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SYNTHESIS OF THE THIAZOLO[3,2-*a*]QUINOLINIUM SYSTEM

D. G. Kim[1]* and E. A. Vershinina[1]

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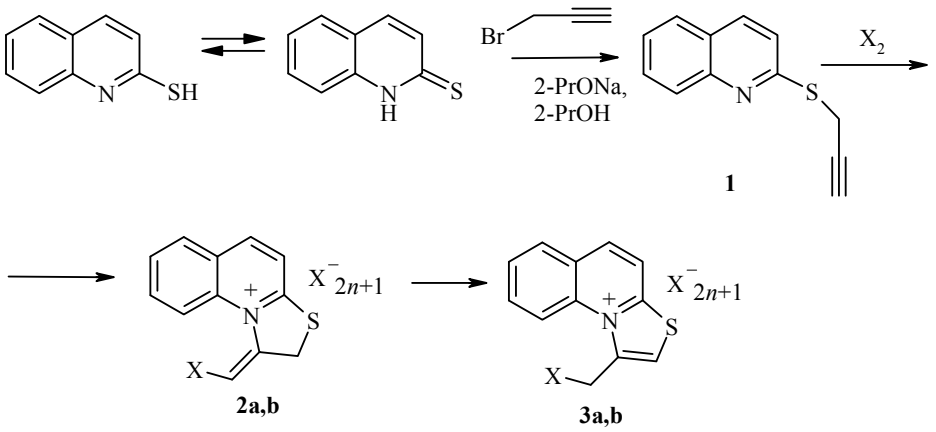
The synthesis of the thiazolo[3,2-*a*]quinolinium system is carried out by dehydration of α-(2-quinolylthio) ketones [1] or α-(quinolylthio)acetic acids [2], and the halocyclization of 2-vinylthioquinoline [3].

We have shown that the reaction of 2-propargylthioquinoline (**1**) with bromine or iodine does not stop at the stage of formation of 1-halomethylidene-1,2-dihydrothiazolo[3,2-*a*]quinolinium halides **2a,b** but further isomerizes to give the 1-halomethylthiazolo[3,2-*a*]quinolinium halides **3a,b**. Compound **1** was prepared by the reaction of 2-mercaptoquinoline with propargyl bromide in the presence of sodium 2-propoxide in 2-propanol.



2, 3 a X = I, *n* = 0; **b** X = Br, *n* = 1

The ^{1}H NMR spectra for compounds **3a**,**b** show signals for the protons of the CH_2I (4.71) or CH_2Br group (4.74 ppm) and for the H-2 proton at 8.09 and 8.04 ppm respectively.

In contrast to compound **1** the 3-formyl-2-propargylthioquinoline reacts with the halogens to form 1-halomethylidene-2H-thiazolo[3,2-*a*]quinolinium halides [4].

^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz) using DMSO-d_6 and with TMS as internal standard. Mass spectra (EI, 70 eV) were taken on a Hewlett-Packard GC/MS instrument with an HP-5890 gas chromatograph.

* To whom correspondence should be addressed, e-mail: kim_dg48@mail.ru.

[1]South Ural State University, Chelyabinsk 454080, Russia.

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2-Propargylthioquinoline(1). 2-Mercaptoquinoline (0.161 g, 1 mmol) was added to a solution of sodium 2-propoxide (prepared from Na (0.023 g, 1 mmol) in 2-propanol (5 ml)) and heated to full solution of the compound. Propargyl bromide (0.180 g, 1.5 mmol) in 2-propanol (2 ml) was then added and refluxed for 3 h. The product was cooled, the precipitated NaBr was filtered off, and the 2-propanol was evaporated. The residue was treated with hexane, filtered, and the hexane distilled off to give compound **1** as a yellow oil. Yield 0.141 g (71%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.15 (1H, t, ^4J = 2.6, CH≡); 4.19 (2H, d, ^4J = 2.6, SCH_2); 7.45 (1H, d, ^3J = 8.65, H-3); 7.54, 7.74, 7.92 (4H, three m, benzene ring); 8.23 (1H, d, ^3J = 8.65, H-4). Mass spectrum, *m/z* (I_{rel}, %): 198 $[M-1]^+$ (100), 167 $[M-32]^+$ (13), 154 $[M-45]^+$ (13) etc. Found, %: C 72.16; H 4.52; N 7.08. $C_{12}H_9NS$. Calculated, %: C 72.33; H 4.55; N 7.03.

1-Iodomethylthiazolo[3,2-*a*]quinolinium Iodide (3a). A solution of iodine (0.064 g, 0.25 mmol) in glacial acetic acid (5 ml) was added to a solution of the sulfide **1** (0.025 g, 0.13 mmol) in glacial acetic acid (3 ml). The black precipitate was filtered off, dried, dissolved in acetone (3 ml), and a solution of NaI in acetone was added. The yellow precipitate formed was filtered off. Yield 0.040 g (70%); mp 178ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.71 (2H, d, ^4J = 1.8, CH_2I); 7.88, 8.10, 8.33, 8.46 (4H, four m, benzene ring); 8.09 (1H, t, ^4J = 1.8, H-2); 8.21 (1H, d, ^3J = 8.8, H-3); 8.93 (1H, d, ^3J = 8.8, H-4). Found, %: C 31.69; H 1.90; I 56.77; N 3.01. $C_{12}H_9I_2NS$. Calculated, %: C 31.81; H 2.00; I 56.02; N 3.09.

1-Bromomethylthiazolo[3,2-*a*]quinolinium Tribromide (3b). A solution of bromine (0.016 ml, 0.30 mmol) in glacial acetic acid (3 ml) was added to a solution of the sulfide **1** (0.030 g, 0.15 mmol) in glacial acetic acid (3 ml). The orange precipitate formed was filtered off, washed with glacial acetic acid, and dried. Yield 0.066 g (85%); mp 120ºC (decomp.). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.74 (2H, d, ^4J = 2.1, CH_2Br); 7.90, 8.10, 8.35, 8.52 (4H, four m, benzene ring); 8.04 (1H, t, ^4J = 2.1, H-2); 8.26 (1H, d, ^3J = 8.8, H-3); 8.95 (1H, d, ^3J = 8.8, H-4); Found, %: C 27.65; H 1.73; Br 61.96; N 2.60. $C_{12}H_9Br_4NS$. Calculated, %: C 27.78; H 1.75; Br 61.60; N 2.70.

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