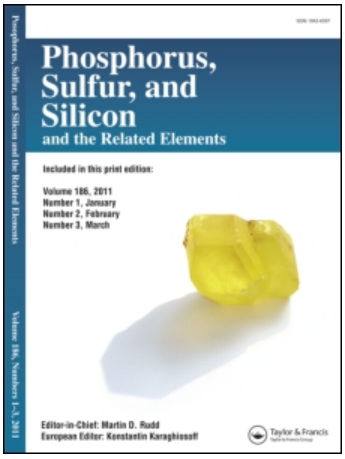

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Synthesis of Novel Trichloro-1,4-Benzoquinonyl-Substituted Heterocycles

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In the reaction of 3,4,6,7-tetrachloro-2,5-dihydroxy-2,3-dihydro-benzo[b]furan with rubeanic acid 2,2'-bis[5-(3,4,6-trichloro-2,5-dihydroxyphenyl)thiazole] and 6-(3,4,6-trichloro-2,5-dihydroxyphenyl)-3-imino-3,4-dihydro-4*H*-1,4-thiazine-3-thione have been synthesized and after the oxidation the corresponding trichloro-1,4-benzoquinonyl-substituted sulfur containing heterocycles were obtained.

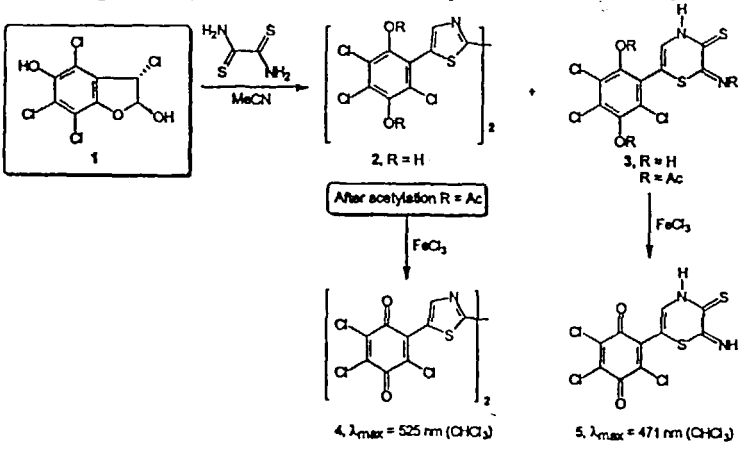
Keywords: 2,3-dihydrobenzo[b]furan; 2,2'-bisthiazole; 3-imino-3,4-dihydro-4*H*-1,4-thiazine-3-thione; intramolecular charge transfer

We have developed our method[1] of the synthesis of trichloro-1,4-benzoquinonyl substituted heterocycles using the recyclization reactions of 3,4,6,7-tetrachloro-2,5-dihydroxy-2,3-dihydrobenzo[b]furan (1) with sulfur containing bifunctional nucleophilic reagents. The reactions of furan 1 with thiosemicarbazide[2] and substituted thiosemicarbazides[3,4] were investigated and the corresponding (3,4,6-trichloro-2,5-dihydroxyphenyl)substituted heterocycles[2,3] as well as [b]-fused benzo[d]furano heterocycles[4] were obtained.

Recently we have investigated the reaction of furan 1 with rubeanic acid. This reaction carried out in boiling acetonitrile led to the mixture of

bis-2,2'-thiazole **2** (R=H, yield 46 %, m.p.330^0 C, with decomp.) and *4H*-1,4-thiazine-3-thione **3** (R = H, yield 28 %, m.p. 240^0 C, decomp.). The acetylation of the hydroquinones **2** and **3** with acetic anhydride in the presence of H_3PO_4 led to the tetraacetate **2** (R = Ac, yield 99 %, m.p. 275-277^0 C) and triacetylderivative **3** (R = Ac, yield 50 %, m.p. 175-176^0 C). In the oxidation reactions of the hydroquinones **2** and **3** (R = H) with $FeCl_3$ in aqueous DMF the corresponding trichloro-1,4-benzoquinonylsubstituted heterocycles **4** (m.p. 310^0 C, decomp.) and **5** (m.p. 180^0 C, decomp.) were obtained.

The long wave band in the electronic spectra of benzoquinones (**4**, λ_{max} 525 nm, log ε 4.13 and **5**, λ_{max} 471 nm, log ε 3.79, in $CHCl_3$) confirms the intramolecular charge transfer between the electron donating sulfur containing heterocycle and the electron accepting quinonoid moiety.



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