Reactions of aminophenols with formaldehyde and hydrogen sulfide

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The reaction of *m*-aminophenol with CH_2O and H_2S (1 : 2 : 1 ratio) afforded 2,12-dioxa-4,14-dithia-6,16-diazatricyclo[15.3.1.1^{7,11}]docosa-1(20),7(22),8,10,17(21),18-hexaene in ~9% yield. Aminophenol *o*- and *p*-isomers react with CH_2O and H_2S (1 : 3 : 2) to form 2- and 4-[4*H*-1,3,5-dithiazin-5(6*H*)-yl]phenols in 86 and 71% yields, respectively. In the crystal structure of the latter, molecules contain dithiazine cycles in the chair conformation with the axial hydroxyphenyl group. Molecular packing represents a combination of molecules forming chains due to the OH...S intermolecular hydrogen bond.

Key words: thiomethylation; *o*-, *m*-, and *p*-aminophenols; formaldehyde; hydrogen sulfide; X-ray diffraction analysis.

We have previously studied the multicomponent condensation of aliphatic[1] and aromatic[2] primary amines, amino acids,[3,4] hydrazine,[5] and their derivatives with H_2S and CH_2O, affording predominantly substituted dithiazines of different structure.

Continuing to study the liquid-phase condensation of H_2S and CH_2O with compounds containing active hydrogen atoms and to develop preparative methods for syntheses of macrocyclic heterocycles and functionally substituted dithiazines, we examined the reactions of bifunctional monomers, *viz.*, *o*-, *m*-, and *p*-aminophenols, with H_2S and CH_2O.

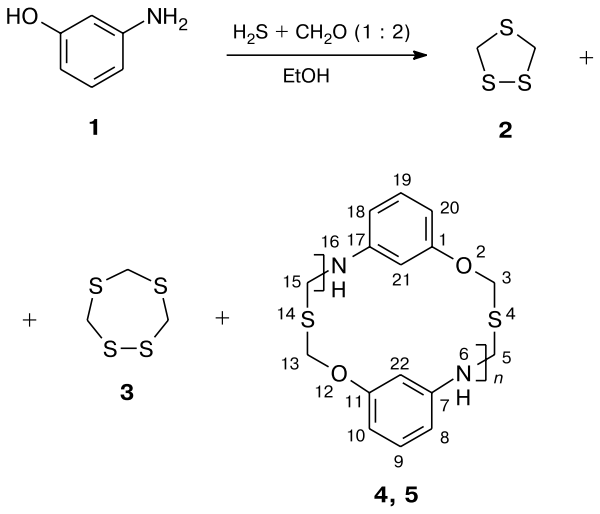
According to available data,[6,7] sulfur-containing macroheterocycles are promising as sensor systems for detection of silver and gold ions and as selective extracting agents and sorbents of noble and rare metals.

Results and Discussion

Thiomethylation of anilines with H_2S and CH_2O is known to form dithiazines and thiazetidines.[2,8,9] In the case of simple phenols, this process proceeds at the aromatic ring.[10] In the present work we found that thiomethylation of aminophenols depends on the mutual arrangement of functional groups in the aromatic ring and proceeds exclusively at these groups.

For example, the reaction of *m*-aminophenol (**1**) with CH_2O and H_2S (1 : 2 : 1 ratio) in EtOH for 3 h at ~40 °C affords a mixture of cyclic sulfides (Scheme 1) consisting of 1,2,4-trithiolane (**2**), 1,2,4,6-tetrathiepane (**3**), and sul-

Scheme 1



4: n = 1 (T = 40 °C, ~9% yield)
5: n = 7 (T = 20 °C, ~39% yield)

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fur-containing macroheterocycle **4** in an overall yield of 40%.

The structures of compounds **2** and **3** were proved by comparing with authentic samples.[11] The IR spectrum of compound **4** exhibits intense bands at 710, 820, 1185, 1375, 1600, 2900, and 3300 cm^{-1}, which indicates that the heterocycle molecule contains the C—S, C—O, C_{Ar}—O, C_{Ar}—N, and C=C (arom.) bonds and the CH_2 and NH groups. The UV spectrum contains a resonance peak at 297.6 nm (ε = 10) assigned to the band of the n—π*-transition, which is characteristic of groups attached to the aromatic ring and having a free electron pair.[12] The ^{1}H NMR spectrum of compound **4** exhibits multiplet signals at δ 6.30—6.88 characteristic of the H atoms bonded to the aromatic ring. Broadened singlets at δ 5.60 and 3.69 belong to the methylene protons arranged between the S and O atoms and between S and N, respectively. The ^{13}C NMR spectrum of compound **4** contains signals at δ 111.03, 126.46, 128.07, 130.93, 148.93, and 155.83 belonging to the C atoms of the aromatic ring and signals at δ 46.38 and 62.97 attributed to the C atoms of the methylene groups localized between the S and N atoms and between S and O, respectively. The mass spectrum of product **4** contains no molecular ion peak but exhibits peaks of ions of the characteristic residual fragments with *m/z* 167 ($[CH_2NHC_6H_4OCH_2S]^+$) and *m/z* 149 ($[C_6H_4NHCH_2SC]^+$) and weak peaks of ions of fragments formed upon thermal decomposition in the mass spectrometer evaporator (*m/z* 279, 258 $[M - CS_2]^+$, 247 and 207). Cryoscopic[13] determinations give a value of 334±10 corresponding to the molecular weight of compound **4**, whereas elemental analysis confirms the molecular formula $C_{16}H_{18}N_2O_2S_2$ for this compound.

Basing on the experimental results obtained, we can conclude that the molecule of compound **4** consists of two aminophenol moieties symmetrically linked through the bismethylenesulfide fragments. No linear oligomer is formed under these conditions: the ^{1}H and ^{13}C NMR spectra of compound **4** exhibit no signals of terminal groups.

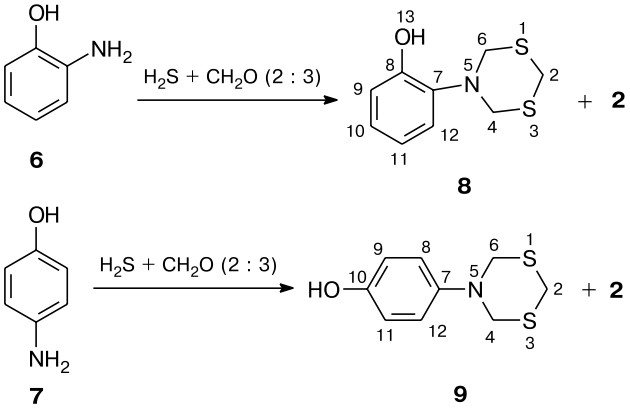
Thus, heterocycle **4** has a structure of 2,12-dioxa-4,14-dithia-6,16-diazatricyclo[15.3.1.1^{7,11}]docosa-1(20),7(22),8,10,17(21),18-hexaene.

The overall yield of heterocycle **4** increases with an increase in the total concentration of the starting reactants (*m*-aminophenol : CH_2O : H_2S = 1 : 2 : 1) in a solution of 95% EtOH. However, along with the increase in this yield, a mixture of other macrocyclic heteroatomic compounds of the type **5** is formed, whose molecules contain two and more aminophenol moieties (M_{cr} = 1333±10,[13] the numerical average value of the cyclooligocondensation degree is ~8). Solubility of such oligomeric macroheterocycles is very low and, hence, these compounds with unique structure are difficult to isolate and purify.

The condensation of aminophenol **1** with CH_2O and H_2S in a ratio of 1 : 3 : 2 affords poorly soluble oligomers, whose identification is very difficult.

Unlike *m*-aminophenol, its *o*- and *p*-isomers (**6** and **7**) undergo multicomponent condensation with H_2S and CH_2O exclusively at the amino group to form dithiazines, namely, 5-(2-hydroxyphenyl)dihydro-1,3,5-dithiazine (**8**) and 5-(4-hydroxyphenyl)dihydro-1,3,5-dithiazine (**9**) in 86 and 71% yields, respectively (Scheme 2).

Scheme 2



p-Dithiazinylphenol **9** has earlier[14] been synthesized by the condensation of NaSH, CH_2O, and *p*-aminophenol but the product was not characterized completely. We proved the structures of compounds **8** and **9** by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. In addition, X-ray diffraction analysis was performed for compound **9**. The mass spectra of products **8** and **9** exhibit the molecular ion peak $[M]^+$ with *m/z* 213. The fragmentation directions differ for both compounds, although the spectrum of each compound contains ions with *m/z* 167, 121, and 107, which are formed by the subsequent detachment of the CH_2S, $(CH_2S)_2$, and $CH_2SCH_2SCH_2$ fragments from the 1,3,5-dithiazine rings. The ^{13}C NMR spectra of compounds **8** and **9** contain signals attributed to the C atoms of the aromatic ring along with the characteristic signals of the dithiazine ring (δ 33.79 and 57.50 (**8**), δ 34.12 and 55.29 (**9**)). The chemical shifts and intensity ratio of the observed signals for the dithiazine ring (δ 4.30 and 4.70 (**8**), δ 4.25 and 4.95 (**9**)) and the corresponding signals of the H atoms of the aromatic ring in the ^{1}H NMR spectra of compounds **8** and **9** confirm the structures proposed for these products.

The X-ray diffraction analysis of compound **9** showed that dithiazine has a chair conformation with the axial hydroxyphenyl group at the nitrogen atom. In crystal, molecules of **9** are linked to form chains due to hydrogen bonds O(1A)—H(10A)...S(2) and O(1)—H(10)...S(2B) (Fig. 1). In addition to the latter, the crystal contains

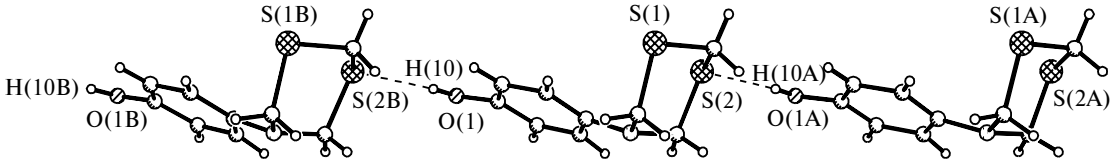


Fig. 1. Geometry of 5-(4-hydroxyphenyl)dihydro-1,3,5-dithiazine (**9**) molecules linked through the OH...S hydrogen bonds in crystal.

weak intermolecular contacts S(1)...S(2) due to which the chains form layers.

Different reactivities of the isomeric aminophenols in the reaction with H_2S and CH_2O are probably due to a change in the basicity[15] and acidity of the amino and hydroxy groups in the composition of the starting phenols, depending on their arrangement in the aromatic ring. According to known data,[16] the basicity of the amino group (K_b) in aminophenols increases in the series *m*-isomer < *o*-isomer < *p*-isomer, and the acidity of the OH group (K_a) decreases in the order *o*-isomer > > *m*-isomer > *p*-isomer (Table 1). Thus, of the three aminophenols, only the *m*-isomer having the amino group with the lowest basicity and the hydroxy group with the sufficient acidity undergoes thiomethylation by the action of CH_2O and H_2S simultaneously at both functional groups to yield macroheterocycles **4** and **5**. However, *o*-aminophenol containing the hydroxy group with the highest acidity does not undergo similar ring closure, probably, due to the appearance of the intramolecular hydrogen bond OH...N.[15] In the case of the *o*- and *p*-isomers, thiomethylation occurs only at the amino group to form the corresponding dithiazines **8** and **9**.

To conclude, the direction of thiomethylation of isomeric aminophenols with H_2S and CH_2O is determined by the basicity and acidity of their functional groups.

Experimental

Reaction products of thiomethylation of aminophenols were analyzed by HPLC on an LKB chromatograph with a photometric detector at a wavelength of 238 nm. Separation was carried out by HPLC at ~20 °C on a metallic column 125×4 mm in size (Separon SGX C_{18}, grain size 5 μm) using an MeCN—H_2O (60 : 40) mixture as eluent, flow rate being 0.2 mL min^{-1}. ^1H NMR spectra were recorded on Bruker AM-300 (300 MHz) and Tesla BS-487 (80 MHz) spectrometers. ^{13}C NMR spectra were obtained on a Jeol-FX 90Q spectrometer (22.50 MHz) using Me_4Si as the internal standard with $CDCl_3$ or DMSO-d_6 as solvents. The IR spectrum was recorded on a Specord 75 IR spectrophotometer in a Nujol suspension. GC-MS analyses of the compounds were carried out on a Finnigan 4021 instrument (glass capillary column 50000×0.25 mm in size, HP-5 stationary phase, helium as carrier gas, temperature programming from 50 to 300 °C with a rate of 5 deg min^{-1}, temperature of the injector 280 °C, temperature of the ion sources 250 °C, 70 eV). Elemental analyses of the samples (C, H, N, O, and S) were conducted on a Carlo Erba 1106 analyzer.[17] Hydrogen sulfide was bubbled and its consumption in mL was monitored using an ANP-10 hose peristatic pump. Melting points were determined on an PHMK 80/2617 instrument; TLC was carried out on Silufol W-254 plates (developing with iodine vapor).

Reaction of *m*-aminophenol with H_2S and CH_2O. A solution of *m*-aminophenol (1.09 g, 0.01 mol) in 95% EtOH (50 mL) was added dropwise for 30 min at 40 °C to a solution of formaldehyde (37%, 1.47 mL, 0.02 mol) saturated with hydrogen sulfide (224 mL, 0.01 mol). The mixture was stirred for 3 h at 40 °C,

Table 1. Influence of the aminophenol structure, reaction temperature, and ratio of the starting reactants on the yield and composition of the reaction products

Aminophenol	K_a[16]	K_b[16]	Amine : CH_2O : H_2S	T/°C	Yield of reaction products (wt.%)				
					2	**3**	**4**	**5**	**8**, **9**
1	$1.4\cdot10^{-10}$	$1.5\cdot10^{-10}$	1 : 2 : 1	20	7	9	—	39	—
	$1.4\cdot10^{-10}$	$1.5\cdot10^{-10}$	1 : 2 : 1*	40	12	20	9	—	—
6	$2\cdot10^{-10}$	$5.2\cdot10^{-10}$	1 : 3 : 2	0	2	—	—	—	86
	$2\cdot10^{-10}$	$5.2\cdot10^{-10}$	1 : 3 : 2	20	4	—	—	—	72
	$2\cdot10^{-10}$	$5.2\cdot10^{-10}$	1 : 3 : 2	40	5	—	—	—	77
	$2\cdot10^{-10}$	$5.2\cdot10^{-10}$	1 : 3 : 2	80	11	—	—	—	49
7	$5\cdot10^{-11}$	$32\cdot10^{-10}$	1 : 3 : 2	0	3	—	—	—	25
	$5\cdot10^{-11}$	$32\cdot10^{-10}$	1 : 3 : 2	20	4	—	—	—	71
	$5\cdot10^{-11}$	$32\cdot10^{-10}$	1 : 3 : 2	40	19	—	—	—	58
	$5\cdot10^{-11}$	$32\cdot10^{-10}$	1 : 3 : 2	80	5	—	—	—	68

* The reaction was carried out with fivefold dilution in EtOH as compared to the previous entry (1 : 2 : 1, 20 °C).

and the precipitate that formed was filtered off. A mixture of products **2—4** was separated by column chromatography on SiO_2 (hexane—AcOEt—$CHCl_3$ (1.5 : 1 : 1) as eluent).

1,2,4-Trithiolane (2).[4,11] M.p. 74—75 °C, R_f 0.91. ^{13}C NMR, δ: 32.7 (s, C(3), C(5)). Mass spectrum, m/z (I_{rel} (%)): 124 $[M]^+$.

1,2,4,6-Tetrathiepane (3).[4,11] M.p. 85—86 °C, R_f 0.76. Mass spectrum, m/z (I_{rel} (%)): 170 $[M]^+$ (57); 124 $[M - CH_2S]^+$ (62); 78 $[M - CH_2SCH_2S]^+$ (100); 45 $[CHS]^+$ (55).

2,12-Dioxa-4,14-dithia-6,16-diazatricyclo[15.3.1.1^{7,11}]docosa-1(20),7(22),8,10,17(21),18-hexaene (4). The yield was 0.31 g (9%), m.p. 173—176 °C, R_f 0.54. M_{cr} = 334±10. Found (%): C, 58.14; H, 5.83; N, 8.98; O, 9.66; S, 18.47. $C_{16}H_{18}N_2O_2S_2$. Calculated (%): C, 57.83; H, 5.42; N, 8.43; O, 9.64; S, 19.28. IR, ν/cm^{-1}: 710, 820, 1185, 1375, 1600, 2900, 3300. UV (DMSO), λ_{max}/nm (ε): 297.6 (10). ^1H NMR (DMSO-d_6), δ: 3.69 (br.s, 4 H, C(5)H_2, C(15)H_2); 5.60 (br.s, 4 H, C(3)H_2, C(13)H_2); 6.30—6.88 (m, 8 H, H arom.). ^{13}C NMR, δ: 46.38 (t, C(5), C(15)); 62.97 (t, C(3), C(13)); 111.03 (d, C(10), C(20)); 126.46 (d, C(21), C(22)); 128.07 (d, C(8), C(18)); 130.93 (d, C(9), C(19)); 148.93 (s, C(7), C(17)); 155.83 (s, C(1), C(11)). Mass spectrum, m/z (I_{rel} (%)): 279 $[MH - SC_2]^+$ (9); 167 $[CH_2NHC_6H_4OCH_2S]^+$ (33); 149 $[C_6H_4NHCH_2SC]^+$ (100); 91 $[OCH_2SCH_2NH]^+$ (9); 44 $[CS]^+$ (74).

Oligomeric cyclic product **5** was prepared similarly to the above-described procedure from the starting reactants taken in the ratio *m*-aminophenol (1.09 g, 0.01 mol) : H_2S : CH_2O = 1 : 1 : 2 in 95% EtOH (10 mL). M.p. 270 °C (with decomp.). Found (%): C, 57.45; H, 5.55; N, 8.27; O, 9.59; S, 19.04. $C_{16}H_{18}N_2O_2S_2$. Calculated (%): C, 57.83; H, 5.42; N, 8.43; O, 9.64; S, 19.28. IR, ν/cm^{-1}: 710, 820, 1185, 1375, 1600, 2900, 3300. M_{cr} = 1333. The numerical mean value of the cyclo-oligocondensation degree is ~8.

Reactions of *o*- and *p*-aminophenols with H_2S and CH_2O. A solution of *o*-aminophenol (0.33 g, 0.003 mol) or *p*-aminophenol (1.09 g, 0.01 mol) in 95% EtOH (10 mL) was added dropwise for 30 min at 20 °C to a solution of formaldehyde (37%, 0.66 mL (0.009 mol) or 2.21 mL (0.03 mol)) saturated with hydrogen sulfide (135 mL (0.006 mol) or 448 mL (0.02 mol), respectively). The mixture was stirred for 3 h at a specified temperature (0, 20, 40, 80 °C), and the product was extracted with chloroform. Mixtures of products **2** and **8** or **2** and **9** were isolated from the organic phase after evaporation of solvents. The reaction products prepared at 40 °C were purified by column chromatography on SiO_2 (toluene—AcOEt—acetone (8 : 1 : 1) as eluent).

5-(2-Hydroxyphenyl)dihydro-1,3,5-dithiazine (8). The yield was 0.55 g (86%), m.p. 102—103 °C, R_f 0.63. Found (%): C, 50.26; H, 5.11; N, 6.11; O, 7.64; S, 30.21. $C_9H_{11}NOS_2$. Calculated (%): C, 50.70; H, 5.20; N, 6.60; O, 7.50; S, 30.00. IR, ν/cm^{-1}: 760, 1100, 1185, 1370, 1600, 2900, 3200—3500. ^1H NMR ($CDCl_3$), δ: 4.30 (br.s, 2 H, C(2)H_2); 4.70 (br.s, 4 H, C(4)H_2, C(6)H_2); 6.10—6.25 (m, 1 H, C(12)H); 6.79—7.21 (m, 3 H, C(9)H, C(10)H, C(11)H); 8.35 (br.s, 1 H, OH). ^{13}C NMR, δ: 33.79 (t, C(2)); 57.50 (t, C(4), C(6)); 115.03 (d, C(9), C(10)); 119.98 (d, C(12)); 127.24 (d, C(11)); 134.73 (s, C(7)); 151.01 (s, C(8)). Mass spectrum, m/z (I_{rel} (%)): 213 $[M]^+$ (23); 167 $[M - CH_2S]^+$ (14); 153 $[M - CH_2SCH_2]^+$ (14); 121 $[M - SCH_2SCH_2]^+$ (100), 107 $[M - CH_2SCH_2SCH_2]^+$ (46), 93 $[C_6H_4OH]^+$ (59), 46 $[CH_2S]^+$ (18); 32 $[S]^+$ (18).

5-(4-Hydroxyphenyl)dihydro-1,3,5-dithiazine (9). The yield was 1.24 g (58%), m.p. 131—132 °C, R_f 0.57. Found (%): C, 50.20; H, 5.60; N, 6.53; O, 7.64; S, 30.13. $C_9H_{11}ONS_2$. Calculated (%): C, 50.70; H, 5.20; N, 6.60; O, 7.50; S, 30.00. IR, ν/cm^{-1}: 690, 830, 1100, 1220, 1600, 2930, 3300. ^1H NMR (DMSO-d_6), δ: 4.25 (br.s, 2 H, C(2)H_2); 4.95 (br.s, 4 H, C(4)H_2, C(6)H_2); 6.82 (d, 2 H, C(8)H, C(12)H, ^3J = 8.8 Hz); 6.99 (d, 2 H, C(9)H, C(11)H, ^3J = 8.8 Hz); 9.00 (br.s, 1 H, OH). ^{13}C NMR, δ: 34.12 (t, C(2)); 55.29 (t, C(4), C(6)); 115.52 (d, C(9), C(11)); 118.85 (d, C(8), C(12)); 137.53 (s, C(7)); 151.19 (s, C(10)). Mass spectrum, m/z (I_{rel} (%)): 213 $[M]^+$ (42); 167 $[M - CH_2S]^+$ (12); 135 $[M - C_6H_6]^+$ (26); 121 $[M - CH_2SCH_2S]^+$ (100); 120 $[M - CH_2SCH_2SH]^+$ (56); 107 $[M - CH_2SCH_2SCH_2]^+$ (36); 93 $[CH_2SCH_2SH]^+$ (18); 46 $[CH_2S]^+$ (35), 45 $[CHS]^+$ (41); 42 $[CH_2NCH_2]^+$ (23).

X-ray diffraction study of compound 9. The crystals were obtained by crystallization from a toluene—AcOEt—acetone (8 : 1 : 1) mixture. Experiment was carried out on a Bruker SMART 1000 CCD Area Detector diffractometer at 120 K (Mo-Kα radiation, $2\theta_{max}$ = 59.82°) for a single crystal 0.5×0.32×0.24 mm in size. The colorless prismatic crystals of $C_9H_{11}NOS_2$ (M = 213.31) are orthorhombic, at 120 K a = 8.471(2) Å, b = 9.443(2) Å, c = 11.988(3) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 959.0(4) Å^3, space group $P2_12_12_1$, Z = 4, d_{calc} = 1.477 g cm^{-3}. After equivalent reflections were averaged, 2789 independent reflections (R_{int} = 0.0198) were obtained and used for structure refinement. The structure was solved by a direct method. All atoms were located in difference electron density syntheses and refined for F^2_{hkl} in the anisotropic approximation (hydrogen atoms were refined in the isotropic approximation). The final R values were R_1 = 0.0258 (calculated by F_{hkl} for 1533 reflections with $I > 2\sigma(I)$), wR_2 = 0.0610 (calculated by F^2_{hkl} for all 2789 reflections involved in refinement at the last stage); GOOF = 0.996, 163 refined parameters. All calculations were performed using the SHELXTL PLUS 5 program package.[18]

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