Syntheses of a Novel Class of 5/6/5-Heterocycles: Convenient Routes from Aldehydes to Bis(1,3,4-thiadiazolo)-1,3,5-triazinium Halides☆

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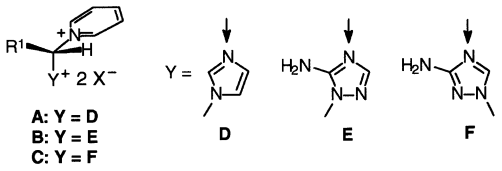
Novel 5/6/5 heterocycles, 1,3,4-thiadiazolo[3,2-*a*]-1,3,4-thiadiazolo[3,2-*d*]-1,3,5-triazinium halides **7**, have been synthesized by the reaction of 2-amino-1,3,4-thiadiazoles **6** with either 1-(haloalkyl)pyridinium halides **4** or *N*,*N*′-methylenebis(pyridinium) dibromides **5**. The tricyclic compounds **7** are generated in the course of several successive reaction steps in which specific proton migrations, bond-breaking and bond-forming processes occur. The structures **7** have been verified by spectral data (^{1}H and ^{13}C NMR, MS), X-ray analysis and ab initio calculations. The latter show that both sp^2-C atoms C(10) and C(12) of **7** are significantly positively charged and, therefore, exhibit electrophilic properties towards the primary amino group of the amino-thiadiazoles **6**. In the course of a multi-step reaction cascade of the **6**/**7** mixture, novel multi-aza/thia heterocycles **8** are formed. The structures of the latter compounds have been confirmed by X-ray analysis as well as by detailed experimental and theoretical NMR-spectroscopic studies.

Introduction

The reasons which focused our interest on the increasingly important field of multi-nitrogen/sulfur heterocycles are their biological activities as well as their synthetic potential. Numerous 1,3,4-thiadiazole derivatives have received considerable attention due to their pharmacological properties and especially because of their applicability in the treatment of various diseases[1]. Monocondensed 1,3,4-thiadiazolo[3,2-*a*]-1,3,5-triazines have been synthesized in order to study their versatility as antifungal agents[2]. Furthermore, poly-nitrogen- and -sulfur-containing five- and six-membered heterocycles seem to becoming more technical significance[3]. There is, however, a dearth of effective methods which allow convenient access to such multicyclic and − if possible − fused ring systems. In this paper we describe synthetic pathways which lead to the title compounds in high yields.The results presented here profit from a preceding study[4] on the synthesis of previously unknown geminal bis(heteroarylium) salts **A**−**C**. These salts can be easily obtained from the reaction of 1-[(alkyl/aryl)chloromethyl]pyridinium chlorides **4** with ambident heterocyclic nucleophiles such as 1-methylimidazole (**D**), or the isomeric aminotriazoles, 5-amino-1-methyl-1*H*-1,2,4-triazole (**E**) and 3-amino-1-methyl-1*H*-1,2,4-triazole (**F**). The structures of the product salts show that alkylation occurs exclusively at the ring-N position of the aminotriazoles as indicated in Figure 1.

Figure 1. Geminal bis(heteroarylium) halides **A**−**C**: Products from the reaction of 1-(haloalkyl)pyridinium halides and the heterocycles **D**−**F**



The geminal bis(heteroarylium) salts **B** and **C** deserve special interest. Due to the nature of the heteroarylium moieties and further properties, these structures could possibly exhibit specific biological activities[5].

Results and Discussion

The 1-(chloroalkyl)pyridinium chlorides **4**, starting material for the title compounds, can be synthesized almost quantitatively by a three-component reaction of a thionyl halide **1** and an aldehyde **2** with a variety of heteroarenes [pyridine (**3**) or pyridine derivatives, methylimidazole, quinolines etc., Scheme 1][6].

If the heterocyclic reactants **D**−**F** are replaced by the double molar amount of closely related nucleophiles (in this case 2-amino-1,3,4-thiadiazoles **6**[7], Scheme 2), a surprising cyclization occurs. In the course of a multi-step cascade reaction and under extrusion of pyridine and ammonium

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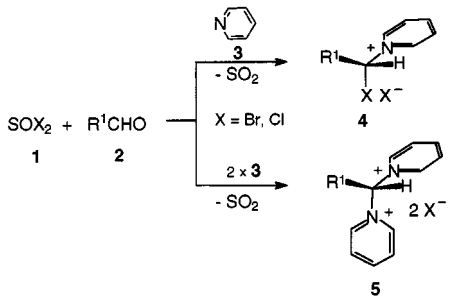
Scheme 1. Syntheses of 1-(haloalkyl)pyridinium halides **4** and geminal (bis)pyridinium halides **5**



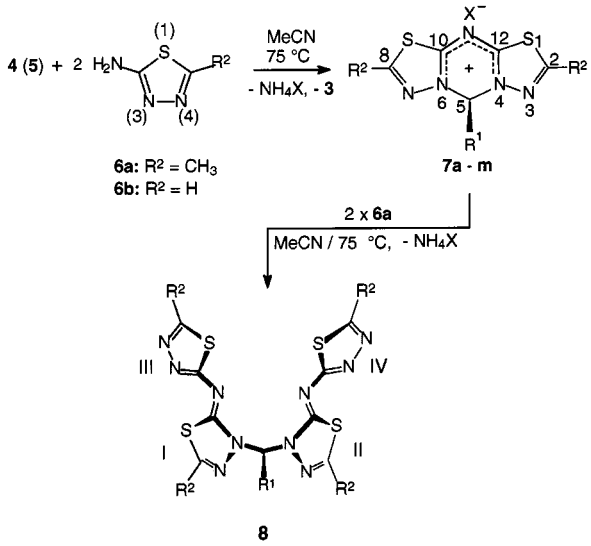
4, **5**	R^1	**4**, **5**	R^1
a	4-$O_2NC_6H_4$	**e**	1-naphthyl
b	4-MeC_6H_4	**f**	C_6H_5
c	*n*Bu	**g**	2-ClC_6H_4
d	4-$MeOC_6H_4$		

chloride or bromide, the reactants **4** and **6** are transformed into the novel tricyclic compounds **7** with almost 80% yield. This cascade is obviously initiated by the electrophilic attack of **4** at the ring-nitrogen atom N(3) of the heterocycles **6** and appears to be very similar to both its methylation of **6** with methyl iodide[8] and the course of the protonation reaction[9]. With respect to this starting point − but not for the consecutive steps which lead to **7** − the aminothiadiazoles **6** show properties related to those of the aminotriazoles **E** and **F**[4]. The selective attack at the N(3) atom goes parallel with the increasing nitrogen-NPA charges of compounds **6**[10] and a decreasing activation barrier for the alkylation of those nitrogen centers[11].To the best of our knowledge, such compounds **7** have not previously been described in the literature. They are the first known representatives of a cationic tricyclic 5/6/5 heterocycle, which is constructed from a central dihydro-1,3,5-triazinium moiety and two *ortho*-condensed 1,3,4-thiadiazole rings[12].

Compounds **7** can be synthesized with comparable yields by means of an alternative procedure, based on the use of geminal bis(pyridinium) salts **5**. The latter are formed in a three-component reaction (vide supra, Scheme 1) employing the double molar amount of pyridine[13].The new tricyclic salts **7** were characterized by NMR-spectroscopic methods, mass spectrometry, and elementary analyses. The structure of cation **7a** was confirmed by X-ray analysis[14]. N*H* signals are not observable in the ^{1}H-NMR spectra. All the *H*C(5) signals in **7** show highfield chemical shift differences of 1−2 ppm as compared with the *H*C(R^1) proton of the respective parent pyridinium halides **4** and **5**. In case of the naphthyl compound **7e** a broad *H*C(5) signal occurs at room temperature, indicating the presence of a conformational equilibrium. Similar measurements at 227 K show two sharp singlets at δ = 9.24 and δ = 8.50 (determined by HMQC correlation) as well as two different sets of proton signals for the naphthyl moieties.

This experimental finding is nicely explained by semiempirical MO calculations (AM1 and PM3)[15] which estimate the barrier for the hindered naphthyl group rotation around the C(5)−C_{naph} bond to be approximately 22 kcal/mol[16]. The other compounds **7** do not exhibit such broad signals for *H*C(5) in the ^{1}H-NMR spectrum. This again agrees with calculational results for further representatives of **7**. For example, the barrier of rotation around the corresponding C(5)−C_{aryl} bond of **7a** (R^1 = 4-$O_2NC_6H_4$) requires only 6.5 kcal/mol.The symmetrical structure of **7** is also supported by ^{13}C-NMR spectra. In addition to the signal of sp^3-hybridized C(5) at δ = 76−78, there are only two chemical shifts (δ = 160 and δ = 166) in almost constant positions which are related to the C(2)/C(8) and C(10)/C(12) carbon atoms. As a consequence, both the *Me*C signals of the methyl groups bound to C(2) and C(8) are also found at identical positions.

Scheme 2. Syntheses of novel 5/6/5 heterocycles **7** and specific aminals **8**

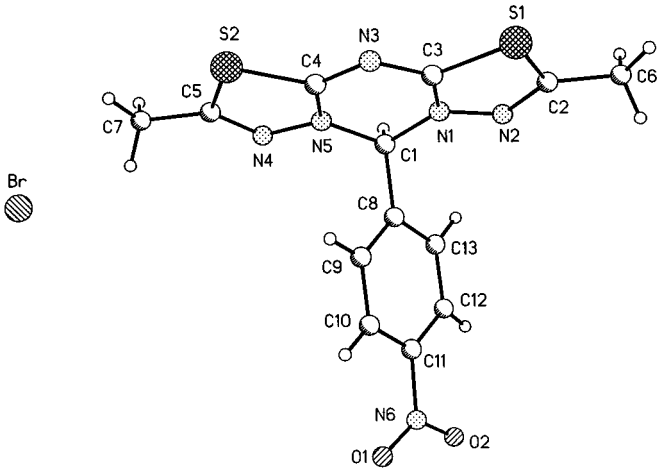


7, **8**	R^1	R^2	X	**7**	R^1	R^2	X
7a, **8a**	4-$O_2NC_6H_4$	Me	Br	**7h**	4-MeC_6H_4	Me	Cl
7b, **8b**	4-MeC_6H_4	Me	Br	**7i**	*n*Bu	Me	Cl
7c, **8c**	*n*Bu	Me	Br	**7j**	4-$O_2NC_6H_4$	H	Br
7d	4-$MeOC_6H_4$	Me	Br	**7k**	4-MeC_6H_4	H	Br
7e	1-naphthyl	Me	Br	**7l**	4-$MeOC_6H_4$	H	Br
7f	C_6H_5	Me	Br	**7m**	1-naphthyl	H	Br
7g	2-ClC_6H_4	Me	Br	**8d**[a]	H	Me	

[a] Model compound used for ab initio calculations.

In order to obtain further insight into the properties of these interesting new compounds, we calculated the cation of **7a** with ab initio methods (up to and including the RHF/6-31+G*//6-31+G* level of theory)[17]. We found acceptable agreement with the X-ray-structural data. The majority of the central azinium ring [N(4), C(12), N(11), C(10) and N(6), numbering: cf. Scheme 2] is almost planar, with the C−N bond lengths in this part of the ring being nearly identical (130−134 pm , ab initio: 132 pm). In contrast to this − and as one would expect − the C(5)−N(4) and C(5)−N(6) bond lengths are significantly longer (145−148 pm, ab initio: 146 pm). The bond angles at the C(5) atom

Figure 2. Crystal structure of **7a**

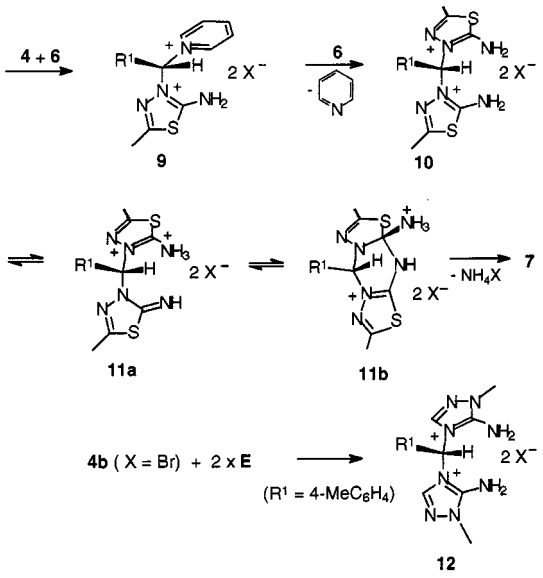


[N(4)−C(5)−N(6): 106.1° (ab initio: 104.1°), N(4)−C(5)−C(phenyl): 114.5°] indicate that the C(5) atom lies clearly "above" the defined plane. These findings demonstrate that the 1,3,5-triazinium ring prefers a quasi half-chair conformation both in the gas phase as well as in the solid state. The structural data of both the *ortho*-condensed 1,3,4-thiadiazole rings do not differ remarkably from that of the parent heterocycles **6a**, **b**[18] or of such moieties in related mercury complexes[19]. These values indicate that the double-bond character of all endocyclic thiadiazole bonds has been preserved. The angles to the connecting centers to the triazinium ring are widened [N(3)−N(4)−C(12)] or contracted [N(4)−C(12)−S(1)] by about 5°.

With a knowledge of the structure, a mechanism for formation of **7** can now be proposed (Scheme 3). We suppose that the reaction begins with two consecutive substitution steps of (a) the halogen atom, and of (b) the pyridine moiety of **4**. This causes the formation of the intermediate bis(heteroarylium) salts **10** via its precursor **9**. All attempts to isolate these structures **9** and **10** with $R^1 \neq H$ failed. The intermediate **10** apparently undergoes a proton shift producing **11a**, which cyclizes to give **11b**[20a]. Under extrusion of NH_3 (observed by isolation of NH_4X) the title compounds **7** are formed. A similar process can be assumed for the formation of **7** via **5**.

In order to support our hypothesis that intermediate **9** is formed in the course of the reaction, we selectively synthesized and isolated a less reactive representative of the **9** family. For this purpose, the formaldehyde-derived salt **4** (R^1 = H, and X = Br)[20b] and **6a** were allowed to react under our standard conditions. Independently from the relative amount of **6a** (e.g. also in the presence of an additional mole of the latter), only monosubstitution of the bromine occurs to give the corresponding pyridinium/thiadiazolium salt **9** (R^1 = H, 62% yield). The corresponding tricyclic product **7** was not formed. We also succeeded in preparing a related intermediate of **10** by treating **4b** (X = Br; Scheme 1) with 5-amino-1-methyl-1*H*-1,2,4-triazole (**E**) to give the novel bis(onium) salt **12** (R^1 = 4-MePh, X = Br) in yields

Scheme 3. Reaction pathway from **4** (or **5**) to the 5/6/5 heterocycles **7**



of about 64%. In this case it was also impossible to detect the corresponding 5/6/5 tricycle.

Applications for the novel substances **7** are conceivable because of a potential biological activity. Appropriate tests are under investigation. Such 5/6/5 heterocycles could also prove to be of particular interest as new precursor for further syntheses in the field of heterocyclic chemistry. As an indication of the fundamental capability of compounds **7** to act as new precursors, it is worth mentioning that compounds **8a**−**8c** are by-products of the cyclization reaction of **4a**, **4b**, and **5c** with **6a**. They have been isolated with ca. 12% yield from the mother liquor after separation of the salts **7**. These results strongly indicate that both the equivalent C(10) and C(12) centers in **7** could be candidates for nucleophilic attack of suitable reactants[21]. Obviously, **6a** can play such a role. The results of these reactions are also interesting from a different point of view. In analogy to the reaction pathway which led to **7** from **4** and **6**, we expected that one of the ring nitrogen atoms in **6a** should act as a nucleophilic center. Surprisingly, the reaction of **6a** with **7b** went in a different direction, which finally led to the formation of compound **8b**. A first synthetic improvement for the synthesis of **8b** by the reaction of **7b** with **6a** (by addition of an excess of **6a** to the solution of **7b** in pyridine) resulted in yields of 30%[22] with this compound being identical to the above-mentioned by-product, isolated from the mother liquor of the reaction of **4b** with **6a**. This reaction again proceeds under extrusion of NH_4Br, which was isolated. The starting material was recovered to a significant extent; further products have not been detected.

The structures of **8** have been confirmed by X-ray analysis[23] (Figure 3) as well as by detailed mass-spectrometric and NMR-spectroscopic[24] investigations. Ab initio calculated ^{13}C-chemical shifts of the model compound **8d** (R^1 = H) agree well with the experimental results (Table 1)[25].

Figure 3. Crystal structure of **8c**; for **8a**: cf. ref.[23]

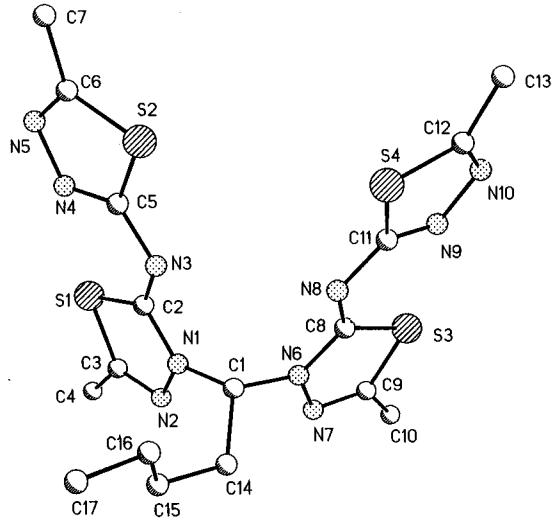


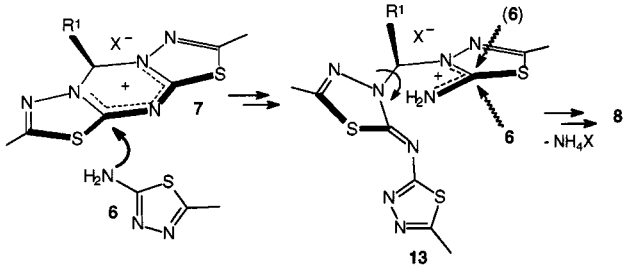
Table 1. Experimentally determined[a] (**8c**) and ab initio calculated[25] (model compound **8d**) ^{13}C-NMR data

C atom[b]	**8c**	**8d**
C(1)	69.40	54.8
C(2)/C(8)	160.40	165.0/163.4
C(3)/C(9)	151.30	135.3/151.4
C(4)C(10)	16.81	16.7.16.7
C(5)/C(11)	171.55	169.6/169.1
C(6)/C(12)	160.40	158.4/159.2
C(7)/C(13)	16.17	16.8/16.8

[a]100 MHz, $CDCl_3$, TMS. − [b] Numbering cf. X-ray, Figure 3.

Scheme 4 shows a characteristic intermediate whose formation again was derived from the structural properties of compounds **8**.

Scheme 4. Proposed reaction pathway for the transformation of **7** by nucleophilic attack of **6**



The NH_2 nitrogen atom of **6a** apparently functions as the nucleophilic center and attacks the trigonal-planar C(10) [or C(12)] carbon atom. After another multi-step reaction which involves several proton migrations followed by a ring-opening reaction, the intermediate **13** could be formed. **13** is then attacked by the second aminothiadiazole molecule (**6**) which finally results in the formation of **8** after the extrusion of NH_4Br.

Due to the influence of the substituent R^1, **6** approaches almost certainly by a less hindered *anti* attack as indicated in Scheme 4. The compounds **8a**−**8c** are representatives of a specific class of bis(azolyl)alkanes[26] ("aminals").The novel classes of compounds **7** and **8** indicate that a variety of interesting applications in different fields of organic and organometallic chemistry can be expected. Tests of the applicability of further (amino)nucleophiles for the transformations of the 5/6/5 heterocycles are currently under investigation.

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Experimental Section

General: Melting points (uncorrected): Lindstrom copper block apparatus. Reagents of commercial quality were purified by common methods. Compounds **4a** (X = Br), **4e** (X = Br), and **4g** (X = Br) were provided[27]. Compounds **4b** (X = Cl), **4b** (X = Br)[6a], **4c** (X = Cl)[4], and **5f**[13a] were prepared according to the literature. − IR: Bio-Rad FTS7. − NMR: Bruker AC 250 (250 MHz and 62.5 MHz, for ^{1}H and ^{13}C, respectively). Bruker DRX 400 (400 MHz and 100 MHz, for ^{1}H and ^{13}C, respectively). For ^{1}H and ^{13}C NMR, $CDCl_3$ (δ_H = 7.24; δ_C = 77.0), and [D_6]DMSO (δ_H = 2.49; δ_C = 39.5) were used as solvents, TMS as internal standard. − MS (CI or FAB): SSQ 710, Finnigan MAT. − Elemental analyses: Leco CHNS-932.

Bis(pyridinium) Dibromides **5**. − *General Procedure:* To a stirred solution of 11.43 g (55 mmol) of **1** (X = Br) in 70 ml of MeCN was added 7.91 g (100 mmol) of pyridine under argon at 0°C followed by aldehyde **2** (50 mmol). The mixture was kept at 0°C for 2 h and then slowly allowed to warm up to room temp. The solutions of crude products were concentrated under reduced pressure. The products were then precipitated by addition of *tert*-butyl methyl ether. The purification of the residues was carried out both by extraction with MeCN and/or acetone, and recrystallization from MeOH with the addition of some drops of HBr.

N,N′-[(4-Methylphenyl)methylene]bis(pyridinium) Dibromide (**5b**): Yield 83%, m.p. 183−186°C (dec.). − ^{1}H NMR ([D_6]DMSO): δ = 2.39 (s, 3 H, MePh), 9.45 (s, 1 H, CH methane), 7.30, 7.43 [2 d, ^3J(H,H) = 8.3 Hz, 4 H, aromatic H], 8.36 (t, 4 H, HC-3/5 pyridinium), 8.89 (t, 2 H, HC-4 pyridinium), 9.35 [d, ^3J(H,H) = 5.8 Hz, 4 H, HC-2/6 pyridinium]. − ^{13}C NMR ([D_6]DMSO): δ = 20.81 (MePh), 87.20 (C methane), 125.91, 128.64, 130.45, 142.14 (aromatic C), 129.23 (C-3 pyridinium), 144.84 (C-2 pyridinium), 149.44 (C-4 pyridinium). − MS (CI); *m/z* (%): 422 (4) [$C_{18}H_{18}Br_2N_2$], 262 (63) [$C_{18}H_{18}N_2$]. − $C_{18}H_{18}Br_2N_2 \times H_2O$ (440.2): calcd. C 49.12, H 4.58, Br 36.31, N 6.36; found C 49.38, H 4.58, Br 36.25, N 6.60.

N,N′-[(n-Butyl)methylene]bis(pyridinium) Dibromide (**5c**): Yield 56%, m.p. 192−193°C (dec.). − ^{1}H NMR ([D_6]DMSO): δ = 0.85 (t, 3 H, CH_3CH_2), 1.26 (m, 2 H, CH_2CH_3), 1.38 (m, 2 H, $CH_2CH_2CH_2$), 3.03 (m, 2 H, CH_2CH_2CH), 8.06 (t, 1 H, CH methane), 8.36 (t, 4 H, HC-3/5 pyridinium), 8.82 (t, 2 H, HC-4 pyridinium), 9.79 [d, ^3J(H,H) = 5.9 Hz, 4 H, HC-2/6 pyridinium]. − ^{13}C NMR ([D_6]DMSO): δ = 22.93 (CH_3), 30.72 (CH_2CH_3), 35.29 ($CH_2CH_2CH_2$), 40.44 (CH_2CH), 96.33 (CH methane), 138.66 (C-3 pyridinium), 153.60 (C-2 pyridinium), 159.56 (C-4 pyridinium). − MS (CI); *m/z* (%): 228 (37) [$C_{15}H_{20}N_2$]. − $C_{15}H_{20}Br_2N_2 \times H_2O$ (406.2): calcd. C 44.36, H 5.46, Br 39.35, N 6.90, O 3.94; found C 45.10, H 5.28, Br 39.31, N 7.07.

N,N′-[(4-Methoxyphenyl)methylene]bis(pyridinium) Dibromide (**5d**): Yield 55%, m.p. 177−179°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 3.83 (s, 3 H, MeOPh), 9.45 (s, 1 H, HC methane), 7.17, 7.42 [2 d, ^3J(H,H) = 8.7 Hz, 4 H aromatic H], 8.36 (t, 4 H, HC-3/5 pyridinium), 8.88 (t, 2 H, HC-4 pyridinium), 9.34 [d, ^3J(H,H) = 6.4 Hz, 4 H, HC-2/6 pyridinium]. − ^{13}C NMR ([D$_6$]DMSO): δ = 55.70 (OMe), 87.07 (C methane), 115.35, 120.28, 130.67, 161.75 (C aromatic), 129.20 (C-3 pyridinium), 144.31 (C-2 pyridinium), 149.31 (C-4 pyridinium). − MS (CI); *m/z* (%): 278 (58) [$C_{18}H_{18}N_2O$]. − $C_{18}H_{18}Br_2N_2O \times H_2O$ (456.2): calcd. C 47.39, H 4.42, Br 35.03, N 6.16; found C 46.98, H 4.30, Br 35.49, N 6.05.

N,N′-[(1-Naphthyl)methylene]bis(pyridinium) Dibromide (**5e**): Yield 46%, m.p. 205−208°C (dec). − ^{1}H NMR ([D$_6$]DMSO): δ = 10.25 (s, 1 H, HC methane), 7.58−8.34 (m, 7 H, naphthyl H), 8.36 (t, 4 H, HC-3/5 pyridinium), 8.94 (t, 2 H, HC-4 pyridinium), 9.33 [d, ^3J(H,H) = 5.8 Hz, 4 H, HC-2/6 pyridinium]. − ^{13}C NMR ([D$_6$]DMSO): δ = 85.20 (C methane), 122.35, 123.96, 125.68, 127.44, 128.16, 128.70, 129.19, 129.46, 133.39, 133.59 (C naphthyl), 129.56 (C-3/5 pyridinium), 144.90 (C-2/6 pyridinium), 149.86 (C-4 pyridinium). − MS (CI); *m/z* (%): 298 (23) [$C_{21}H_{18}N_2$]. − $C_{21}H_{18}Br_2N_2$ (458.2): calcd. C 55.05, H 3.96, Br 34.88, N 6.11; found C 54.84, H 4.09, Br 34.74, N 6.13.

1,3,4-Thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Halides **7**. − *General Procedure:* 10 mmol of **6a** or **6b** were suspended in 60 ml of MeCN and treated at room temp. with 5 mmol of compound **4** or **5**. After heating to 75°C (12 h), the solution was concentrated to 1/3 of its initial volume. Crystallization was completed at ca. 2°C. From the separated crystalline material the NH_4X by-product was washed off with water. The crude product salts **7** were recrystallized from MeOH or EtOH (in some cases under addition of *tert*-butyl methyl ether).

4(6),5-Dihydro-2,8-dimethyl-5-(4-nitrophenyl)-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7a**):Yield 56% from **4a** (X = Br) and **6a**, m.p. 295°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2 .61 (s, 6 H, MeC-2/6), 8.13 (s, 1 H, HC-5), 8.11 [d, ^3J(H,H) = 9.0 Hz, 2 H, aromatic H], 8.34 [d, ^3J(H,H) = 9.2 Hz, 2 H, aromatic H]. − ^{13}C NMR ([D$_6$]DMSO): δ = 16.89 (MeC-2/8), 77.58 (C-5), 124.14, 130.69, 139.61, 149,23 (C aromatic), 161.07 (C-2/8), 167.40 (C-10/12). − MS (CI); *m/z* (%): 427 (4) [$C_{13}H_{11}BrN_6O_2S_2$], 347 (15) [$C_{13}H_{11}N_6O_2S_2$]. − $C_{13}H_{11}BrN_6O_2S_2$ (427.3): calcd. C 36.54, H 2.59, Br 18.70, N 19.67, S 15.01; found C 36.68, H 2.70, Br 18.83, N 19.52, S 15.10.

4(6),5-Dihydro-2,8-dimethyl-5-(4-methylphenyl)-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7b**):Yield 68% from **4b** (X = Br) and **6a**, 74% from **5b** and **6a**, m.p. 254−255°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.33 (s, 3 H, MePh), 2.61 (s, 6 H, MeC-2/8), 7.91 (s, 1 H, HC-5), 7.30 [d, ^3J(H,H) = 8.1 Hz, 2 H, aromatic H], 7.58 [d, ^3J(H,H) = 8.1 Hz, 2 H, aromatic H]. − ^{13}C NMR ([D$_6$]DMSO): δ = 16.86 (MeC-2/8), 20.84 (MePh), 78.80 (C-5), 128.53, 129.74, 131.21, 141.32 (C aromatic), 160.55 (C-2/8), 166.90 (C-10/12). − MS (CI); *m/z* (%): 396 (12) [$C_{14}H_{14}BrN_5S_2$], 316 (46) [$C_{14}H_{14}N_5S_2$]. − $C_{14}H_{14}BrN_5S_2$ (396.3): calcd. C 42.43, H 3.56, Br 20.16, N 17.67, S 16.18; found C 42.60, H 3.55, Br 20.05, N 17.52, S 16.16.

5-(n-Butyl)-4(6),5-dihydro-2,8-dimethyl-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7c**): Yield 78% from **5c** and **6a**, m.p. 244−246°C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 0.84 (t, 3 H, CH_3CH$_2$), 1.15 (m, 2 H, CH_2CH$_2$CH$_3$), 1.31 (m, 2 H, CH$_2$CH_2CH$_3$), 2.41 (m, 2 H, CH$_2$CH_2CH), 2.74 (s, 6 H, MeC-2/8), 7.27 (t, 1 H, HC-5). − ^{13}C NMR ($CDCl_3$): δ = 13.66 (*C*H$_3$CH$_2$), 17.78 (MeC-2/8), 21.78 (*C*H$_2$CH$_3$), 24.14 (CH$_2$*C*H$_2$CH$_2$), 32.13 (CH$_2$*C*H$_2$CH), 79.73 (C5), 159.84 (C2/8), 168.18 (C10/12). − MS (CI); *m/z* (%): 362 (12) [$C_{11}H_{16}BrN_5S_2$], 282 (100) [$C_{11}H_{16}N_5S_2$]. − $C_{11}H_{16}BrN_5S_2$ (362.3): calcd. C 36.47, H 4.45, Br 22.05, N 19.33, S 17.70; found C 36.71, H 4.56, Br 21.87, N 19.25, S 18.11.

4(6),5-Dihydro-5-(4-methoxphenyl)-2,8-dimethyl-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7d**): Yield 65% from **5d** (X = Br) and **6a**, m.p. 190−192°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.61 (s, 6 H, MeC-2/8), 3.79 (s, 3 H, MeOPh), 7.88 (s, 1 H, HC-5), 7.03 [d, ^3J(H,H) = 8.7 Hz, 2 H, aromatic H], 7.64 [d, ^3J(H,H) = 8.7 Hz, 2 H, aromatic H]. − ^{13}C NMR ([D$_6$]DMSO): δ = 16.83 (MeC-2/8), 55.42 (MeOPh), 78.73 (C-5), 114.51, 126.12, 130.29, 161.33 (C aromatic), 160.47 (C-2/8), 166.87 (C-10/12). − MS (CI); *m/z* (%): 412 (0.8) [$C_{14}H_{14}BrN_5OS_2$], 332 (12) [$C_{14}H_{14}N_5OS_2$]. − $C_{14}H_{14}BrN_5OS_2$ (412.3): calcd. C 40.78, H 3.42, Br 19.38, N 16.99, S 15.55; found C 40.65, H 3.51, Br 19.29, N 16.87, S 15.35.

4(6),5-Dihydro-2,8-dimethyl-5-(1-naphthyl)-1,3,4-thiadiazolo-[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7e**): Yield 76% from **4e** and **6a**, 59% from **5e** and **6a**, m.p. 256−257°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.54 (s, 6 H, MeC2/8), 8.73 (br. s, 1 H, HC-5), 7.60−8.19 (m, 7 H, naphthyl H). − ^{13}C NMR ([D$_6$]DMSO): δ = 16.84 (MeC2/8), 76.60 (C5), 121.48, 125.58, 126.70, 128.28, 129.26, 130.09, 133.32 (C naphthyl), 160.93 (C2/8), 167.25 (C10/12). − MS (CI); *m/z* (%): 432 (7) [$C_{17}H_{14}BrN_5S_2$], 352 (43) [$C_{17}H_{14}N_5S_2$]. − $C_{17}H_{14}BrN_5S_2$ (432.4): calcd. C 47.23, H 3.26, Br 18.48, N 16.20, S 14.83; found C 47.71, H 3.48, Br 18.39, N 16.11, S 14.96.

4(6),5-Dihydro-2,8-dimethyl-5-phenyl-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7f**): Yield 69% from **5f** and **6a**, m.p. 205−208°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.61 (s, 6 H, MeC-2/8), 7.96 (s, 1 H, HC-5), 7.52−7.69 (m, 5 H, aromatic H). − ^{13}C NMR ([D$_6$]DMSO): δ = 16.89 (MeC-2/8), 78.78 (C-5), 128.66, 129.23, 131.34, 133.95 (C aromatic), 160.68 (C-2/8), 167.01 (C-10/12). − MS (CI); *m/z* (%): 382 (39) [$C_{13}H_{12}BrN_5S_2$], 302 (90) [$C_{13}H_{12}N_5S_2$]. − $C_{13}H_{12}BrN_5S_2$ (382.3): calcd. C 40.84, H 3.16, Br 20.90, N 18.32, S 16.77; found C 40.50, H 3.39, Br 20.34, N 17.94, S 16.73.

5-(2-Chlorophenyl)-4(6),5-dihydro-2,8-dimethyl-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7g**): Yield 70% from **4g** (X = Br) and **6a**, m.p. 256−258°C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 2.60 (s, 6 H, MeC2/8), 8.54 (s, 1 H, HC-5), 7.41−7.53 (m, 3 H, aromatic H), 7.78 [d, ^3J(H,H) = 6,9 Hz, aromatic H]. −^{13}C NMR ($CDCl_3$): δ = 17.43 (MeC-2/8), 80.59 (HC-5), 127.93, 129.99, 131.33, 133,15, 133.29, 133,93 (C aromatic), 158.99 (C-2/8), 168.10 (C-10/12). − MS (CI); *m/z* (%) 418 (94) [$C_{13}H_{11}BrClN_5S_2$], 338 (25) [$C_{13}H_{11}ClN_5S_2$]. − $C_{13}H_{11}BrClN_5S_2$ (416.7): calcd. C 37.47, H 2.66, Br 19.17, Cl 8.51, N 16.81, S 15.39; found C 37.53, H 2.78, Br 19.36, Cl 8.59, N 16.74, S 15.71.

4(6),5-Dihydro-2,8-dimethyl-5-(4-methylphenyl)-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Chloride (**7h**): Yield 67% from **4b** (X = Cl) and **6a**, m.p. 260−261°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.33 (s, 3 H, MePh), 2.61 (s, 6 H, MeC-2/8), 7.90 (s, 1 H, HC-5), 7.30, 7.58 (2 d, ^3J(H,H) = 8.1 Hz, 4 H, aromatic H). − ^{13}C NMR ([D$_6$]DMSO): δ = 16.80 (MeC-2/8), 20.84 (MePh), 78.78 (C5), 128.53, 129.74 131.23, 141.83 (C aromatic), 160.60 (C-2/8), 166.95 (C-10/12). − MS (CI); *m/z* (%): 352 (17) [$C_{14}H_{14}ClN_5S_2$], 316 (32) [$C_{14}H_{14}N_5S_2$]. − $C_{14}H_{14}ClN_5S_2$ (351.9): calcd. C 47.79, H 4.01, Cl 10.08, N 19.90, S 18.22; found C 47.01, H 4.07, Cl 9.74, N 19.58, S 18.16.

5-(n-Butyl)-4(6),5-dihydro-2,8-dimethyl-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Chloride (**7i**):Yield 60%

from **4c** (X = Cl) and **6a**, m.p. 129−130°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 0.82 (t, 3 H, C*H*$_3$CH$_2$), 1.23−1.36 (m, 4 H, CH$_3$C*H*$_2$C*H*$_2$), 2.46 (m, 2 H, CH$_2$C*H*$_2$CH), 2.71 (s, 6 H, MeC-2/8), 7.08 (t, 1 H, HC-5). − ^{13}C NMR ([D$_6$]DMSO): δ = 16.91 (MeC-2/8), 13.55 (*C*H$_3$CH$_2$), 21.38 (CH$_3$*C*H$_2$), 23.63 (CH$_2$*C*H$_2$CH$_2$), 32.73 (CH$_2$*C*H$_2$CH), 77.99 (HC-5), 160.55 (C2/8), 167.62 (C10/12), only NMR-spectroscopically analyzed.

4(6),5-Dihydro-5-(4-nitrophenyl)-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7j**): Yield 56% from **4a** (X = Br) and **6b**, m.p. 241−243°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 8.12, 8.34 [2 d, ^3J(H,H) = 8.7 Hz, 4 H, aromatic H], 8.28 (s, 1 H, HC-5), 9.38 (s, 2 H, HC-2/8). − ^{13}C NMR ([D$_6$]DMSO): δ = 77.97 (C-5), 124.14, 130.80, 139.58, 149.21 (C aromatic), 151.72 (C-2/8), 167.26 (C-10/12). − MS (CI); *m/z* (%): 399 (6) [C$_{11}$H$_7$BrN$_6$O$_2$S$_2$], 319 (30) [C$_{11}$H$_7$N$_6$O$_2$S$_2$]. − C$_{11}$H$_7$BrN$_6$O$_2$S$_2$ × MeOH (431.2): calcd. C 33.42, H 2.57, Br 18.53, N 19.49, S 14.87; found C 33.23, H 2.29, Br 18.85, N 19.73, S 15.16.

4(6),5-Dihydro-5-(4-methylphenyl)-1,3,4-thiadiazolo[3.2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7k**): Yield 67% from **4b** (X = Br) and **6b**, m.p. 243−245°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.33 (s, 3 H, MePh), 7.30, 7.58 [2 d, ^3J(H,H) = 8.1 Hz, 4 H, aromatic H], 8.05 (s, 1 H, HC-5), 9.35 (s, 2 H, HC-2/8). − ^{13}C NMR ([D$_6$]DMSO): δ = 20.85 (MePh), 79.19 (C-5), 128.60, 129,67, 131.20, 141.34 (C aromatic), 151.14 (C-2/8), 166.81 (C-10/12). − MS (CI); *m/z* (%): 288 (21) [C$_{12}$H$_{10}$N$_5$S$_2$]. − C$_{12}$H$_{10}$BrN$_5$S$_2$ (368.3): calcd. C 39.14, H 2.74, Br 21.70, N 19.02, S 17.41; found C 39.08, H 2.74, Br 21.92, N 19.06, S 17.36.

4(6),5-Dihydro-5-(4-methoxyphenyl)-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7l**): Yield 64% from **5d** and **6b**, m.p. 213−215°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 3.78 (s, 3 H, MeOPh), 7.07, 7.64 [2 d, ^3J(H,H) = 8.8 Hz, 4 H, aromatic H], 8.03 (s, 1 H, HC-5), 9.34 (s, 2 H, HC-2/8). − ^{13}C NMR ([D$_6$]DMSO): δ = 55.44 (MeO), 79.15 (C-5), 114.47, 126.05, 130.29, 161.36 (C aromatic), 151.02 (C-2/8), 166.76 (C-10/12). − MS (CI); *m/z* (%): 384 (0.8) [C$_{12}$H$_{10}$BrN$_5$OS$_2$], 304 (20) [C$_{12}$H$_{10}$N$_5$OS$_2$]. − C$_{12}$H$_{10}$BrN$_5$OS$_2$ (384.3): calcd. C 37.51, H 2.62, Br 20.79, N 18.23, S 16.69; found C 37.21, H 2.77, Br 21.48, N 18.37, S 16.69.

4(6),5-Dihydro-5-(1-naphthyl)-1,3,4-thiadiazolo[3,2-a]-1,3,4-thiadiazolo[3,2-d]-1,3,5-triazinium Bromide (**7m**): Yield 55% from **5e** and **6b**, m.p. 244°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 7.60−8.19 (m, 7 H, naphthyl H), 8.87 (br. s, 1 H, HC-5), 9.31 (s, 2 H, HC-2/8). − ^{13}C NMR ([D$_6$]DMSO): δ = 77.08 (C-5), 121.62, 125.51, 126.71, 128.26, 129.12, 130.14, 132.27, 133.33 (C naphthyl), 151.45 (C-2/8), 167.23 (C-10/12). − MS (CI); *m/z* (%): 404 (3) [C$_{15}$H$_{10}$BrN$_5$S$_2$], 324 (40) [C$_{15}$H$_{10}$N$_5$S$_2$]. − C$_{15}$H$_{10}$BrN$_5$S$_2$ (404.3): calcd. C 44.56, H 2.49, Br 19.76, N 17.32, S 15.86; found C 44.31, H 2.67, Br 19.42, N 17.09, S 15.62.

N^4,N$^{4'}$-[(4-Methylphenyl)methane]bis(5-amino-1-methyl-1H-1,2,4-triazolium) Dibromide (**12**, R^1 = 4-MePh): Yield 64% from **4b** (X = Br) and **E**[28], m.p. 178°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.37 (s, 3 H, MePh), 3.70 (s, 6 H, NCH$_3$), 7.30−7.38 [2 d, ^3J(H,H) = 8.38 Hz, 4 H, aromatic H], 8.02 (s, 1 H, methane H), 8.49 (s, 2 H, CH triazolium), 8.99 (s, 4 H, NH$_2$). − ^{13}C NMR ([D$_6$]DMSO): δ = 20.73 (MePh), 35.41 (CH$_3$N), 65.81 (C methane), 126.34, 127.50, 129.99, 140.74 (C aromatic), 136.73 (HC triazolium), 149.00 (NH$_2$C triazolium). − MS (FAB); *m/z* (%): 299 (60) [C$_{14}$H$_{20}$N$_8$], 201 (100) [C$_{11}$H$_{13}$N$_4$]. − C$_{14}$H$_{20}$Br$_2$N$_8$ × H$_2$O (478.2): calcd. C 35.16, H 4.64, Br 33.42, N 23.43; found C 34.98, H 4.65, Br 33.22, N 22.88.

N-[3-(2-Amino-5-methyl-1,3,4-thiadiazolio)methyl]pyridinium Dibromide (**9**, R^1 = H, X = Br): Yield 62% from **4** (R^1 = H, X = Br)[20b] and **6a**, m.p. 200−202°C (dec.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.50 (s, 3 H, Me thiadiazolium), 6.95 (s, 2 H, methane H), 8.28 (t, 2 H, pyridinium 3/5-H), 8.76 (t, 1 H, pyridinium 4-H), 9.23 [d, ^3J(H,H) = 5.60 Hz, 2 H, pyridinium 2/6-H], 10.80 (s, 2 H, NH$_2$). − ^{13}C NMR ([D$_6$]DMSO): δ = 16.19 (Me thiadiazolium), 68.39 (C methane), 128.29 (C-3/5 pyridinium), 144.98 (C-2/6 pyridinium), 148.07 (C-4 pyridinium), 155.96 (C-5 thiadiazolium), 169.75 (C-2 thiadiazolium). − MS (FAB); *m/z* (%): 208 (33) [C$_9$H$_{12}$N$_4$S]. − C$_9$H$_{12}$Br$_2$N$_4$S (368.1): calcd. C 29.37, H 3.29, Br 43.41, N 15.22, S 8.71; found C 29.38, H 3.29, Br 42.83, N 15.49, S 8.75.

Exemplary, in case of the syntheses of compounds **7a−7c** the filtrates of crude products were concentrated to dryness. The residues were purified by column chromatography (silica gel 60, 0.063−0.2 mm, ethyl acetate/methanol). **8a−8c** were isolated in yields of 10−15%.

Bis{2,3-dihydro-5-methyl-2-[(5-methyl-1,3,4-thiadiazol-2-yl)-imino]-1,3,4-thiadiazol-3-yl}(4-nitrophenyl)methane (**8a**): M.p. 280−282°C. − IR (ATR): ṽ = 1578 cm^{-1}(m, C=N exocyclic). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.45 (s, 6 H, Me thiadiazole I/II), 2.57 (s, 6 H, Me thiadiazole III/IV), 7.74 [d, ^3J(H,H) = 8.47 Hz, 2 H, aromatic H], 8.27 [d, ^3J(H,H) = 8.61 Hz, 2 H, aromatic H], 8.50 (s, 1 H, methane H). − ^{13}C NMR ([D$_6$]DMSO): δ = 15.79 (Me thiadiazole III/IV), 16.68 (Me thiadiazole I/II), 68.94 (C methane), 123.63, 129.60, 140.66, 147.83 (C aromatic), 152.55 (C-5 thiadiazole I/II), 159.73 (C-2 thiadiazole I/II), 160.23 (C-5 thiadiazole II/IV)), 170.51 (C-2 thiadiazole III/IV). − MS (CI): *m/z* (%): 560 (90) [C$_{19}$H$_{17}$N$_{11}$O$_2$S$_4$ + H$^+$]. − C$_{19}$H$_{17}$N$_{11}$O$_2$S$_4$ (559.7): calcd: C 40.78, H 3.06, N 27.53, S 22.91, O 5.72; found C 41.26, H 3.34, N 27.24, S 22.03.

Bis{2,3-dihydro-5-methyl-2-[(5-methyl-1,3,4-thiadiazol-2-yl)-imino]-1,3,4-thiadiazol-3-yl}(4-methylphenyl)methane (**8b**): M.p. 259−261°C. − In addition to the isolation from the mother liquor this compound **8b** could be alternatively prepared by the reaction of **7b** with **6a**: To a solution of 0.75 g (6.5 mmol) of **6a** in 100 ml of pyridine was added 1.20 g (3 mmol) of **7b** at room temp. The mixture was stirred for 15 h at 80°C. After evaporation of the pyridine under reduced pressure, the residue was triturated with CHCl$_3$ to separate the formed NH$_4$Br and remaining **6a**. The CHCl$_3$ filtrate was concentrated again and the residue was washed with MeOH. The precipitate was filtered off, washed with cold MeOH and then recrystallized from CH$_2$Cl$_2$/*tert*-butyl methyl ether. Yield 30%[22]; m.p. 259−261°C. − IR (ATR): ṽ = 1576 cm^{-1} (m, C=N exocyclic). −^{1}H NMR (CDCl$_3$): δ = 2.34 (s, 3 H, MePh), 2.45 (s, 6 H, MeC-5 thiadiazole I/II), 2.63 (s, 6 H, MeC-5 thiadiazole III/IV), 7.18 (s, 4 H, aromatic H), 8.63 (s, 1 H, methane H). − ^{13}C NMR (CDCl$_3$): δ = 16.17 (Me thiadiazole III/IV), 16.81 (Me thiadiazole I/II), 21.12 (MePh), 69.40 (C methane), 127.70, 129.28, 131.10, 138.80 (C aromatic), 151.30 (C-5 thiadiazole I/II), 160.04 (C-2 thiadiazole I/II), 160.40 (C-5 thiadiazole III/IV), 171.55 (C-2 thiadiazole III/IV). − MS (CI): *m/z* (%): 529 (5) [C$_{20}$H$_{20}$N$_{10}$S$_4$ + H$^+$]. − C$_{20}$H$_{20}$N$_{10}$S$_4$ (528.7): calcd. C 45.44, H 3.81, N 26.49, S 24.26; found C 45.28, H 3.92, N 26.18, S 24.20.

1,1-Bis{2,3-dihydro-5-methyl-2-[(5-methyl-1,3,4-thiadiazol-2-yl)imino]-1,3,4-thiadiazol-3-yl}pentane (**8c**): M.p. 187−189°C. − IR (ATR): ṽ = 1577 cm^{-1}(m, C=N exocyclic). − ^{1}H NMR (CDCl$_3$): δ = 0.89 (t, 3 H, C*H*$_3$CH$_2$), 1.34 (m, 2 H, CH$_2$C*H*$_2$CH$_2$), 1.40 (m, 2 H, CH$_3$C*H*$_2$CH$_2$), 2.44 (t, 2 H, CH$_2$C*H*$_2$CH), 7.35 (t, 1 H, CH$_2$C*H*NN), 2.47 (s, 6 H, Me thadiazole I/II) 2.67 (s, 6 H, Me thiadiazole III/IV). − ^{13}C NMR (CDCl$_3$): δ = 13.82 (*C*H$_3$CH$_2$), 22.15 (CH$_3$*C*H$_2$), 27.00 (CH$_2$*C*H$_2$CH$_2$), 32.12 (*C*H$_2$CH), 68.12

(CH_2CHNN), 16.27 (Me thiadiazole III/IV), 16.79 (Me thiadiazole I/II), 151.26 (C-5 thiadiazole I/II), 159.79 (C-2 thiadiazole I/II), 160.26 (C-5 thiadiazole III/IV)), 171.71 (C-2 thiadiazole III/IV). – MS (CI): *m/z* (%); 495 (48) [$C_{17}H_{22}N_{10}S_4 + H^+$]. – $C_{17}H_{22}N_{10}S_4$ (497.7): calcd. C 41.28, H 4.48, N 28.32, S 25.92; found C 40.92, H 4.47, N 28.30, S 25.40.

☆ Dedicated to Professor Dr. Dr. h.c. mult. *Alan R. Katritzky* on occasion of his 70th birthday.

[1] K. Miyamoto, R. Koshiurura, M. Mori, H. Yokoi, C. Mori, T. Hasegawa, *Chem. Pharm. Bull.* **1985**, *33*, 5126–5129.

[2] [2a] M. M. El-Kerdawy, S. M. Bayomi, I. A. Shekata, R. A. Glemion, *J. Heterocycl. Chem.* **1987**, *24*, 501–504. – [2b] R. A. Coburn, B. Bhooshan, *J. Org. Chem.* **1973**, *38*, 3868–3871.

[3] Without completeness, for recently developed synthetic procedures and for applications compare the following examples: polysulfur/nitrogen heterocycles seem to be useful candidates for optical and electronic switches, e.g. tetrathiafulvalenes and related compounds serve as components in charge-transfer complexes. – [3a] C. F. Marcos, C. Polo, O. A. Rakitin, C. W. Rees, T. Torraba, *Angew. Chem.* **1997**, *109*, 283–285; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 281–283. – [3b] S. Nakatsuji, Y.Amano, H. Kawamura, H. Anzai, *Liebigs Ann.* **1997**, 729–732, and references cited therein.

[4] E. Anders, K. Wermann, B. Wiedel, J.-J. Vanden Eynde, *Liebigs Ann.* **1997**, 745–752.

[5] For example see: [5a] J. B. Polya in *Comprehensive Heterocyclic Chemistry* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon, Oxford **1984**, p. 733. – [5b] *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford **1996**, vol. 1. – [5c] E. Lukevits, *Khim. Geterosikl. Soedin.* **1995**, *6*, 723–734; *Chem. Abstr.* **1996**, *124*, 105358e.

[6] For syntheses and applications see: [6a] E. Anders, J. Tropsch, *Bull. Soc. Chim. Belg.* **1987**, *96*, 719–720. – [6b] A. Maquestiau, E. Anders, A. Mayence, J.-J. Vanden Eynde, *Chem. Ber.* **1991**, *124*, 2013–2017. – [6c] J.-J. Vanden Eynde, A. Mayence, A. Maquestiau, E. Anders, *Synth. Commun.* **1992**, *22*, 3141–3150. – [6d] J.-J. Vanden Eynde, J. Godin, A. Mayence, A. Maquestiau, E. Anders, *Synthesis* **1993**, 867–869, and references cited therein.

[7] [7a] M. Freund, G. Meinecke, *Ber. Dtsch. Chem. Ges.* **1896**, 2511– 2517. – [7b] Commercially available product: Sigma-Aldrich Chemie GmbH, Steinheim, Germany.

[8] G. Werber, F. Buccheri, M. Gentile, *J. Heterocycl. Chem.* **1977**, *14*, 1263–1265.

[9] L. Antolini, A. Cornia, A. C. Fabretti, W. Malavasi, *J. Crystallogr. Spectrosc. Res.* **1993**, *23*, 967–971, and references cited therein.

[10] Natural population analysis for: **6a**: $q_{N3} = -0.400$; $q_{N4} = -0.296$; $q_{NH2} = -0.913$. **6b**: $q_{N3} = -0.404$; $q_{N4} = -0.269$; $q_{NH2} = -0.912$. – [10a] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[11] Relative energies [kcal/mol] of S_N2-TS$^{\neq}$ of a model-reaction of **6a** and **6b** with MeCl, respectively, (ab initio MP2/6-31+G*// MP2/6-31+G*; ZPE corr.): 1-Me-**6a**$^+$ = 50.5; 3-Me-**6a**$^+$ = 0.0; 4-Me-**6a**$^+$ = 0.4; $MeNH_2$-**6a**$^+$ = 25.7; 1-Me-**6b**$^+$ = 52.0; 3-Me-**6b**$^+$ = 0.0; 4-Me-**6b**$^+$ = −1.0; $MeNH_2$-**6b**$^+$ = 25.3.

[12] For the application of salts **4** for further cyclization reactions cf.: [12a] J.-J. Vanden Eynde, P. D'Orazio, A. Maquestiau, E. Anders, *Tetrahedron* **1992**, *48*, 1263–1268. [12b] J.-J. Vanden Eynde, A. Mayence, A. Maquestiau, E. Anders, *Bull. Soc. Chim. Belg.* **1992**, *101*, 801–806.

[13] Previous routes to geminal bis(pyridinium) salts: [13a] F. Kröhnke, H. Leister, *Chem. Ber.* **1958**, *91*, 1295–1300. – [13b] B. Almarzoqi, A. V. George, N. S. Isaacs, *Tetrahedron* **1986**, *42*, 601–607.

[14] Crystal data for **7a** : $C_{13}H_{11}BrN_6O_2S_2$, M_r = 427.31 g mol^{-1}, colourless prism, size 0.30 × 0.28 × 0.15 mm, triclinic, space group *P*1bar, a = 6.851(1), b = 7.892(1), c = 16.023(2) Å, α = 76.22(1), β = 87.31(1), γ = 83.10(1)°, V = 835.2(2) Å^3, T = 20°C, Z = 2, $\rho_{calcd.}$ = 1.699 g cm^{-3}, μ(Mo-K_α) = 27.31 cm^{-1}, absorption correction: ψ scan, trans.(min): 0.37, trans.(max): 0.39, F(000) = 428, 3858 reflections in +h, ±k, ±l, measured in the range 2.62° ≤ Θ ≤ 28.01°, 3858 independent reflections, R_{int} = 0.0470, 1783 reflections with $F_o > 4\,\sigma(F_o)$, the structure was solved by direct methods, refined by full-matrix least-squares techniques against F^2, the hydrogen atoms were located from the difference map and refined isotropically, only the hydrogen atoms of the methyl group were included at calculated positions with fixed thermal parameters, all nonhydrogen atoms were refined anisotropically, 237 parameters, $R1_{obs}$ = 0.0495, wR^2_{obs} = 0.0969, GOOF = 1.105, largest difference peak and hole: 0.361/−0.308 e Å^{-3}. Characteristic bond lengths [pm] and angles [°], [ab initio values]: N1–C3 130.3(6) [132.1], N1–C1 144.9(7) [146.4], N3–C3 134.3(6) [131.7], N3–C4 132.1(7) [131.7], N5–C4 132.7(6) [132.1], N5–C1 147.6(6) [146.4], C1–C8 152.3(7) [151.6], N1–N2 139.3(5) [136.4], N2–C2 127.8(6) [126.7], S1–C3 172.8(6) [176.0], S1–C3 172.0(6) [172.2]; N1–C1–N5 106.1(4) [104.1], N1–C1–C8 110.2(4) [112.9], N5–C1–C8 114.5(4) [112.9], C8–C1–H1 114(3) [110.3], N1–C1–H1 109(3) [108.1], N5–C1–H1 103(3) [108.1], C3–N1–C1 123.9(4) [124.9], N1–C3–N3 126.4(5) [125.6], C4–N3–C3 113.5(5) [113.0], N3–C4–N5 124.6(5) [124.2], C4–N5–C1 124.2(4) [124.9], C3–N1–N2 118.0(4) [117.5], N1–C3–S1 108.7(4) [109.3], C3–S1–C2 89.5(3) [88.2], N2–C2–S1 114.6(4) [114.1].

[15] [15a] M. J. S. Dewar, E. G. Zoebisch, E. F.Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909. – [15b] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209–220.

[16] Dieder angles N5–C1–$C1_{naphthyl}$–$C9_{naphthyl}$ of the conformers at 227 K: −63° and 118.7°.

[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binlley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. Q. A. Pople, *Gaussian 94, Revision E.1*, Gaussian, Inc., Pittsburgh, PA, USA, **1995**.

[18] T. La Cour, *Acta Crystallogr.* **1994**, *B30*, 1642–1643.

[19] L. Antolino, A. Cornia, A. C. Fabretti, W. Mulavasi, *J. Crystallogr. Spectrosc. Res.* **1993**, *23*, 967–971.

[20] [20a] These mechanistic alternatives have been investigated by PM3-MO calculations. This method definitely predicts the pathway via **11a** to be energetically favoured. – [20b] Synthesized from CH_2O, $SOBr_2$, and pyridine; publication in preparation: Salts **4** and **9** with R^1 = H appear to be less reactive towards nucleophilic replacements of the bromine (salt **4**) or the pyridine moiety (salt **9**), compared with cations with R^1 = Ph or Me. An explanation was found on the basis of semiempirical and ab initio calculations.

[21] This is supported by the ab initio calculated net charges (as they result from an natural population analysis; cf. ref.[10a]. Both C atoms are significantly positively charged: $q_{C3} = q_{C4} = +0.40$, for completeness: $q_{C1} = +0.25$, $q_{N1} = q_{N5} = -0.32$ (numbering cf. Figure 2).

[22] The reaction conditions have not been optimized for that synthesis.

[23] Crystal data for **8c** : $C_{17}H_{22}N_{10}S_4$, M_r = 494.69 g mol^{-1}, colourless prism, size 0.35 × 0.32 × 0.20 mm, triclinic, space group *P*1bar, a = 8.7332(4), b = 9.7892(6), c = 14.9130(9) Å, α = 104.414(2), β = 91.959(3), γ = 106.430(3)°, V = 1176.8(1) Å^3 , T= −90°C, Z = 2, $\rho_{calcd.}$ = 1.396 g cm^{-3}, μ(Mo-K_α) = 4.31 cm^{-1}, F(000) = 516, 2994 reflections in +h, ±k, ±l, measured in the range 4.73° ≤ Θ ≤ 23.47°, 2994 independent reflections, R_{int} = 0.041, 2580 reflections with $F_o > 4\,\sigma(F_o)$, the structure was solved by direct methods, refined by full-matrix least-squares techniques against F^2, the hydrogen atoms were included at calculated positions with fixed thermal parameters, all nonhydrogen atoms were refined anisotropically, 280 parameters, R_{obs} = 0.0497, wR^2_{obs} = 0.1367, GOQF = 1.009, largest difference peak and hole: 0.320/−0.337 e Å^{-3}. Characteristic bond lengths [pm] and [°], [ab initio values]: N(1)–C(1) 146.1(4) [144.0], N(6)–C(1) 146.9(4) [144.7], N(1)–C(2) 136.6(4) [135.3], N(6)–C(8) 136.4(5) [135.2], N(3)–C(2) 130.2(4) [127.6], N(8)–C(8) 129.7(5) [127.8], N(3)–C(5) 135.6(4) [136.4], N(8)–C(11) 135.7(4) [136.2], N(4)–C(5) 129.6(5) [127.8], N(9)–C(11) 129.7(5) [127.9], N(4)–N(5) 139.2(4) [136.5], N(9)–N(10) 138.4(5) [136.6], N(5)–C(6) 128.8(5) [127.2], N(10)–C(12) 129.4(6) [127.1], N(1)–N(2) 137.9(4) [136.2]. N(6)–N(7) 137.4(4) [136.1]. N(7)–C(9) 128.4(5) [126.1], N(2)–C(3) 128.2(4) [126.0], C(1)–C(14) 151.2(5) [–]; N(1)–C(1)–N(6) 108.1(3) [112.3], N(6)–C(1)–C(14) 113.0(3) [–], N(1)–C(1)–C(14) 112.2(3) [–], C(2)–N(1)–C(1) 124.2(3)

[123.9], N(3)−C(2)−N(1) 121.9(3) [121.1], C(2)−N(3)−C(5) 118.5(3) [120.3], N(3)−C(5)−S(2) 119.7(3) [119.4], C(6)−S(2)−C(5) 87.7(2) [86.4], C(7)−C(6)−S(2) 124.3(3) [123.2]. The intensity data for the compounds were collected with an Enraf−Nonius CAD4 diffractometer for **7a** and with a Nonius−Kappa CCD for **8a** and **8c**. The following programs were used: data reduction: MOLEN, DENZO; structure solution: SHELXS; structure refinement: SHELXL-93; structure presentation: SHELXL/PC. Further details of the crystal structure investigations are available on requests from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-408232 (**7a**), -408233 (**8a**), -408234 (**8c**), the names of the authors, and the journal citation.

[24] The ^{1}H- and ^{13}C-NMR signals could be assigned unambiguously to thiadiazole ring I/II and III/IV (cf. Scheme 2) by suitable NOESY-, HMQC-, and HMBC correlations. An NOE in **8c**, which is caused by the correlation of the protons at C-3 of the pentane moiety (δ = 1.34) with Me protons of the thiadiazole rings I/II (δ = 2.47), is very important to the structure characterization. **7c** does not exhibit such an effect. Further selected cross peaks are: HMQC: ^{1}H(2.47)/^{13}C(16.79) for Me thiadiazole I/II; ^{1}H(2.67)/^{13}C(16.27) for Me thiadiazole III/IV; HMBC: ^{1}H(7.54, CH, pentane-1)/^{13}C(159.79, C-2, thiadiazole I/II); ^{1}H(2.47, Me thiadiazole I/II)/^{13}C(151.26, C-5, thiadiazole I/II); ^{1}H(2.67, Me thiadiazole III/IV/^{13}C(160.26, C-5, thiadiazole III/IV).

[25] J. R. Cheeseman, G. W. Trucks, A. T. Keith, M. J. Frisch, *J. Chem. Phys.* **1996**, *104*, 5497−5509. (Basis set: HF/6-31+G*//6-31+G*, method: NMR = GIAO in Gaussian 94).

[26] [26a] E. Diez-Barra, A. de la Hoz, A. Sanchez-Migallon, J. Tejeda, *Heterocycles* **1992**, *34*, 1365−1373, and references cited therein. − [26b] Related bis(azolyl)alkanes with 2,3-dihydro-1,3,4-thiadiazole moieties, cf.: K. N. Zelenin, V. A. Khrustalev, V. V.Alekseev, P. A. Sharbatyan, A. T. Lebedev, *Chem. Heterocycl. Compd. (Engl. Transl.)* **1982**, *18*, 683−689; *Khim. Geterosikl. Soedin* **1982**, 904−910; D. M. Evans, D. R. Taylor, *J. Chem. Soc., Chem. Commun.* **1982**, 188−189; D. M. Evans, L. Hill, D. R. Taylor, M. Myers, *J. Chem. Soc., Perkin Trans. 1* **1986**, 1499−1506; related imino-bridged 1,3,4-thiadiazoles: C. T. Supuran, *Rev. Roum. Chim.* **1995**, *40*, 643−652.

[27] We thank Dr. A. Opitz (Hans-Knöll-Institut für Wirkstoff-Forschung, Jena) for providing us with a sample of that unpublished compound.

[28] J.-L. Barascut, R.-M. Claramunt, J. Elguero, *Bull. Soc. Chim. Fr.* **1973**, 1849−1853.

[98260]