NEW METHOD FOR THE SYNTHESIS OF TETRAHYDRO-1,4-THIAZINO[2,3,3,4-i,j]QUINOLINIUM SALTS. PREPARATION OF 2-HYDROXO- AND 2-MERCAPTO-2-METHYLTETRAHYDRO-1,4-THIAZINO[2,3,3,4-i,j]QUINOLINIUM HALIDES

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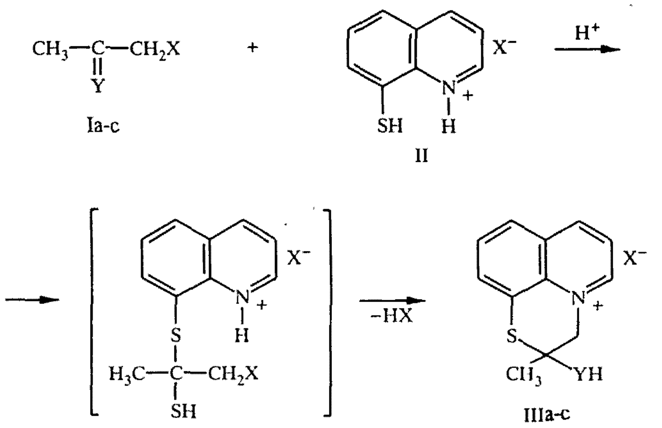
The known route for the synthesis of tetrahydro-1,4-dithazino[2,3,3,4-i,j]quinolinium salts of type III is a three stage process. Potassium 8-mercaptoquinolinate is S-alkylated with 2-chloroethanol, the S-alkyl substituent is C-halogenated with thionyl chloride and intramolecular quaternisation of the quinoline nitrogen then occurs [1].

We have developed a new route to the salts III based on the reaction of mercaptoquinolinium halides II with monohalogenated acetones and thioacetones Ia to Ic in ethanol or dimethylformamide at 20°C in the presence of the corresponding hydrogen halide.



I, IIIa X = Cl, Y = O; I, IIIb X = Cl, Y = S; I, IIIc X = Br, Y = S

The reaction goes in one step to give the previously unknown water soluble 2-hydroxy- and 2-mercaptosubstituted 2-methyltetrahydro-1,4-dithazino[2,3,3,4-i,j]quinolinium halides IIIa-c in yields of 81-87%.

Salt formation begins with the addition of the thiol group of compound II to the carbonyl or thiocarbonyl group of acetones Ia-c (observed experimentally) and is completed by intramolecular cyclisation, coupled with quaternisation of the quinoline nitrogen and loss of hydrogen halide.

The polarogram of compound IIIb in dimethylformamide containing 0.05 mole/liter Bu_4NClO_4 showed one anodic and two cathodic one electron waves with $E_{1/2}$ at −0.20, −0.63 and −1.99 V respectively corresponding to formation of the mercury mercaptide [2], reversible reduction of the $C{=}N^+$ group in the aromatic heterocycle [3] and reduction of H^+ generated from the thiol in dimethylformamide [4].

Salt IIIa ($C_{12}H_{12}ClNOS$). T_{dec} 115-116°C. ^1H NMR spectrum ($CDCl_3$): 2.15 (3H, s, CH_3), 3.93 (2H, s, N^+CH_2), 7.80-8.19 (6H, m, H_{arom}), 11.27 ppm (1H, s OH).

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Salt IIIb ($C_{12}H_{12}ClNS_2$). T_{dec} 205-207°C. ^1H NMR spectrum (D_2O): 2.01 (3H, s, CH_3), 3.98 (1H, s SH), 5.28 (2H, s, N^+CH_2), 8.19-9.16 ppm (6H, m, H_{arom}). ^{13}C NMR Spectrum: 30.32 (CH_3), 44.96 ($-C-$), 70.16 (CH_2), 150.44 ($C{=}N^+$).

Salt IIIc ($C_{12}H_{12Br}ClNS_2$). T_{dec} 193-195°C. ^1H NMR spectrum (D_2O): 2.07 (3H, s, CH_3), 5.37 (2H, s, N^+CH_2), 8.04-8.19 ppm (H_{arom}).

The elemental analysis results for C, H, Br, Cl, N, and S agree with the calculated values.

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