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Preparation and Photoisomerization of 2-Formylcinnamaldehyde in Solution

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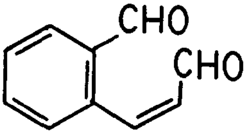
Abstract Naphthalene, in dilute aqueous solution, reacts with ozone to form one or both isomers of 2-formylcinnamaldehyde; an equilibrium mixture of the isomers also results upon irradiation of the E-isomer with long wavelength ultraviolet light.

The ozonolysis of naphthalene in organic solvents has been studied extensively; in water, fewer investigations have been reported. Owing to the frequent occurrence of naphthalene and its derivatives in polluted waters, we undertook an investigation of its reactions with ozone in buffered aqueous solution. Previous work has shown that the major non-peroxidic products, in both aqueous and non-aqueous solvents, are o-phthaldehyde, phthaldehydic acid, and phthalic acid.[1,2] Intermediate products have been postulated. We report here on the formation and properties of 2-formylcinnamaldehyde, the first stable product of ozonolytic ring cleavage of naphthalene in aqueous solution.

2-Formylcinnamaldehyde (1, double-bond stereochemistry unspecified) was first observed, along with many other oxygenated products, in the ozonolysis of kerosene in heterogeneous, aqueous-buffered systems. In order to characterize the products further, individual constituents of kerosene were ozonized. When naphthalene, dissolved in water (ca. 1 x 10^{-4} M), was treated with one or more equivalents of ozone at pH 5 (acetate buffer), two major products were observed. These products were two closely related isomers separable by capillary gas chromatography. The mass spectra were nearly identical, having major ions at m/z 77, 103, and 131 with relative intensities of 25%, 20%, and 100%, respectively. When a moderate excess (200-300% of theoretical) of ozone was used, or when the product mixture was allowed to stand for several hours in room light before analysis, the later-eluting isomer was the major product. Otherwise, the earlier-eluting isomer predominated. A very small molecular ion peak



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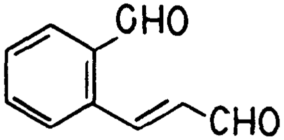
was observed at m/z 160; this corresponds to $C_{10}H_8O_2$, or formally an introduction of two oxygen atoms into naphthalene. A logical structure for one of the isomers is the Z-isomer 1. The literature does not appear to contain reference to 1 as an identified product of naphthalene ozonolysis in solution, although it has been hypothesized as an intermediate.[1,2] Recently, Zadok et al. isolated 1 and its E-isomer 2 as products of the reaction of florisil-supported naphthalene with vapor-phase ozone molecules generated by microwave discharge.[3]



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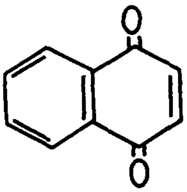
The E-isomer (2) has also been synthesized by a different pathway,[4] and the mass spectrum of this material was virtually identical to those of our compounds. When naphthalene was ozonized in a preparative-scale experiment in aqueous acetone, the isomer which was isolated (silica gel column chromatography) had the same gas chromatographic retention time and mass spectrum as the later-eluting isomer; its NMR spectrum showed one-proton olefinic hydrogen signals at 6.70 and 8.60 ppm downfield from tetramethylsilane with the expected coupling constant (J = 16 hz) for E-protons. Accordingly, we assign structure 2 to this material, and 1 to the earlier-eluting isomer. The proton NMR spectrum for 2 nicely complements that recently reported for 1.[3] Other physical and spectroscopic properties of the later-eluting material were consistent with its proposed structure, 2.

When the ozonolysis of naphthalene was run at pH 9, only one of the two isomers of the dialdehyde product (apparently 2, based on its retention time) was observed, but in addition 1,4-naphthoquinone (3) was positively identified and phthalic acid was tentatively identified. The formation of 3 is probably due to 1,4-addition of ozone to naphthalene.[3]



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Several minor oxidized products could not be conclusively identified. The preferential formation of 2 at higher pH may be explained by competing reactions of the zwitterionic, ring-opened intermediate 4 (Figure 1). Protonation, which should be faster at low pH, would afford intermediate 5; this species could undergo direct nucleophilic attack by water on the hydroxyl oxygen, with the products being the Z-isomer 1 and hydrogen peroxide. At higher pH, protonation of 4 may be slow relative to its tautomerization to the benzylic carbocation 6, capable of free rotation. Reconversion of this cation to the styryl form would lead to a mixture of Z- and E-isomers, but the E-isomer may be more thermodynamically stable and lead preferentially to the E-dialdehyde 2.

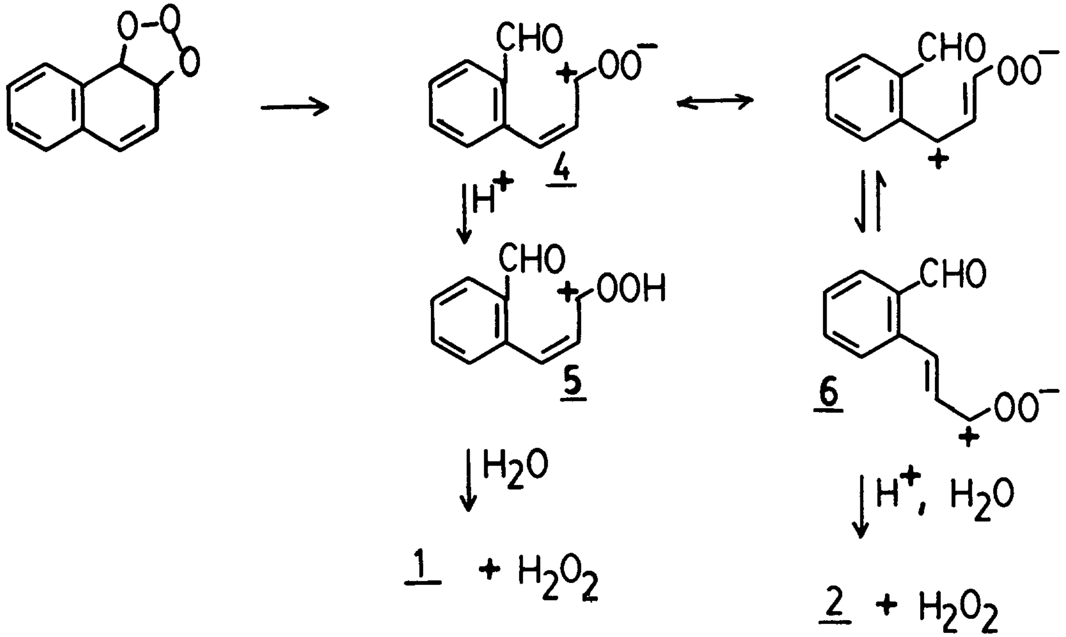

Figure 1

Substituted styrenes are well known to undergo direct Z-E photoisomerization reactions to give equilibrium mixtures. A methylene chloride solution of the E-isomer, when exposed to Pyrex-filtered UV from a medium-pressure mercury arc, showed a decrease in the concentration of the E-isomer, and the appearance of comparable quantities of the earlier-eluting Z-isomer. Olefins also undergo sensitized Z-E photoisomerizations, and since naphthalene is a good photosensitizer with strong absorptions in the solar UV, it is possible that it could promote the isomerization of its ozonolysis products.[5]

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