Thiomethylation of aromatic amines: efficient method for the synthesis of heterocyclic compounds

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Primary aromatic amines were thiomethylated by formaldehyde and hydrogen sulfide. *N*-Substituted 1,3-thiazetidines, 4,5-dihydro-1,3,5-dithiazines, 3,4,5,6-tetrahydro-2*H*-1,3,5-thiadiazines, and 4,5-dihydro-1,3,5-oxathiazines were prepared for the first time starting from *meta*- and *para*-toluidines, *meta*-, *para*-, and *ortho*-anisidines, and *para*-xylidine. Amines characterized by higher mobility of hydrogen atoms produced previously unknown four-membered thiazetidines, whereas amines characterized by lower mobility of hydrogen atoms gave six-membered thiadiazines. The sorption properties with respect to silver were studied for the compounds, which were prepared from *p*-toluidine and *p*-anisidine.

Key words: thiomethylation, primary aromatic amines, O,N,S-containing heterocyclic compounds, formaldehyde, hydrogen sulfide, 1,3-thiazetidines, 4,5-dihydro-1,3,5-dithiazines, 3,4,5,6-tetrahydro-2*H*-1,3,5-thiadiazines, 4,5-dihydro-1,3,5-oxathiazines, sorption of precious metals.

The reactions of formaldehyde and hydrogen sulfide with amines open up new possibilities for the synthesis of heterocycles containing simultaneously the oxygen, nitrogen, and sulfur atoms. This synthesis was first carried out using the reaction of methylamine with formaldehyde and hydrogen sulfide as an example.[1,2] Later on, acyclic bis(4-morpholinomethyl)- and bis(1-piperidinomethyl) sulfides and selenides have been prepared by these reactions starting from piperidine and morpholine, respectively.[3—5]

Recently, we have demonstrated that thiomethylation of amino acids can be used for preparing difficultly accessible carboxy-containing 1,3,5-dithiazine derivatives.[6] The resulting heterocyclic compounds exhibit high complex-forming ability with respect to silver. Such heterocyclic compounds hold considerable promise as sorbents[7,8] and biologically active compounds.[9]

Taking into account the practical value of O,N,S-containing compounds and also with the aim of extending the field of application of thiomethylation, we studied liquid-phase condensation of formaldehyde and hydrogen sulfide with primary aromatic amines, which have not been earlier involved in such transformations.

Results and Discussion

Liquid-phase thiomethylation of primary aromatic amines by formaldehyde and hydrogen sulfide was carried out in a two-phase water—diethyl ether medium, which provided solubility of formaldehyde and hydrogen sulfide in water and solubility of aromatic amines in ether. We examined *meta*- (**1a**) and *para*-toluidines (**1b**), *meta*- (**1c**), *para*- (**1d**), and *ortho*-anisidines (**1e**), and *para*-xylidine (**1f**). Crystalline products **2—5** were prepared by bubbling hydrogen sulfide through a solution of formaldehyde in water in a molar ratio of 2 : 3 followed by the addition of a solution of amine **1** in diethyl ether at the temperature from 0 to 40 °C. The conversions of the starting amines were ≥90% (Scheme 1), except for *ortho*-substituted aromatic amine, *viz.*, *o*-anisidine (**1e**), whose conversion was 20%.

According to the data from HLPC, the reactions of *meta*- (**1a,c**) and *para*-substituted anilines (**1b,d**) at 20 and 40 °C afforded mixtures of compounds **2—4** with the predominant formation of one of them. The compositions of heterocycles **2—4** depend on the nature of amine, the ratio between the starting reagents, and the reaction temperature (Table 1).

For toluidines **1a,b**, a decrease in the temperature to 0 °C led to a decrease in the selectivity of the reaction. Under these conditions, thiazetidines **2a,b** and thiadiazines **4a,b** were produced in equal amounts, whereas dithiazines **3a,b** were prepared in lower yields. The inverse dependence was observed for *p*-xylidine (**1f**), *i.e.*, only dithiazine **3f** was generated upon a decrease in the temperature to 0 °C.

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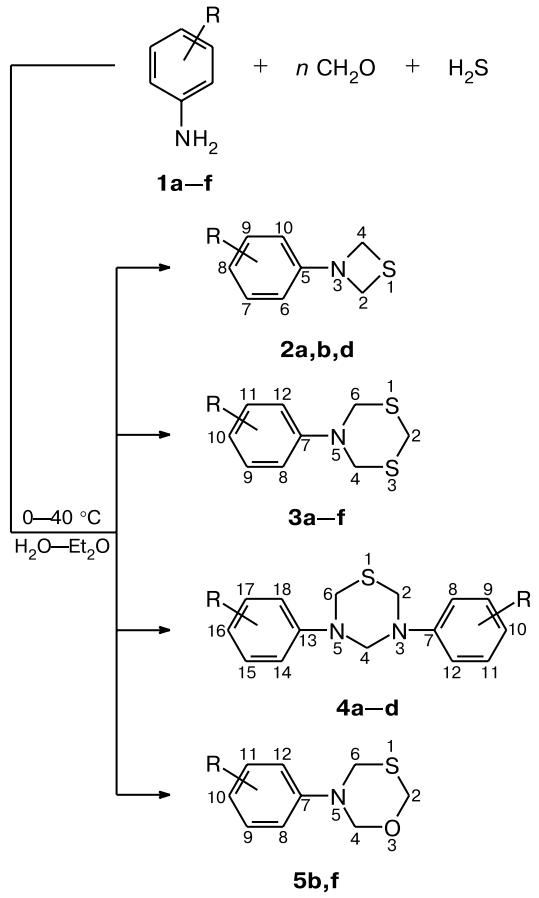
Scheme 1



R = *m*-CH_3 (**a**); *p*-CH_3 (**b**); *m*-OCH_3 (**c**); *p*-OCH_3 (**d**); *o*-OCH_3 (**e**); 2,5-$(CH_3)_2$ (**f**); *n* = 1—6

The composition of the products of thiomethylation of toluidines **1a,b** depends ambiguously on the excess of formaldehyde with respect to amine (6 : 1, see Table 1). The reaction of *m*-toluidine (**1a**) afforded thiazetidine **2a** as the major product (in 66% yield) and 1,3,5-dithiazine **3a** as a by-product (8%), whereas the reaction of *p*-toluidine (**1b**) gave rise to 1,3,5-dithiazine **3b** as the major product (28%), 1,3,5-oxathiazine **5b** (6%) being formed along with heterocycles **2b—4b** (52%).

The following dependence was found: four-membered thiazetidine **2a** was predominantly prepared from *m*-toluidine (**1a**), dithiazines **3** were generated from all anilines (see Table 1), whereas thiadiazines **4** were predominantly produced from *p*-toluidine (**1b**). Apparently, these results can be attributed to the difference in the mobility of the hydrogen atoms in the starting anilines. For example, less basic *m*-toluidine (**1a**) gave thiazetidine **2a**, whereas more basic *p*-toluidine (**1b**) produced thiadiazine **4b**. These facts are in agreement with the data published in the literature[10] according to which the rate of the reaction of toluidines with formaldehyde decreases in the following series: *m*-toluidine > *o*-toluidine > *p*-toluidine.

Oxathiazine **5** was generated only from *p*-toluidine (**1b**) and *p*-xylidine (**1f**) in a yield of no higher than 6% (see Table 1).

Heterocyclic compounds **2—5** were isolated in individual form by column chromatography. The mass spectrum of product **2a** has the molecuar ion peak $[M]^+$ at *m/z* 165 and the fragmentation ion peaks $[M - S]^+$, $[M - CH_2S]^+$, $[M - CH_2SCH_2]^+$, and $[M - NCH_2SCH_2]^+$ at *m/z* 133, 119, 105, and 91, respectively, corresponding to the characteristic fragments formed from $[M]^+$ by the abstraction of the sulfur atom and thiomethylene groups, among them those involving the nitrogen atom. The ^{1}H NMR spectrum shows a signal at δ_H 4.87 assigned to the protons of the CH_2 groups of the thiazetidine ring and signals for the protons of the aromatic moiety containing the methyl group at δ_H 6.58—7.22 and 2.35[11] (Table 2). The ^{13}C NMR spectrum has a signal for the carbon atom of the thiazetidine ring of **2a** at δ_C 56.75 (Table 3). In the IR spectrum of product **2a**, the stretching vibration band of the amino group at 3150 cm^{-1} disappears. The stretching vibration band of the methyl group is observed at 2850 cm^{-1} and absorption characteristic of the aromatic ring is observed at 1600 cm^{-1}. The absorption band at 1050 cm^{-1} is assigned to stretching vibrations of the C—N bond. Weak absorption of the C—S bond is observed at 580—650 cm^{-1} (see Table 2).

The structure of thiadiazine **4b** as *N*,*N*-disubstituted tetrahydro-2*H*-1,3,5-thiadiazine was established based on spectroscopic data (see Tables 2 and 3). The mass spectrum of product **4b** shows the molecular ion $[M]^+$ at *m/z* 284 and the fragmentation ions $[M - H_2S]^+$, $[M - CH_2NPhCH_3]^+$, $[M - SCH_2NPhCH_3]^+$, $[CH_3PhNCH_2]^+$, $[CH_3PhN]^+$, and $[CH_3Ph]^+$ at *m/z* 250, 165, 133, 119, 105, and 91, respectively. The ^{1}H NMR spectrum has signals at δ_H 4.90 and 5.09 with the integral intensity ratio of 2 : 1, which are assigned to the methylene protons located between the S and N atoms and between two nitrogen atoms, respectively. In addition, the spectrum has signals of the methyl group and aromatic protons at δ_H 2.30 and 6.91—7.01, respectively (see Table 2). The ^{13}C NMR spectrum shows a signal for two carbon atoms located between the S and N atoms at δ_C 54.29 and a signal for one carbon atom located between two nitrogen atoms at δ_C 70.10.

We studied the sorption properties of a mixture of the products of thiomethylation of *p*-toluidine (**1b**) and *p*-anisidine (**1d**) with respect to silver. Solutions of wastes from photographic industry were used as a source of silver. The sorption was carried out in a static mode in a solution of the metal extracted and determined photometrically on a KFK-2 instrument according to standard procedures.[12] Based on the kinetic curves, it was found that the equilibrium was attained after 100 min of expo-

Table 1. Effects of the structure of aromatic amines, reaction temperature, and ratio between the starting reagents on the yields and compositions of the reaction products

Starting compound	R[a]	T/°C	Amine : CH_2O : H_2S[b]	Y[c] (wt.%)	Reaction products (%)				
					1	**2**	**3**	**4**	**5**
1a	*m*-CH_3	20	1 : 1 : 1	15	80	—	20	—	—
		0	1 : 3 : 2	32	6	43	12	39	—
		20	1 : 3 : 2	20	5	60	25	10	—
		40	1 : 3 : 2	36	2	98	—	—	—
		0	1 : 6 : 4	77	5	85	10	—	—
1b	*p*-CH_3	20	1 : 2 : 2	28	6	—	62	32	—
		0	1 : 3 : 2	30	6	38	15	36	5
		20	1 : 3 : 2	64	1	5	92	2	—
		40	1 : 3 : 2	62	3	—	52	45	—
		0	1 : 6 : 4	61	5	20	45	20	10
1c	*m*-OCH_3	20	1 : 3 : 2	24	5	—	65	30	—
1d	*p*-OCH_3	20	1 : 2 : 2	14	8	92	—	—	—
		20	1 : 3 : 2	21	—	60	10	30	—
1e	*o*-OCH_3	20	1 : 3 : 2	10	80	—	20	—	—
1f	*p*-$(CH_3)_2$	0	1 : 3 : 2	18	68	—	32	—	—
		20	1 : 3 : 2	16	53	—	41	—	6

[a] The position in the starting amine.
[b] The molar ratio between the starting reagents.
[c] The total yield of the products.

sure of the sorbent (solid phase) to a solution of the metal extracted at room temperature. The maximum capacity of the mixture of the products derived from *p*-toluidine and *p*-anisidine was 1.1 and 0.76 g g^{-1}, respectively. An increase in the temperature to 80 °C led to a decrease in the time required for the attainment of equilibrium to 5—10 min, the sorbent capacity remaining virtually unchanged. The degree of extraction of silver is close to 100%.

To summarize, we studied for the first time thiomethylation of aromatic amines giving rise to practically valuable heterocyclic O,N,S-containing compounds. We synthesized previously unknown derivatives of 1,3-thiazetidine, 1,3,5-dithiazine, 1,3,5-thiadiazine, and 1,3,5-oxathiazine.

Experimental

The ^1H and ^{13}C NMR spectra of compounds **2a**, **3b**, and **4a,b,d** were recorded on a Bruker AM-300 spectrometer operating at 300 MHz. The ^1H and ^{13}C NMR spectra of all other compounds were measured on a Jeol FX 90 Q spectrometer operating at 89.55 and 22.50 MHz, respectively using $CDCl_3$ as the solvent. The IR spectra were recorded on a Specord 75 IR spectrophotometer in Nujol mulls with KBr. The mass spectra were obtained on an MX 1320 instrument with direct inlet of samples at 100—150 °C and 70 eV. Thin-layer chromatography was carried out on Silufol UV-254 silica gel using a 9 : 1 benzene—ethanol mixture as the eluent. The HPLC analysis was performed on an Altex chromatograph (Separon C_{18} column, 150×4), λ = 254 nm. Bubbling of hydrogen sulfide was controlled using an ANP-10 peristaltic pump.

Thiomethylation of aromatic amines 1a—f. Calculated amounts of a formaldehyde solution were placed in a temperature-controlled three-neck flask equipped with a magnetic stirrer, a reflux condenser, and a bubbler. Hydrogen sulfide (prepared from calculated amounts of Na_2S and HCl) was bubbled at a rate of 2.8 L h^{-1} to form a CH_2O : H_2S mixture in a ratio of 3 : 2. Then the corresponding amine dissolved in diethyl ether was added dropwise to the reaction mixture. In the experiments, the temperature was varied from 0 to 40 °C. The molar ratio between the reagents was also varied (amine : CH_2O = 1—6). The crystals that precipitated were filtered off and dried. The products were separated by column chromatography. The physicochemical and spectroscopic characteristics are given in Tables 2 and 3.

3-(3-Methylphenyl)-1,3-thiazetidine (2a). The yield was 66%, m.p. 184—185 °C, R_f 0.34. MS, m/z (I_{rel} (%)): 165 $[M]^+$ (26), 133 $[M - S]^+$ (69), 119 $[M - CH_2S]^+$ (75), 105 $[M - CH_2SCH_2]^+$ (82), 91 $[M - NCH_2SCH_2]^+$ (29). Found (%): C, 65.54; H, 6.83; N, 8.15; S, 19.48. $C_9H_{11}NS$. Calculated (%): C, 65.46; H, 6.67; N, 8.48; S, 19.39.

3-(4-Methylphenyl)-1,3-thiazetidine (2b). The yield was 12%, m.p. 171—172 °C, R_f 0.34. MS, m/z (I_{rel} (%)): 165 $[M]^+$ (25), 133 $[M - S]^+$ (10), 119 $[M - CH_2S]^+$ (29), 105 $[M - CH_2SCH_2]^+$ (14), 91 $[M - NCH_2SCH_2]^+$ (19). Found (%): C, 65.87; H, 6.74; N, 8.23; S, 19.16. $C_9H_{11}NS$. Calculated (%): C, 65.46; H, 6.67; N, 8.48; S, 19.39.

3-(4-Methoxyphenyl)-1,3-thiazetidine (2d). The yield was 13%, m.p. 119—120 °C, R_f 0.33. MS, m/z (I_{rel} (%)): 181 $[M]^+$ (4), 149 $[M - S]^+$ (4), 135 $[M - CH_2S]^+$ (88), 121 $[M - CH_2SCH_2]^+$ (14), 107 $[M - NCH_2SCH_2]^+$ (4), 92 $[M - CH_3NCH_2SCH_2]^+$ (37). Found (%): C, 59.89; H, 6.27;

Table 2. ^{1}H NMR and IR spectra of compounds **2—5**

Compound	δ (*J*/Hz)	IR, ν/cm^{-1}
2a	2.35 (s, 3 H, Me); 4.87 (m, 4 H, NCH_2S); 6.62 (s, 1 H, C_6H_4); 6.64 and 6.70 (d, 2 H, Ph, J = 7.8); 7.17 (t, 1 H, C_6H_4, J = 7.8)	1050 (C—N), 580—650 (C—S)
2b	2.08 (s, 3 H, Me); 5.04 (m, 4 H, NCH_2S); 6.47—7.07 (m, 4 H, C_6H_4)	1600, 2850
2d	3.84 (s, 3 H, OMe); 4.63 (m, 4 H, NCH_2S); 6.70—7.28 (m, 4 H, C_6H_4)	
3a	2.10 (s, 3 H, Me); 3.80 (s, 2 H, SCH_2S); 4.03 (s, 4 H, CH_2N); 6.82—7.32 (m, 4 H, C_6H_4)	1050 (C—N), 580—650 (C—S)
3b	2.23 (s, 3 H, Me); 4.00 (s, 2 H, SCH_2S); 4.97 (s, 4 H, CH_2N); 6.98 and 7.15 (both d, 4 H, C_6H_4, J = 8.5)	1600, 2850
3c	3.82 (s, 3 H, OMe); 3.88 (s, 2 H, SCH_2S); 4.38 (s, 4 H, CH_2N); 7.04—7.36 (m, 4 H, C_6H_4)	
3d	3.62 (s, 3 H, OMe); 3.74 (s, 2 H, SCH_2S); 4.30 (s, 4 H, CH_2N); 6.83—7.21 (m, 4 H, C_6H_4)	
3e	3.67 (s, 3 H, OMe); 3.88 (s, 2 H, SCH_2S); 4.30 (s, 4 H, CH_2N); 6.54—6.77 (m, 4 H, C_6H_4)	
3f	2.07 and 2.20 (both s, 3 H each, Me); 3.50 (s, 2 H, SCH_2S); 4.36 (s, 4 H, CH_2N); 6.74—7.07 (m, 3 H, C_6H_3)	
4a	2.30 (s, 6 H, Me); 4.82 (s, 4 H, SCH_2N); 5.33 (s, 4 H, NCH_2N); 6.60—7.15 (m, 8 H, 2 C_6H_4)	1150 (C—N), 1600, 2850
4b	2.25 (s, 6 H, Me); 4.90 (s, 4 H, SCH_2N); 5.09 (s, 2 H, NCH_2N); 6.91 (d, 4 H, C_6H_4, ^3J = 8.5); 7.01 (d, 4 H, C_6H_4, ^3J = 8.5)	
4c	3.82 (s, 6 H, OMe); 4.80 (s, 4 H, SCH_2N); 4.91 (s, 4 H, NCH_2N); 7.21—7.36 (m, 8 H, 2 C_6H_4)	
4d	3.42 (s, 6 H, OMe); 4.63 (s, 4 H, SCH_2N); 4.80 (s, 2 H, NCH_2N); 6.72—6.95 (m, 8 H, 2 C_6H_4)	
5b	2.36 (s, 3 H, Me); 4.34 (s, 2 H, NCH_2S); 4.71 (s, 2 H, SCH_2O); 5.25 (s, 2 H, NCH_2O); 6.52—7.11 (m, 4 H, C_6H_4)	1050 (C—N), 580—650 (C—S)
5f	2.12 and 2.28 (both s, 3 H each, Me); 4.09 (s, 2 H, NCH_2S); 4.53 (s, 2 H, SCH_2O); 4.78 (s, 2 H, NCH_2O); 6.34—6.99 (m, 3 H, C_6H_3)	1600, 2850

Table 3. ^{13}C NMR spectra of compounds **2—5**

Compound	δ (*J*/Hz)*
2a	22.02 (q, Me); 56.75 (t, C(2), C(4)); 112.02 (d, C(10)); 115.53 (d, C(6)); 120.35 (d, C(8)); 129.19 (d, C(7)); 139.07 (s, C(9)); 144.21 (s, C(5))
2b	19.93 (q, Me); 56.54 (t, C(2), C(4)); 114.42 (d, C(6), C(10)); 118.71 (d, C(7), C(9)); 129.44 (s, C(8)); 141.21 (s, C(5))
2d	55.57 (q, OMe); 57.32 (t, C(2), C(4)); 114.88 (d, C(6), C(10)); 115.85 (d, C(7), C(9)); 137.90 (s, C(5)); 152.46 (s, C(8))
3a	21.88 (q, Me); 33.26 (t, C(2)); 56.67 (t, C(4), C(6)); 115.14 (d, C(12)); 117.93 (d, C(8)); 119.17 (d, C(10)); 129.12 (d, C(9)); 138.35 (s, C(11)); 143.68 (s, C(7))
3b	20.19 (q, Me); 33.65 (t, C(2)); 53.81 (t, C(4), C(6)); 117.02 (d, C(8), C(12)); 126.64 (s, C(10)); 128.44 (d, C(9), C(11)); 144.46 (s, C(7))
3c	34.70 (t, C(2)); 55.12 (q, OMe); 58.18 (t, C(4), C(6)); 104.28 (d, C(8)); 109.94 (d, C(10)); 112.8 (d, C(12)); 129.91 (d, C(11)); 145.97 (s, C(7)); 160.47 (s, C(9))
3d	30.92 (t, C(2)); 55.37 (q, OMe); 57.19 (t, C(4), C(6)); 114.81 (d, C(9), C(11)); 115.72 (d, C(8), C(12)); 137.83 (s, C(7)); 152.33 (s, C(10))
3e	33.52 (t, C(2)); 47.30 (t, C(4), C(6)); 55.89 (q, OMe); 111.69 (d, C(9)); 120.99 (d, C(12)); 122.55 (d, C(11)); 123.92 (d, C(10)); 138.55 (s, C(7)); 147.00 (s, C(8))
3f	17.59 and 21.57 (both q, Me); 33.07 (t, C(2)); 56.74 (t, C(4), C(6)); 112.01 (d, C(12)); 119.56 (d, C(10)); 130.03 (d, C(9)); 131.00 (s, C(8)); 135.56 (s, C(11)); 143.94 (s, C(7))
4a	21.81 (q, Me); 54.04 (t, C(2), C(6)); 69.51 (t, C(4)); 111.82 (d, C(8), C(18)); 114.16 (d, C(12), C(14)); 120.14 (d, C(10), C(16)); 128.66 (d, C(11), C(15)); 138.30 (s, C(9), C(17)); 144.18 (s, C(7), C(13))
4b	20.40 (q, Me); 54.29 (t, C(2), C(6)); 70.10 (t, C(4)); 117.92 (d, C(8), C(12), C(14), C(18)); 129.32 (d, C(9), C(11), C(15), C(17)); 129.82 (s, C(10), C(16)); 145.51 (s, C(7), C(13))
4c	46.08 (t, C(2), C(6)); 55.12 (q, OMe); 65.72 (t, C(4)); 103.76 (d, C(8), C(14)); 104.83 (d, C(10), C(16)); 107.40 (d, C(12), C(18)); 128.93 (d, C(11), C(17)); 150.32 (s, C(7), C(13)); 157.93 (s, C(9), C(15))
4d	55.20 (t, C(2), C(6)); 55.94 (q, OMe); 71.17 (t, C(4)); 114.92 (d, C(9), C(11), C(15), C(17)); 120.28 (d, C(8), C(12), C(14), C(18)); 142.34 (s, C(7), C(13)); 154.62 (s, C(10), C(16))
5b	20.19 (q, Me); 53.62 (t, C(6)); 71.70 (t, C(2)); 82.43 (t, C(4)); 118.97 (d, C(8), C(12)); 126.84 (s, C(10)); 129.64 (d, C(9), C(11)); 141.41 (s, C(7))
5f	19.09 and 21.55 (both q, Me); 53.34 (t, C(6)); 72.15 (t, C(2)); 81.45 (t, C(4)); 110.45 (d, C(12)); 118.91 (d, C(10)); 124.50 (d, C(9)); 124.89 (s, C(8)); 134.32 (s, C(11)); 147.20 (s, C(7))

* In $CDCl_3$.

N, 7.53; O, 8.53; S, 17.78. $C_9H_{11}NOS$. Calculated (%): C, 59.67; H, 6.08; N, 7.73; O, 8.84; S, 17.68.

5-(3-Methylphenyl)perhydro-1,3,5-dithiazine (3a). The yield was 8%, m.p. 154—155 °C, R_f 0.83. MS, m/z (I_{rel} (%)): 211 $[M]^+$ (27), 165 $[M - CH_2S]^+$ (7), 133 $[M - SCH_2S]^+$ (17), 119 $[M - SCH_2SCH_2]^+$ (40). Found (%): C, 56.78; H, 6.36; N, 6.28; S, 30.58. $C_{10}H_{13}NS_2$. Calculated (%): C, 56.87; H, 6.16; N, 6.64; S, 30.33.

5-(4-Methylphenyl)perhydro-1,3,5-dithiazine (3b). The yield was 59%, m.p. 147—148 °C, R_f 0.83. MS, *m/z* (I_{rel} (%)): 211 $[M]^+$ (29), 165 $[M - CH_2S]^+$ (8), 133 $[M - SCH_2S]^+$ (29), 119 $[M - SCH_2SCH_2]^+$ (100). Found (%): C, 56.63; H, 6.24; N, 6.31; S, 30.82. $C_{10}H_{13}NS_2$. Calculated (%): C, 56.87; H, 6.16; N, 6.64; S, 30.33.

5-(3-Methoxyphenyl)perhydro-1,3,5-dithiazine (3c). The yield was 16%, m.p. 119—120 °C, R_f 0.84. MS, *m/z* (I_{rel} (%)): 227 $[M]^+$ (69), 181 $[M - CH_2S]^+$ (4), 149 $[M - SCH_2S]^+$ (4), 135 $[M - SCH_2SCH_2]^+$ (88). Found (%): C, 52.97; H, 5.45; N, 6.27; O, 7.27; S, 28.04. $C_{10}H_{13}NOS_2$. Calculated (%): C, 52.86; H, 5.72; N, 6.17; O, 7.05; S, 28.19.

5-(4-Methoxyphenyl)perhydro-1,3,5-dithiazine (3d). The yield was 2%, m.p. 109—110 °C, R_f 0.84. MS, *m/z* (I_{rel} (%)): 227 $[M]^+$ (14), 181 $[M - CH_2S]^+$ (4), 149 $[M - SCH_2S]^+$ (4), 135 $[M - SCH_2SCH_2]^+$ (86). Found (%): C, 52.64; H, 5.52; N, 6.02; O, 7.23; S, 28.59. $C_{10}H_{13}NOS_2$. Calculated (%): C, 52.86; H, 5.72; N, 6.17; O, 7.05; S, 28.19.

5-(2-Methoxyphenyl)perhydro-1,3,5-dithiazine (3e). The yield was 2%, m.p. 104—105 °C, R_f 0.84. MS, *m/z* (I_{rel} (%)): 227 $[M]^+$ (14), 181 $[M - CH_2S]^+$ (6), 149 $[M - SCH_2S]^+$ (6), 135 $[M - SCH_2SCH_2]^+$ (82). Found (%): C, 52.71; H, 5.46; N, 6.15; O, 7.18; S, 28.50. $C_{10}H_{13}NOS_2$. Calculated (%): C, 52.86; H, 5.72; N, 6.17; O, 7.05; S, 28.19.

5-(2,5-Dimethylphenyl)perhydro-1,3,5-dithiazine (3f). The yield was 7%, m.p. 127—128 °C, R_f 0.81. Found (%): C, 59.14; H, 6.45; N, 6.37; S, 28.04. $C_{11}H_{15}NS_2$. Calculated (%): C, 58.67; H, 6.67; N, 6.22; S, 28.44.

3,5-Bis(3-methylphenyl)-3,4,5,6-tetrahydro-2*H*-1,3,5-thiadiazine (4a). The yield was 13%, m.p. 196—197 °C, R_f 0.21. MS, *m/z* (I_{rel} (%)): 284 $[M]^+$ (23), 250 $[M - H_2S]^+$ (6), 165 $[M - CH_2NPhCH_3]^+$ (37), 133 $[M - SCH_2NPhCH_3]^+$ (27), 119 $[CH_3PhNCH_2]^+$ (100), 105 $[CH_3PhN]^+$ (8), 91 $[CH_3Ph]^+$ (62). Found (%): C, 71.67; H, 7.15; N, 9.74; S, 11.44. $C_{18}H_{20}N_2S$. Calculated (%): C, 71.83; H, 7.04; N, 9.86; S, 11.27.

3,5-Bis(4-methylphenyl)-3,4,5,6-tetrahydro-2*H*-1,3,5-thiadiazine (4b). The yield was 28%, m.p. 161—162 °C, R_f 0.22. MS, *m/z* (I_{rel} (%)): 284 $[M]^+$ (23), 250 $[M - H_2S]^+$ (6), 165 $[M - CH_2NPhCH_3]^+$ (37), 133 $[M - SCH_2NPhCH_3]^+$ (27), 119 $[CH_3PhNCH_2]^+$ (100), 105 $[CH_3PhN]^+$ (8), 91 $[CH_3Ph]^+$ (62). Found (%): C, 71.58; H, 7.21; N, 9.80; S, 11.41. $C_{18}H_{20}N_2S$. Calculated (%): C, 71.83; H, 7.04; N, 9.86; S, 11.27.

3,5-Bis(3-methoxyphenyl)-3,4,5,6-tetrahydro-2*H*-1,3,5-thiadiazine (4c). The yield was 7%, m.p. 153—154 °C, R_f 0.23. Found (%): C, 64.68; H, 6.39; N, 8.71; O, 10.21; S, 10.01. $C_{17}H_{20}N_2O_2S$. Calculated (%): C, 64.56; H, 6.33; N, 8.86; O, 10.13; S, 10.13.

3,5-Bis(4-methoxyphenyl)-3,4,5,6-tetrahydro-2*H*-1,3,5-thiadiazine (4d). The yield was 6%, m.p. 145—146 °C, R_f 0.23. Found (%): C, 64.47; H, 6.24; N, 8.75; O, 10.40; S, 10.14. $C_{17}H_{20}N_2O_2S$. Calculated (%): C, 64.56; H, 6.33; N, 8.86; O, 10.13; S, 10.13.

5-(4-Methylphenyl)perhydro-1,3,5-oxathiazine (5b). The yield was 6%, m.p. 124—125 °C, R_f 0.67. Found (%): C, 61.44; H, 6.37; N, 7.23; O, 8.32; S, 16.64. $C_{10}H_{13}NOS$. Calculated (%): C, 61.53; H, 6.67; N, 7.18; O, 8.21; S, 16.41.

5-(2,5-Dimethylphenyl)perhydro-1,3,5-oxathiazine (5f). The yield was 1%, m.p. 122—123 °C, R_f 0.69. Found (%): C, 62.97; H, 7.53; N, 6.54; O, 7.32; S, 15.64. $C_{11}H_{15}NOS$. Calculated (%): C, 63.16; H, 7.18; N, 6.70; O, 7.66; S, 15.30.

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