Synthesis of Zwitterionic Compounds: Fully Saturated Pyrimidinylium and 1,3-Diazepinylium Derivatives via the Novel Rearrangement of 3-Oxobutanoic Acid Thioanilide Derivatives

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An unusual rearrangement following cyclization of 2-anilino-2-ethoxy-3-oxothiobutanoic acid with aliphatic 1,3- as well as 1,4-diamine leads to zwitterionic derivatives of 2-hydroxypropanoic acid. Moreover, with aromatic 1,2-diamines, fused heterocyclic systems such as pteridine, quinoxaline, and pyrido[2,3-*b*]pyrazine are obtained.

Introduction

Several types of saturated pyrimidine and 1,3-diazepine derivatives are used in industry and in the pharmaceutical field, which explains the interest in new and better strategies for the construction of these heterocyclic systems.

For example, saturated pyrimidine derivatives are useful as transport molecules for tumor inhibition,[1] as well as antidepressants and sedatives.[2] On the other hand, 1,3-diazepine derivatives exhibit activity on the central nervous system.[3] Some derivatives of saturated 1,3-diazepines have been selected as promising candidates for potential anticancer drugs[4] and as antagonists of arginine vasopressin.[5]

Certain fully saturated derivatives of pyrimidine have other industrial applications, e.g., as antioxidants[6] and catalysts.[7] Moreover, saturated 1,3-diazepine derivatives are known as insecticidal[8] and fungicidal agents.[9]

We report here a novel and convenient route to synthesize zwitterionic derivatives of saturated pyrimidine as well as the 1,3-diazepine system starting from 2-anilino-2-ethoxy-3-oxothiobutanoic acid anilide[10] **1** and appropriate aliphatic diamines.

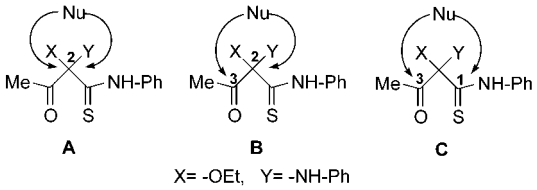
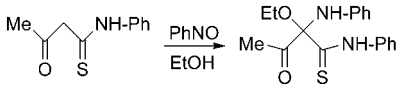


Figure 1.

Scheme 1



In the course of our research into the structure and reactivity of 3-oxothio acid derivatives, we have prepared easily accessible building block **1** by the one-pot, tandem condensation/addition reaction of 3-oxothiobutanoic acid anilide with nitrosobenzene in ethanol at room temperature (Scheme 1).

The high degree of functionalization of thioanilide **1** allows this compound to react with binucleophiles on any of the three electrophilic carbons C-1, C-2, and C-3. As a consequence, attack is possible in ways (A−C) depicted in Figure 1.

Putting these considerations into practice, we were able to apply compound **1** in the synthesis of various heterocyclic systems. Each of these modes of reaction with binucleophiles has been exploited in the synthesis of a variety of heterocyclic systems, as described below. As an extension of our previous[10,11] works, we envisaged that binucleophilic attack of aliphatic 1,3- and 1,4-diamines should provide C-2 disubstituted heterocyclic systems.

Results and Discusion

Our main experiments focused on attempts to carry out the synthesis of heterocyclic six- and seven-membered ring systems, by exploiting the reactivity of the electro-

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(11) Further investigations on that problem are in progress.

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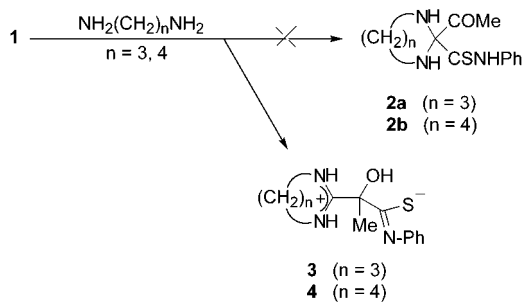
Scheme 2



philic center at C-2 of compound **1** with binucleophiles such as aliphatic 1,3- and 1,4-diamines (path A). The strong electrophilicity of the C-2 carbon substituted by two good leaving groups (EtO− and PhNH−) is enhanced additionally by the electron-withdrawing character of the neighboring carbonyl group (C3) and thiocarbonyl group (C1).

Treatment of 2-anilino-2-ethoxy-3-oxothiobutanoic acid **1** with 1,3-diaminopropane in molar ratio 1:1 in toluene provided, after 5 min heating, crystalline compound **3** (Scheme 2). The yields of **3** and **4** were readily increased over 60% by the addition of amine in excess (molar ratio 1:2). NMR analysis of the product obtained indicated that the reaction had yielded exclusively compound **3**—different from the expected **2a** (Scheme 2). In the IR spectra of compound **3**, the presence of carbonyl group was not observed, whereas MS as well as elemental analysis were in agreement with the expected compound **2a**. An analogous reaction with 1,4-diaminobutane afforded the hexahydro-1,3-diazepine system **4**, but with 1,2-diaminoethane the corresponding imidazolidine was not obtained. Probably, insufficient stereoelectronic stabilization of imidazolidine caused its ring opening.[11]

The structure of compound **3** was determined by single-crystal X-ray analysis (Nonius KappaCCD diffractometer) and indicates that cyclization with 1,3-diaminopropane took place with novel rearrangement of starting 3-oxothiobutanoic acid leading to 2-hydroxy-2-(1′,3′,4′,5′,6′-pentahydropyrimidin-2′-ylium-2′-yl)-1-phenyliminopropane-1-thiolate, $C_{13}H_{17}N_3OS$. A perspective view of the molecule with the atoms numbering scheme is given in Figure 2.

The compound **3** crystallizes in a relatively high-symmetry, trigonal crystal system, space group *R*-3, but the diffraction data were collected as full sphere in the reciprocal space, up to 2θ equal 60.20°. A very high total of 23 223 reflections were collected and merged to give 4017 unique reflections with fairly low values of R_{int} = 0.0368 and R_σ = 0.0241. No systematic absence violations, neither inconsistent equivalents were detected, which confirms the correctness of the space group assignment. The structure was solved and refined using the SHELX-97 system.[12] In the course of refinement, all hydrogen atoms were found from the Fourier map and included in full-matrix least-squares refinement with no signs of divergence. The final discrepancy factors were fairly low, wR2 = 0.1251, R1 = 0.0681 for all data, and R1 = 0.0429 for $F_o > 4\sigma(F_o)$, goodness of fit being 1.047. The number of refined parameters was 231 against 4017 data, which gives a good observations-to-parameters ratio above 17. The final difference Fourier map of electron density was flat with the highest peak of 0.29 and deepest hole of −0.27 e Å^{-3}. Extensive discussion of the details of crystal structure analysis is important for a univocal proof of the localization of protons at nitrogen atoms of the pyrimidine ring (N7, N11) and the exclusion of another possibility of proton localization at the thioanilide moiety.

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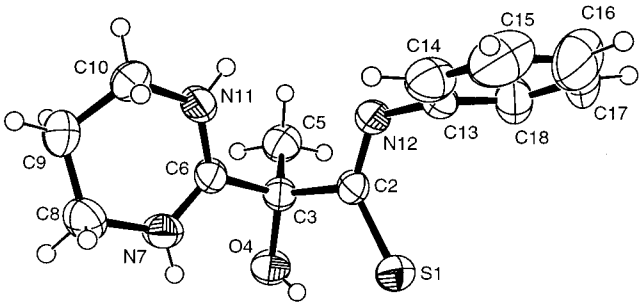


Figure 2.

The zwitterionic region comprising atoms C6, N7, and N11 (Figure 2) has the vicinity with flat conformation: bond angles with apexes at N7 and N11 have values of 123.9(2)° and 122.3(2)°, respectively. The sum of bond angles around C6 is exactly 360.0(2)°, proving flat conformation of its adjacent atoms (C6, N7, N11, C3). Bond distances C6−N7 and C6−N11 are 1.303(2) and 1.310(2) Å, respectively, which is between typical values for single and double C−N bonds. Very slight difference in these bond lengths might be due to different hydrogen bonds the two nitrogen atoms N7 and N11 are involved in: intramolecular N7−H9···O4 (2.616 Å, 110.0°) and both intramolecular, N11−H15···N12 (3.010 Å, 103.7°), and intermolecular, N11−H15···N12 (3.071 Å, 141.6°). The latter fact may be responsible for the slightly higher than average thermal parameter of H15, equal to 0.10(1), which is, however, within the usual limits of 1.5 times U_{eq} of the heavy atom to which it is attached (N11 has U_{eq} = 0.0645). The thermal parameter of H9 equals a typical 0.059(5). Crystallographically, there is nothing unusual about the geometry of the N7−C6−N11 fragment. The distance N7−H9 is 0.81(3) Å and N11−H15 0.86(3) Å, which is rather short, but not unusual. The sum of the three bond angles with apex at N7 is 360° (C6−N7−C8 = 123.9(1)°; C6−N7−H9 = 117.3(1.4)°; C8−N7−H9 = 118.8(1.5)°) indicating flat conformation; the same holds for N11 (sum 359.9°: C6−N11−C10 = 122.3(2)°; C6−N11−H15 = 121.5(2.0)°; C10−N11−H15 = 116.1(2.0)°). This means that neither N7, nor N11 have sp^3 hybridization with one hydrogen missing, thus proving the zwitterionic character of this molecular fragment. This solid-state observation is consistent with NMR results obtained in solution.

The pentahydropyrimidine moiety C6−N7−C8−C9−C10−N11 has a (relatively rare) sofa conformation with C9 being the flap atom. The middle part of the molecule comprises a nearly planar quasi-ring S1−C2−C3−O4 closed by the O4−H10···S1 hydrogen bond (2.86 Å). Except for atoms C9 and C5, the entire molecule consists of three nearly planar fragments: (1) the planar part of the pyrimidine ring, (2) the quasi-ring S1−C2−C3−O4−H10, and (3) the planar phenyl ring consisting of atoms C13 through C18. The angles between respective LSQ planes are: (1)−(2) 74.2°, (2)−(3) 101.2°, and (1)−(3) 116.0°.

Scheme 3

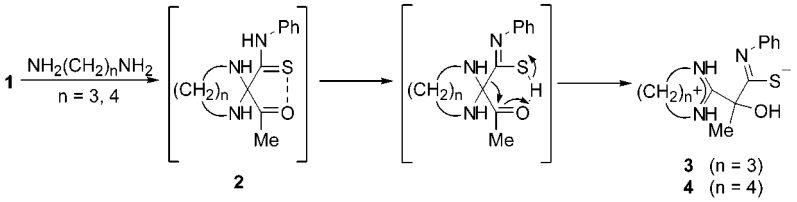
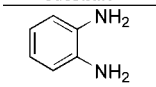
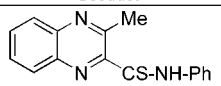
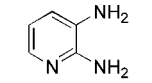
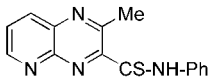
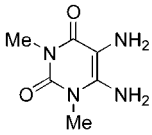
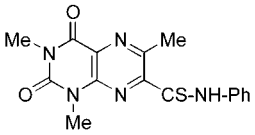


Table 1. Fused Heterocyclic Systems Obtained from 1 and Aromatic 1,2-Diamines

Substrate	Product	No.	yield (%)
		**5**	65
		**6**	50
		**7**	67

The probable pathway leading to the formation of zwitterionic products **3** and **4** involves the facile attack of binucleophiles on electrophilic C-2 center of compound **1** (Scheme 3). The resulting intermediate aminal **2** may form the sterically constrained "pseudospiro" system, disubstituted at C-2 by two electron-withdrawing groups. Intramolecular donor−acceptor interaction[13] between sulfur of the thiocarbonyl group and oxygen of the carbonyl group may promote protonation of the oxygen. The key step can be regarded as a sigmatropic rearrangement. It should be stressed that in compound **1**, where the bulky sulfur atom was replaced by oxygen, no reaction with aliphatic diamine was observed.

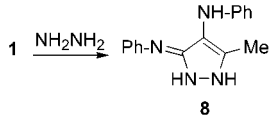
X-ray results (distance C8−C10 equal 2.456(3) Å) indicated that stereoelectronic stabilization of diaminocarbenium ions at position 2 of 1,3,4,5,6-pentahydropyrimidine as well as 1,3,4,5,6,7-hexahydro-1,3-diazepine systems is most favorable in six- and seven-membered rings.

The ^{1}H and ^{13}C NMR and MS spectra of compounds **3** and **4** were consistent with the structures deduced by X-ray crystallography.

The signal in the ^{1}H NMR spectra of **3** and **4** at δ_H = 8.55−9.00 ppm (s, 2H) is remarkable due to the presence of two equivalent polar NH groups of the heterocyclic ring. Moreover, compounds **3** and **4** show signals in the range 1.94−3.53 ppm corresponding to the CH_2 groups of the ring. Resonance in the ^{13}C NMR spectra of **3** at δ_C = 181 (s, C=S) is consistent with polar character of the thiocarbonyl group. Zwitterionic compounds **3** and **4** appeared to be very stable and soluble in boiling water.

Binucleophilic attack at C-2 and C-3 (path B) was employed in order to synthesize fused heterocyclic systems such as quinoxaline, pteridine, and pyrido[2,3-*b*]-pyrazine[14] (Table 1). In such reactions with aromatic 1,2-diamines, reagent **1** serves as an equivalent of the unknown (unstable) 2,3-dioxothiobutanoic acid anilide. These reactions also demonstrate the concept of using compound **1** as an excellent equivalent of an α-diketo unit, very useful for construction of heterocyclic systems.

Scheme 4



These fused nitrogen-containing heterocyclic systems (**5**−**7**) are common as synthetic dyestuffs and natural pigments. The pteridine[15] derivatives such as folic acid are naturally occurring growth factors, which are required by all higher animals.[16]

Some derivatives of quinoxaline system were studied as NMDA/glycine and AMPA receptor antagonists.[17,18]

Various pyridopyrazine derivatives have shown interesting pharmacological properties.[19,20]

The reactivity of **1** via path C was exemplified by the reaction with hydrazine, leading to pyrazole derivatives **8** (Scheme 4).

A reagent such as hydrazine attacks the acetyl carbonyl group as well as the thiocarbonyl carbon, but heterocyclization goes via the enolic form of 3-oxothiobutanoic acid anilide **1**, with the elimination of ethanol. The structure of compound **8** was confirmed by NMR and MS analysis.

Conclusion

We have explored the reactivity of 2-anilino-2-ethoxy-3-oxothiobutanoic acid anilide **1** in the synthesis of pentahydropyrimidine and hexahydro-1,3-diazepine derivatives (via path A) as well as fused heterocyclic systems (via path B). The reaction with hydrazine confirmed the possibility of heterocyclization on pathway C.

The good leaving groups at C-2 of compound **1** offer entry to the process of heterocyclization followed by a novel rearrangement of 3-oxothiobutanoic acid to 2-hydroxypropanoic acid derivatives.

The unusual rearrangement following cyclization gives easily, in one-pot reaction, new zwitterionic compounds **3** and **4**. The zwitterionic form of the products makes them easily accessible reagents for a cycloaddition process, as well as interesting compounds for bioactivity

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investigations. On the other hand, functionality in compound **1** also offers the possibility of versatile synthesis of fused heterocyclic systems, such as quinoxaline, pteridine and pyrido[2,3-*b*]pyrazine.

Experimental Section

Melting points were determined on an electrothermal IA9000 digital melting point apparatus and are uncorrected. The IR spectra were obtained on a Bruker IFS 48 spectrometer at room temperature. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AMX 500 NMR spectrometer using TMS as internal standard. Chemical shifts are reported in ppm downfield from TMS.

General Procedure for the Preparation of 3 and 4. A solution of 0.5 g (1.52 mmol) **1** and 3.04 mmol of corresponding diamine in toluol was refluxed for 5 min. Cooling the mixture yielded white crystals, which were purified by recrystallization from ethanol.

2-Hydroxy-2-(1′,3′,4′,5′,6′-pentahydropyrimidin-2′-ylium-2′-yl)-1-phenyliminopropane-1-thiolate (3): yield 95%; colorless needles; mp 181 °C; IR (KBr) 3168, 2929, 1654 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.55 (s, 2H, 2 × NH), 7.00−7.40 (m, 5H, Ph), 3.34 (t, 4H, J = 5.5 Hz, 2 × NCH_2), 1.95 (quintet, 2H, J = 5.5 Hz, CH_2), 1.84 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 189.1 (CS), 165.9 (NCN), 147.7, 128.6, 124.1, 122.3, 75.0 (CO), 39.35 (NCH_2), 31.68 (CH_3), 18.8 (CH_2); EIMS *m*/*z* 264 (M^+, 1), 127 (M^+ − PhNHCS, 100), 85 (M^+ − (PhNHCS + CH_3CO), 4). Anal. Calcd for $C_{13}H_{17}N_3OS$ (263.4): C, 59.29; H, 6.51; N, 15.96; S, 12.18. Found: C, 59.33; H, 6.74; N, 15.72; S, 12.29.

2-Hydroxy-2-(1′,3′,4′,5′,6′,7′-hexahydro-1,3-diazepin-2′-ylium-2′-yl)-1-phenyliminopropane-1-thiolate (4): yield 65%; colorless crystals; mp 114 °C; IR (KBr) 3142, 2995, 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.5−9.0 broad (s, 2H, 2 × NH), 7.06−7.36 (m, 5H, Ph), 3.53 (m, 4H, 2 × NCH_2), 1.94 (tt, J = 5.75 Hz, 4H, 2 × CH_2), 1.83 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 187.4 (CS), 170.6 (NCN), 149.3, 128.6, 123.7, 122.1, 75.7 (CO), 45.2 (NCH_2), 31.5 (CH_3), 26.9 (CH_2); EIMS *m*/*z* 141 (M^+ − PhNHCS, 100), 99 (M^+ − (PhNHCS + CH_3CO), 12). Anal. Calcd for $C_{14}H_{19}N_3OS$ (277.4): C, 60.62; H, 6.90; N, 15.15; S, 11.56. Found: C, 60.25; H, 6.73; N, 15.19; S, 11.36.

General Procedure for the Preparation of 5−8. A solution of 0.5 g (1.52 mmol) **1** and 1.52 mmol of corresponding diamine in ethanol was refluxed for 3 h. Cooling the mixture yielded crystals that were purified by recrystallization from ethanol.

3-Methyl-2-phenylthiocarbamoylquinoxaline (5): yield 65%; yellow crystals; mp 162 °C. IR (KBr) 3249, 1623, 1594, 1179 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.01 (s, 1H, CS−NH), 8.01 (d, 2H, J = 7.50 Hz, Ph), 7.89 (d, 1H, J = 8.30 Hz), 7.86 (d, 1H, J = 8.30 Hz), 7.74 (t, 1H, J = 6.88 Hz), 7.68 (t, 1H, J = 6.88 Hz), 7.45 (t, 2H, J = 7.56 Hz, Ph), 7.31 (t, 1H, J = 7.50 Hz), 2.99 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 192.05, 152.62, 150.38, 141.75, 138.56, 138.22, 130.97, 129.84, 129.47, 129.06, 128.39, 127.10, 122.72, 24.97. EIMS *m*/*z* 279 (M^+, 100), 246 (55), 143 (M^+ − PhNHCS, 56), 102 (23) Anal. Calcd for $C_{16}H_{13}N_3S$ (279.4) C, 68.79; H, 4.69; N, 15.04; S, 11.48. Found: C, 68.99; H, 4.45; N, 15.21; S, 11.51..

2-Methyl-3-phenylthiocarbamoylpyrido[2,3-*b*]pyrazine (6): yield 50%; yellow needles; dec 230 °C; IR (KBr) 3243, 1623, 1596, 1161 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.1 (s, 1H, CSNH), 9.03 (dd, 1H, J = 4.26, 1.87 Hz), 8.18 (d, 2H, J = 7.55 Hz, Ph), 8.10 (dd, 1H, J = 8.29, 1.87 Hz), 7.58 (dd, 1H, J = 8.29, 4.26 Hz), 7.52 (t, 2H, J = 7.55 Hz, Ph), 7.37 (t, 1H, J = 7.55 Hz, Ph), 3.07 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 191.9, 156.5, 154.1, 152.4, 149.4, 138.8, 138.2, 133.7, 129.1, 127.2, 125.0, 122.7, 24.6; EIMS *m*/*z* 280 (M^+, 100), 247 (66), 144 (M^+ − PhNHCS, 38), 103 (35). Anal. Calcd for $C_{15}H_{12}N_4S$ (280.4) C, 64.26; H, 4.31; N, 19.98; S, 11.44. Found: C, 64.06; H, 4.15; N, 19.98; S, 10.86.

1,3,6-Trimethyl-2,4-dioxo-7-phenylthiocarbamoylpteridine (7): yield 67%; yellow crystals; mp 114 °C; IR (KBr) 3469, 1718, 1662, 1113 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.76 (s, 1H, CSNH), 7.86−7.84 (m, 2H, Ph), 7,32−7,29 (m, 2H, Ph), 7,24−7,21 (m, 1H, Ph), 3.64 (s, 3H, NCH_3), 3.38 (s, 3H, NCH_3), 2.94 (s, 3H, C−CH_3); ^{13}C NMR ($CDCl_3$) δ 189.2, 159.8, 159.6, 150.1, 148.5, 146.0, 138.7, 128.6, 126.8, 122.5, 120.3, 28.7, 28.3, 24.3; EIMS *m*/*z* 341 (M^+, 100), 308 (85), 249 (6), 232 (7), 128 (7). Anal. Calcd for $C_{16}H_{15}N_5O_2S$ (341.4) C, 56.29; H, 4.43; N, 20.51; S, 9.39. Found: C, 56.33; H, 4.09; N, 20.20; S, 9.15.

4-Anilino-5-phenylimino-3-methylpyrazoline (8). Hydrazine monohydrate was used: yield 47%; colorless crystals; mp 184 °C; IR (KBr) 3393, 1598, 1550 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 11.72 (s, 1H, PhNH), 7.441−7.403 (m, 3H), 7.13−7.09 (m, 2H), 7.06−7.03 (m, 2H), 6.70 (s, 1H), 6.67−6.64 (m, 1H), 6.57−6.54 (m, 1H), 6.52−6.50 (m, 2H), 2.01 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 148.3, 143.6, 128.7, 128.3, 117.6, 116.3, 114.9, 112.4, 108.0, 9.2; EIMS *m*/*z* 264 (M^+, 100), 173 (12), 146 (10), 131 (8), 119 (14), 104 (27), 93 (21). Anal. Calcd for $C_{16}H_{16}N_4$ (264.3) C, 72.70; H, 6.10; N, 21.20. Found: C, 72.73; H, 5.90; N, 21.54.

Supporting Information Available: Details of the crystal structure investigation. This material is available free of charge via the Internet at http://pubs.acs.org.

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