Reaction of (alkylthio)chloroacetylenes with thiourea

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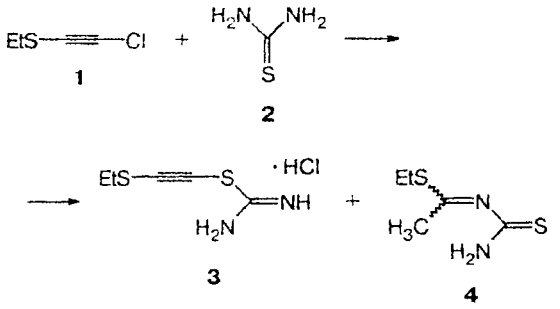
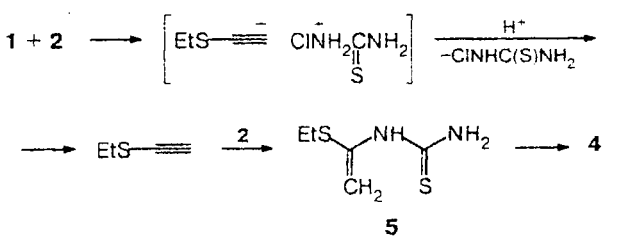
The information on interaction of halogenoacetylenes with amides of thiocarbonic acid is confined to data on the reaction of bromoethynyl(phenyl)ketone with phenyl substituted thioureas leading to the hydrobromides of *N*-substituted 4-benzoyl-2-imino-1,3-thiazoles and proceeding, according to the authors' opinion, through the stage of formation of *S*-ethynylisothiouronic salts.[1]

Using (ethylthio)chloroacetylene (**1**) as an example, we demonstrated for the first time that (alkylthio)-chloroacetylenes react with thiourea (**2**) under mild conditions (20 °C, 24 h, acetone) forming not only the expected *S*-(ethylthioethynyl)isothiouronium chloride (**3**) but also *N*-[1-(ethylthio)ethylidene]thiourea (**4**) in 23 and 31% yields, respectively.



A probable scheme of formation of compound **4** involves halophilic attack of acetylene **1** by the thiourea molecule leading to ethylthioacetylene, which further reacts with thiourea affording *N*-vinylthiourea (**5**). The latter is converted into *N*-ethylidenethiourea **4** as a result of prototropic isomerization.

The scheme of formation of compound **4**, as well as preparative conditions for the reaction of (organylthio)chloroacetylenes with thiourea, are now being studied. Reaction of thiourea with readily available (alkylthio)chloroacetylenes[2] may provide a real pathway for synthesis of new polyfunctional nitrogen- and sulfur-containing unsaturated compounds, which are promising biologically active compounds and complexing agents.



***S*-(Ethylthioethynyl)isothiouronium chloride (3)**, yield 23%, m.p. 84—86 °C. ^{1}H NMR (90 MHz, DMSO-d_6), δ: 1.27 (t, 3 H, CH_3); 2.93 (q, 2 H, CH_2S); 9.31, 9.60 (both br.s, 3 H, NH, NH_2). ^{13}C NMR: 15.8 (CH_3); 28.2 (CH_2S); 104.4 (C≡C); 166.0 ($SC(NH_2)$=N—). IR (KBr)/cm^{-1}: 3450—3000 (νNH); 2970, 2925 (νCH); 2732 (ammonium band); 2192 (νC≡C); 1651 (νC=N); 1615 pl (δNH); 1426 (δCH_2); 687, 621 (νCS). Found (%): C, 29.98; H, 4.68; Cl, 19.28; N, 15.14; S, 3180. $C_5H_9ClN_2S_2$. Calculated (%): C, 30.53; H, 4.61; Cl, 18.61; N, 14.24; S, 32.60.

***N*-[1-(Ethylthio)ethylidene]thiourea (4)**, yield 31%, m.p. 102—104 °C. ^{1}H NMR (90 MHz, CD_3OD), δ: 1.13 (t, 3 H, CH_3); 1.71 (s, 3 H, CH_3); 2.76 (q, 2 H, CH_2S). ^{13}C NMR: 15.6 (CH_3); 29.4 (CH_2S); 32.3 (CH_3); 135.0 (C=N, J = 35.4 Hz); 167.3 (C=S). IR (KBr)/cm^{-1}: 3490 ($\nu_{as}NH$); 3394 (ν_sNH); 2967, 2927, 2866 (νCH); 1696 (νC=N); 1631 (δNH_2); 1531 (δN—C(S)—N); 1447, 1417, 1355 (δCH_3); 1318 (νC=S); 1213 (νC—N); 670, 532 (νC—S). Found (%): C, 37.96; H, 5.68; N, 16.64; S, 39.80. $C_5H_{10}N_2S_2$. Calculated (%): C, 37.01; H, 6.21; N, 17.26; S, 39.52.

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