Efficient method for a synthesis of *N*-substituted dithiazinanes via transamination of *N*-methyl-1,3,5-dithiazinane with arylamines and hydrazines

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Dedicated to Professor Usein M. Dzhemilev on the occasion of his 65th birthday

DOI: http://dx.doi.org/10.3998/ark.5550190.0012.810

Abstract

The efficient method for a synthesis of *N*-substituted dithiazinanes based on the transamination reaction of *N*-methyl-1,3,5-dithiazinane with arylamines and hydrazines in the presence of Sm and Co catalysts has been developed.

Keywords: Transamination, dithiazinanes, arylamines, phenylenediamines, hydrazines, catalysis

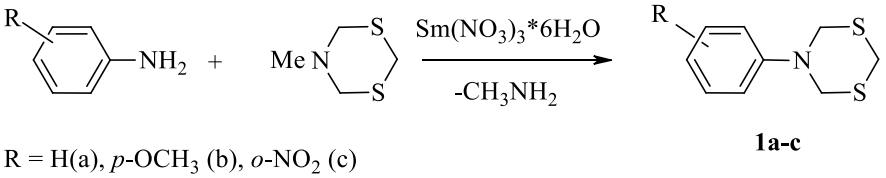
Introduction

Dithiazinanes have attracted notable research interest due to its applicability in synthesis of biologically active compounds,[1-5] as sorbents for noble metals,[6] and even as food additives in some countries.[7-13] Cyclothiomethylation of primary amines with CH_2O and H_2S is one of the first and well-known procedures to synthesize *N*-substituted 1,3,5-dithiazinanes.[14] In recent years, this reaction have been extensively studied on the example of aliphatic[15,16] and aromatic amines,[17,18] aminophenols,[19] amino acids,[20,21] hydrazine and its derivatives.[22–25] Nevertheless, this method has definite limitation associated with the use of gaseous H_2S and aqueous solution of CH_2O. As a rule, these reactions furnish a mixture of heterocyclic compounds. At the same time, the synthesis of *N*-substituted 1,3,5-dithiazinanes by thermal transamination of *N*-*tert*-butyl-1,3,5-dithiazinane with the aid of 1,3,5-trimethyltriazinane (68 °C, 3 h) has been also reported.[26]

Results and discussion

In order to develop more effective method for synthesizing *N*-substituted 1,3,5-dithiazinanes with high selectivity and yields we have studied the catalytic reaction of primary arylamines and hydrazines with *N*-methyl-1,3,5-dithiazinane as a synthetic equivalent of H_2S and CH_2O. Preliminary experiments showed that non-catalytic interaction between equimolar amount of *N*-methyl-1,3,5-dithiazinane and aniline ($CHCl_3$, 20 °C, 3 h) affords *N*-phenyl-1,3,5-dithiazinane **1a** in low yields (less than 10%).

To optimize overall product yield we performed this transamination reaction in the presence of transition metal-based (Cu, Pd, Co, Mn, Ti, Hf, V, Fe, Sm) catalysts, which showed high catalytic activity in the aminomethylation reaction of CH acids with *gem*-diamines.[27] For a series of catalysts tested, the catalytic activity of $Sm(NO_3)_3*6H_2O$ (5 mol%) was the highest. In this case, *N*-phenyl-1,3,5-dithiazinane **1a** (Scheme 1) has been obtained at r. t. for 3 h in 68% yield. Under optimized conditions (5 mol% $Sm(NO_3)_3*6H_2O$, 20 °C, 3 h, $CHCl_3$) *p*-anizidine entered into reaction with *N*-methyl-1,3,5-dithiazinane to give 5-(4-methoxyphenyl)-1,3,5-dithiazinane **1b** in 70% yield. The interaction between *N*-methyl-1,3,5-dithiazinane and *o*-nitroaniline was found to afford 5-(2-nitrophenyl)-1,3,5-dithiazinane **1c** in 64% yield.



R = H(a), *p*-OCH_3 (b), *o*-NO_2 (c)

1a-c

Scheme 1

The NMR experiments showed that the samarium ions are coordinated by the nitrogen atom of arylamine to form the intermediate complex. In the ^1H and ^{13}C NMR spectra of this complex the signals attributable to protons of the amino group and the carbon atom associated with the nitrogen atom, respectively, were shifted in a higher field as compared to those appeared in the spectra of initial arylamine. Probably, under reaction conditions, the N-H bond in original arylamine is activated due to the coordination of the lone electron pair of the nitrogen atom with the metal ion. As a result, transamination of *N*-methyl-1,3,5-dithiazinane occurs giving rise to thermodynamically more stable *N*-aryl-1,3,5-dithiazinane.

As reported,[28] the multicomponent condensation of *o*-, *m*-, and *p*-phenylenediamines with H_2S and CH_2O proceeds unambiguously giving rise to a mixture of heterocyclic compounds for *o*-isomer, and a mixture of macroheterocycles in the case of *m*-isomer. The thiomethylation reaction of *p*-phenylenediamine with the above reagents has failed.

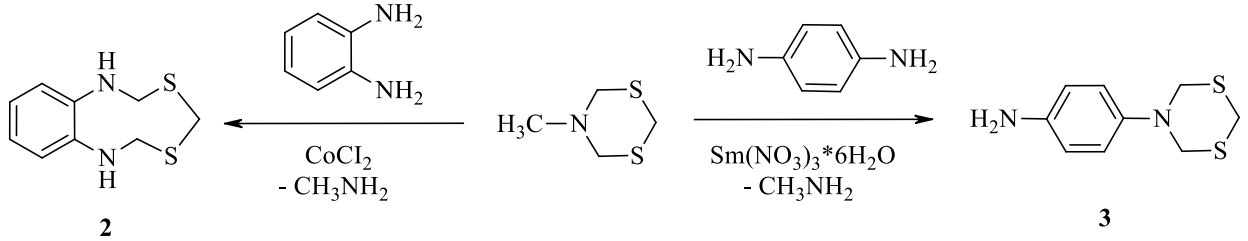
We have examined the transamination reaction of *N*-methyl-1,3,5-dithiazinane with phenylenediamines (*o*- and *p*-isomers) in the presence of transition metal-based (Sm, Cu, Pd, Co, Fe, Ni) catalysts. It became clear that *o*-phenylenediamine enters into reaction with equimolar

amount of *N*-methyl-1,3,5-dithiazinane under above optimized conditions (5 mol% $CoCI_2$, 20 °C, 3 h, $CHCl_3$) furnishing 1,2,6,7-tetrahydro-3,5,1,7-benzodithidiazonine **2** in 75% yield (Scheme 2).

The ^{1}H NMR spectrum of **2** contains the broadened singlets [δ 4.29 and 4.76 (1:2 ratio)] of the methylene protons located between two sulfur atoms as well as S and N atoms respectively. Two duplets and two triplets for the aromatic protons at δ 6.72–8.29 are also observed. The ^{13} C NMR spectra of **2** exhibit the triplet signals belonging to the C-4 and C-2(C-6) atoms at δ 32.50 and 55.16 ppm respectively. The mass spectrum of compound **2** has the molecular ion peak at *m/z* 212 $[M]^+$ as well as characteristic fragment ion peaks at *m/z* 134 $[M\text{-}SCH_2S]^+$, *m/z* 120 $[M\text{-}CH_2SCH_2S]^+$, *m/z* 92 $[CH_2SCH_2S]^+$, *m/z* 78 $[C_6H_6]^+$, and *m/z* 46 $[CH_2S]^+$. The spectral results have confirmed the structure of compound **2** namely 1,2,6,7-tetrahydro-3,5,1,7-benzodithidiazonine.

Unlike *o*-phenylenediamine, its *p*-isomer reacts with *N*-methyl-1,3,5-dithiazinane under the action of 5 mol% $Sm(NO_3)_3$*$6H_2O$ (20 °C, 3 h, DMF) involving only one NH_2 group to form 4-(1,3,5-dithiazinane-5-yl)phenylamine **3** in 70% yield.

In the ^{1}H NMR spectrum of compound **3**, the methylene protons of the 1,3,5-dithiazinane ring located between two S atoms and also S and N atoms appear as broadened singlets at δ 4.25 and 4.97. The aromatic protons resonated at δ_H 6.7–7.7. The ^{13}C NMR spectrum of **3** exhibits triplets at δ 34.30 and 55.40 assigned to the C-2 and C-4 (C-6) atoms of the 1,3,5-dithiazinane ring. According to these spectroscopic results, under reaction conditions the transamination product **3** namely 4-(1,3,5-dithiazinane-5-yl)phenylamine is formed.



2 **3**

Scheme 2

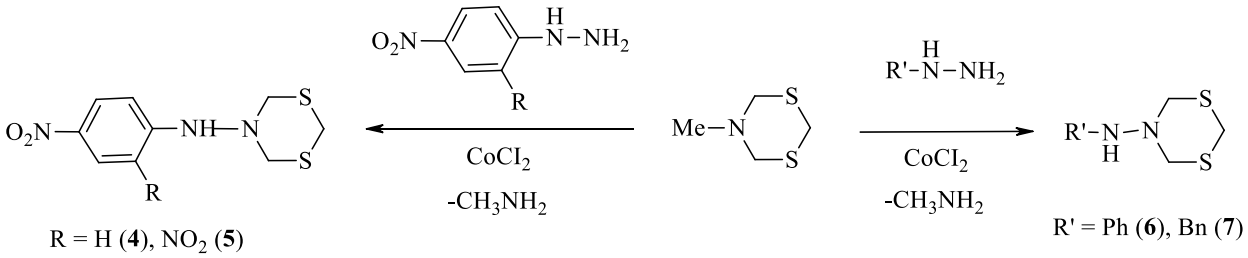
The positive results on catalytic cyclothiomethylation of arylamines providing formation of dithiazinanes **1–3** have encouraged us and gave hope for the successful implementation of *N*-methyl-1,3,5-dithiazinane transamination with aryl hydrazine (Scheme 3).

As an example, we have employed the transamination reaction of *N*-methyl-1,3,5-dithiazinane with 4-nitrophenylhydrazine, which in the presence of 5 mol% $CoCl_2$ under selected conditions (20 °C, 3 h) afforded 4-nitrophenyl-1,3,5-dithiazinane-5-amine **4** in 78% yield.

The formation of dithiazinane ring was indicated by ^{1}H and ^{13} C NMR spectral data. Thus, in the ^{1}H NMR spectrum of compound **4** we observed two characteristic singlets at δ_H 3.7 and 4.4 ppm with an intensity ratio of 1: 2 due to the methylene protons. The aromatic protons resonated

at a lower field at δ_H 6.7–8.07 ppm. In the ^{13}C NMR spectrum of **4** the carbon C-2 и C-4 (C-9) atoms manifest themselves by triplet signals at δ 33.30 and 57.40 ppm respectively. Mass-spectrum of **4** is characterized by the presence of the molecular ion peak at *m/z* 258 $[M]^+$ as well as characteristic fragment ion peaks at *m/z*134 $[M\text{-}SCH_2S]^+$, *m/z* 120 $[M\text{-}CH_2SCH_2S]^+$, *m/z* 92 $[CH_2SCH_2S]^+$, *m/z* 78 $[C_6H_6]^+$, and *m/z* 46 $[CH_2S]^+$. These spectral data have confirmed the proposed by us structure of compound **4**.

In an analogous fashion, we have successfully performed the transaminatiom reaction of *N*-methyl-1,3,5-dithiazinane with 2,4-dinitrophenylhydrazine mediated by 5 mol% $CoCl_2$ under optimized conditions (20 °C, 3 h, $CHCl_3$) providing 2,4-dinitrophenyl-1,3,5-dithiazinane-5-amine **5** in 75% yield.



Scheme 3

Catalytic transamination of *N*-methyl-1,3,5-ditiazinane with phenyl- and benzylhydrazines, in contrast to the well-known[25] procedure based on cyclothiomethylation with H_2S and CH_2O, provides high yields (more than 80%) of individual *N*-phenyl-1,3,5-dithiazinane-5-amine **6** and *N*-benzyl-1,3,5-dithiazinane-5-amine **7**. In the absence of a catalyst the transamination products **1–7** were obtained in 5–15% yield. It should be noted that, unlike the transamination procedure, thiomethylation of phenyl- and benzylhydrazines by a classical method using CH_2O and H_2S, as mentioned above, affords a mixture of heterocyclic compounds.[25] Furthermore, under these conditions one can not thiomethylate nitrophenyhydrazines.

Conclusions

In summary we have developed an efficient method for synthesizing a variety of *N*-substituted 1,3,5-ditiazinanes via catalytic transamination of *N*-methyl-1,3,5-ditiazinane with arylamines and arylhydrazines. Unique structure of *N*-substituted 1,3,5-ditiazinanes opens up new possibilities for using these classes of compounds as potential biologically active compounds, food additives, extractants and other valuable substances.

Experimental Section

General. Progress of the reaction was monitored by thin-layer chromatography (TLC) using Silufol W-254 plates and iodine vapor as a revealing agent. Analysis of the reaction products was performed by high performance liquid chromatography (HPLC) using Beckman Altex gradient liquid Chromatograph (model 330, U.S.A.) with UV detection at 340 nm. The one-dimensional (^{1}H, ^{13}C) and two dimensional homo- (COSY) and heteronuclear (HSQC, HMBC) NMR spectra were recorded in $CDCl_3$ on a spectrometer Bruker Avance 400 [400.13 MHz (^{1}H) and 100.62 MHz (^{13}C)] in accordance with a standard Bruker protocol. Infrared spectra (IR) spectra were recorded using a Specord IR-75 instrument in liquid paraffin and in KBr pellets. Chromato-mass spectrometric analysis of compounds was performed on a Finnigan 4021 instrument (glass capillary column 50000x0.25mm, stationary phase HP-5, helium as the carrier gas, temperature programming from 50 to 300 ºC at a rate of 5 ºC min^{-1}, evaporator temperature 280 °C, the temperature of the ion source 250 °C [EI, 70 eV]) and also using SHIMADZU QP-2010Plus instrument (Supelco PTE-5 capillary column 30m x 0.25mm). Elemental analysis of the samples was carried out using Carlo Erba Elemental Analyzer model 1106. The products were isolated by column chromatography on silica gel SiO_2. Compounds **1a**, **1b**, **6** and **7** were identified by comparison with the known samples.[17,25]

Transamination of *N*-methyl-1,3,5-dithiazinane with arylamines and hydrazines

The calcined and argon-filled Schlenk vessel equipped by magnetic stirrer under continuous stirring was charged with $CHCI_3$ (5 mL), $Sm(NO_3)_3$*$6H_2O$ (or $CoCl_2$) catalyst (0,16 mmol), the corresponding arylamine or hydrazine (10 mmol) and *N*-methyl-1,3,5-dithiazinane (11 mmol). The reaction mixture was stirring at r.t. (~20 ºC) for 3 h. The end products **1–7** were purified by column chromatography on silica gel SiO_2 and identified by means of spectral methods.

5-(2-Nitrophenyl)-1,3,5-dithiazinane (1c). Yield 64%. ^{1}H NMR δ 3.38 (s, 2H, C(2)H_2); 4.75 (s, 4H, C(4)H_2, C(6)H_2); 6.74 (t, 1H, C(10)H, *J* = 7.4 Hz); 7.13 (d, 1H, C(12)H, *J* = 7.4 Hz); 7.55 (t, 1H, C(11)H, *J* = 7.4 Hz); 8.06 (d, 1H, C(9)H, *J* = 7.4 Hz) ppm. ^{13}C NMR δ 43.0 (t, C(2)); 63.4 (t, C(4), C(6)); 115.6 (d, C(10)); 116.2 (d, C(12)); 126.1 (d, C(9)); 135.9 (d, C(11)); 143.0 (s, C(8)); 143.3 (s, C(7)) ppm. Anal. Calcd for $C_9H_{10}N_2O_2S_2$: C, 44.61; H, 4.16; N, 11.56; S, 26.47%. Found: C, 44.84; H, 4.33; N, 11.05; S, 26.47%.

1,2,6,7-Tetrahydro-3,5,1,7-benzodithiadizonine (2). Yield 75 %. ^{1}H NMR δ 4.29 (br s, 2H, CH_2 (2)); 4.76 (br s, 4H, CH_2 (4, 9)); 6.72 (d, 1H, CH (10)); 6.79 (t, 1H, CH (11)); 7.02 (t, 1H, CH (12)); 8.29 (d, 1H, CH (13)) ppm. ^{13}C NMR δ 32.50 (t, C-2); 55.16 (t, C-4, C-9); 116.75 (d, C-10, C-13); 120.26 (d, C-11, C-12); 134.77 (s, C-6, C-7) ppm. MS *m/z*: 212 $[M]^+$ (20); 134 $[M\text{-}SCH_2S]^+$ (15); 133 $[M\text{-}SCH_2SH]^+$ (100); 120 $[M\text{-}CH_2SCH_2S]^+$ (20); 119 $[M\text{-}CH_2SCH_2SH]^+$ (85); 92 $[CH_2SCH_2S]^+$ (20); 78 $[C_6H_6]^+$ (15); 46 $[CH_2S]^+$ (65). Anal. Calcd for $C_9H_{12}S_2N_2$: C, 50.91; H, 5.70; N, 13.19; S, 30.20%. Found: C, 50.82; H, 5.67; N, 13.20; S, 30.71%.

(1,3,5-Dithiazinane-5-yl)phenylamine (3). Yield 70%. IR ν 720 1500, 1650, 2900, 3300 cm^{-1}. ^{1}H NMR δ 4.25 (br s, 2H, CH_2 (2)); 4.97 (br s, 4H, CH_2 (4, 6)); 6.7 (d, 2H, CH (8, 12)); 7.7 (d,

2H, CH (9, 11)) ppm. ^{13}C NMR δ 34.3 (t, C(2)); 55.4 (t, C(6,4)); 115,4 (d, C(8,12)); 116,6 (d, C(9,11)) ppm. Anal. Calcd for $C_9H_{12}S_2N_2$: C, 50.91; H, 5.70; N, 13.19; S, 30.20%. Found: C, 50.80; H, 5.63; N, 13.10; S, 30.50%.

***N*-(4-Nitrophenyl)-1,3,5-dithiazinane-5-amine (4).** Yield 82%. ^{1}H NMR δ 3,6 (s, 1H, NH (7)); 3.7 (s, 2H, CH_2 (2)); 4.4 (s, 4H, CH_2 (4,6)); 6.7 (s, 2H, CH (10,12)); 8.07 (s, 2H, CH (9,13)) ppm. ^{13}C NMR δ 36.3 (t, C(2)); 57.4 (t, C(6,4)); 112,4 (d, C(13,9)); 123,6 (d, C(12,10)); 141,7 (s, C(11)); 154,3 (s, C(8)) ppm. MS *m/z*: 258 $[M]^+$ (20); 134 $[M\text{-}SCH_2S]^+$ (15); 133 $[M\text{-}SCH_2SH]^+$ (100); 120 $[M\text{-}CH_2SCH_2S]^+$ (20); 119 $[M\text{-}CH_2SCH_2SH]^+$ (85); 92 $[CH_2SCH_2S]^+$ (20); 78 $[C_6H_6]^+$ (15); 46 $[CH_2S]^+$ (65). Anal. Calcd for $C_9H_{11}N_3O_2S_2$: C,42.01; H,4.31; N,16.33; S,24.92; O, 12.43%. Found: C,41.95; H,4.29; N,16.25; S,24.88; O, 12.28%.

***N*-(2,4-Dinitrophenyl)-1,3,5-dithiazinane -5-amine (5).** Yield 79%. ^{1}H NMR δ 3,3 (s, 1H, NH (7)); 4.1 (s, 2H, CH_2 (2)); 4.4 (s, 4H, CH_2 (4,6)); 7.9 (d, H, CH (13)); 8.2 (d, H, CH (12)); 9.1 (s, H, CH (10)) ppm. ^{13}C NMR δ 35.1 (t, C(2)); 56.5 (t, C(6,4)); 115,2 (d, C(13)); 122,3 (d, C(12)); 128,4 (s, C(9)); 130,8 (s, C(12)); 134,5 (s, C(11)); 154,5 (s, C(8)) ppm. Anal. Calcd for $C_9H_{10}N_4O_4S_2$: C, 35.75; H, 3.33; N, 18.53; S, 21.17; O, 21.21%. Found: C, 35.63; H, 3.27; N, 18.36; S, 21.09; O, 21.15%.

***N*-Phenyl-(perhydro-1,3,5-dithiazine-5-yl)amine (6).** Yield 71%. R_f 0.54 (C_6H_{14}-C_6H_6, 1:3). IR ν 750, 1380, 1600, 2900, 3300–3400 (br) cm^{-1}. ^{1}H NMR δ 4.79 (s, 2H, $H_2C(2)$); 5.20 (s, 4H, $H_2C(4,6)$); 7.37–8.13 (m, 5H, H_2C (8–13)) ppm. ^{13}C NMR δ 32.19 (t, C(2)); 58.64 (t, C(4,6)); 114.45 (d, C(9,13)); 120.28 (d, C(10,12)); 129.13 (d, C(11)); 145.87 (s, C(8)) ppm. MS *m/z*: 212 $[M]^+$ (91); 166 $[M\text{-}CH_2S]^+$ (7); 134 $[M\text{-}SCH_2S]^+$ (48); 120 $[M\text{-}CH_2SCH_2S]^+$ (100). Anal. Calcd for $C_9H_{12}N_2S_2$: C, 50.94; H, 5.66; N, 13.21; S,30.19%. Found: C, 51.23; H, 5.47; N, 13.27; S, 30.03%.

***N*-Benzyl-(perhydro-1,3,5-dithiazine-5-yl)amine (7).** Yield 63%. R_f 0.28 (CCl_4-EtOEt, 5:1). ^{1}H NMR δ 4.25 (s, 2H, $H_2C(2)$); 4.63 (s, 2H, $H_2C(8)$); 4.72 (s, 4H, $H_2C(4,6)$); 7.87–8.05 (br s, 5H, H_2C (9–14)) ppm. ^{13}C NMR δ 31.74 (t, C(2)); 58.17 (t, C(4,6)); 59.03 (t, C(8)); 127.34 (d, C(12)); 128.42 (d, C(11,13)); 129.04 (d, C(10,14)); 138.15 (s, C(9)) ppm. MS *m/z*: 226 $[M]^+$ (30); 192 $[M\text{-}H_2S]^+$ (5); 147 $[M\text{-}C_6H_5\text{-}2)]^+$ (10); 131 $[C_6H_5CH_2NNC]^+$ (58); 118 $[C_6H_5CHNN]^+$ (23); 91 $[CHSCH_2S]^+$ (100); 77 $[C_6H_5]^+$ (58); $[SCH]^+$ (80). Anal. Calcd for $C_{10}H_{14}N_2S_2$: C, 53.10; H,6.19; N,12.39; S, 28.32%. Found: C, 53.07; H, 6.30; N, 12.38; S, 28.63%.

Acknowledgements

The authors thank the Russian Foundation of Basic Research and President RF for financial support (Grants 08-03-00789 and NSh-2349.2008.3).

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