PREPARATION OF 3-SUBSTITUTED 2-DIMETHYLAMINO-5-(3,5,6-TRICHLORO-1,4-BENZOQUINON-2-YL)THIAZOLIUM SALTS

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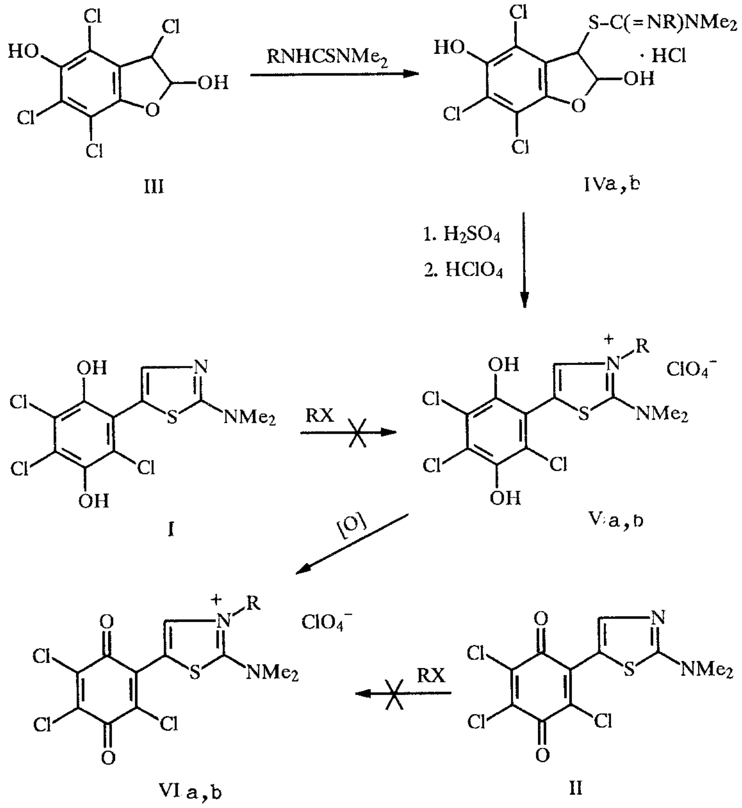
We have previously reported [1] the preparation of 2-dimethylamino-5-(2,5-dihydroxy-3,4,6-trichloro- and 3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazoles (I, II). 2-Dialkylamino-substituted thiazoles are readily alkylated on the nitrogen atom of the thiazole ring forming thiazolium salts [2, 3]. However, on account of the specific properties of the thiazoles I and II which we prepared earlier [1], we were unable to effect their alkylation by such reagents as methyl iodide or dimethyl sulfate.

To solve this problem we propose a new method of constructing a thiazole ring with a quaternized nitrogen atom. It has been established that in the reaction of 2,5-dihydroxy-3,4,6,7-tetrachlorocoumaran (III) with trisubstituted thioureas, the corresponding thiuronium salts IVa, b are formed and these are cyclized in sulfuric acid with subsequent treatment of the reaction mixture with perchloric acid. 3-Substituted 2-dimethylamino-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazolium perchlorates (Va, b) are obtained, the hydroquinone fragments of which are readily oxidized to 1,4-benzoquinone with the formation of thiazolium salts VIa, b. The latter are of interest for the study of intra- and intermolecular charge transfer.



IV-VI a R=Me; b R=Ph

Hydrochlorides of 2,4-Dihydroxy-3-trimethyl- or N,N-Dimethyl-N′-phenylisothioureido-4,6,7-trichlorocoumaran (IVa, b). Coumaran III (3 mmole) [4] and trimethyl- or N,N-dimethyl-N′-phenylthiourea (3 mmole) were stirred in 6 ml acetone for 4 h at room temperature. The colorless crystals which formed were filtered off and washed with a small quantity of acetone.

Compounds, yields (5), mp: IVa, 92, 169-170°C; IVb, 87, 176-177°C. IR spectrum (cm^{-1}): IVa 1632, 1408, 1380, 1322, 1280, 1234, 1170, 1071, 1054, 1010; IVb 1618, 1590, 1564, 1494, 1404, 1380 1306, 1276, 1254, 1220, 1189, 1176, 1074, 1054, 1010.

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2-Dimethylamino-3-methyl- or phenyl-5-(2,5-dihydroxy-3,4,6-trichlorophenyl)thiazolium Perchlorates (Va, b). Thiuronium salts IVa or IVb (2 mmole) were dissolved in 3 ml sulfuric acid and kept for 3 h at 60°C. The mixture was cooled and 5 ml 75% perchloric acid added and then diluted with 40 ml water. The colorless crystals which formed were filtered off and dried in air. Mp: Va >190°C (decomp.); Vb >150°C (decomp.). IR spectra (cm^{-1}): Va 3096, 1608, 1540; Vb 3572, 3512, 3320, 3092, 1628, 1610, 1588, 1540, 1492. Yields: Va 99%, Vb 98%.

2-Dimethylamino-3-methyl- or phenyl-5-(3,5,6-trichloro-1,4-benzoquinon-2-yl)thiazolium Perchlorates (VIa, b). To a solution of 2 mmole compound Va or Vb in 10 ml acetonitrile was added 2.2 mmole 1,4-benzoquinone and the mixture stirred 2 h. The acetonitrile was reduced by approximately 2/3 and the residue diluted with 40 ml water. The dark red crystals were separated, washed with hot water, and dried in air. They were recrystallized from methanol. IR spectrum (cm^{-1}): VIa 2924, 2856, 1708, 1676, 1604, 1560, 1544, 1508; VIb 3320, 2928, 1672, 1602, 1572, 1548. UV spectrum [λ_{max}, nm (log ε)]: VIa 537 (3.56), 495 (3.60), 354 (3.50), 290 (4.25). Yields: VIa 68%, VIb 62%.

Elemental analyses of the compounds prepared were in agreement with calculated values.

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