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REACTION OF 6,7-DICHLOROQUINOLINE-5,8-QUINONE WITH THIOSULFONIC ACID SALTS

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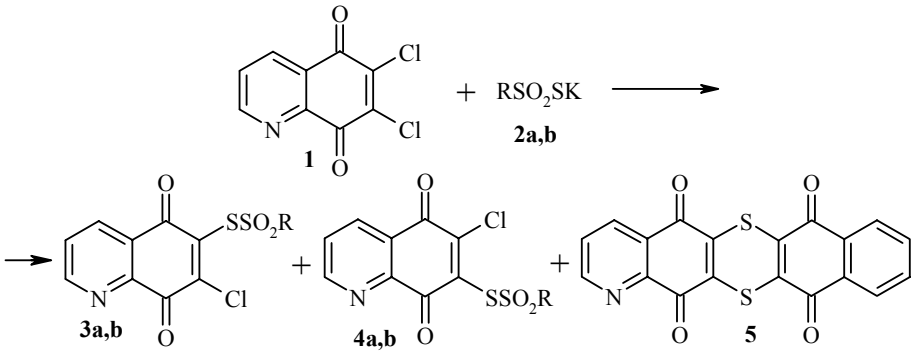
Keywords: S-(7-chloroquinoline-5,8-quinone-6-yl) thiosulfonic acid esters, 6,7-dichloroquinoline-5,8-quinone.

Derivatives of 5,8-quinolinequinone have stimulated considerable interest as biologically active compounds [1], but no data are available on synthesis of its derivatives containing a thiosulfonate moiety. Continuing our research on thiosulfonic acid esters in the heterocyclic series [2, 3], we have studied the reaction of thiosulfonic acid salts with 6,7-dichloroquinoline-5,8-quinone. In acetone at low temperature (from -18 to -10°C), the chlorine atoms are easily substituted by a thiosulfonate moiety with formation of two monosubstitution products **3a,b** and **4a,b** with a predominant amount of **3a,b**, and also compound **5**, the amount of which depends on the reaction conditions (temperature, solvent, and rate at which the salt **2a,b** is added). The structure of the products **3a,b** and **4a,b** obtained has been confirmed by elemental analysis, IR spectroscopy, and an alternate synthesis for verifying identity.



a R = 4-$MeCONHC_6H_4$, **b** R = 4-MeC_6H_4

S-(7-Chloroquinoline-5,8-quinon-6-yl) Ester of 4-Acetylaminobenzenethiosulfonic Acid (3a). Yield 37%; mp 120°C. IR spectrum (KBr), ν, cm^{-1}: 1136, 1344 (SO_2), 1564, 1592 (Ar), 1620 (C=N), 1680, 1536, 1288 (I, II, III amide bands of secondary amides), 1690, 1708 (C=O), 3328 (NH). Found, %: C 47.95; H 2.83; Cl 8.12; N 6.37; S 14.85; $C_{17}H_{11}ClN_2O_5S_2$. Calculated, %: C 48.29; H 2.62; Cl 8.38; N 6.62; S 15.17.

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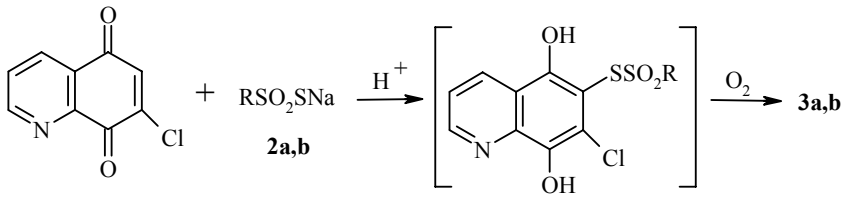

S-(7-Chloroquinoline-5,8-quinon-6-yl) Ester of 4-Methylbenzenethiosulfonic Acid (3b). Yield 40%; mp 94-95°C. IR spectrum (KBr), ν, cm^{-1}: 1112, 1312 (SO_2), 1564, 1578, 1592 (Ar), 1624 (C=N), 1660, 1680 (C=O). Found, %: C 50.13; H 2.85; Cl 8.95; N 3.56; S 16.45. $C_{16}H_{10}ClNO_4S_2$. Calculated, %: C 50.59; H 2.65; Cl 9.33; N 3.69; S 16.88.

S-(6-Chloroquinoline-5,8-quinone-7-yl) Ester of 4-Acetylaminobenzenethiosulfonic Acid (4a). Yield 18%; mp 177-178°C. IR spectrum (KBr), ν, cm^{-1}: 1140, 1336 (SO_2), 1568, 1594 (Ar), 1620 (C=N), 1656, 1540, 1292 (I, II, III amide bands of secondary amides), 1690, 1712 (C=O), 3308 (NH). Found, %: C 48.52; H 2.86; Cl 8.07; N 6.75; S 15.32. $C_{17}H_{11}ClN_2O_5S_2$. Calculated, %: C 48.29; H 2.62; Cl 8.38; N 6.62; S 15.17.

S-(6-Chloroquinoline-5,8-quinon-7-yl) Ester of 4-Methylbenzenethiosulfonic Acid (4b). Yield 20%; mp 105-106°C. IR spectrum (KBr), ν, cm^{-1}: 1136, 1336 (SO_2), 1576, 1588, 1600 (Ar), 1620 (C=N), 1664, 1686 (C=O). Found, %: C 50.21; H 2.81; Cl 9.12; N 3.78; S 16.98. $C_{16}H_{10}ClNO_4S_2$. Calculated, %: C 50.59; H 2.65; Cl 9.33; N 3.69; S 16.88.

Quino[7',6':5,6][1,4]dithiino[2,3-*g*]quinoline-5,7,12,14-tetrone (5). Yield 9.8%; mp >300°C. Found, %: C 58.96; H 1.15; S 17.15. $C_{18}H_6N_2O_4S_2$. Calculated, %: C 57.14; H 1.60; N 7.40; S 16.95.

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