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OXIDATION-REDUCTION REACTIONS OF 1,3-DITHIOLES AND THEIR IONS

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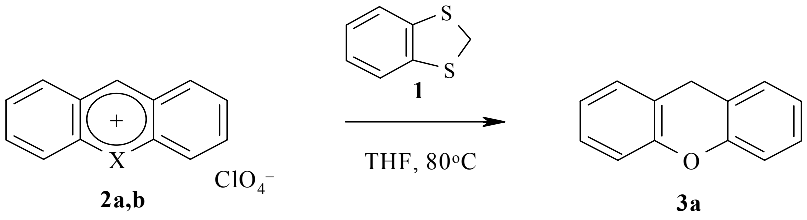
Keywords: 4-aryl-1,3-dithioles, 1,3-benzodithiole, dibenzothiopyran, 1,3-benzodithiolium and 4-aryl-1,3-dithiolium ions, dibenzopyrilium cation, 10-methyl-9,10-dihydroacridine.

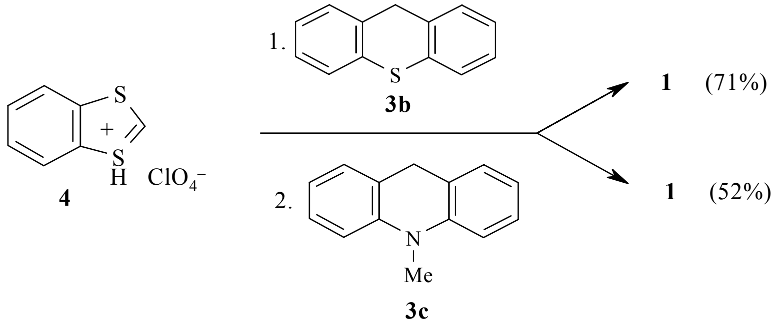
The transfer reaction of hydrogen from the C–H group of an organic compound to an electrophilic substrate is of interest as a model of fermentation processes [1]. 1,3-Dithioles are hetero analogs of the 10-methyl-9,10-dihydroacridine NADH model. Despite the fact that there are many known examples of the shift of hydride ion from heterocyclic donors to organic cations [2] or protonated imines [3, 4] there is, at this time, only one example of the oxidation of 1,3-benzodithiole by trityl ion [5].

We have found that 1,3-benzodithiole (**1**) can reduce dibenzopyrilium perchlorate (but not the dibenzothiopyrilium ion **2b**) to give the dibenzopyran **3a** in 60% yield.



2 a X = O, **b** X = S

On the other hand, the dibenzothiopyran (**3b**) reduces the 1,3-benzodithiolium cation (**4**) to 1,3-benzodithiole **1** and we can conclude that compound **1** is a stronger donor of hydride ion when compared with the dibenzopyran **3a** but weaker than the dibenzothiopyran **3b**.



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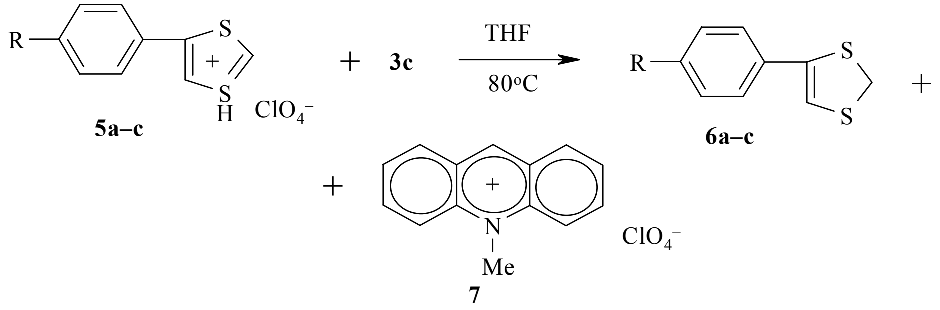
10-Methyl-9,10-dihydroacridine (**3c**) behaves similarly to compound **3b**. On the basis of this data the place of the 1,3-benzodithiole **1** in the known series of hydride mobility [6] can be determined as **3c**>**3b**>**1**>**3a**. The reaction of perchlorate **4** with substances **3b** and **3c** takes place at 80°C over 1 h. When acetonitrile or acetic acid are used as solvent in the reaction of compounds **4** and **3b** only traces of the 1,3-benzodithiole **1** were identified by ^{1}H NMR spectroscopy.

According to known data [7] the reaction of the 4-phenyl-1,3-dithiolium ion with 1,3,5-cycloheptatriene is accompanied by formation of a mixture of 4-phenyl-1,3-dithiolium and tropylium perchlorates. We have shown, for the first time, that the 4-aryl-1,3-dithiolium perchlorates **5a-c** are reduced by compound **3c** to give the 4-aryl-1,3-dithioles **6a-c** in 58, 62, and 58% yields respectively. The 10-methyl-9,10-dihydroacridinium perchlorate **7** is formed in close to quantitative yield.



5,6 a R = H, **b** R = Br, **c** R = Cl

The ^{1}H NMR spectra were recorded on a Mercury 300 (300 MHz) instrument using $CDCl_3$ with HMDS as internal standard. Mass spectra were taken on an HP 6890/MSD 5973 instrument.

4-Phenyl-1,3-dithiole (6a). Mp 45-46°C (mp 45-48°C [8]). ^{1}H NMR spectrum, δ, ppm: 4.47 (2H, s, CH_2); 6.26 (1H, s, CH, Het); 7.23-7.41 (5H, m, C_6H_5).

4-(4-Bromophenyl)-1,3-dithiole (6b). Mp 95-96°C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 4.50 (2H, s, CH_2); 6.29 (1H, s, CH, Het); 7.20 (2H, d, J =8.4, Ar); 7.37 (2H, d, J = 8.4, Ar). Mass spectrum, m/z (I_{rel}, %): 259 $[M]^+$ (100), 258 $[M-1]^+$ (97), 212 (18), 179 (3), 89 (52), 76 (5).

4-(4-Chlorophenyl)-1,3-dithiole (6c). Mp 69-71°C. ^{1}H NMR Spectrum, δ, ppm (J, Hz): 4.50 (2H, s, CH_2); 6.27 (1H, s, CH, Het); 7.22 (2H, d, J = 8.7, Ar); 7.27 (2H, d, J = 8.7, Ar). Mass spectrum, m/z (I_{rel}, %): 214 $[M]^+$ (100), 213 $[M-1]^+$ (97), 179 (10), 168 (34), 89 (32), 76 (23).

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