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SHORT COMMUNICATIONS

New Method for Preparation of *N*-Alkyl-1,3-dithiolan-2-imines

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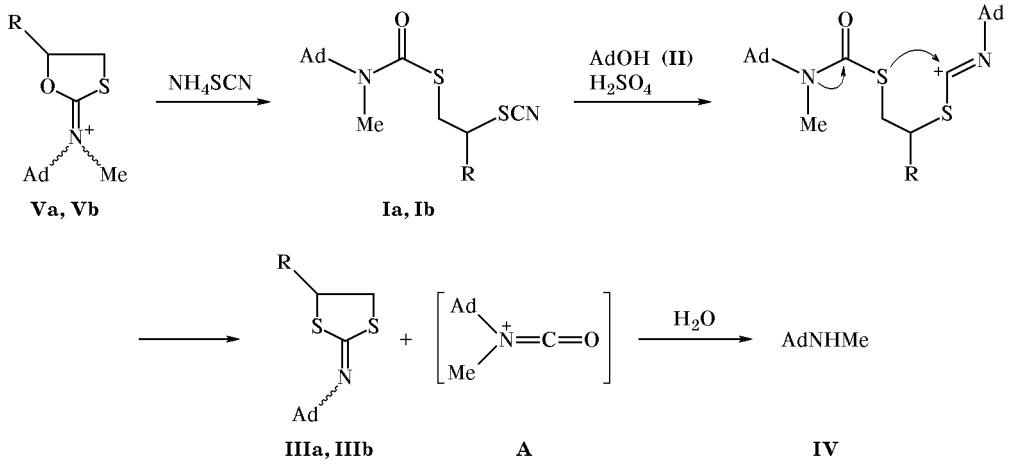
The procedure developed previously for the preparation of *N*-alkyl-1,3-oxathiolan-2-imines is based on intramolecular stabilization of thionitrilium cation via reaction with the neighboring hydroxy group [1]. In this case, the thionitrilium cation is formed by addition of tertiary carbenium ion, which competes with protonation of the nitrogen atom. The latter process, i.e., protonation of the nitrogen atom in α-hydroxy thiocyanates, also gives rise to cyclization leading to 1,3-oxathiolan-2-imines [2]. Attempts to effect intramolecular reaction of thionitrilium cation with carboxamido or ureido group with a view to obtain cyclic product were unsuccessful. The reaction of 1-hydroxyadamantane with thiocyanoacetamide gave 2-(1-adamantylsulfanyl)acetamide [3].

We have found that thionitrilium cation generated by addition of 1-adamantyl cation to the nitrogen atom of a thiocyanato group may be stabilized via reaction not only with neighboring hydroxy group (followed by elimination of proton) but also with a thiocarbamate moiety. Thus, *S*-(2-thiocyanatoethyl) *N*-(1-adamantyl)-*N*-methyl(thiocarbamate) (**Ia**) and *S*-(2-thiocyanatopropyl) *N*-(1-adamantyl)-N-methyl-(thiocarbamate) (**Ib**) reacted with 1-hydroxyadamantane (**II**) in concentrated sulfuric acid through addition of 1-adamantyl cation at the lone electron pair on the nitrogen atom of the thiocyanato group. The resulting thionitrilium cation attacks the neighboring sulfur atom to give *N*-(1-adamantyl)-1,3-dithiolan-2-imine (**IIIa**) or *N*-(1-adamantyl)-5-methyl-1,3-dithiolan-2-imine (**IIIb**), respectively. Presumably, decomposition of the thiocarbamate group involves elimination of 1-adamantyl(carbonyl)methylammonium cation **A** which undergoes hydrolysis to 1-adamantyl(methyl)-amine (**IV**) (Scheme 1). It should be noted that the thiocarbamate moiety itself is sufficiently stable under conditions of this reaction. For example, a procedure is known for the preparation of 1-adamantyl(thiocarbamates) from 1-hydroxyadamantane and alkyl thiocyanates in concentrated sulfuric acid [4, 5].

Like *N*-alkyl-1,3-oxathiolan-2-imines [1], *N*-(1-adamantyl)-1,3-dithiolan-2-imines **IIIa** and **IIIb** exist as

Scheme 1.



R = H (**a**), Me (**b**), Ad = 1-adamantyl.

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mixtures of *Z* and *E* isomers due to restricted rotation about the double C=N bond. This is confirmed by the NMR spectra. The proposed procedure is fairly simple, and it ensures high yields of *N*-alkyl-1,3-dithiolan-2-imines; it is superior to the previously known methods based on reactions of thiiranes with aryl and alkyl isothiocyanates, which give rise mainly to polymeric products [2].

Thiocarbamates **Ia** and **Ib** were synthesized by reaction of *N*-(1-adamantyl)-*N*-methyl-1,3-oxathiolan-2-iminium salt (**Va**) [1] and *N*-(1-adamantyl)-*N*,5-dimethyl-1,3-oxathiolan-2-iminium salt (**Vb**) [6], respectively, with ammonium thiocyanate.

***S*-(2-Thiocyanatoethyl) 1-adamantyl(thiocarbamate) (Ia).** A mixture of 4.8 g (0.013 mol) of *N*-(1-adamantyl)-*N*-methyl-1,3-oxathiolan-2-iminium methyl sulfate (**Va**), 2 g (0.026 mol) of ammonium thiocyanate, and 10 ml of dimethylformamide was stirred for 24 h at room temperature. The mixture was then poured into 100 ml of water, and the precipitate was filtered off and purified by chromatography on silica gel using chloroform as eluent. Yield 2.6 g (63%), mp 95–97°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.69 m (6H, Ad), 2.15 m (9H, Ad), 2.95 s (3H, CH_3N), 3.18 m (4H, CH_2S). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.9 (Ad), 30.3 (CH_3N), 30.5 (CH_2S), 34.0 (CH_2S), 36.1 (Ad), 39.6 (Ad), 60.1 (Ad), 111.5 (SCN), 165.1 (C=O).

***S*-(2-Thiocyanatopropyl) 1-adamantyl(thiocarbamate) (Ib)** was synthesized in a similar way from 5 g (0.013 mol) of *N*-(1-adamantyl)-*N*,5-dimethyl-1,3-oxathiolan-2-iminium methyl sulfate (**Vb**) and 2 g (0.026 mol) of ammonium thiocyanate. Yield 3.1 g (72%), mp 53–55°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.47 d (3H, CH_3, J = 6.6 Hz), 1.70 m (6H, Ad), 2.12 m (9H, Ad), 2.87 s (3H, CH_3N), 3.06 m (2H, CH_2S), 3.4 m (1H, CHS).

***N*-(1-Adamantyl)-1,3-dithiolan-2-imine (IIIa).** Compound **Ia**, 2.1 g (6.7 mmol), was added with stirring at 0°C to a solution of 1.5 g (10 mmol) of 1-hydroxyadamantane in a mixture of 10 ml of concentrated sulfuric acid and 5 ml of glacial acetic acid. The mixture was stirred for 20 h at 0–5°C and poured onto ice, excess 1-hydroxyadamantane was filtered off, the filtrate was neutralized with sodium carbonate, and the precipitate was filtered off and purified by chromatography on silica gel using chloroform as eluent. Yield 1.54 g (93%), mp 116–117°C. IR spectrum (KBr), ν, cm^{-1}: 1591 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.70 m (6H, Ad), 1.99 m (6H, Ad), 2.12 m (3H, Ad), 3.30 t (2H, CH_2S, J = 6.5 Hz), 3.66 t (2H, CH_2S, J = 6.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.5 (Ad), 36.3 (Ad), 40.1 (CH_2S), 40.7 (Ad), 45.2 (CH_2S), 58.2 (Ad), 159.3 (C=N).

Sodium hydroxide, 10 g, was added to the aqueous mother liquor, and the solution was extracted with chloroform to isolate 0.2 g of 1-adamantyl(methyl)-amine (**IV**). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.59 m (10H, Ad, NH), 2.02 m (Ad), 2.40 d (3H, CH_3, J = 5.9 Hz).

***N*-(1-Adamantyl)-5-methyl-1,3-dithiolan-2-imine (IIIb)** was synthesized as described above for compound **IIIa** from 1.5 g (10 mmol) of 1-hydroxyadamantane and 2.2 g (6.8 mmol) of carbamate **Ib**. Yield 1.55 g (89%), mp 74–75°C. IR spectrum (KBr), ν, cm^{-1}: 1596 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.53 d (J = 5.5 Hz) and 1.56 d (J = 5.5 Hz) (3H, CH_3); 1.71 m (6H, Ad); 1.99 m (6H, Ad); 2.12 m (3H, Ad); 3.0 d.d (J = 8.6, 11.0 Hz), 3.31 m (J = 4.5, 11.0 Hz), and 3.64 d.d (J = 4.5, 11.0 Hz) (2H, CH_2S); 3.80 m and 4.12 m (1H, CHS). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.0 (CH_3), 19.5 (CH_3), 29.3 (Ad), 36.1 (Ad), 36.7 (CH_2S), 40.5 (Ad), 43.3 (CH_2S), 46.4 (CHS), 51.2 (CHS), 57.9 (Ad), 159.5 (C=N). Mass spectrum (FAB), *m*/*z* (I_{rel}, %): 135 (100) $[Ad]^+$, 268 (73) $[M + H]^+$.

***N*-(1-Adamantyl)-*N*-methyl-1,3-oxathiolan-2-iminium methyl sulfate (Va).** A mixture of 5 g (0.021 mol) of *N*-(1-adamantyl)-1,3-oxathiolan-2-imine, 10 ml (0.10 mol) of dimethyl sulfate, and 20 ml of chloroform was kept for 24 h at room temperature. The solvent was distilled off, the residue was extracted with diethyl ether to remove excess dimethyl sulfate, and the product was purified by chromatography on silica gel using chloroform as eluent. Yield 7.2 g (94%), n_D^{20} = 1.4970. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.71 m (6H, Ad), 2.22 m (9H, Ad), 3.40 s (3H, CH_3N), 3.65 s (3H, CH_3O), 3.99 t (2H, CH_2S, J = 7.2 Hz), 5.29 t (2H, CH_2O, J = 7.2 Hz).

***N*-(1-Adamantyl)-*N*,5-dimethyl-1,3-oxathiolan-2-iminium methyl sulfate (Vb)** was synthesized as described above for compound **Va** from 5 g (0.020 mol) of *N*-(1-adamantyl)-5-methyl-1,3-oxathiolan-2-imine and 10 ml (0.10 mol) of dimethyl sulfate. Yield 7.1 g (94%), n_D^{20} = 1.4975. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.70 m (6H, Ad), 1.78 d (3H, CH_3, J = 6.1 Hz), 2.22 m (9H, Ad), 3.41 s (3H, CH_3N), 3.56 d.d (1H, CH_2S, J = 11.4, 3.2 Hz), 3.71 s (3H, CH_3O), 4.17 d.d (1H, CH_2S, J = 11.4, 6.4 Hz), 5.79 m (1H).

The IR spectra were measured on a Shimadzu S-8400 Fourier spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol EX-90 spectrometer at a frequency of 90 MHz (^{1}H) or 22 MHz (^{13}C); the

solvent signal was used as internal reference. The mass spectrum (fast atom bombardment) was obtained at the EPSRC MS Center, Wales University, Swansea, Great Britain.

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REFERENCES

1. Shiryaev, A.K., Moiseev, I.K., and Popov, V.A., *Zh. Org. Khim.,* 1992, vol. 28, p. 418.
2. Fokin, A.V. and Kolomiets, A.F., *Khimiya tiiranov* (Chemistry of Thiiranes), Moscow: Nauka, 1978.
3. Shiryaev, A.K. and Moiseev, I.K., *Russ. J. Org. Chem.,* 2001, vol. 37, p. 746.
4. Klimochkin, Yu.N. and Moiseev, I.K., *Zh. Org. Khim.,* 1987, vol. 23, p. 2026.
5. Klimochkin, Yu.N., Moiseev, I.K., Abramov, O.V., Vladyko, G.V., Korobchenko, L.V., and Boreko, E.I., *Khim.-Farm. Zh.,* 1991, vol. 25, p. 49.
6. Shirayev, A., Kong, P., and Moiseev, I.K., *Synthesis,* 1997, p. 38.