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Synthesis of 3-alkyl-5-allylamino-2-benzoylimino-1,3,4-thiadiazoles via Dimroth rearrangement

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Abstract: A facile access to 3-alkyl-5-*N*-allylamino-2-*N*′-benzoylimino-1,3,4-thiadiazoles via Dimroth rearrangement is reported. Alkylation of 5-allylamino-4-benzoyl-1,2,4-triazole-3-thione with alkyl halides in basic alcohol solution is regioselective. A mechanism for the formation of a 1,3,4-thiadiazole ring by 1,2,4-triazole recyclization is proposed. The obtained compounds were characterized by NMR, elemental analysis and X-ray diffraction analysis.

Keywords: alkylation; Dimroth rearrangement; 1,3,4-thiadiazole; 1,2,4-triazole.

Introduction

1,3,4-Thiadiazoles possess a wide range of biological activities including antimicrobial [1–3], antifungal [4], antituberculosis [5], anti-inflammatory [6], anticancer [7], antioxidant [8] and antidepressant activity [9]. Some drugs (Figure 1) containing an amino-substituted 1,3,4-thiadiazole ring, are used in medicinal practice [2, 3].

1,3,4-Thiadiazoles are available by (i) cyclization of acylhydrazines [9], thiocarbazides [10], thiosemicarbazides [11], dithiocarbazates [12], thioacylhydrazines [13] and bithioureas [14], (ii) by rearrangement of other heterocycles, like 1,3,4-oxadiazole [15], 1,3,4-thiadiazine [16] and imidazoloiminophosphorane [17] and (iii) by tandem 1,3-dipolar cycloaddition reaction [18]. Herein, we summarize a fortuitous synthesis of substituted 5-amino-2-imino-1,3,4-thiadiazoles from 1,2,4-triazole derivatives in the hope that this procedure will enrich the list of simple and versatile methods for thiadiazole ring formation and can help chemists in preparation of methazolamide-like pharmaceuticals.

Previously, we have shown [19, 20] that 5-allylamino-1,2,4-triazole-3-thiones are useful intermediate products in ring anellation reactions; we have also shown that the presence of an aroyl substituent in the 4-position of 1,2,4-triazole-3-thiones allows for use of these compounds as ligands for complexation of heavy metals cations [21]. Our group has continued to investigate the chemical properties of the 5-amino-4-aroyl-1,2,4-triazole-3-thione system, particularly its behavior in basic medium toward treatment with alkyl halides. Herein, we wish to report a facile synthetic method for construction of substituted 5-amino-2-imino-1,3,4-thiadiazoles by alkylation of 5-allylamino-4-benzoyl-1,2,4-triazole-3-thione with primary alkyl halides in basic alcohol solution. We believe that this reaction proceeds by Dimroth rearrangement.

Results and discussion

The starting allylaminotriazole **2** was obtained by cyclization of bis-thiourea **1**, obtained in turn by the reaction of benzoyl isothiocyanate with allyl thiosemicarbazide according to the literature [19]. The reaction of triazole **2** with a primary alkyl halide was carried out in methanol in the presence of potassium hydroxide. Analysis of the NMR spectra of the obtained products indicated the formation of *N*-alkylated 1,3,4-thiadiazole **3** in each case instead of S-alkylation.

Thus, the ^{1}H NMR spectra of alkylated products **3** do not contain the peak at 12–13 ppm which is a signal of NH-proton of triazole ring seen in the spectrum of a triazole **2**, and the corresponding proton signals of an alkyl group are observed in the aliphatic area. A signal for protons of the exocyclic N-CH_2 group in thiadiazole **3b–f** appears at about 4.27–5.46 ppm. This is in contrast to a higher-field resonance of S-CH_2 group protons (at 3.76–3.98 ppm) observed for *S*-alkylated 3-mercapto-1,2,4,-triazoles [22]. The ^{13}C NMR spectra of compounds **3** reveal low-field signals of heterocyclic nodal carbons at 172 ppm (thiadiazole C-2) and 161 ppm (thiadiazole C-5)

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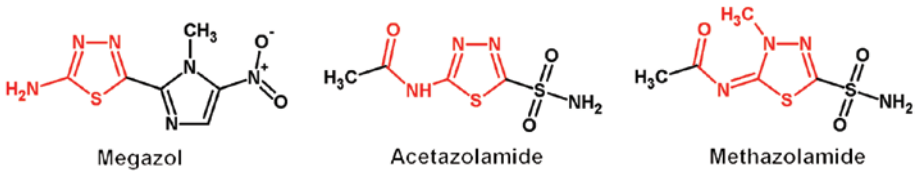


Figure 1 Drugs containing amino-substituted 1,3,4-thiadiazole ring.

in addition to a signal at 159 ppm for a carbonyl function. If these products of alkylation were the isomeric triazoles **A** (Scheme 1), the nodal C-3 and C-5 triazole signals would have appeared at a higher field (smaller chemical shift) [23–25]. The structure of thiadiazole **3c** was also unambiguously confirmed by X-ray crystallographic analysis of its dibromo derivative **4.** Compound **4** was used because a crystal of **3** suitable for X-ray analysis could not be prepared (Scheme 2). Thus, the bromination of thiadiazole **3c** leads to a simple addition product **4** without halocyclization in contrast to related reports [19, 20, 26–33] but in agreement with a similar transformation [34]. X-ray crystallographic analysis of dibromide **4** (Figure 2 and Tables 1S, 2S) provides confirmation of the structure of the alkylation products (Scheme 1). A mechanism for the formation of the thiadiazole ring is suggested in Scheme 3. It is proposed that recyclization is carried out

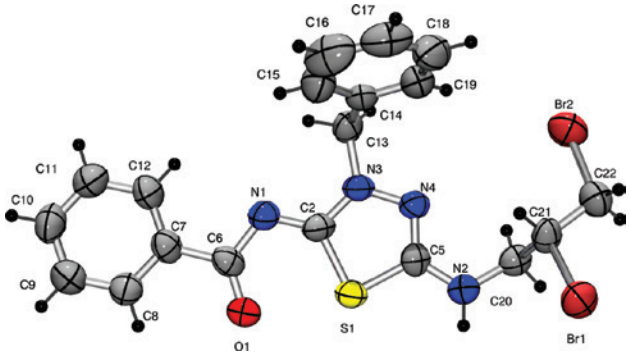
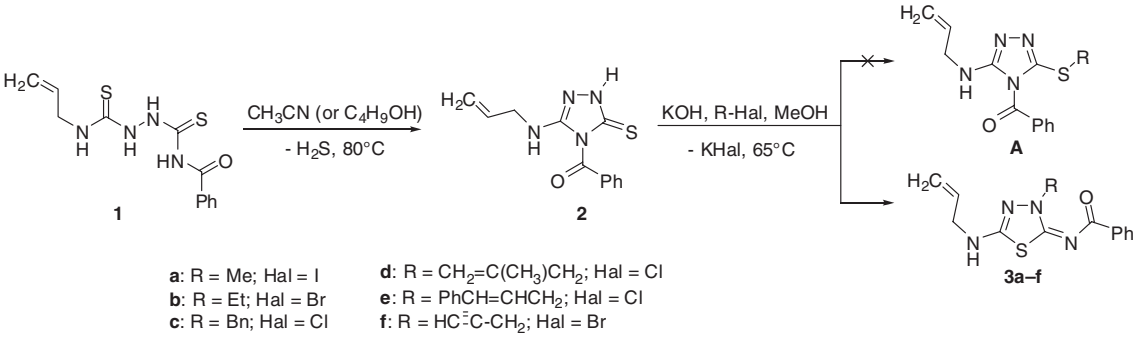
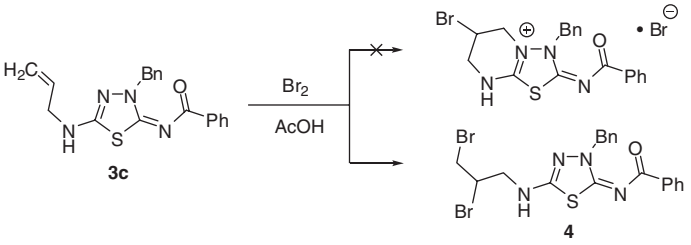


Figure 2 Structure of compound **4** as obtained by X-ray diffraction analysis.

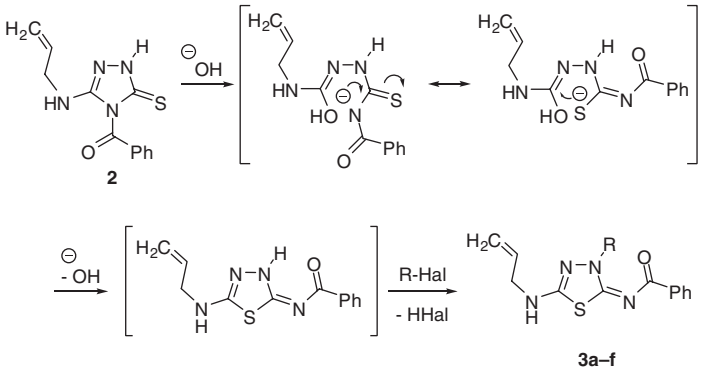
through the Dimroth rearrangement with cleavage of a triazole ring under the action of hydroxide anion. The next stage is the formation of the 1,3,4-thiadiazole ring



Scheme 1 Synthetic approach to 1,3,4-thiadiazoles **3**.



Scheme 2 Synthesis of thiadiazole **4**.



Scheme 3 Mechanistic proposal for the formation of the 1,3,4-thiadiazole ring.

and then alkylation of its anion form with formation of products **3**. This unexpected rearrangement under basic conditions can be explained by the high stability of 5-amino-substituted 4-carbonyl-1,3,4-thiadiazoles [16].

Conclusions

3-Alkyl-5-*N*-allylamino-2-*N'*-benzoylimino-1,3,4-thiadiazoles are easily accessible by treatment of 5-alkylamino-4-benzoyl-1,2,4-triazol-3-thiones with alkyl halides in hydroxide alcohol solution.

Experimental

^{1}H NMR (500 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Brucker Avance 500 and Varian VXR 400 instruments, respectively, in DMSO-d_6. The melting points were determined on a Stuart SMP30 instrument. Elemental analyses were performed on Elementar Vario MICRO cube analyzer. All reagents were obtained from commercial suppliers and used without any further purification.

X-ray diffraction analysis

The structure of **4** was obtained by X-ray diffraction studies performed at room temperature (293(2) K) on an automatic diffractometer Oxford Diffraction Xcalibur, interpreted by a direct method and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the SHELX-97 program package [35]. The program WinGX [36] was used to analyze the structure and to produce the illustrations. All C–H hydrogen atoms were placed in calculated positions and refined as a riding model. For all distances, bonds and valence angles the expected values were found in the molecule of dibromide **4**.

X-ray crystal data [35]: M 510.25, colorless crystal, crystal size ca. 0.55×0.03×0.02 mm. Monoclinic, space group $P2_1/c$, a = 5.6367(5) A, b = 19.4588(15) A, c = 18.6097(19) A, β = 95.511(8)°, V = 2031.7(3) A^3, Z = 4, Dcalc. = 1.668 g/cm^3, μ = 4.109 mm^{-1}, F(000) = 1016. The intensity data were collected within the range of 3.04 ≤ θ ≤ 28.36°, using Mo-Kα radiation (λ = 0.71078 Å). The intensities of 14314 reflections were collected (4324 unique reflections). The multi-scan absorption correction (the minimum and maximum transmission 0.211 and 0.922) was applied. In the refinement, 4324 reflections (1791 reflections with I ≥ 2σ(I)) were used. Convergence was obtained at R_F = 0.1597 and wR^2 = 0.0952 for all reflections and R_F = 0.0475 and wR^2 = 0.0677, GOF = 0.984.

Synthesis of 5-allylamino-3-R-1,3,4-thiadiazol-2(3*H*)-ylidenebenzamide 3a–f

5-Allylamino-4-benzoyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (**2**, 5.0 mmol) was stirred in methanol (20 mL) containing potassium hydroxide (6.0 mmol) untill a clear solution was formed. An alkylating agent (6.0 mmol) was then added and the mixture was heated under reflux for 2 h. After cooling the precipitated product **3** was filtered, washed with cold water-methanol solution (1:1), dried and crystallized from water-ethanol (1:2) mixture.

5-Allylamino-3-methyl-1,3,4-thiadiazol-2(3*H*)-ylidenebenzamide (3a) This compound was obtained from **2** and methyl iodide; yield 60%; light-yellow crystals; mp 169.8–170.5°C; ^{1}H NMR: δ 8.20 (d, 2H), 7.80 (t, 1H), 7,50 (m, 3H), 5.92 (m, 1H), 5.28 (d, 1H), 5.17 (d, 1H), 3.87 (m, 2H), 3.81 (s, 3H); ^{13}C NMR: δ 172.3, 161.0, 158.5, 136.8, 134.7, 132.0, 129.3, 128.6, 116.7, 45.9, 45.9, 37.6. Anal. Calcd for $C_{13}H_{14}N_4OS$: C, 56.91; H, 5.14; N, 20.42; S, 11.69. Found: C, 56.62; H, 5.30; N, 20.26; S, 11.45.

5-Allylamino-3-ethyl-1,3,4-thiadiazol-2(3*H*)-ylidenebenzamide (3b) This compound was obtained from **2** and ethyl bromide; yield 55%; colorless crystals; mp 129.8–131.1°C; ^{1}H NMR: δ 8.18 (d, 2H), 7.76 (t, 1H), 7.50 (m, 3H), 5.92 (m, 1H), 5.26 (d, 1H), 5.15 (d, 1H), 4.27 (q, 2H), 3.86 (m, 2H), 1.35 (t, 3H); ^{13}C NMR: δ 172.3, 160.5, 158.6, 136.9, 134.7, 132.0, 129.2, 128.6, 116.8, 45.9, 45.5, 13.7. Anal. Calcd for $C_{14}H_{16}N_4OS$: C, 58.31; H, 5.59; N, 19.43; S, 11.12. Found: C, 58.10; H, 5.72; N, 19.18; S, 10.97.

5-Allylamino-3-benzyl-1,3,4-thiadiazol-2(3*H*)-ylidenebenzamide (3c) This compound was obtained from **2** and benzyl chloride; yield 66%; colorless crystals; mp 243.5–244.0°C; ^{1}H NMR: δ 8.21 (d, 2H),

7.88 (t, 1H), 7.44 (m, 3H), 5.91 (m, 1H), 5.46 (s, 2H), 5.26 (d, 1H), 5.15 (d, 1H), 3.84 (m, 2H). Anal. Calcd for $C_{19}H_{18}N_4OS$: C, 65.12; H, 5.18; N, 15.99; S, 9.15. Found: C, 65.01; H, 5.32; N, 15.68; S, 9.37.

5-Allylamino-3-methallyl-1,3,4-thiadiazol-2(3*H*)-ylidenebenzamide (3d) This compound was obtained from **2** and methallyl chloride; yield 71%; white powder; mp 123.8–124.7°C; ^{1}H NMR: δ 8.17 (d, 2H), 7.79 (t, 1H), 7.49 (m, 3H), 5.92 (m, 1H), 5.26 (d, 1H), 5.15 (d, 1H), 4.93 (s, 1H), 4.82 (s, 2H), 4.80 (s, 1H), 3.84 (m, 2H), 1.71 (s, 3H); ^{13}C NMR: δ 172.4, 161.6, 158.4, 140.1, 136.8, 134.6, 132.2, 129.3, 128.7, 116.7, 113.5, 55.4, 45.9, 20.5. Anal. Calcd for $C_{16}H_{18}N_4OS$: C, 61.12; H, 5.77; N, 17.82; S, 10.20. Found: C, 60.71; H, 6.03; N, 17.16; S, 9.99.

5-Allylamino-3-cinnamyl-1,3,4-thiadiazol-2(3*H*)-ylidenebenzamide (3e) This compound was obtained from **2** and cinnamyl chloride; yield 67%; yellow powder; mp 156.4–158.5°C; ^{1}H NMR: δ 8.21 (d, 2H), 7.81 (t, 1H), 7.23–7.55 (m, 8H), 6.70 (d, 1H), 6.45 (m, 1H), 5.91 (m, 1H), 5.28 (d, 1H), 5.15 (d, 1H), 5.04 (d, 2H), 3.86 (m, 2H); ^{13}C NMR: δ 172.4, 161.2, 158.6, 136.8, 136.5, 134.6, 133.7, 132.2, 129.4, 129.2, 128.7, 128.4, 127.0, 123.6, 116.8, 52.2, 46.0. Anal. Calcd for $C_{21}H_{20}N_4OS$: C, 67.00; H, 5.35; N, 14.88; S, 8.52. Found: C, 66.70; H, 5.84; N, 14.46; S, 8.22.

5-Allylamino-3-propargyl-1,3,4-thiadiazol-2(3*H*)-ylidenebenzamide (3f) This compound was obtained from **2** and propargyl bromide; yield 48%; colorless crystals; mp 177.3–177.6°C; ^{1}H NMR: δ 8.20 (d, 2H), 7.86 (t, 1H), 7.52 (m, 3H), 5.92 (m, 1H), 5.28 (d, 1H), 5.16 (d, 1H), 5.09 (s, 2H), 3.87 (m, 2H), 3.41 (s, 1H); ^{13}C NMR: δ 172.6, 161.5, 158.4, 136.3, 134.6, 132.5, 129.4, 128.7, 116.9, 78.1, 76.2, 45.9. Anal. Calcd for $C_{15}H_{14}N_4OS$: C, 60.38; H, 4.73; N, 18.78; S, 10.75. Found: C, 60.04; H, 4.98; N, 18.46; S, 10.33.

***N*-[3-Benzyl-5-(2,3-dibromopropylamino)-3*H*-[1,3,4]thiadiazol-2-ylidene]benzamide (4)** A solution of bromine (10.0 mmol) in acetic acid was dropwise added to the solution of triazole **3c** (10.0 mmol) in acetic acid with constant stirring at room temperature during 30 min. The precipitated product was filtered, washed with acetone and crystallized from a water–ethanol–dioxane (1:2:1) mixture to give compound **4** as fine white needles suitable for X-ray diffraction analysis; yield 74%; mp 285.4–287.2°C; ^{1}H NMR: δ 8.21 (d, 2H), 8.03 (t, 1H), 7.30–7.58 (m, 8H), 5.47 (s, 2H), 4.61 (m, 1H), 3.98 (m, 2H), 3.80 (m, 1H), 3.66 (m, 1H). Anal. Calcd for $C_{19}H_{18}Br_2N_4OS$: C, 44.72; H, 3.56; N, 10.98; S, 6.28. Found: C, 44.98; H, 3.82; N, 10.81; S, 6.09.

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