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1,2-SHIFT IN THE ANODIC OXIDATION OF AROMATIC COMPOUNDS

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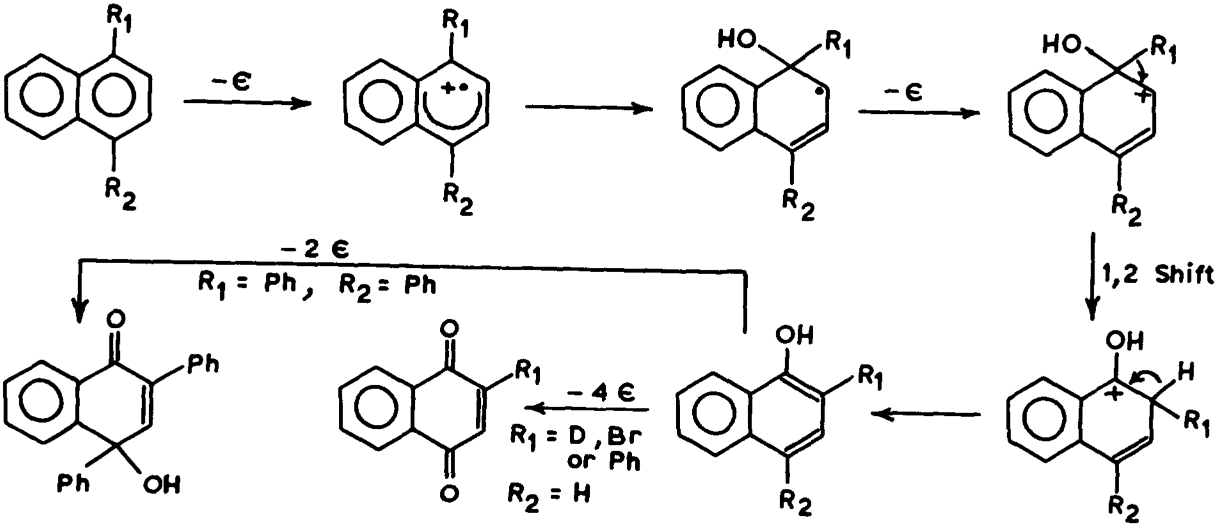
Abstract: The 1,2-shift observed during oxidation of organic substrates can arise by involvement of cation radicals.

Anodic oxidation of aromatic hydrocarbons, like naphthalene have been reported on an electrode consisting of a mixture of naphthalene and carbon pressed into platinum gauze matrix in 1% aqueous sulphuric acid[1]. The product in the case of naphthalene are 1,4-naphthoquinone and other condensed quinones. It has been postulated that 1-naphthol is a necessary intermediate[1].

Involvement of cation radicals in the anodic oxidation of aromatic compounds is a well accepted tenet of electro organic chemistry[2]. To test whether cation radical involvement results in a 1,2-shift[3], mechanistically distinct, but phenomenologically similar to the well known NIH shift[4,5,6], we have examined the oxidation of some 1-substituted naphthalene derivatives (Table 1). It can be seen that in all the compounds studied, a 1,2-shift, is observed which may be a general feature of ion radical involvement and can be visualised by the mechanism shown in Scheme 1.

These experiments clearly demonstrate that the 1,2-shift observed in aromatic hydroxylations are not necessarily diagnostic of the intermediacy of arene oxide[5,6].



SCHEME 1

Table I: Anodic Oxidation of Naphthalene and its Derivatives.

Substrate[a]	Reaction conditions[b] (hr)	(°C)	Product[c]	Yield[d] (%)	mp. (°C)	Lit.mp (°C)
Naphthalene	2	25	1,4-Naphthoquinone	20	123-125	123-125[7]
1-Bromonaphthalene	4	25	4-Bromo, 1,2-naphthoquinone	9	152-153	154[8]
			2-Bromo, 1,4-naphthoquinone	7	131	130-131[9]
			1,4-naphthoquinone	6	124	123-125[7]
1-Phenylnaphthalene	2	50	2-phenyl, 1,4-naphthoquinone	7	111	111-112[6]
			5-phenyl, 1,4-naphthoquinone	5	168-169	169-170[11]
1,4-Diphenyl naphthalene	2	50	4-Hydroxy, 2,4-diphenyl 1(4H)-naphthalene	10	152-153	152-153[12]

(a) 2 m mol of organic substrates were used. (b) Electrolysis was carried out in a beaker, containing the organic substrate dissolved in dimethylformamide (DMF) and IM sulphuric acid (50:50) mixture, fitted with platinum wire gauze anode and graphite carbon cathode. The power source for the electrolysis is Aplab LVA 50/2. The current was kept constant at 1 ampere during electrolysis. (c) The products were isolated by preparative TLC over silicagel (benzene) and identified by comparison with authentic samples (mp, IR and NMR). (d) Yields of the products were based on the unrecovered starting materials. The other products were dark in colour and polymeric in nature. (e) 1,4-Dideuterionaphthalene gave deuterated 1,4-naphthoquinones, which contained 2-deuterio 1,4-naphthoquinone; NMR,δ: quinonoid hydrogens = 2:1·5 (should be 1:1 if there is no deuterium in the quinonoid positions), Mass. M$^+$ peaks m/e 158, 159 and 160.

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