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Photooxidation of Monothioanthraquinone and its 2-Methyl Derivative

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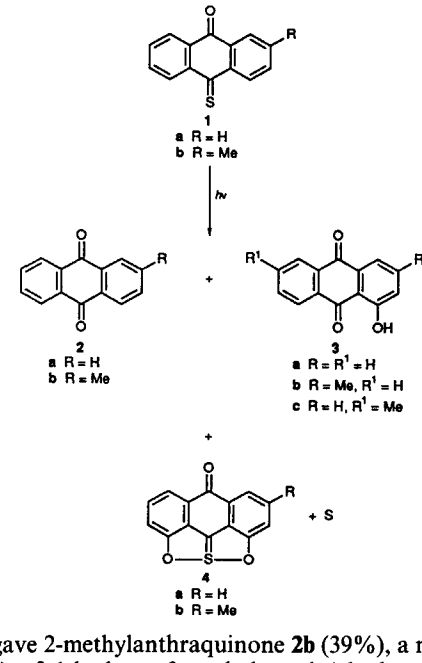
When exposed to visible light, chloroform solutions of monothioanthraquinone and 2-methyl-10-monothioanthraquinone undergo photoconversion to form the oxidation products anthraquinones **2**, α-hydroxyanthraquinones **3** and anthradioxathiapentalenes **4**.

One distinctive feature of thiocarbonyl compounds is their reduced stability when exposed to light. Monothioanthraquinone **1a** in solutions of normal hydrocarbons is photochemically converted at room temperature in air to anthraquinone.[1]

We have found that on passing from hydrocarbon to chloroform solutions, monothioanthraquinone **1a**[2] undergoes photooxidation and desulfurization, with oxygen atoms introduced into those positions *peri* to the thiocarbonyl group. Thus, when exposed to light with $\lambda_{exc} > 400$ nm (DRSh-250 lamp) in aerobic conditions at room temperature, compound **1a** in chloroform solution ($c = 10^{-3}$ mol dm^{-3}) was converted during 25–30 h to anthraquinone **2a** (yield† 44%), 1-hydroxyanthraquinone **3a** (18%) and the anthradioxathiapentalene **4a**‡ (6.5%). The photolysate also contained sulfur (90%) and insignificant amounts of unidentified compounds. When the solution was exposed to sunlight or when chloroform was substituted by other solvents (acetonitrile, toluene), conversion of monothioanthraquinone **1a** proceeded in a similar way, though was more sluggish. We can suggest that the photooxidation products **3a** and **4a** were also formed in solutions of normal hydrocarbons[1] but remained undetected because of the low concentration of monothioanthraquinone **1a**.

A similar transformation has also been found for 2-methyl-10-monothioanthraquinone **1b**.§ Its photolysis in chloroform



solution gave 2-methylanthraquinone **2b** (39%), a mixture (*ca.* 1:1, 23%) of 1-hydroxy-3-methyl- and 1-hydroxy-6-methylanthraquinones **3b** and **3c**,¶ anthradioxathiapentalene **4b**‖

† Here and below, yields after chromatographic separation are given (Silufol UV-254, benzene as eluent).

‡ Compound **4a**: m.p. >230°C (decomp.), ^{1}H NMR ($CDCl_3$) δ 7.57 (dd, ^4J 1.5, ^3J 8 Hz, 2-H, 8-H), 7.87 (t, 3-H, 7-H), 7.94 (dd, 4-H, 6-H); IR (KBr) $\nu_{C=O}$/cm^{-1} 1670; UV (C_2H_5OH) λ_{max}/nm (1g ε) 205 (4.14), 242 (3.90), 334 (3.47), 385 sh (3.00), 402 sh (2.98), 530 (3.50); M_r 254.0067 (Calc. 254.0038).

§ Compound **1b** [m.p. 161–164°C, ^{1}H NMR ($CDCl_3$) δ 2.38 (s, CH_3), 7.67 (m, 3-H, 6-H, 7-H), 8.08 (m, 1-H, 8-H), 8.44 (m, 4-H, 5-H); IR (KBr) ν/cm^{-1} 1670 (C=O), 1220 (C=S); M_r 238.0455 (Calc. 254.0452)] was obtained by a standard procedure,[2] by the reaction of 2-methyl-10-diazoanthrone with sulfur in DMF in the presence of pyridine (140°C, 15 min, yield 42%). 2-Methyl-10-diazoanthrone [m.p. 144–147°C, ^{1}H NMR ($CDCl_3$) δ 2.30 (s, CH_3), 6.76–7.60 (m, 3-H, 4-H, 5-H, 6-H, 7-H), 8.00–8.43 (m, 1-H, 8-H); IR (KBr) ν/cm^{-1} 2060 (N=N), 1635 (C=O)] was obtained by treatment of 2-methylanthrone with tosyl azide in alcohol in the presence of piperidine (yield 79%).

¶ The ratio of isomers **3b** and **3c** was established by the comparison of the ^{1}H NMR spectrum of the mixture [($CDCl_3$) δ 2.42 (s, 3H), 2.52 (s, 3H), 7.07 (d, ^4J 1.5 Hz, 1H), 7.28 (dd, ^4J 1.5, ^3J 8 Hz 1H), 7.64 (m, 3H), 7.76 (m, 3H), 8.05 (d, ^4J 1.5 Hz, 1H), 8.16 (d, ^3J 8 Hz, 1H), 8.25 (m, 2H), 12.54 (s, 1H), 12.64 (s, 1H)] with the spectrum of 1-hydroxy-3-methylanthraquinone **3b**[5] [($CDCl_3$) δ 2.42 (s, CH_3), 7.05 (d, ^4J 1.5 Hz, 2-H) 7.58 (d, ^4J 1.5 Hz, 4-H), 7.75 (m, 6-H, 7-H), 8.24 (m, 5-H, 8-H), 12.51 (s, OH)], a sample of which was provided by V. V. Russkikh, and with the spectrum of 1-hydroxy-6-methylanthraquinone **3c**.[6]

‖ Compound **4b**: m.p. 218–222°C, ^{1}H NMR ($CDCl_3$) δ 2.59 (s, CH_3), 7.32 (s, 2-H), 7.54 (d, ^3J 8 Hz, 8-H), 7.72 (s, 4-H), 7.82 (t, 7-H), 7.87 (d, 6-H); IR (KBr) $\nu_{C=O}$/cm^{-1} 1670; UV ($CHCl_3$) λ_{max}/nm (1g ε) 342 (3.81), 389 sh (3.41) 410 sh (3.37), 536 (3.86); M_r 268.0188 (Calc. 268.0194).

(6%) and sulfur (81%). Formation of the hydroxy derivatives **3b** and **3c**, as well as the anthradioxathiapentalenes **4a** and **4b**, indicates that the positions being oxidized in the photolysis of monothioanthraquinones **1** are those anthraquinone positions *peri* to the thiocarbonyl (but not the carbonyl) group.

The anthraquinone derivatives have been reported in the literature to undergo photohydroxylation with participation of oxygen from the solvent or the air (see, *e.g.*, ref. 3). The photochemical formation of anthradioxathiapentalene derivatives was observed for the first time. When the photolysis of monothioanthraquinone **1a** was performed in chloroform purified from hydroxy-containing impurities (alcohol, water), no significant changes in reaction route or product yield were observed, while in ethanol monothioanthraquinone **1a** very readily underwent thermal desulfurization.[1] This may indicate that the photochemical transformation of solutions of monothioanthraquinones **1** involves oxygen dissolved in organic solvents.

The photooxidation of monothioanthraquinones **1** as well as of other thioketones,[4] begins with attack of singlet oxygen on the thiocarbonyl group. The main route of the subsequent transformation of the resulting intermediate is desulfurization, though the sterically close position of reactive α-carbons can give rise to processes which lead to oxygen-containing derivatives **3** and **4**.

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