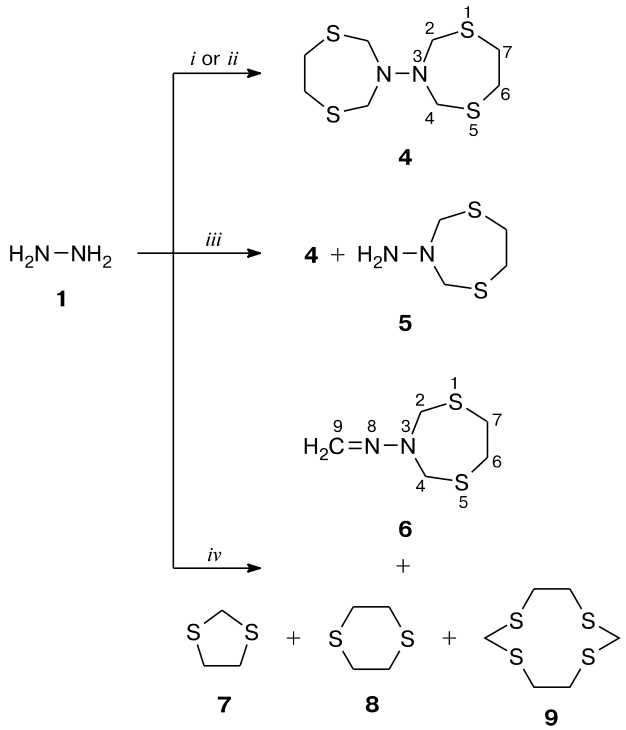
factors (temperature, concentration of the starting reagents, order of mixing, and pH) to examine their effect on the reaction pathway.

It turned up that this reaction produces no annulated heterocycles, in contrast to similar reactions between hydrazine, H_2S, and aldehydes RCHO (R = H and Me). For instance, condensation of hydrazine (**1**) with formaldehyde (**2**) and ethane-1,2-dithiol (**3**) in a ratio of 1 : 4 : 2 at 0—70 °C without any acid or base (pH 3.15—3.20) and in the presence of a base (pH 11.50—11.70) selectively gives 3,3′-bi(1,5,3-dithiazepane) (**4**) in 81 and 79% yields, respectively. An increase in the reaction temperature to 80 °C leads to a 1 : 2 mixture of compound **4** and 3-amino-1,5,3-dithiazepane (**5**) in a total yield of 93%. Heterocyclization in the presence of HCl (pH 0.45—0.5) gives 3-methylideneamino-1,5,3-dithiazepane (**6**) and sulfur-containing products **7**—**9** derived from CH_2O and ethane-1,2-dithiol in a total yield of 99% (Scheme 1). Note that the range of products in the above reactions does not vary with the concentrations or order of mixing of the starting reagents.

Scheme 1



Reagents and conditions: *i*. **1**—**2**—**3**, 1 : 4 : 2, 0—70 °C (pH 3.15—3.20); *ii*. **1**—BuONa—**2**—**3**, 1 : 4 : 4 : 2, 0—70 °C (pH 11.50—11.70); *iii*. **1**—**2**—**3**, 1 : 4 : 2, 80 °C, (pH 3.15—3.20); *iv*. **1**—HCl—**2**—**3**, 1 : 4 : 4 : 2, 20 °C, (pH 0.45—0.5).

Thus, by varying the conditions for the three-component reaction between hydrazine, ethane-1,2-dithiol, and CH_2O, we obtained three types of dithiazepane derivatives: 3,3′-bi(1,5,3-dithiazepane) (**4**), 3-amino-1,5,3-dithiazepane (**5**), and 3-methylideneamino-1,5,3-dithiazepane (**6**). According to our experimental data, the heterocyclization is only selective in the synthesis of 3,3′-bi(1,5,3-dithiazepane) (**4**); at 20—25 °C, its yield is 80%.

The structure of 3,3′-bi(1,5,3-dithiazepane) (**4**) was proved by ^1H and ^{13}C NMR spectroscopy and X-ray diffraction. The ^1H NMR spectra show narrow singlets for the protons at the C(2) and C(4) atoms (δ_H 4.55) as well as for the protons at the C(6) and C(7) atoms (δ_H 2.94). This suggests a rapid inversion of the rings on the NMR time scale. In the ^{13}C NMR spectra, the corresponding carbon atoms resonate at δ_C 56.18 and 37.84, respectively.

In the crystal, both dithiazepane rings adopt the *twist-chair* conformation;[9] the torsion angle C(1)—N(1)—N(2)—C(5) is 82.1(1)° (Fig. 1).

The C(4)—S(2) and C(5)—S(3) bonds are longer by 0.03—0.04 Å than the topologically equivalent C(1)—S(1) and C(8)—S(4) bonds. In conjunction with the near-180° pseudotorsion angles *lp*—N—C—S (*lp* stands for the lone electron pair), this suggests the presence of strong stereoelectronic couplings *lp*—N—C—S in structure **4**. At the same time, the N(2)—C(5) and N(2)—C(8) bond lengths differ only by 0.003(1) Å, although the N(2)—C(8) bond is involved in the coupling *lp*—N—C—S and hence should have been shortened by 0.02 Å (Table 1). Apparently, the coupling *lp*—N(1)—N(2)—C(8) is also effective here, thus lengthening the N(2)—C(8) bond. Analogous reasoning holds for the N(1)—C(1) bond, although its shortening relative to the N(1)—C(4) bond is more appreciable (0.01(1) Å).

The ^1H NMR spectra exhibit two singlets at δ_H 2.87 and 3.61, with an integral intensity ratio of 1 : 1, for the methylene protons of the dithiazepane ring in compound **5**, which suggests a rapid inversion of the seven-membered ring in $CDCl_3$. The signals for the C(2), C(4) and C(6), C(7) atoms of compound **5** are shifted upfield compared to the corresponding signals for bicyclane **4**. In the ^{13}C NMR spectrum, compound **6** is manifested as three characteristic signals at δ_C 35.13 (C(2), C(4)), 59.01 (C(6), C(7)), and 130.00 (methylidene C(9)).

The IR spectra of compounds **4**—**6** show absorption bands at 1020—1150 (C—N stretching) and 580—750 cm^{-1} (C—S stretching). The mass spectrum of compound **6**

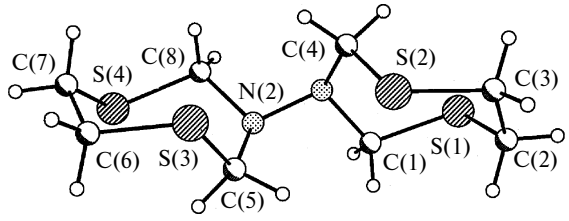


Fig. 1. Structure of 3,3′-bi(1,5,3-dithiazepane) (**4**) in the crystal.

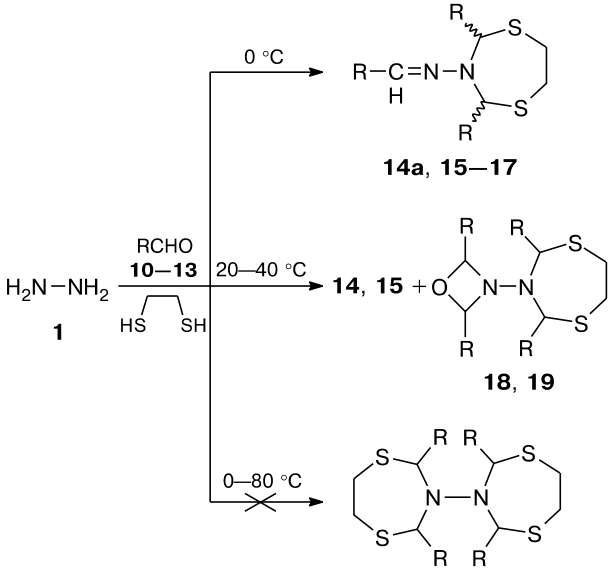
Table 1. Selected bond lengths in compound **4**

Bond	*d*/Å	Bond	*d*/Å
S(1)—C(1)	1.8020(3)	S(4)—C(8)	1.8062(3)
S(1)—C(2)	1.8162(4)	S(4)—C(7)	1.8167(4)
S(2)—C(3)	1.8102(4)	S(1)—C(2)	1.4250(3)
S(2)—C(4)	1.8393(3)	N(1)—C(4)	1.4485(3)
S(3)—C(6)	1.8145(4)	N(1)—C(1)	1.4603(4)
S(3)—C(5)	1.8395(3)		

contains a molecular ion peak with *m/z* 162 ($[M]^+$) and characteristic peaks with *m/z* 101 ($[M - CHNN(CH_2)_2S]^+$), 92 ($[SCH_2CH_2S]^+$), 73 ($[NNCHS]^+$), 60 ($[NCHS]^+$), 55 ($[CHNNCH_2]^+$), and 27 ($[NCH]^+$).

The use of higher aliphatic aldehydes **10**—**13** (acetaldehyde, propanal, butanal, and pentanal) in three-component heterocyclization with hydrazine and ethane-1,2-dithiol under optimized conditions (0 °C, N_2H_4 : RCHO : $(CH_2SH)_2$ = 1 : 4 : 2) selectively gives the corresponding 2,4-dialkyl-3-alkylideneamino-1,5,3-dithiazepanes **14**—**17** (R = methyl, ethyl, propyl, and butyl; alkylidene is ethylidene, propylidene, butylidene, and pentylidene) in 63, 69, 74, and 76% yields, respectively. Note that this reaction produces dimethyldithiazepane as the only isomer **14a**, while ethyl, propyl, and butyl derivatives **15**—**17** are mixtures of three stereoisomers (Scheme 2).

Scheme 2



R = Me (**10**, **14**, **18**), Et (**11**, **15**, **19**), Pr^n(**12**, **16**), Bu^n(**13**, **17**)

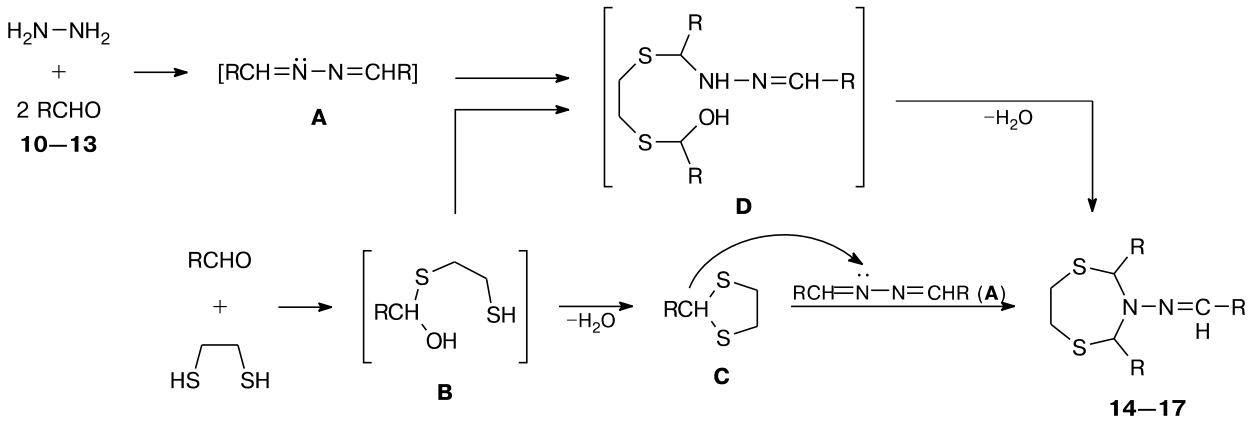
Attempted synthesis of tetraalkylated 3,3′-bi(1,5,3-dithiazepanes) at elevated temperature through involvement of both the amino groups of hydrazine failed under the chosen reaction conditions. Imines **14**—**17** were obtained as major heterocyclization products. Only the reactions with acetaldehyde and propanal gave 2,4-dialkyl-3-(2,4-dialkyl-1,3-oxazetan-3-yl)-1,5,3-dithiazepanes **18** and **19** as minor products (5—7%) (GC-MS). Apparently, the synthesis of tetraalkylated 3,3′-bi(1,5,3-dithiazepanes) is precluded by steric hindrances. At the same time, since higher aliphatic aldehydes are less electrophilic than formaldehyde, the three-component reaction between hydrazine, aldehydes, and ethane-1,2-dithiol proceeds more slowly and involves several steps. Initially, a nucleophilic N atom of intermediate aldazine **A** is attacked by intermediate **B** or **C**, probably giving adduct **D** (Scheme 3). The alkyl substituents make intermediates **B**—**D** less reactive; consequently, the reaction stops to yield monodithiazepanes **14**—**17**.

The formation of 2,4-dialkyl-3-alkylideneamino-1,5,3-dithiazepanes **14a** and **15**—**17** was confirmed by IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, and mass spectrometry. The mass spectra of this homologous series contain the corresponding molecular ion peaks with *m/z* 204, 246, 288, and 330 ($[M]^+$) and characteristic peaks due to the fragmentation of $[M]^+$. The ^{13}C NMR spectra of compounds **14a** and **15**—**17** show characteristic signals for the AlkCH=N— group as well as signals for the dithiazepane ring at δ_C 34—36 ($S(CH_2)_2S$) and 63—68 (NCH(R)S). According to GC-MS data, 3-ethylideneamino-2,4-dimethyl-1,5,3-dithiazepane (**14**) was detected as isomer **14a** only, while compounds **15**—**17** form three stereoisomers, one of them being dominant (^{13}C and ^1H NMR data). For the major stereoisomers of compounds **14**—**17**, we determined the Kovats indices (I_K).[10]

The use of phenylhydrazine (**20**) and benzylhydrazine (**21**) in three-component reactions with ethane-1,2-dithiol and formaldehyde (or acetaldehyde) leads to 3-anilino- and 3-benzylamino-1,5,3-dithiazepanes **22** and **24** or the corresponding 2,4-dimethylated derivatives **23** and **25**, regardless of the pH of the medium. Higher aliphatic aldehydes RCHO (R = Et, Pr^n, and Bu^n) under these reaction conditions yield dithio acetals **26**—**28** and the corresponding hydrazones **29**—**31**, probably because of the lower reactivity of aliphatic aldehydes **11**—**13** (Scheme 4).

The ^1H NMR spectrum of compound **22** shows singlets at δ_H 3.08 (—CH_2CH_2—) and 4.31 (—NCH_2S—) and multiplets at δ_H 6.86—7.28 (Ph). In the ^{13}C NMR spectrum of compound **22**, the signal at δ_C 35.46 is due to the carbon atoms of the fragment —SCH_2CH_2S— in the dithiazepane ring. The mass spectrum of compound **22** contains a molecular ion peak with *m/z* 226 ($[M]^+$) and characteristic peaks with *m/z* 180 ($[M - CH_2S]^+$), 118 ($[C_6H_5NHNCH]^+$), 106 ($[C_6H_5NHN]^+$), 91 ($[C_6H_5N]^+$), 77 ($[C_6H_5]^+$), 51 ($[CN—NC]^+$), and 46 ($[CH_2S]^+$). The formation of three diastereomers of 3-anilino-2,4-dimethyl-1,5,3-dithiazepane **23** is evident from triple sets of signals in the ^1H and ^{13}C NMR spectra, which remain unchanged in a temperature range from 20 to 40 °C.

Scheme 3



R = Me (**10**, **14**), Et (**11**, **15**), Pr^n (**12**, **16**), Bu^n (**13**, **17**)

The Kovats indices were determined for compounds **22** and **23b**.

In the ^{1}H NMR spectrum of a mixture of stereoisomers **23a**—**c**, the signal for the ring H(2) and H(4) protons in the major isomer **23b** appears as a quartet at δ_H = 4.51 (J = 6.8 Hz). In the two other isomers **23a,c**, these protons are manifested as broadened singlets because of a rapid (on the NMR time scale) conformational change. Note that their chemical shifts differ largely (δ_H 4.90 and 4.15, respectively; Fig. 2). According to the integral intensity ratio of the signals, isomers **23a,c** are minor products (**23a** : **23b** : **23c** = ~1 : 5 : 1). Therefore, major isomer **23b** in $CDCl_3$ predominantly exists as one conformer, in contrast to minor isomers **23a,c**, the configurations of which are described below.

In the ^{13}C NMR spectrum of stereoisomers **23a**—**c**, the chemical shifts of the signals for the C(2) and C(4) atoms can easily be differentiated as well. A heteronuclear HSQC experiment gave the following correlations:

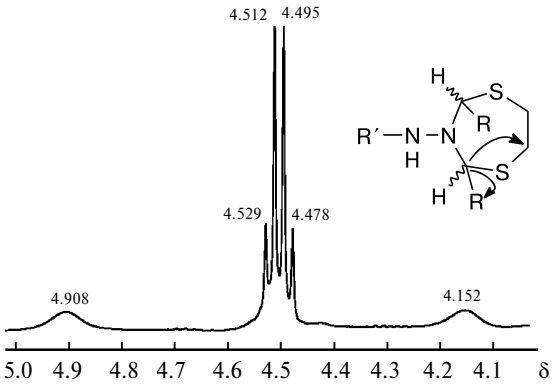
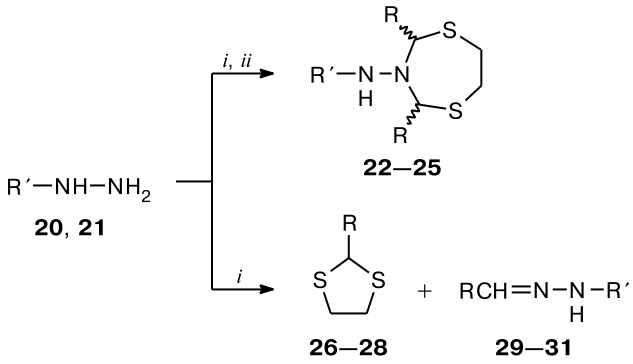


Fig. 2. ^{1}H NMR spectrum of a mixture of isomers **23a**—**c** (the fragment containing the signals for the H(2) and H(4) protons is shown only) and heteronuclear HMBC spin-spin couplings in compounds **23a**—**c**.

Scheme 4

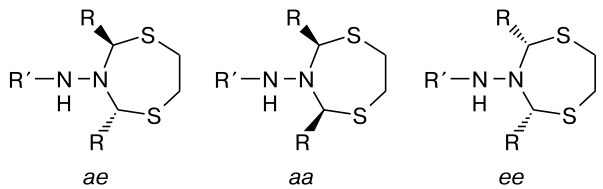


R′ = Ph (**20**, **22**, **23**, **29**—**31**), Bz (**21**, **24**, **25**); R = H (**22**, **24**), Me (**23**, **25**), Et (**26**, **29**), Pr^n (**27**, **30**), Bu^n (**28**, **31**)

Reagents and conditions: *i*. **20**—RCHO (**2**, **10**—**13**)—$(CH_2SH)_2$, 1 : 2 : 1, 0—70 °C (pH 3.15—3.20); *ii*. **20**—BuONa—RCHO—$(CH_2SH)_2$, 1 : 2 : 1, 0—70 °C (pH 11.50—11.70).

δ_H(4.90) ↔ δ_C(67.01), δ_H(4.51) ↔ δ_C(72.26), and δ_H(4.15) ↔ δ_C(68.10). For each stereoisomer, all signals were assigned from heteronuclear spin-spin couplings (HMBC) (see Fig. 2).

For stereochemical identification of compounds **23a**—**c**, we compared experimental and theoretical data. Conformational analysis of 2,4-substituted isomers **23a**—**c** with axial-axial (*aa*), axial-equatorial (*ae*), and equatorial-



equatorial (*ee*) arrangements of the methyl substituents was performed using the quantum chemical DFT approach (B3LYP, 6-31G(d,p)) (Table 2).

There are three minima on the potential energy surface for two isomeric structures **23a** and **23c** which correspond to the conformations *chair* **F**, *twist* **Q**, and *boat* **H** (Fig. 3).

But there are only two minima for isomer **23b**. The global minimum corresponds to the *chair* conformer **F** (ΔG_{rel}^{298} = 6.5 kcal mol^{-1}). This makes it evident that stereoisomer **23b** with the diaxially arranged substituents must incur the conformational shift **F** $\rightleftharpoons$ **Q** observed in the ^{1}H and ^{13}C NMR spectra. In addition, the energy barrier to the forward conformational change is higher (TS_{FQ} = = 7.5 kcal mol^{-1}) than the barriers in the other isomers (TS_{FQ} = 6.7 kcal mol^{-1} (**23a**); TS_{FH} = 6.0 kcal mol^{-1} (**23c**)). The differences between the ΔG values of the stereoisomers in their most stable conformations are

Table 2. Relative thermodynamic parameters of the stable conformers of compounds **14**, **17**, and **23** (the lowest-energy rotamers formally derived by rotation about the N—N bond of the substituent are cited)

Compound	Conformation	Configuration	E /Hartree	ΔG_{rel}^{298} for the conformers	ΔG^{298} for the isomers
				kcal mol^{-1}	
14	**F**	*ae*	1180.831408	0	0
	chair	*aa*	1180.840919	5.9	
		ee	1180.835589	2.6	
17		*ae*	1337.997151	1.6	
		aa	1337.994537	0	0
		ee	1337.998869	2.7	
23		*ae*	1373.737276	5.7	
		aa	1373.728564	0	0
		ee	1373.731834	9.6	
14	**Q**	*ae*	1180.877092	3.6	
	twist	*aa*	1180.835316	0	2.5
		ee	1180.838171	4.2	
17		*ae*	1337.994865	0	3.2
		aa	1337.997097	1.6	
		ee	1337.994524	3.9	
23		*ae*	1373.736679	0	2.1
		aa	1373.736767	6.5	
		ee	1373.739866	5.9	
14	**H**	*ae*	1180.847046	9.8	
	boat	*aa*	1180.841021	0	3.4
		ee	1180.841021	6.0	
17		*ae*	1338.005521	5.7	
		aa	1337.785633	4.6	2.2
		ee	1337.996441	0	
23		*ae*	1373.865347	13.2	
		aa		—	
		ee	1373.864379	0	5.5

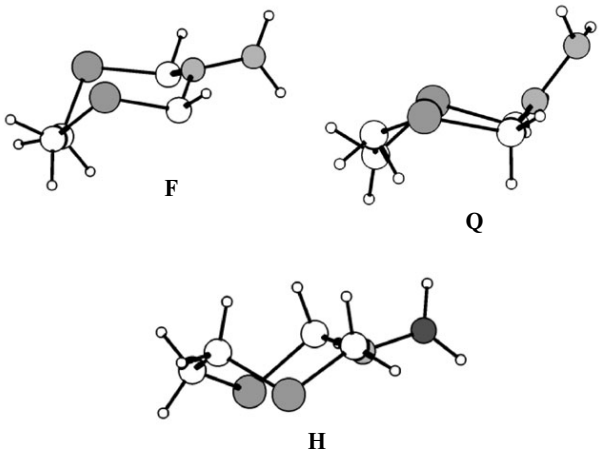


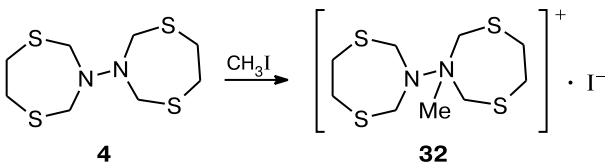
Fig. 3. Conformers **F**, **Q**, and **H** of compounds **14**, **17**, and **23**.

ΔG_{rel}^{298}(*aa*—*ae*) = 2.1 kcal mol^{-1} and ΔG_{rel}^{298}(*aa*—*ee*) = = 5.5 kcal mol^{-1} (see Table 2). Therefore, it is isomer **23b** that should be expected to form under thermodynamic control.

Thus, the methyl substituents in stereoisomers **23a** and **23c** are arranged *ae* and *ee*, respectively. This is confirmed by a moderate upfield shift of the signal for the characteristic H(2) and H(4) protons in the heterocycle of stereoisomer **23c** because of a 1,3-coupling between the axial protons in any of its conformers. Based on theoretical and experimental data, we concluded that *aa* stereoisomer **23b** in the *chair* conformation is the major reaction product. Similar calculations performed for imines **14** and **17** showed that the *aa* stereoisomer is most stable for compound **17** as well. However, the energy differences between the isomers of imine **17** are small (ΔG = 2.2 and 3.2 kcal mol^{-1}, see Table 2) and the integral intensities of the corresponding signals in the ^{1}H and ^{13}C NMR spectra are almost equal. As for compound **14**, the formation of the only stereoisomer is probably due to steric hindrances. Based on our calculations, we identified 3-ethylideneamino-2,4-dimethyl-1,5,3-dithiazepane as *ae* stereoisomer **14a**.

Because accessible starting materials and easy synthesis make 3,3′-bi(1,5,3-dithiazepane) (**4**) most promising for practical application, we studied the fungicidal activity of its solution in DMF and water-soluble adduct **32** prepared by N-quaternization of compound **4** with MeI.

Scheme 5



4 **32**

Fungicidal activity was examined in tests with the microscopic fungi *Bipolaris sorokiniana*, *Fusarium oxysporium*, *Aspergillus fumigatus*, *Aspergillus niger*, and *Paecilomyces variotii*, which cause various diseases in crops (including root rot in cereals and wood[11]). The mold species *Aspergillus fumigatus* and *Aspergillus niger* are also common contaminants of various natural and synthetic materials, which can provoke allergic reactions and mycosis in people with weakened immune systems.[12]

First, we tested the solvent (DMF) and revealed no negative effect on the growth of the test cultures of the above fungi. The effect of a solution of bi(dithiazepane) **4** in DMF on the test cultures is species-specific and dependent on the concentration of compound **4**. For instance, compound **4** completely suppresses the growth of *Paecilomyces variotii* in a concentration of ≥0.13% and inhibits the growth of the other test cultures in a concentration range from 0.04 to 0.2% (Table 3).

Water-soluble adduct **32** proved to be ineffective against the growth of the test cultures of the microscopic fungi (Table 4).

To sum up, 3,3′-bi(1,5,3-dithiazepane) (**4**) has a fungistatic effect on *Bipolaris sorokiniana*, *Fusarium oxysporium*,

Table 3. Effect of 3,3′-bi(1,5,3-dithiazepane) (**4**) on the growth of test fungi (incubation period 7 days)[a]

Test culture	Processes occurring at the concentration of **4** in DMF				
	0.04%	0.09%	0.13%	0.16%	0.2%
Bipolaris sorokiniana	Sporogenesis	Growth inhibition	Growth suppression, $d = 13.0\pm2.9$	Growth suppression, $d = 12.8\pm0.8$[b]	Growth inhibition
Fusarium oxysporum	Growth suppression, $d = 11.7\pm3.1$[c]	Growth inhibition	Growth suppression, $d = 17.3\pm5.6$	Growth suppression, $d = 17.8\pm4.2$	Growth suppression, $d = 16.3\pm7.8$[c]
Aspergillus fumigatus	Growth suppression, $d = 14.3\pm3.1$	Growth inhibition	Growth suppression, $d = 21.3\pm3.1$[b]	No growth	Growth suppression, $d = 23.3\pm4.1$[c]
A.niger	Sporogenesis	Growth inhibition	Growth inhibition	No growth	Growth suppression, $d = 19.0\pm2.7$[b]
Paecilomyces variotii	Sporogenesis	Growth inhibition	No growth	No growth	No growth

[a] In a control group, sporogenesis always occurs; *d* is the diameter of the growth suppression zone.
[b] Outside the effective area of compound **4**, the growth of fungi is inhibited.
[c] Within the effective area of compound **4**, the growth of fungi is inhibited; outside, sporogenesis occurs.

Table 4. Fungicidal activity of aqueous solutions of quaternized 3,3′-bi(1,5,3-dithiazepane) derivative **32** (incubation period 7 days)[a]

Test culture	Processes occurring at the concentration of adduct **32** in water				
	0.04%	0.09%	0.13%	0.16%	0.2%
Bipolaris sorokiniana	Sporogenesis	Sporogenesis	Growth inhibition	Growth inhibition	Growth inhibition
Fusarium oxysporum	Sporogenesis	Sporogenesis	Growth inhibition	Growth inhibition	Growth suppression, $d = 15.3\pm1.6$[c]
Aspergillus fumigatus	Sporogenesis	Growth inhibition	Sporogenesis	Sporogenesis	Sporogenesis
A.niger	Sporogenesis	Sporogenesis[b]	Sporogenesis	Sporogenesis	Sporogenesis[b]
Paecilomyces variotii	Sporogenesis	Sporogenesis[b]	Sporogenesis[b]	Sporogenesis	Sporogenesis[b]

[a] In a control group, sporogenesis always occurs.
[b] The color of spore-producing colonies is atypical of this species.
[c] Outside the effective area of compound **32**, typical sporogenesis occurs.

Aspergillus fumigatus, and *Aspergillus niger* and a fungicidal effect on *Paecilomyces variotii*.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 and 100.62 MHz, respectively) in $CDCl_3$. IR spectra were recorded on a Specord 75 IR spectrophotometer (Nujol, KBr). GC-MS analysis was carried out on a Finnigan 4021 instrument (glass capillary column 50 000×0.25 mm, HP-5 stationary phase, helium as a carrier gas, programmed temperature rise from 50 to 300 °C, heating rate 5 deg min^{-1}, injector temperature 280 °C, ion source temperature 250 °C, 70 eV). Elemental analysis was done on a Carlo Erba 1106 analyzer. Reaction products were separated by column chromatography on SiO_2. Thin-layer chromatography was carried out on Silufol W-254 plates; spots were visualized with the iodine vapor.

An X-ray diffraction study of compound **4** was carried out on a SMART APEX II CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω scan mode). The structure was solved by the direct methods and refined anisotropically on F^2_{hkl} by the full-matrix least-squares method. The hydrogen atoms were located in the difference electron-density maps and refined isotropically. The crystallographic parameters and data collection and refinement statistics for compound **4** are summarized in Table 5. All calculations were performed with the SHELXTL PLUS program package.[13]

Heterocyclization of hydrazine hydrate with aldehydes and ethane-1,2-dithiol. A three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel was maintained at a given temperature and charged with acetaldehyde, propanal, butanal, or pentanal (0.2 mol). Ethane-1,2-dithiol (0.1 or 0.07 mol) was added dropwise with stirring for 3 h to a desired RCHO : **3** ratio of 2 : 1 or 3 : 2. Then hydrazine hydrate (0.05 mol) was added dropwise and the reaction mixture was stirred at a specific temperature (0, 20, 40, or 70 °C) for 3.5 h (see Scheme 1, pathway *i*). Alternative pathways involved BuONa—BuOH (**1** : BuONa = 1 : 2) (see Scheme 1, pathway *ii*), water at 80 °C (see Scheme 1, pathway *iii*), and aqueous 37% HCl (**1** : HCl = 1 : 2) (see Scheme 1, pathway *iv*). After completion of the reaction, the mixture was neutralized with HCl (pathway *ii*) or NaOH (pathway *iv*). The products were extracted with chloroform, the extracts were dried with $CaCl_2$ and concentrated on a rotary evaporator, and the residues were separated by column chromatography on SiO_2 (C_6H_6—AcOEt—$CHCl_3$ = = 5 : 1 : 1 (for compounds **5** and **6**)).

3,3′-Bi(1,5,3-dithiazepane) (4). Yield 81 (pathway *i*) and 79% (pathway *ii*). Colorless crystals, R_f 0.55 ($CHCl_3$), m.p. 121—122 °C. ^{1}H NMR (20 °C), δ: 2.94 (s, 8 H, CH_2); 4.55 (s, 8 H, CH_2). ^{13}C NMR, δ: 37.84; 56.18. I_K = 2526. MS, *m/z* (I_{rel} (%)): 268 $[M]^+$ (40); 162 $[CH_2N_2CH_2CH_2SCH_2CH_2S]^+$ (70); 106 $[CH_2SCH_2CH_2S]^+$ (100); 92 $[SCH_2CH_2S]^+$ (15); 60 $[NCH_2S]^+$ (35); 57 $[N_2CH_2CH_2]^+$ (12); 42 $[CH_2NCH_2]^+$ (12). Found (%): C, 35.50; H, 5.43; N, 10.24; S, 47.48. $C_8H_{16}N_2S_4$. Calculated (%): C, 35.79; H, 6.01; N, 10.43; S, 47.77.

3-Amino-1,5,3-dithiazepane (5). Yield 37% (pathway *iii*), R_f 0.75. ^{1}H NMR (20 °C), δ: 2.87 (s, 4 H, CH_2); 3.61 (s, 2 H, NH_2); 4.67 (s, 4 H, CH_2). ^{13}C NMR, δ: 31.61; 65.85. MS, *m/z* (I_{rel} (%)): 149 $[M - H]^+$ (50); 105 $[NH_2NHCH_2SCH_2CH_2]^+$ (70); 60 $[NCH_2S]^+$ (40); 57 $[N_2CH_2CH_2]^+$ (100); 45 $[NH_2NHCH_2]^+$ (20).

3-Methylideneamino-1,5,3-dithiazepane (6). Yield 49% (pathway *iv*), R_f 0.54. ^{1}H NMR (20 °C), δ: 3.32 (s, 4 H, CH_2); 4.15 (s, 4 H, CH_2); 6.72 (s, 2 H, CH_2). ^{13}C NMR, δ: 35.13; 59.01; 131.00. I_K = 1493. MS, *m/z* (I_{rel} (%)): 162 $[M]^+$ (60); 106 $[CH_2SCH_2CH_2S]^+$ (70); 73 $[NNCH_2S]^+$ (25); 60 $[NCHS]^+$ (100); 55 $[CHNNCH_2]^+$ (50); 27 $[NCH]^+$ (45).

1,3-Dithiolane (7). Yield 30% (pathway *iv*). The product obtained is identical with 1,3-dithiolane described earlier.[14] MS, *m/z* (I_{rel} (%)): 106 $[M]^+$ (95); 78 $[SCH_2S]^+$ (56); 60 $[CH_2CH_2S]^+$ (94); 45 $[CHS]^+$ (100).

1,4-Dithiane (8). Yield 9% (pathway *iv*). The product obtained is identical with 1,4-dithiane described earlier.[15] MS, *m/z* (I_{rel} (%)): 120 $[M]^+$ (80); 92 $[SCH_2CH_2S]^+$ (20); 60 $[CH_2CH_2S]^+$ (40); 45 $[CHS]^+$ (60).

1,3,6,8-Tetrathiecane (9). Yield 12% (pathway *iv*). MS, *m/z* (I_{rel} (%)): 212 $[M]^+$ (80); 106 $[CH_2SCH_2CH_2S]^+$ (70); 92 $[SCH_2CH_2S]^+$ (35); 60 $[CH_2CH_2S]^+$ (100); 45 $[CHS]^+$ (60).

3-Ethylideneamino-2,4-dimethyl-1,5,3-dithiazepane (14a). Light yellow oil, yield 63% (pathway *i*). ^{1}H NMR (20 °C), δ: 1.42 (s, 6 H, Me); 1.89 (m, 3 H, Me); 2.88 (m, 4 H, CH_2); 4.85 (m, 2 H, CH); 7.12 (m, H, CH_{Ar}). ^{13}C NMR, δ: 19.14; 22.06; 35.61; 63.27; 146.02. I_K = 1560. MS, *m/z* (I_{rel} (%)): 204 $[M]^+$ (40);

Table 5. Crystallographic parameters and the data collection and refinement statistics for compound **4**

Parameter	Value
Molecular formula	$C_8H_{16}N_4S_4$
Molecular mass	268.51
T/K	100
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2
a/Å	6.61880(10)
b/Å	8.9581(2)
c/Å	11.0195(2)
α/deg	68.4428(8)
β/deg	75.5200(8)
γ/deg	88.4911(10)
V/Å^3	586.802(19)
d_{calc}/g cm^{-3}	1.520
μ/cm^{-1}	7.73
F(000)	284
$2\theta_{max}$/deg	115
Number of measured reflections	91041
Number of unique reflections	16128
Number of reflections with $I < 2\sigma(I)$	13750
Number of parameters refined	191
R_1	0.0218
wR_2	0.0643
GOOF	1.003
Residual electron density /e Å^{-3}, ρ_{min}/ρ_{max}	0.667/0.331

162 $[NCH(CH_3)SCH_2CH_2S\ CH(CH_3)]^+$ (13); 120 $[CH(CH_3)SCH_2CH_2S]^+$ (35); 105 $[CHSCH_2CH_2S]^+$ (100); 92 $[SCH_2CH_2S]^+$ (30); 69 $[CH_3CHNNCH]^+$ (52); 59 $[NCHS]^+$ (57); 57 $[N_2CH_2CH_2]^+$ (12); 45 $[CHS]^+$ (40); 42 $[CH_3NCH]^+$ (72). Found (%): C, 46.92; H, 7.56; N, 13.69; S, 31.24. $C_8H_{16}N_2S_2$. Calculated (%): C, 47.02; H, 7.89; N, 13.71; S, 31.38.

2,4-Diethyl-3-propylideneamino-1,5,3-dithiazepanes (15a—c) (5 : 1 : 1). Light yellow oil, yield 69% (pathway *i*). ^{1}H NMR (20 °C), δ: 0.94 (t, 6 H, Me, ^3J = 7.5 Hz); 1.03 (t, 3 H, Me, ^3J = 7.5 Hz); 1.66 (sextet, 2 H each, CH_{2a}, J = 7.2 Hz (**15b**,**c**)); 1.72 (sextet, 2 H, CH_{2a}, J = 7.5 Hz (**15a**)); 1.81 (sextet, 2 H each, CH_{2b}, J = 7.2 Hz (**15b**,**c**)); 2.01 (sextet, 2 H, CH_{2b}, J = 7.5 Hz (**15a**)); 2.24 (m, 2 H, CH_2); 2.82—2.97 (m, 4 H, CH_2); 4.76 (t, 4 H, CH_2(2), CH_2(4), J = 6.2 Hz); 6.90 (t, H, CH_{Ar}, ^3J = 5.0 Hz). ^{13}C NMR, δ: 11.48; 11.58; 26.64; 28.54; 34.78; 68.32 (**15b**); 74.26 (**15a**); 72.12 (**15c**); 143.18 (**15b**); 147.00 (**15a**,**c**). I_K = = 1776 (**15a**). **15a**. MS, m/z (I_{rel} (%)): 246 $[M]^+$ (5); 190 $[NCH(C_2H_5)SCH_2CH_2SCH(C_2H_5)]^+$ (7); 134 $[CH(C_2H_5)SCH_2CH_2S]^+$ (23); 112 $[CH_3CH_2CHNNCH(C_2H_5)]^+$ (25); 105 $[CHSCH_2CH_2S]^+$ (100); 83 $[CH_3CH_2CH_2NNCH]^+$ (60); 56 $[CH_3CH_2CHN]^+$ (30); 45 $[CHS]^+$ (22); 41 $[CH_2CH_2CH]^+$ (41).

3-Butylideneamino-2,4-dipropyl-1,5,3-dithiazepane (16a). Light yellow oil, yield 74% (pathway *i*). ^{1}H NMR (20 °C), δ: 0.81—0.90 (m, 9 H, Me); 1.28—1.62 (m, 6 H, CH_2); 2.63—2.65 (m, 4 H, CH_2); 2.65—2.79 (m, 2 H, CH_2); 3.50—3.70 (m, 4 H, CH_2); 4.70—4.80 (m, 4 H, CH_2); 6.85 (m, H, CH_{Ar}). ^{13}C NMR, δ: 13.63; 13.77; 20.06; 20.56; 28.66; 34.62; 37.57; 66.23; 141.77. I_K = 1996. MS, m/z (I_{rel} (%)): 288 $[M]^+$ (3); 148 $[CH(C_3H_7)SCH_2CH_2S)]^+$ (20); 105 $[CHSCH_2CH_2S]^+$ (100); 97 $[CH_3CH_2CH_2CHNNCH]^+$ (50); 70 $[CH_3CH_2\ CH_2CHN]^+$ (18); 55 $[CH_3CH_2\ CH_2C]^+$ (45); 43 $[CH_2CH_2CH_2]^+$ (30). Found (%): C, 58.07; H, 9.63; N, 9.59; S, 22.11. $C_{14}H_{28}N_2S_2$. Calculated (%): C, 58.28; H, 9.78; N, 9.71; S, 22.23.

2,4-Dibutyl-3-pentylideneamino-1,5,3-dithiazepanes (17a—c) (*Faa*). Light yellow oil, yield 76% (pathway *i*). ^{1}H NMR (20 °C), δ: 1.61—1.67 (m, 9 H, Me); 2.42—2.61 (m, 18 H, CH_2); 4.72 (t, 2 H, CH_2, J = 6.2 Hz (**17b**)); 4.79—4.82 (t, 2 H each, CH_2 (**17a,c**)); 6.41—6.42 (m, H, CH_{Ar}). ^{13}C NMR, δ: 18.62; 20.26; 24.48; 25.26; 28.57; 31.32; 33.80; 34.82; 67.95 (**17b**); 74.08 (**17a**); 73.32 (**17c**); 131.85 (**17b**); 131.91 (**17a**); 131.81 (**17c**). I_K = 2258 (**17a**). **17a**. MS, m/z (I_{rel} (%)): 330 $[M]^+$ (3); 162 $[CH(C_4H_9)SCH_2CH_2S)]^+$ (20); 111 $[CH_3CH_2CH_2CH_2CHNNCH]^+$ (35); 105 $[CHSCH_2CH_2S]^+$ (100); 84 $[CH_3CH_2CH_2CH_2CHN]^+$ (26); 69 $[CH_3CH_2CH_2CH_2C]^+$ (30); 56 $[CH_3CH_2CH_2CH_2]^+$ (19); 43 $[CH_2CH_2CH_2]^+$ (28).

3-(2,4-Dimethyl-1,3-oxazetan-3-yl)-2,4-dimethyl-1,5,3-dithiazepane (18) (pathway *i*). MS, m/z (I_{rel} (%)): 248 $[M]^+$ (40); 162 $[NCH(CH_3)SCH_2CH_2SCH(CH_3)]^+$ (15); 120 $[CH(CH_3)SCH_2CH_2S]^+$ (37); 105 $[CHSCH_2CH_2S]^+$ (100); 92 $[SCH_2CH_2S]^+$ (32); 86 $[NCH(CH_3)OCH(CH_3)]^+$ (32); 69 $[CH_3CHNNCH]^+$ (54); 59 $[NCHS]^+$ (57); 57 $[N_2CH_2CH_2]^+$ (12); 45 $[CHS]^+$ (40); 42 $[CH_3NCH]^+$ (72).

3-(2,4-Diethyl-1,3-oxazetan-3-yl)-2,4-diethyl-1,5,3-dithiazepane (19) (pathway *i*). MS, m/z (I_{rel} (%)): 304 $[M]^+$ (5); 190 $[NCH(C_2H_5)SCH_2CH_2SCH(C_2H_5)]^+$ (5); 134 $[CH(C_2H_5)SCH_2CH_2S]^+$ (21); 115 $[NCH(C_2H_5)OCH(C_2H_5)]^+$ (31); 112 $[CH_3CH_2CHNNCH(C_2H_5)]^+$ (23); 105 $[CHSCH_2CH_2S]^+$ (100); 83 $[CH_3CH_2CH_2NNCH]^+$ (58); 56 $[CH_3CH_2CHN]^+$ (28); 45 $[CHS]^+$ (20); 41 $[CH_2CH_2CH]^+$ (39).

Heterocyclization of phenyl- and benzylhydrazines with aldehydes and ethane-1,2-dithiol (general procedure). A three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel was maintained at a given temperature and charged with formaldehyde, acetaldehyde, propanal, butanal, and pentanal (0.1 mol). Ethane-1,2-dithiol (0.05 mol) was added dropwise with stirring for 3 h to a desired RCHO : **3** ratio of 2 : 1. Then phenylhydrazine or benzylhydrazine (0.05 mol) was added dropwise and the reaction mixture was stirred at a specific temperature (0, 20, 40, or 70 °C) for 3.5 h (see Scheme 4, pathway *i*). An alternative pathway involved BuONa—BuOH (**20** : BuONa = = 1 : 2) (see Scheme 4, pathway *ii*). After completion of the reaction, the mixture was neutralized with HCl (pathway *ii*). The products were extracted with chloroform, the extracts were dried with $CaCl_2$ and concentrated on a rotary evaporator, and the residues were separated by column chromatography on SiO_2 (C_6H_6—AcOEt—$CHCl_3$ = 5 : 1 : 1 (compounds **29**—**31**)).

3-Anilino-1,5,3-dithiazepane (22). Light yellow oil, yield 87 (pathway *i*) and 66% (pathway *ii*). ^{1}H NMR (20 °C), δ: 3.08 (s, 4 H, CH_2); 4.31 (s, 4 H, CH_2); 6.18 (s, H, NH); 6.96 (d, 4 H, CH_2, J = 8 Hz); 6.88 (t, 2 H, CH_2, J_1 = 7.6 Hz, J_2 = 7.2 Hz); 7.26 (t, 4 H, CH_2, J_1 = 7.6 Hz, J_2 = 8 Hz). ^{13}C NMR, δ: 35.46; 61.19; 114.51; 120.15; 129.35; 146.02. I_K = 2118. MS, m/z (I_{rel} (%)): 226 $[M]^+$ (60); 147 $[NNCH_2SCH_2CH_2SCH]^+$ (50); 120 $[NCH_2SCH_2CH_2S]^+$ (100); 106 $[C_6H_5NHN]^+$ (15); 91 $[C_6H_5N]^+$ (35); 77 $[C_6H_5]^+$ (23); 75 $[NHNCH_2S]^+$ (25); 60 $[NCH_2S]^+$ (25); 46 $[CH_2S]^+$ (10). Found (%): C, 52.94; H, 6.16; N, 12.24; S, 28.18. $C_{10}H_{14}N_2S_2$. Calculated (%): C, 53.06; H, 6.23; N, 12.38; S, 28.33.

3-Anilino-2,4-dimethyl-1,5,3-dithiazepanes (23a—c). Orange oil, yield 75 (pathway *i*) and 73% (pathway *ii*). ^{1}H NMR (20 °C), δ: 1.45 (d, 6 H, Me, J = 6.8 Hz); 3.02—3.18 (m, 4 H, CH_2); 4.51 (q, 2 H, CH, ^2J = 6.8 Hz (**23b**)); 4.90 (br.s, 2 H, CH_2 (**23a**)); 4.15 (br.s, 2 H, CH_2 (**23c**)); 6.03 (s, H, NH (**23b**)); 5.76 (s, H, NH (**23a**,**c**)); 6.91—6.94 (m, 3 H, CH_{Ar} (**23b**)); 6.75—6.89 (m, 3 H each, CH_{Ar} (**23a**,**c**)); 7.19—7.29 (m, 2 H, CH_{Ar}). ^{13}C NMR, δ: 21.59; 34.47; 72.26 (**23b**); 67.10 (**23a**); 68.10 (**23c**); 112.33; 118.22; 129.13 (**23b**); 129.25 (**23a,c**); 150.44 (**23b**); 148.32 (**23a,c**). I_K = 2144 (**23a**). MS, m/z (I_{rel} (%)): 254 $[M]^+$ (8); 161 $[NCH(CH_3)SCH_2CH_2SCHCH_2]^+$ (25); 134 $[NCH(CH_3)SCH_2CH_2S]^+$ (100); 106 $[C_6H_5NN]^+$ (25); 78 $[C_6H_6]^+$ (5); 60 $[NCH_2S]^+$ (10).

3-Benzylamino-1,5,3-dithiazepane (24). Light yellow oil, yield 77 (pathway *i*) and 69% (pathway *ii*). ^{1}H NMR (20 °C), δ: 2.51 (s, 4 H, CH_2); 3.52 (s, 2 H, CH_2); 4.71 (s, 4 H, CH_2); 6.15 (br.s, 1 H, NH); 7.09—7.24 (m, 5 H, CH_{Ar}). ^{13}C NMR, δ: 37.35; 53.80; 59.15; 122.24; 125.41; 127.97; 141.65. Found (%): C, 54.33; H, 6.13; N, 11.09; S, 26.57. $C_{11}H_{16}N_2S_2$. Calculated (%): C, 54.96; H, 6.71; N, 11.65; S, 26.68.

3-Benzylamino-2,4-dimethyl-1,5,3-dithiazepane (25). Light yellow oil, yield 69 (pathway *i*) and 63% (pathway *ii*). ^{1}H NMR (20 °C), δ: 1.43 (br.s, 6 H, Me); 2.67 (s, 4 H, CH_2); 3.99 (s, 2 H, CH_2); 4.23 (m, 4 H, CH_2); 6.35 (br.s, 1 H, NH); 7.11—7.33 (m, 5 H, CH_{Ar}). ^{13}C NMR, δ: 22.55; 34.76; 53.82; 61.15; 121.77; 124.39; 126.37; 142.24. Found (%): C, 58.01; H, 7.35; N, 10.22; S, 23.61. $C_{13}H_{20}N_2S_2$. Calculated (%): C, 58.16; H, 7.51; N, 10.44; S, 23.89.

2-Ethyl-1,3-dithiolane (26). Yield 35% (pathway *i*). The product obtained is identical with 2-ethyl-1,3-dithiolane described earlier.[16] MS, m/z (I_{rel} (%)): 134 $[M]^+$ (70); 105 $[CHSCH_2CH_2S]^+$ (100); 74 $[CH_3CH_2CHS]^+$ (10); 59 $[CHSCH_2]^+$ (20); 45 $[CHS]^+$ (65).

2-Propyl-1,3-dithiolane (27). Yield 27% (pathway *i*). The product obtained is identical with 2-propyl-1,3-dithiolane described earlier.[16] MS, *m/z* (I_{rel} (%)): 148 $[M]^+$ (50); 105 $[CHSCH_2CH_2S]^+$ (100); 77 $[SCHS]^+$ (10); 55 $[CH_2CH_2CH_2CH]^+$ (25); 45 $[CHS]^+$ (35).

2-Butyl-1,3-dithiolane (28). Yield 10% (pathway *i*). The product obtained is identical with 2-butyl-1,3-dithiolane described earlier.[16] MS, *m/z* (I_{rel} (%)): 162 $[M]^+$ (20); 105 $[CHSCH_2CH_2S]^+$ (100); 69 $[CH_2CH_2CH_2CH_2CH]^+$ (10); 61 $[SCH_2CH_2]^+$ (20); 45 $[CHS]^+$ (15).

Propanal *N*-phenylhydrazone (29). Yield 60% (pathway *i*), R_f 0.35. The product obtained is identical with propanal *N*-phenylhydrazone described earlier.[17] ^{1}H NMR (20 °C), δ: 1.14 (m, 3 H, Me); 1.98 (m, 2 H, CH_2); 3.15 (s, 1 H, NH); 6.79—7.31 (m, 5 H, CH_{Ar}). ^{13}C NMR, δ: 10.77; 28.13; 113.68; 119.12; 129.20; 147.50; 149.81. MS, *m/z* (I_{rel} (%)): 148 $[M]^+$ (100); 119 $[C_6H_5NHNCH]^+$ (15); 106 $[C_6H_5NHN]^+$ (15); 92 $[C_6H_5NH]^+$ (80); 77 $[C_6H_5]^+$ (30); 41 $[CHCH_2CH_2]^+$ (10).

Butanal *N*-phenylhydrazone (30). Yield 70% (pathway *i*), R_f 0.30. The product obtained is identical with butanal *N*-phenylhydrazone described earlier.[17] ^{1}H NMR (20 °C), δ: 1.02 (m, 3 H, Me); 1.61 (m, 2 H, CH_2); 2.33 (m, 2 H, CH_2); 6.03 (m, 1 H, CH); 6.21 (s, 1 H, NH); 6.83—7.31 (m, 5 H, CH_{Ar}). ^{13}C NMR, δ: 13.92; 21.19; 34.53; 113.68; 112.93; 118.20; 129.25; 147.40; 149.85. MS, *m/z* (I_{rel} (%)): 162 $[M]^+$ (100); 133 $[C_6H_5NHNCHCH_2]^+$ (30); 119 $[C_6H_5NHNCH]^+$ (15); 106 $[C_6H_5NHN]^+$ (45); 92 $[C_6H_5NH]^+$ (95); 77 $[C_6H_5]^+$ (50); 41 $[CHCH_2CH_2]^+$ (10).

Pentanal *N*-phenylhydrazone (31). Yield 90% (pathway *i*), R_f 0.27. The product obtained is identical with pentanal *N*-phenylhydrazone described earlier.[17] ^{1}H NMR (20 °C), δ: 0.92 (m, 3 H, Me); 1.53 (m, 2 H, CH_2); 2.29 (m, 2 H, CH_2); 6.00 (m, 1 H, CH); 6.15 (s, 1 H, NH); 6.79—7.26 (m, 5 H, CH_{Ar}). ^{13}C NMR, δ: 13.22; 21.89; 25.89; 33.94; 116.78; 121.12; 126.55; 147.37; 149.07. MS, *m/z* (I_{rel} (%)): 176 $[M]^+$ (80); 147 $[C_6H_5NHNCHCH_2CH_2]^+$ (10); 133 $[C_6H_5NHNCHCH_2]^+$ (60); 119 $[C_6H_5NHNCH]^+$ (50); 106 $[C_6H_5NHN]^+$ (50); 92 $[C_6H_5NH]^+$ (100); 77 $[C_6H_5]^+$ (50); 41 $[CHCH_2CH_2]^+$ (10).

3-(1,5,3-Dithiazepan-3-yl)-3-methyl-1,5,3-dithiazepanium iodide (32). A flask equipped with a mechanical stirrer was charged with 3,3′-bi(1,5,3-dithiazepane) **4** (10 mmol) in $CHCl_3$. Iodomethane (10 mmol) was added and the reaction mixture was stirred at ~20 °C for 6 h. Then water (5 mL) was added. The aqueous phase was concentrated to give compound **32**. On cooling, it was recrystallized from water. The yield was 88%. ^{1}H NMR (20 °C), δ: 2.50 (s, 3 H, Me); 2.94 (s, 8 H, CH_2); 4.55 (s, 8 H, CH_2). ^{13}C NMR, δ: 15.01; 37.84; 56.18. Calculated (%): C, 26.34; H, 4.67; N, 6.83; S, 31.24; I, 30.92. $C_9H_{19}N_2S_4I$. Found (%): C, 26.16; H, 4.43; N, 6.24; S, 31.20; I, 30.92.

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