REACTION OF 2-MERCAPTOTHIAZOLINE WITH α-HALOGENOCARBONYL COMPOUNDS

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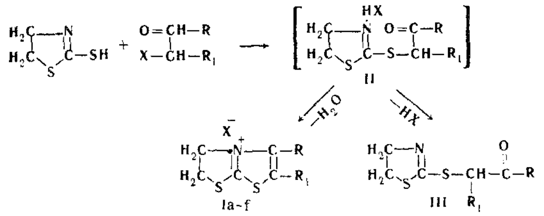
Condensation of 2-mercaptothiazoline with α-halogeno-carbonyl compounds at 100° gives 2, 3-dihydrothiazolo[2, 3-b]thiazolium salts.

Reaction of 2-mercaptothiazoles with α-halogenocarbonyl compounds is known to give 2-β-ketoalkyl (aryl) mercaptothiazoles [1], while 2-mercaptoimidazole [2], 2-mercaptoimidazoline [3], and thilactams [4] react as cyclic thioamides, to give thiazole derivatives. It was of interest to investigate the reaction 2-mercaptothiazoline with α-halogenocarbonyl compounds. When equimolecular quantities of 2-mercaptothiazoline and α-halogenoketones or aldehydes are heated together in the absence of solvent at 100°, salt-like compounds are formed, and their compositions and properties are those of 2,3-dihydrothiazole[2,3-b]thiazolium salts (I):



a $R=R_1=H$;
b $R=CH_3$, $R_1=H$;
c $R=H$, $R_1=CH_3$;
$X=Cl$, Br, I, ClO_4
d $R=C_6H_5$, $R_1=H$;
e $R=R_1=-(CH_2)_4-$;
f $R=R_1=C_6H_5$;

When the reactions are run in solvents (benzene, ethanol), it is in some cases possible to isolate the intermediate 2-β-ketoalkyl(aryl)mercaptothiazonlines (e. g. IId) as their hydrohalides. Alkali converts the latter to the corresponding base III, heat to salts I. Thus the reaction investigated is one of the variants of the Hantzsch general method of synthesizing thiazoles. The salts I were used to prepare polymethine dyes.

EXPERIMENTAL

2, 3-Dihydrothiazolo[2, 3-b]thiazolium perchlorate (Ia). A mixture of 6.1 g (0.051 mole) 2-mercaptothiazoline and 6.3 g (0.051 mole) bromoacetaldehyde was heated for 6 hr at 100°. After cooling the reaction product was dissolved in 20 ml water, and 25 ml 30% aqueous solution of $NaClO_4$ added. The precipitate was filtered off and washed with acetone and ether. Yield 5.5 g (48.2%), mp 202–205°* (ex EtOH). Found: N 5.69; 5.60%, calculated for $C_5H_6ClNO_4S_2$: N 5.77%.

5-Methyl-2, 3-dihydrothiazolo[2, 3-b]thiazolium chloride (Ib, X = Cl). A mixture of 5.85 g (0.05 mole) 2-mercaptothiazoline and 4.65 g (0.05 mole) chloroacetone was heated for 1 hr at 100°. After cooling 10 ml EtOH was added to the reaction products, and the precipitate was filtered off and washed with acetone and ether. Mass 5.4 g (51%), mp 227–228°. To purify the product, it was dissolved in 50 ml EtOH and precipitated with ether. Yield 4.2 g (40%), mp 235–236°. Found: N 6.96; 7.01%, calculated for $C_6H_8ClNS_2$: N 7.23%.

Bromide (Ib, X = Br). This was prepared similarly to the above, using bromoacetone. Yield 31.8%, mp 235° (ex EtOH). Found: N 5.88; 5.83%, calculated for $C_6H_8BrNS_2$: N 5.87%.

Iodide (Ib, X = I). Obtained in 64.6% yield by adding a KI solution to an aqueous solution of the bromide. Colorless crystals, mp 219–220° (ex EtOH).

6-Methyl-2, 3-dihydrothiazolo [2, 3-b] thiazolium bromide (Ic, X = Br). A mixture of 5.85 g (0.05 mole) 2-mercaptothiazoline and 6.85 g (0.05 mole) α-bromopropionaldehyde were heated together for 5 hr at 100°. The reaction products were triturated with 10 ml EtOH. The precipitate was filtered off and recrystallized from EtOH. Yield 2.5 g (25.7%), mp 240–242°. Found: N 5.65; 5.64%, calculated for $C_6H_8BrNS_2$: N 5.87%.

5-Phenyl-2, 3-dihydrothiazolo[2, 3-b]thiazolium bromide (Id, X = Br). A mixture of 15 g (0.125 mole) mercaptothiazoline and 25 g (0.125 mole) phenacylbromide was heated for 2 hr in 100°. 50 ml acetone was added to the cold reaction products. The precipitate was filtered off and washed with acetone and ether. Yield 32 g (84.8%), mp 231° (ex EtOH). Found: N 4.47; 4.43%, 'calculated for $C_{11}H_{10}BrNS_2$: N 4.66%.

5, 6-Tetramethylene-2, 3-dihydrothiazolo[2, 3-b]thiazolium bromide (Ie, X = Br). A mixture of 8.3 g (0.07 mole) 2-mercaptothiazoline and 12.3 g (0.07 mole) α-bromocyclohexanone was heated for 30 min at 100°. The reaction products were triturated with 8 ml EtOH. The precipitate was filtered off, washed with acetone and EtOH, and recrystallized from EtOH. Yield 14 g (71.2%), mp 240–241°. Found: N 4.94; 4.89%, calculated for $C_9H_{12}BrNS_2$: N 5.03%.

5, 6-Diphenyl-2, 3-dihydrothiazolo[2, 3-b]thiazolium bromide (If, X = Br). A mixture of 5.1 g (0.042 mole) 2-mercaptothiazoline and 9 g (0.042 mole) desyl chloride was heated for 4 hr at 100°. The reaction product was dissolved in 75 ml water and boiled with 1 g decolorizing charcoal. The solution was filtered, 9 g KBr in 15 ml water added. The oil that separated crystallized by trituration with 10 ml acetone. Yield 4 g (28.4%), mp 265° (ex EtOH). Found: N 3.54; 3.66%, calculated for $C_{17}H_{14}BrNS_2$: N 3.75%.

2-Phenacylmercaptothiazoline hydrobromide (IIc). A solution of 2.5 g (0.0126 mole) phenacyl bromide in 5 ml benzene was added to a warm solution of 1.5 g (0.0126 mole) 2-mercaptothiazoline in 20 ml benzene. The crystals that came down were filtered off and recrystallized from 1% hydrobromic acid. Yield 3.1 g (97.5%), mp 150–152°. Found: N 4.62; 4.70; Br 25.38; 25.36; S 20.49; 20.35%, calculated for $C_{11}H_{11}NOS_2 \cdot HBr$: N 4.48; Br 25.08; S 20.15%

2-Phenacylmercaptophenazoline (IIIc). 0.4 g NaOH in 5 ml water was added to a solution of 1 g hydrobromide IIc in 10 ml water. The resultant precipitate was filtered off, washed with water, and recrystallized from EtOH. Yield 0.6 g (81%), mp 61–62°. Found: N 6.07; 6.05; S 27.20; 27.22%, calculated for $C_{11}H_{11}NO_2S_2$: N 5.87; S 26.91%.

5-Phenyl-2, 3-dihydrothiazolo[2, 3-b]thiazolium bromide (Ic). 1 g 2-phenacylmercaptothiazoline hydrobromide was heated for 10 min at 150°. The cold reaction product was triturated with 5 ml EtOH. The precipitate was filtered off and recrystallized from EtOH. Yield 0.6 g (60%), mp 229–231°. Found: N 4.86; 4.99; Br 26.45; 26.47%, calculated for $C_{11}H_{10}NS_2$: N 4.66; Br 26.61%. Undepressed mixed mp with the product obtained by heating 2-mercaptothiazoline with phenacyl bromide in the absence of solvent.

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*All I salts melted with decomposition.

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