

SHORT  
COMMUNICATIONSSynthesis of 4-Bromomethylidene-1,3-thiazolidin-2-imine  
Hydrobromide

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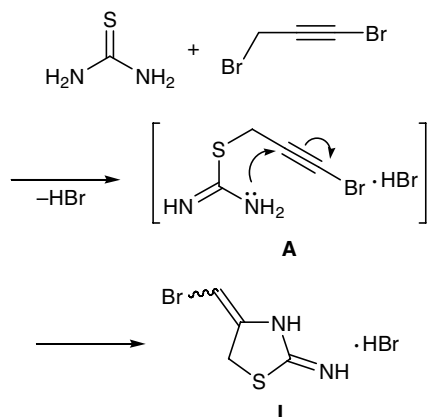
Reactions of thiourea with haloacetylenes provide a convenient synthetic route to functionalized thiazines and thiazoles. Substituted thioureas were reported to react with 1-bromo-2-benzoylacetylene in acetonitrile to give 4-benzoyl-2-iminothiazolium bromides [1], while in acetic acid in the presence of boron trifluoride–ether complex, 1,3-thiazine-6-thione hydrobromides were obtained [2]. Reactions of 3-bromoprop-1-yne with thiourea in methanol on heating lead to substituted thiazoles [3]. Chloro(ethylsulfanyl)acetylene reacts with thiourea under mild conditions (20°C, 24 h, acetone), yielding *S*-(ethylsulfanyl-ethyl)isothiuronium chloride [4].

We have found that the reaction of thiourea with 1,3-dibromopropyne in acetic acid or anhydrous methanol gives 4-bromomethylidene-1,3-thiazolidin-2-imine hydrobromide (**I**). The process is likely to involve formation of intermediate *S*-(3-bromoprop-2-yn-1-yl)isothiuronium bromide **A**, and intramolecular attack by the amino group on the carbon atom at the triple bond results in ring closure to thiazolidin-2-

iminium salt **I**. The structure of compound **I** was proved by the spectral data and elemental analysis. The IR spectrum of **I** lacked C≡C absorption band but contained bands at 1630 and 3085 cm<sup>-1</sup>, which are typical of C=C bond and endocyclic NH group. Compound **I** showed in the <sup>1</sup>H NMR spectrum signals from protons in the =CHBr and NH groups at δ 4.55 and 7.92 ppm, respectively. The double-bonded carbon atoms of the C=CHBr fragment resonated in the <sup>13</sup>C NMR spectrum at δ<sub>C</sub> 74.01 and 46.71 ppm.

**4-Bromomethylidene-1,3-thiazolidin-2-imine hydrobromide (I)**. A solution of 0.99 g (5 mmol) of 1,3-dibromoprop-1-yne in 20 ml of glacial acetic acid was added to a solution of 0.38 g (5 mmol) of thiourea in 15 ml of glacial acetic acid, and the mixture was stirred for 6 h at 20°C (it turned light yellow). The mixture was cooled to 0°C, and the colorless crystals were filtered off, washed with cold diethyl ether, and dried under reduced pressure. Yield 0.75 g (55%), mp 133–135°C. When the reactant ratio **I**:**II** was 1:2 or 2:1, the yield was 73% or 44%, respectively. When the reaction was carried out in anhydrous methanol at 20°C, the yield was 26%. IR spectrum, ν, cm<sup>-1</sup>: 3280 (=NH); 3085 (NH); 1595, 1630 (C=N, C=C); 1435 (δCH<sub>2</sub>); 1260 (C–N); 680 (C–S). <sup>1</sup>H NMR spectrum, δ, ppm: 9.21 s (1H, HN=C), 7.92 s (1H, NH), 4.55 s (1H, =CHBr), 4.21 s (2H, CH<sub>2</sub>). <sup>13</sup>C NMR spectrum, δ<sub>C</sub>, ppm: 20.55 (C<sup>5</sup>), 46.71 (CHBr), 74.01 (C<sup>4</sup>), 168.17 (C<sup>2</sup>). Found, %: C 17.56; H 2.30; Br 58.45; N 10.07; S 11.36. C<sub>4</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>2</sub>S. Calculated, %: C 17.52; H 2.19; Br 58.39; N 10.22; S 11.68.

The IR spectrum was recorded in KBr on a Specord 75IR spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured from solutions in DMSO-*d*<sub>6</sub> on a Bruker



DPX-400 spectrometer (400.13 and 100.61 MHz, respectively) using hexamethyldisiloxane as internal reference.

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