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A REEXAMINATION OF THE ACID CATALYZED ADDITION OF ETHANETHIOL TO NAPHTHOQUINONE

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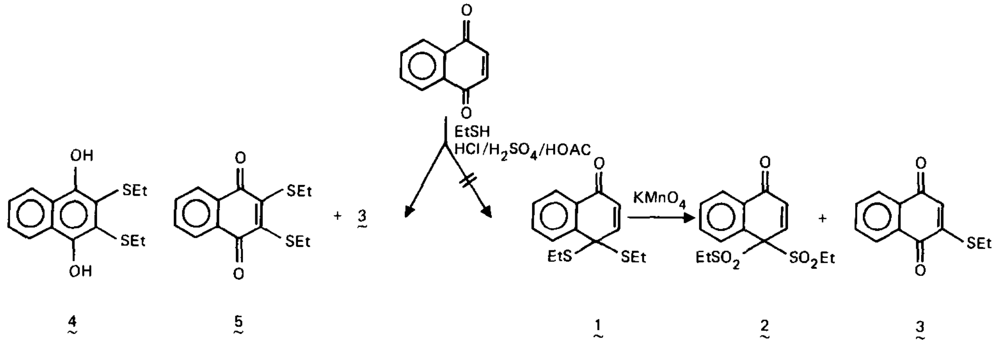
Abstract: The reaction of ethanethiol with naphthoquinone under acidic conditions has been shown to proceed by addition to the olefin, analogous to other nucleophiles, and does not yield ketal products as previously reported.

In conjunction with a review of nucleophilic additions to the carbonyl group of quinone compounds, we became interested in the 1927 report of Recsei in which some unusual addition and oxidation reactions of 1,4-benzo- and 1,4-naphthoquinones with ethanethiol were described[2]. He reported that the reaction of ethanethiol and naphthoquinone in the presence of acetic acid, dry HCl gas, and a catalytic amount of H_2SO_4 led to the formation of thioketal 1. Subsequent oxidation of 1 with permanganate resulted in the formation of the disulfone 2 and 2-thioethyl-1,4-naphthoquinone, 3. This early work of Recsei is often cited in the quinone literature,[3a,b] because it represents one of a limited number of routes to the synthetically useful quinone ketals[4] and because it suggests a course for the acid catalyzed attack of the sulfur nucleophile on the quinone nucleus which is quite different from that observed with other nucleophiles.



Snell and Weissberger[5] questioned the assignment of the disulfone structure to compound 2 based upon elemental analysis data, but these authors failed to propose an alternative. We have, therefore, reexamined the work of Recsei and describe our results in the present communications.

In a 50 ml three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a gas dispersion tube were placed 1.5g of 1,4-naphthoquinone (9.5 mmole), 15 ml of glacial acetic acid, and two drops of concentrated sulfuric acid. Dry HCl gas was introduced into the flask at room tempertaure via the dispersion tube at a rate of 3 ml/min and the addition funnel was charged with 1.4 ml of ethanethiol (19 mmole). The mercaptan was added dropwise over a period of 15 minutes and the combined reactants were allowed to stir for 30 minutes. An additional 1.4 ml of ethanethiol (19 mmole) were added dropwise, introduction of HCl gas was discontinued and the solution was allowed to stir at room temperature. Analysis by thin layer chromatography (1:9, EtOAc:Hexane) indicated that the starting material had been consumed and three products were present. The materials were isolated by chromatography on silica gel. The first compound eluted was recrystallized from hexane to a yield a solid (4, 0.40g) with the following spectroscopic properties: nmr ($CDCl_3$) δ 8.18 (m,2), 7.49 (m,2), 7.25 (s,2), 2.85 (q, J = 7Hz), 1.15 (t, J = 7Hz); ir (KBr) 3350, 1560, 1390, 1080, 880, 765 cm^{-1}; ms(70eV) m/e 280, 257, 234, 217, 189, 183. The singlet at 7.25 rapidly exchanged with D_2O. The second compound eluted was recrystallized from ethanol to give a red compound with black reflex (5, 0.45g): mp 82-83°C [lit.[6] 83-84°C]; nmr ($CDCl_3$) δ 8.00 (m,2), 7. 60 (m,2), 3.3 (q, J = 8Hz), 1.34 (t, J = 8Hz); ir (KBr) 1645, 1590, 1480, 1275, 1140, 700 cm^{-1}; ms (70eV) m/e 278, 249, 216. The final compound eluted was recrystallized from $CHCl_3$ to give a yellow solid (3, 1.05g): mp 141-142°C [lit.[6] 142-143°C]; nmr ($CDCl_3$) δ 7.90 (m,4), 6.55 (s,1), 2.85 (q, J = 8Hz), 1.45 (t, J = 8Hz); ir (KBr) 1665, 1640, 1335, 865, 775, 695, 610 cm^{-1}; ms (70eV) m/e 218, 189, 89, 76.

These data are consistent with the reaction sequence indicated in which the acid catalyzed addition of ethanethiol yields a mixture of 1,4- dihydroxy-2,3-dithioethylnaphthalene (4), 2,3-dithioethyl-1,4-naphthoquinone (5) and 2-thioethyl-1,4-naphthoquinone (3). Confirmation of these assignments was obtained by the independent synthesis of 4[7] which was reduced with zinc and acetic acid to give 3. Oxidation of the crude naphthoquinone/ethanethiol/acid reaction mixture as described by Recsei[2] using potassium permanganate gave only compounds 4 and 5 in 35% and 50% yield, respectively. No evidence for sulfone containing products was obtained. It appears that our compound 5 is the material previously described as the disulfone 2.[2]

The reaction of 1,4-benzoquinone and ethanethiol under the previously described conditions gave a complicated mixture of products which we have not succesfully identified. By analogy to the above results, we propose that the products are the mono- and poly-thioethyl derivatives of 1,4-benzoquinone. This mixture did not appear to change on permanganate oxidation.

It has thus been established that under acidic conditions ethanethiol adds to naphthoquinone in a manner analogous to that of other nucleophiles such as alcohols[8], phosphines[9] and amines[10] and does not yield ketal products as previously reported[2].

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