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SHORT COMMUNICATIONS

Adamantylation of Thiocyanatoacetamide and Thiocyanatoacetylurea

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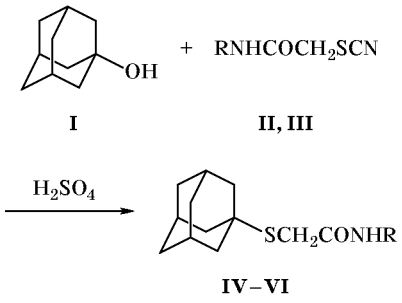
We showed in [1] that α-hydroxy thiocyanates can be alkylated by tertiary carbocations, following the Ritter reaction pattern; intermediate thionitrilium cation is stabilized through intramolecular cyclization involving the neighboring hydroxy group to form 2-alkylimino-1,3-oxathiolanes. With the goal of searching for other functional groups capable of stabilizing thionitrilium cations via intramolecular interaction, we examined the reactions of 1-hydroxyadamantane (**I**) with thiocyanatoacetamide (**II**) and thiocyanatoacetylurea (**III**) in concentrated sulfuric acid. However, these reactions gave unexpected products formally resulting from replacement of the cyano group by adamantyl (compounds **IV**, **V**, and **VI**).



II, **IV**, R = H; **III**, **V**, R = $CONH_2$; **VI**, R = 1-adamantyl.

The reaction with thiocyanatoacetamide was accompanied by formation of the second product, *N*-(1-adamantyl)(1-adamantylthio)acetamide (**VI**). It is likely to result from adamantylation of sulfide **IV** at the nitrogen atom with excess 1-hydroxyadamantane. The same products were obtained by adamantylation of (carbamoylthio)acetamide (**VII**) and (carbamoylthio)acetylurea (**VIII**) which were synthesized by hydrolysis of thiocyanatoacetamide and thiocyanatoacetylurea, respectively. These data indicate faster solvolysis of the thiocyanato group (which can be facilitated by intramolecular catalysis), as compared to the addition of adamantyl cation to the nitrogen atom of the thiocyanato group. As a result, adamantyl cation attacks the sulfur atom of the carbamoylthio group thus formed, and decomposition of the latter yields sulfides **IV** and **V**. The low yields of the adamantylation products may be due to concurent transformations of acetamide derivatives **II** and **VII** and urea derivatives **III** and **VIII**. This assumption is supported by the presence in the reaction mixtures of a considerable amount of unreacted 1-hydroxyadamantane and evolution of carbon dioxide during the process.

Thiocyanatoacetamide (II). A mixture of 5 g (0.053 mol) of chloroacetamide, 4.5 g (0.059 mol) of ammonium thiocyanate, and 20 ml of ethanol was refluxed for 2 h. The solvent was removed under reduced pressure, and the residue was recrystallized from 50 ml of water. Yield 2.4 g (38%), mp 111–112°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 3460, 3360, 3220, 2220, 1720, 1625, 1490. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.00 s (2H, CH_2S), 7.51 s (1H, NH), 7.83 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 36.8 (CH_2S), 113.1 (SCN), 167.6 (C=O).

***N*-(Thiocyanatoacetyl)urea (III)** was synthesized as described above for compound **II** from 10 g of *N*-(chloroacetyl)urea. Yield 5.1 g (44%), mp > 220°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 3400, 3220, 3150, 1720, 1680, 1600, 1505. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 4.16 s (2H, CH_2S), 7.44 s (2H, NH_2), 10.53 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 37.1 (CH_2S), 112.6 (SCN), 153.4 (C=O), 168.1 (C=O).

(1-Adamantylthio)acetamide (IV). To a solution of 1.5 g (0.01 mol) of 1-hydroxyadamantane in 10 ml of concentrated sulfuric acid at 5–10°C we added in small portions while stirring 1 g (8.6 mmol) of thio-

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cyanatoacetamide. The mixture was stirred for 30 min and poured onto ice, and the products were extracted into chloroform. By chromatography on silica gel with chloroform as eluent we isolated 0.92 g (48%) of (1-adamantylthio)acetamide (**IV**), mp 131–132°C (from cyclohexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.75 m (6H, Ad), 1.93 m (6H, Ad), 2.11 m (3H, Ad), 3.27 s (2H, CH_2S), 6.96 s (2H, NH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.5 (Ad), 30.2 (CH_2S), 35.3 (Ad), 43.0 (Ad), 45.4 (Ad), 172.4 (C=O). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 135 (100) $[Ad]^+$, 136 (33), 167 (14), 225 (40) $[M]^+$, 226 (14), 227 (4).

We also isolated 0.14 g (4%) of *N*-(1-adamantyl)-(1-adamantylthio)acetamide (**VI**), mp 132–133°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.79 m (12H, Ad), 1.96 m (6H, Ad), 2.13 m (12H, Ad), 3.26 s (2H, CH_2S), 6.94 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.3 (Ad), 29.6 (Ad), 31.3 (CH_2S), 36.0 (Ad), 36.2 (Ad), 41.2 (Ad), 43.2 (Ad), 45.7 (AdS), 52.0 (AdN), 169.2 (C=O).

***N*-[(1-Adamantylthio)acetyl]urea (V)** was synthesized as described above for compound **IV** from 1.5 g (10 mmol) of 1-hydroxyadamantane, 1.2 g (7.5 mmol) of *N*-(thiocyanatoacetyl)urea and 10 ml of concentrated sulfuric acid. Yield 0.86 g (42%). IR spectrum (KBr), ν, cm^{-1}: 3375, 3220, 3130, 3050, 1720, 1700, 1585. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.76 m (6H, Ad), 1.96 m (6H, Ad), 2.11 m (3H, Ad), 3.44 s (2H, CH_2S), 7.38 s (1H, NH), 7.76 s (1H, NH), 10.28 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 29.3 (Ad), 30.6 (CH_2S), 35.8 (Ad), 43.0 (Ad), 45.1 (AdS), 153.6 (C=O), 172.4 (C=O). Mass spectrum (FAB), *m*/*z*: 269 $[M+H]^+$, 291 $[M+Na]^+$, 537 $[2M+H]^+$, 559 $[2M+Na]^+$.

(Carbamoylthio)acetamide (VII). Thiocyanatoacetylurea, 1 g (8.6 mmol), was added in small portions at 5–10°C to 10 ml of concentrated sulfuric acid. The mixture was kept for 1 h at that temperature and was poured onto ice. The precipitate was filtered off, washed with water, and dried. Yield 0.89 g (78%), mp 147–148°C. IR spectrum (KBr), ν, cm^{-1}: 3460, 3360, 3220, 1720, 1625, 1490. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.97 s (2H, CH_2S), 5.61 s (2H, NH_2), 7.18 s (1H, NH_2), 7.67 s (1H, NH_2). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 33.2 (CH_2S), 167.4 ($CONH_2$), 171.5 ($SCONH_2$).

***N*-[(Carbamoylthio)acetyl]urea (VIII)** was synthesized as described above for compound **VII** from 1 g (6.3 mmol) of *N*-(thiocyanatoacetyl)urea and 10 ml of concentrated sulfuric acid. Yield 0.88 g (79%), mp 164–165°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 3440, 3380, 3280, 1725, 1635, 1495, 1430, 1210, 1135, 1000, 830. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.59 s and 3.70 s (2H, CH_2S), 7.30 s (2H, NH_2), 7.70 s (2H, NH_2), 10.22 s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 33.5 (CH_2S), 153.8 ($NHCONH_2$), 166.4 (CONH), 170.7 ($SCONH_2$).

The IR spectra were recorded on an IKS-22 spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained on a JEOL EX90 instrument at 90 and 22 MHz, respectively; the solvent signals were used as internal reference. The mass spectra were recorded at the EPSRC Mass Spectrometry Center, Wales University, Swansea, Great Britain.

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