Synthesis of *N*-substituted 4-benzoyl-2-iminothiazolium bromides

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Substituted thioureas react with 1-bromo-2-benzoylacetylene in various solvents at 20 °C to give the corresponding *N*-substituted 4-benzoyl-2-(R-imino)-3-R'-thiazolium bromides.

Key words: 1-bromo-2-benzoylacetylene, substituted thioureas, reaction, intramolecular cyclization; *N*-substituted 4-benzoyl-2-iminothiazolium bromides, IR spectra, ^{1}H and ^{13}C NMR spectra.

It is known that the reaction of substituted thioureas with phenyl ethynyl ketone in the presence of HCl leads to the formation of 2-imino-4-phenyl-1,3-thiazine hydrochlorides.[1] When thiourea reacts with substituted α-acetylenic ketones in ethanol in the presence of sodium ethoxide, substituted pyrimidine-2-thiones form.[2] The reaction of thiourea and its derivatives with α-acetylenic ketones in methanol at 20 °C leads to a mixture of *E,Z*- and *Z,Z*-bis(acylvinyl) sulfides.[3,4] The interaction between substituted thioureas and phenylpropiolyl chloride in benzene on heating results in 5-benzylidene-2-phenyliminothiazolidine-4-ones.[5]

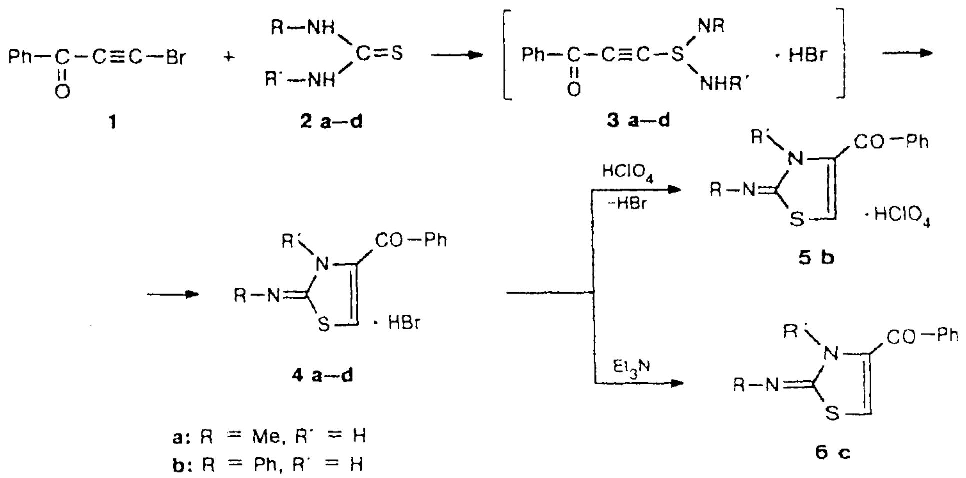
To investigate the reactivity of 2-benzoyl-1-bromoacetylene (**1**), we studied its interaction with substituted thioureas (**2a—d**) (Scheme 1) and found that *N*-substituted 4-benzoyl-2-iminothiazolium bromides (**4a—d**) form with an equimolar ratio of the reagents at 20 °C in acetonitrile, methanol, or benzene in the absence of catalysts.

Thioureas **2a—d** seem to react with acetylene **1** according to the mechanism of nucleophilic substitution of bromine[6] to give intermediate ethynyl sulfides **3a—d** which undergo intramolecular cyclization resulting in *N*-substituted 4-benzoyl-2-iminothiazolium bromides **4a—d**.

4-Benzoyl-2-phenylimino-*3H*-thiazolium perchlorate (**5b**) was obtained on heating compound **4b** with perchloric acid in 88% yield.

A free base, 4-benzoyl-3-phenyl-2-phenyliminothiazoline (**6c**), was formed upon heating a solution of hydrobromide **4c** in ethanol with an equimolar amount of triethylamine.

Scheme 1



a: R = Me, R' = H
b: R = Ph, R' = H
c: R = R' = Ph
d: R = 2-pyridyl, R' = Me

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The structures of compounds **4a—d**, **5b**, and **6c** synthesized were confirmed by ^{1}H NMR and IR spectroscopic data as well as by ^{13}C NMR spectra (**4b** and **4c**). The absorption bands of the C—S bond (680—700 cm^{-1}), the carbonyl group (1630—1645 cm^{-1}), and the C=N group (1650—1660 cm^{-1}) are present in the IR spectra of compounds **4a—d** and the absorption bands of the ring N—H group (3100—3150 cm^{-1}) are observed for **4a,b**.

Experimental

^{1}H NMR spectra (in DMSO-d$_6$) were obtained on a BS-487C spectrometer (80 MHz), and ^{13}C NMR spectra (in DMSO-d$_6$) were obtained on a FX-90Q spectrometer (22.49 MHz) with HMDS as the internal standard. IR spectra were recorded on a Specord IR-75 instrument in pellets with KBr.

4-Benzoyl-2-phenylimino-*3H*-thiazolium bromide (4b). A solution of 2-benzoyl-1-bromoacetylene (**1**) (1.04 g, 5 mmol) in 10 mL of acetonitrile was added dropwise with stirring to a suspension of phenylthiourea (**2b**) (0.76 g, 5 mmol) in 10 mL of acetonitrile and stirred at 20 °C for 2 h. The precipitate formed was filtered off and recrystallized from acetonitrile, and bromide **4b** was obtained, yield of 1.4 g (78%), m.p. 282—284 °C (when the reaction was carried out in benzene and methanol at 20 °C, the yields of bromide **4b** were 76 and 58%, respectively). Found (%): C, 53.4; H, 3.6; Br, 22.3; N, 7.8; S, 8.6. $C_{16}H_{13}BrN_2OS$. Calculated (%): C, 53.2; H, 3.6; Br, 22.2; N, 7.8; S, 8.9. ^{1}H NMR, δ: 6.95 (s, 1 H, CH—S); 7.82—8.26 (m, 10 H, 2 Ph); 10.38 (s, 1 H, NH). ^{13}C NMR, δ: 120.36 (C(5)); 137.17 (C(2)); 169.66 (C(4)); 182.96 (C=O); 130.67, 134.03, 134.55, 135.97 (PhN); 127.75, 129.03, 129.92, 130.36 (PhCO).

4-Benzoyl-2-methylimino-*3H*-thiazolium bromide (4a) was obtained from thiourea **2a** (0.45 g, 5 mmol) and ketone **1** (1.04 g, 5 mmol) similarly to salt **4b**. The yield of bromide **4a** was 0.96 g (64%), m.p. 215—217 °C (from acetonitrile). Found (%): C, 44.0; H, 3.5; Br, 26.9; N, 9.5; S, 10.9. $C_{11}H_{11}BrN_2OS$. Calculated (%): C, 44.2; H, 3.7; Br, 26.8; N, 9.4; S, 10.7. ^{1}H NMR, δ: 6.92 (s, 1 H, CH—S); 3.05 (s, 3 H, Me); 7.85—8.20 (m, 5 H, Ph); 10.32 (s, 1 H, NH).

4-Benzoyl-3-phenyl-2-phenyliminothiazolium bromide (4c) was obtained from thiourea **2c** (1.14 g, 5 mmol) and ketone **1** (1.04 g, 5 mmol) similarly to salt **4b**. The yield of bromide **4c** was 1.5 g (69%), m.p. 284—286 °C (from acetonitrile). Found (%): C, 60.2; H, 4.00; Br, 18.4; N, 6.5; S, 7.3. $C_{22}H_{17}BrN_2OS$. Calculated (%): C, 60.4; H, 3.9; Br, 18.3; N, 6.4; S, 7.3. ^{1}H NMR, δ: 6.87 (s, 1 H, CH—S); 7.67—8.24 (m, 15 H, 3 Ph). ^{13}C NMR, δ: 125.73 (C(5)); 128.34—137.31 (3 Ph); 140.30 (C(2)); 172.56 (C(4)); 187.28 (C=O).

4-Benzoyl-3-methyl-2-(2-pyridyl)iminothiazolium bromide (4d) was obtained from ketone **1** (1.04 g, 5 mmol) and *N*-(2-pyridyl)-*N'*-methylthiourea (**2d**) (0.77 g, 5 mmol) similarly to salt **4b**. The yield of bromide **4d** was 1.1 g (55%), m.p. 191—193 °C (from ethanol). Found (%): C, 51.1; H, 3.8; Br, 21.5; N, 11.4; S, 8.4. $C_{16}H_{14}BrN_3OS$. Calculated (%): C, 51.1; H, 3.7; Br, 21.3; N, 11.2; S, 8.5. ^{1}H NMR, δ: 1.97 (s, 3 H, Me); 6.57 (s, 1 H, CH—S); 7.65—8.24 (m, 9 H, Ph, C_5H_4N).

4-Benzoyl-2-phenylimino-*3H*-thiazolium perchlorate (5b). A solution of perchloric acid (0.1 g, 1 mmol) in 5 mL of water was added slowly with vigorous stirring to a hot solution of bromide **4b** (0.36 g, 1 mmol) in 10 mL of water. The reaction mixture was heated to 60 °C, stirred for 1 h, and cooled to 20 °C. The precipitate formed was filtered off, recrystallized from ethanol, and dried *in vacuo*. The yield of perchlorate **5b** was 0.33 g (88%), white needles, m.p. 215—217 °C. Found (%): C, 50.5; H, 3.4; Cl, 9.3; N, 7.4; S, 8.4. $C_{16}H_{13}ClN_2O_5S$. Calculated (%): C, 50.4; H, 3.4; Cl, 9.5; N, 7.3; S, 8.4. IR, ν/cm^{-1}: 685 (C—S); 1080 (ClO_4^-); 1605 (C=C); 1642 (C=O); 1650 (C=N); 3100 (NH). ^{1}H NMR, δ: 6.90 (s, 1 H, CH—S); 7.80—8.28 (m, 10 H, 2 Ph); 10.45 (s, 1 H, NH).

4-Benzoyl-3-phenyl-2-phenyliminothiazoline (6c). A solution of triethylamine (0.15 g, 1.6 mmol) in 5 mL of ethanol was added with vigorous stirring to a solution of bromide **4c** (0.68 g, 1.6 mmol) heated to 60 °C in ethanol, stirred for 1 h, and cooled to 20 °C. The yellow precipitate formed was filtered off, washed on the filter with cold ethanol, and dried *in vacuo*. The yield of thiazoline **6c** was 0.42 g (76%), yellow flakes, m.p. 153—155 °C. Found (%): C, 74.4; H, 4.5; N, 8.1; S, 8.9. $C_{22}H_{16}N_2OS$. Calculated (%): C, 74.2; H, 4.5; N, 7.9; S, 9.0. IR, ν/cm^{-1}: 690 (C—S); 1608 (C=C); 1640 (C=O); 1660 (C=N). ^{1}H NMR, δ: 6.95 (s, 1 H, CH—S); 7.88—8.28 (m, 15 H, 3 Ph). ^{13}C NMR, δ: 123.60 (C(5)); 136.54 (C(4)); 138.36 (C(2)); 114.36, 121.26, 129.45, 151.36 (PhN); 127.24, 127.69, 129.45, 157.87 (PhN=C); 128.54, 128.86, 133.35, 138.10 (Ph—CO); 183.49 (C=O).

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