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Oxidation of 2-Methylnaphthalene with Ozone

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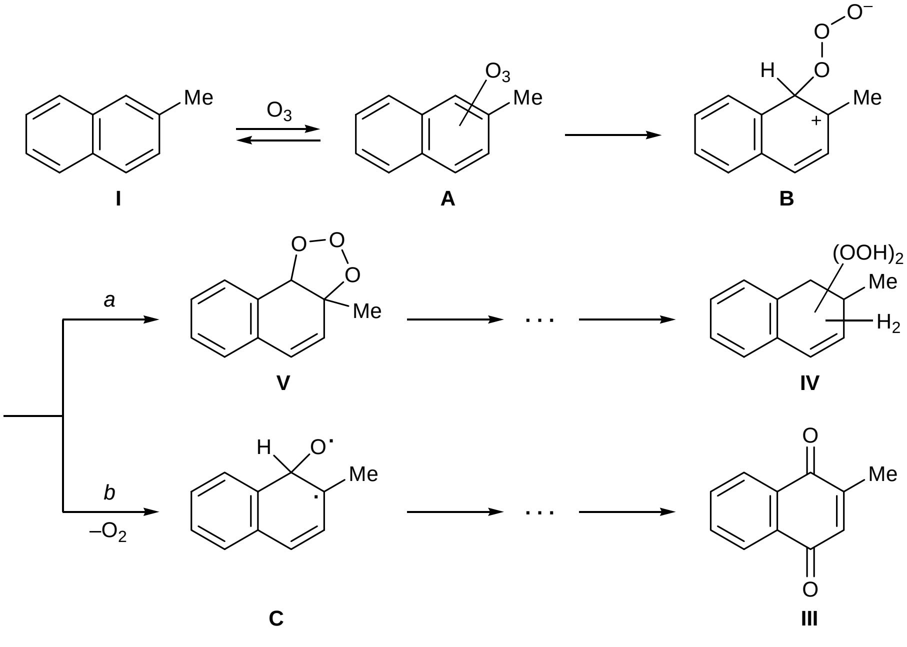
Abstract—In the oxidation of 2-methylnaphthalene with ozone in acetic acid, the oxidant reacts mainly at the double bonds of the substituted aromatic ring to give peroxy compounds. In the presence of cobalt diacetate and sodium bromide, oxidation of the 2-methyl group occurs with formation of 2-naphthoic acid. The major product in the oxidation of 2-methylnaphthalene with ozonated transition metal compounds is 2-methyl-1,4-naphthoquinone.

The reaction of ozone with 2-methylnaphthalene (**I**) attracts interest from the viewpoint of development of selective procedures for the synthesis of 2-naphthoic acid (**II**) and 2-methyl-1,4-naphthoquinone (**III**). However, published data on this reaction are few in number: In 1957, Bailey and Garsia-Sharp [1] showed that ozonation of 2-methylnaphthalene (**I**) occurs at the methyl-substituted ring with rupture of the aromatic system.

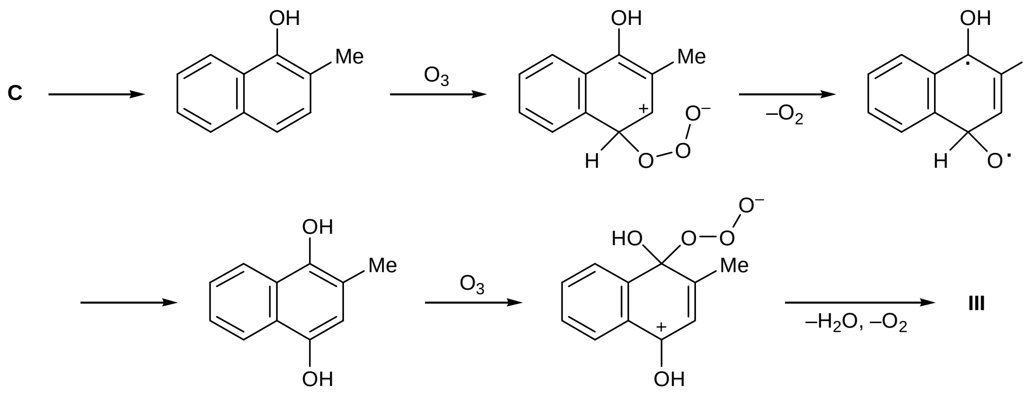
We have found that the reaction of 2-methylnaphthalene (**I**) with ozone, depending on the conditions, may result not only in rupture of the aromatic system but also in formation of 2-naphthoic acid (**II**) or quinone (**III**). The major products of the oxidation of **I** in acetic acid are hydroperoxides **IV** (84%); also, unidentified tarry compounds and small amounts of acid **II** (2%) and quinone **III** (1.5%) are formed. The reaction follows the first-order kinetics with respect to the reactants, in keeping with the radical ion mechanism. The oxidation of 1 mol of **I** requires 1.86 mol of ozone [2]. Hydroperoxides **IV** are stable to the action of ozone; they react with potassium iodide with liberation of iodine in an amount equivalent to two hydroperoxy groups per molecule.

The above stated is consistent with the modern views on the mechanism of ozonation of aromatic

Scheme 1.



Scheme 2.



compounds [3, 4]. In the first stage, ozone reacts with the substituted aromatic ring in **I** to give π-complex **A**; charge transfer in the latter leads to formation of σ-complex **B** whose further transformations can follow two pathways. The first pathway (*a*) leads to ozonide **V** and then to hydroperoxides **IV**. According to pathway *b*, dissociation of the O–O bond in **B** gives structure **C** which is then converted into quinone **III** (Scheme 1). Presumably, the transformation of **V** into hydroperoxides **IV** follows the scheme proposed in [1] for the ozonation of **I** in aqueous methanol .

The mechanism of formation of naphthoquinones was not described previously; it is now in the development stage. Quinone **III** is presumed to be formed according to the scheme proposed in [5] for the oxidation of anthracene to anthraquinone (Scheme 2).

Scheme 3 [6] illustrates the formation of 2-naphthoic acid (**II**).

Scheme 3.

$$ArCH_3 + O_3 \longrightarrow ArCH_2^{\bullet} + HO^{\bullet} + O_2$$

$$ArCH_2^{\bullet} + O_2 \longrightarrow ArCH_2O_2^{\bullet}$$

$$2\,ArCH_2O_2^{\bullet} \longrightarrow \text{Products}$$

The selectivity of oxidation of the methyl group increases in the presence of cobalt bromide catalyst. At 373 K and a catalyst concentration of 0.015 M, the yield of acid **II** rises from 2 to 90%. In this case, no destructive oxidation of the aromatic system occurs since ozone reacts with the reduced form of the catalyst, Co(II)Br$^-$. The reactive catalytic species Co(II)Br$^{\bullet}$ is then reduced via oxidation of the methyl group in the substrate [7, 8] (Scheme 4).

Scheme 4.

$$\text{Co(II)Br}^- + O_3 + H^+ \longrightarrow \text{Co(II)Br}^{\bullet} + HO^{\bullet} + O_2$$

$$ArCH_3 + \text{Co(II)Br}^{\bullet} \longrightarrow ArCH_2^{\bullet} + \text{Co(II)Br}^- + H^+$$

The above data show that, under conditions of noncatalytic and catalytic ozonation, the main products in the oxidation of arene **I** may be either hydroperoxides **IV** or napththoic acid **II**. Quinone **III** cannot be obtained by these reactions. We previously [9] proposed a procedure for the synthesis of quinone **III**, which involves initial ozonation of a mixture of Cr(III) and Mn(II) salts according to Scheme 5.

Scheme 5.

$$\text{Mn(II)} + O_3 + H^+ \longrightarrow \text{Mn(III)} + HO^{\bullet} + O_2$$

$$\text{Cr(III)} + 3\,\text{Mn(III)}^{\bullet} \longrightarrow \text{Cr(VI)} + 3\,\text{Mn(II)}$$

In the second step, 2-methylnaphthalene (**I**) is oxidized with the resulting ozonated chromium(VI) and manganese(III) compounds. 2-Methyl-1,4-napththoquinone (**III**) is thus obtained in 70% yield.

EXPERIMENTAL

The ozonation process was studied in a catalytic reactor maintained at a constant temperature. The reaction was carried out in the kinetic mode (the reactor was shaken at a frequency of 7 s^{-1}) [10]. The concentrations of 2-methylnaphthalene (**I**) and 2-methyl-1,4-naphthoquinone (**III**) were determined by gas–liquid chromatography on an LKhM-80 instrument equipped with a flame ionization detector and a 2-m column packed with 5 wt % of PNFS-6 on Chromaton N-AW; injector temperature 250°C, oven temperature 160°C. The concentration of hydroperoxides **IV** was determined by iodometric titration, and naphthoic acid **II** was quantitated by potentiometric titration in acetone.

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