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PHOTO-OXIDATION OF BENZENE IN AQUEOUS SOLUTION

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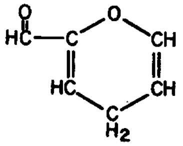
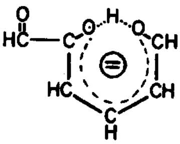
A novel, acidic photo-oxidation product of benzene has been obtained, for which tentatively the structure: α-formyl-γ-pyrane (I) is proposed.


I


II

Preparation: An aerated solution of benzene in water (5 l, pH = 5, 1 M phosphate buffer*) was irradiated by a submerged Philips TUV 30 W low-pressure mercury lamp, while being cooled with water. A circulating benzene phase extracted I from the irradiated aqueous solution and transferred it to 2 N aqueous sodium hydroxide (150 ml).

Percolation with ether of the alkaline extract at pH = 11 removed phenol (1,2) and neutral contaminants; subsequent percolation at pH = 8 afforded I in dilute ethereal solution, the residue of which upon repeated high-vacuum sublimation yielded I in the form of colourless needles, which melted at -25 °C while decomposing. Although I is formed with a spectrophotometrically estimated quantum yield of 5-10%, only 100-150 mg could be isolated after 24 hours of irradiation - i.e. about 0.1% overall quantum yield.

The properties of I determined so far are given below. It should be emphasized, however, that the solutions decompose rapidly** which was very troublesome, especially in the NMR and IR analyses.

UV absorption spectra. Besides end absorption below 2200 Å (0.1 mmol/l) one sharp band prevails: In water at pH ≤7, λ_{max} = 2940 Å (ε = 12,500), extractable with organic solvents (e.g. cyclohexane, λ_{max} = 2900 Å); at pH > 12 λ_{max} = 3080 Å (ε = 25,000), not extractable. Similar pH-dependent UV spectra were obtained upon irradiation of oxygenated 1 : 1 aqueous-ethanolic solutions of toluene, o- and m-xylene, tert-butylbenzene, chlorobenzene and diphenyloxide.

NMR and IR spectra indicate the absence of carboxylic acid and of hydroxyl groups. The following NMR signals may be attributed to I (CCl_4 solution, δ in ppm relative to TMS, all single lines): 9.4 ppm (relative intensity 1): one aldehydic proton; 7.3 (1) and 6.7 (2): 3 olefinic protons; 3.4 (2): 2 allylic protons (Cf. furane: 7.5 and 6.5 ppm, furfural: 9.5, 7.5 and 6.4 ppm (ref. 3); γ-pyrane 6.7, 4.6 and 2.7 ppm (ref. 4)).

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* Buffering at this pH enhances the rate of extraction of I, without unduly inhibiting its formation which occurs in the pH range 4-8, with an optimum at pH = 7.

** Product I was found to be relatively stable only in very dilute solutions (in perfectly dry ether and in aqueous alkali) and in the form of the dry salts (see below).

In the IR-spectrum, bands at 1670, 2715 and 2810 cm^{-1} confirm the presence of a conjugated aldehyde group; strong bands at 1191 and 1000 cm^{-1} suggest a divinyl ether group.

Sodium and barium salts of I could be obtained from their rapidly discolouring concentrated solutions in absolute ethanol by precipitation with dry ether. The colourless salts, relatively stable under dry nitrogen, decompose violently without melting at about 120 °C. Their elemental compositions suggest that these salts are derived from a dibasic acid $C_6H_8O_3$ and retain one molecule of ethanol:

Sodium salt $C_6H_6O_3Na_2 \cdot C_2H_5OH$; found (theor. for $C_8H_{12}O_4Na_2$): C 43.2% (44.0); H 5.2% (5.5); O 31 ± 3% (29.5); Na 24 ± 3% (21.2). According to an X-ray powder diagram no sodium carbonate, hydroxide or ethoxide was present. NMR spectrum (D_2O, 0.5 N in NaOH): Signals at 8.4 ppm (relative intensity 1) and at 6.2-6.5 (4, 3 lines) are attributed to the ionic form II of I; furthermore there is a sharp, intense signal at 4.9 ppm (HOD).

Barium salt; found (theor. for $C_8H_{12}O_4Ba$): C 33.0% (31.2); H 3.9% (3.9); O 19.7% (20.7); Ba 45.0% (44.5).

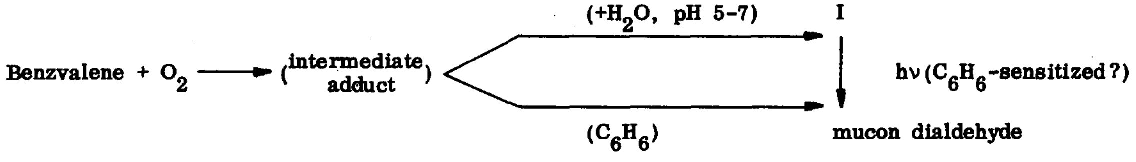
The above properties distinguish I from mucon dialdehyde (5), known as a benzene photo-oxidation product (1,2,6), as also from the weak monobasic acid cyclopentadienyl aldehyde (7). Composition and NMR spectra of the salts suggest that salt formation by I involves abstraction of an (allylic) proton and addition of a hydroxide ion. Formation of a resonance-stabilized dianion by ring opening may be represented by II.

Chemical properties. Spectrophotometry revealed that I reacts with aldehyde reagents such as dimedone and semicarbazide hydrochloride, but no stable products could be isolated. Adduct formation with sodium bisulphite occurs, and was found to be partly reverted by the addition of strong mineral acid. Nearly all attempts to reduce I failed or gave unstable products. Sodium borohydride in a neutral aqueous solution, surprisingly, gave fulvene, identified by its characteristic UV absorption spectrum (8), in a high yield (about 70%).

Mechanistic considerations. Its highly characteristic pH-dependent UV absorption spectrum allows of a sensitive and unambiguous detection of traces of the unstable product I. These absorption spectra were also observed upon addition in the dark of oxygen-saturated ice-water to previously irradiated oxygen-free solutions of benzene in methanol and isopropanol. Hence a metastable, oxidizable photo-isomer of benzene is probably involved as an intermediate. Such an isomer, viz. benzvalene has been isolated in neutral systems, which with acid formed derivatives of bicyclo[3.1.0]hex-2-ene (11). Furthermore, in acidic aqueous solution photo-addition of water to benzene (12) was found to prevail over photo-oxidation to I as well as to mucon dialdehyde (2). This strongly suggests that both photo-oxidation of aqueous benzene to I and acid-catalysed photo-addition of water yielding 4-exo-hydroxy-bicyclo[3.1.0]hex-2-ene (12) proceed via the same metastable intermediate, viz. benzvalene.

Possibly, a relation exists between formation of I, and of mucon dialdehyde (1,2,6), since both are formed photochemically in aqueous oxygenated benzene solution in the same pH range (Cf. 2). Analogous ring openings of other pyrane derivatives (9,10), suggest that the conversion of α-formyl-γ-pyrane (I) into mucon dialdehyde is feasible. The primary formation of mucon dialdehyde, followed by its conversion to I seems less likely, since prolonged irradiation yields more mucon dialdehyde, whereas I can only be obtained in quantity when it is extracted as soon as it is formed.

It should be noted that formation of I requires the presence of water at pH 5 to 7; in the absence of water, mucon dialdehyde seems to be formed directly (6). This may indicate that benzvalene and oxygen form an intermediate adduct, which in the presence of water at pH 5 to 7 undergoes a proton shift to give I, whereas in the absence of water the intermediate adduct rearranges to mucon dialdehyde. Further irradiation of I in aqueous solution, perhaps photosensitized by benzene, could give mucon dialdehyde by photochemical ring opening (Cf. 9,10).



The high reactivity of the intermediate, assumedly benzvalene, towards oxygen, may be surprising in view of the fact that formation of products in singlet ground state (I as well as mucon dialdehyde) would be both spin- and symmetry-forbidden. Thus, intermediate steps must be involved in which both spin and symmetry restrictions are circumvented. It should be borne in mind that the stability of the highly strained benzvalene with respect to conversion to benzene, owing to the forbiddenness of the latter conversion, implies a relatively low-lying, unoccupied level in benzvalene. Thus, interaction with oxygen may conceivably give a relatively stable, triplet-state intermediate adduct, which subsequently converts to ground state I or mucon dialdehyde. This would obtain, regardless of whether the intermediate adduct would be a triplet biradical, an insertion product of oxygen into a carbon-carbon or into a carbon-hydrogen bond.

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