

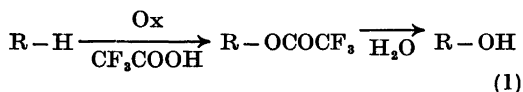
## Anodic Synthesis of Fluorinated Quinones\*

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Anodic oxidation of hexafluorobenzene and octafluoronaphthalene in trifluoroacetic acid yields after hydrolysis of the initial products tetrafluorobenzoquinone and hexafluoronaphthoquinone in 75 % and 60 % yields, respectively. An attempt to isolate octafluorobiphenylquinone after anodic oxidation of decafluorobiphenyl failed.

In recent years trifluoroacetic acid has found increased use as a solvent in anodic oxidation studies. In particular the study of anodically generated radical cations has been extended greatly due to the enhanced stability of these species in trifluoroacetic acid.<sup>2</sup> Besides the stabilizing effect on radical cations, trifluoroacetic acid has the advantage of a high anodic discharge potential, about 2.4 V *vs.* SCE.<sup>3</sup> It is therefore possible to oxidize aliphatic hydrocarbons in trifluoroacetic acid, the products being alkyl trifluoroacetates.<sup>4-7</sup> Furthermore, benzene and deactivated benzenes are oxidized in trifluoroacetic acid yielding phenols after hydrolysis [eqn. (1)].<sup>8-11</sup>



R = alkyl or aryl

In a recent communication we described an unusual anodic displacement reaction.<sup>12</sup> When 2- or 4-fluoroanisole was oxidized in acetic acid containing sodium acetate, 2- and 4-acetoxyanisole, respectively, were the reaction products.

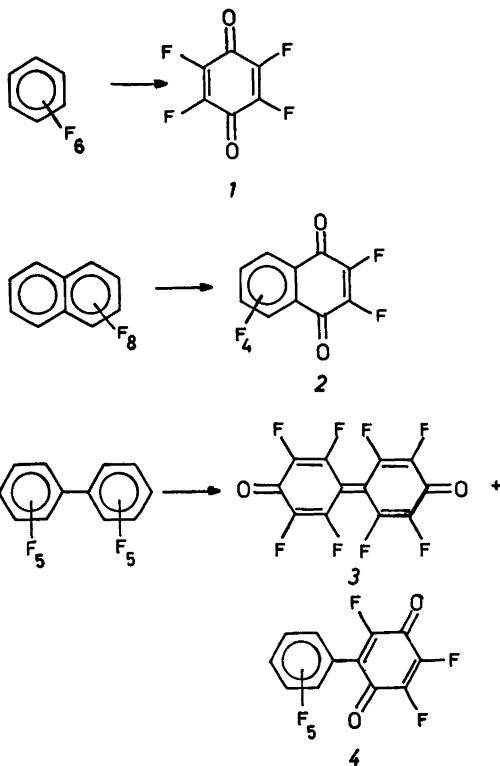
\* Cf. Ref. 1.

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Since neither 4-fluorotoluene nor fluorobenzene gave any products resulting from displacement of fluorine on anodic oxidation in the same medium, we undertook a study of the anodic oxidation of polyfluorinated arenes. As these compounds only contain fluorine substituents displacement of fluorine or addition to the aromatic rings would be the probable reaction paths. Voltammetric data in fluorosulfonic acid have been reported for some polyfluorinated arenes.<sup>13</sup> In this medium stable radical cation were produced. In our study trifluoroacetic acid containing potassium trifluoroacetate was used as an electrolyte.

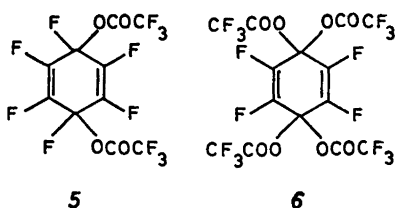
### RESULTS

Anodic oxidation was carried out at a platinum electrode in trifluoroacetic acid with potassium trifluoroacetate as the supporting electrolyte. Trifluoroacetic anhydride was added in order to remove residual water, thereby avoiding hydrolysis of the products during the electrolysis. The polyfluorinated arene was added and electrolysis was carried out until 3 F/mol of substrate had been passed. Hexafluorobenzene gave tetrafluorobenzoquinone, 1, in 75 % yield. Hexafluoronaphthoquinone, 2, was obtained in 60 % yield from the oxidation of octafluoronaphthalene. When we tried to produce the fluorinated biphenylquinone, 3, by oxidation of decafluorobiphenyl, we did not obtain reproducible results. The <sup>19</sup>F NMR spectrum of the product was complex and not in agreement with 3 as the sole product. On the other hand, we observed an MS fragment with *m/e* 136 which can be explained on the basis of 3 (see Experimental). Our failure to



obtain a single product might be due in part to an unselective oxidation yielding a mixture of 3 and 4. The latter has been obtained by nitric acid oxidation of decafluorobiphenyl.<sup>14</sup> However, since one might assume that 3 is a very powerful oxidant, it is possible that it does not survive the work-up procedure completely. Unsubstituted diphenylquinone is known to be almost as powerful an oxidant as DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) and the fluorinated analogue (3) should be even stronger.<sup>15</sup>

Our synthetic procedure compares favourably with those previously reported. Thus, 1 has been prepared by passing tetrachlorobenzoquinone over potassium fluoride at elevated



temperature,<sup>16,17</sup> and 2 has been obtained by nitric acid oxidation of octafluoronaphthalene.<sup>18</sup> Halogenated quinones are known to be useful reagents in organic synthesis<sup>15,19</sup> and acceptors in charge-transfer complexes.<sup>20</sup>

We have not made any investigation into the mechanism of the reaction leading to the quinones. However, we may assume that intermediates such as 5 and/or 6 are formed, since the quinones are not formed until water is added to the electrolysis solution.

## EXPERIMENTAL

**Experimental.** The electrolysis cell consisted of a 20 ml water-jacketed, flat-bottomed, glass cylinder equipped with a four-neck flat flange lid, a platinum foil anode (area 6 m<sup>2</sup>), a platinum wire cathode, a drying tube and a magnetic stirring bar. The electrodes were connected to a constant current power supply (Radiak 60 V/2 A). Anodic oxidation was carried out in trifluoroacetic acid (10 ml) containing potassium trifluoroacetate (1 M), trifluoroacetic anhydride (0.5 ml), and the substrate (5 mmol) at a constant current of 100 mA until 3 F/mol of substrate had been passed. The reaction mixture was then poured into 50 % nitric acid (200 ml). The resulting mixture was extracted with dichloromethane (5 × 50 ml). The dichloromethane phases were washed with water and dried over anhydrous sodium sulfate (the work-up procedure should be carried out rapidly in order to avoid oxidation of water by the quinone). After filtration and evaporation *in vacuo* a coloured residue was obtained. Upon addition of pentane the quinone precipitated and was filtered off.

**Tetrafluorobenzoquinone, 1.** Yield 680 mg (75 %), m.p. 174–179 °C (lit.<sup>16</sup> m.p. 179 °C), MS (IP 70 eV; *m/e* (% rel. int.)): 180 (100, M), 124 (100, M–2 CO), 62 (40). <sup>19</sup>F NMR (94 MHz, CDCl<sub>3</sub>, trifluoroacetic acid as reference): δ –70.15.

**Hexafluoronaphthoquinone, 2.** Yield 800 mg (60 %), m.p. 264–269 °C (lit.<sup>18</sup> m.p. 273.5–274.5 °C). MS: 266 (96, M), 238 (50, M–CO), 210 (100, M–2 CO), 148 (27), 62 (5). <sup>19</sup>F NMR: δ –61.1 (s), –59.1 (m), –65.7 (m).

The product from the oxidation of decafluorobiphenyl gave the following MS data: 328 (61, M), 300 (71, M–CO), 272 (100, M–2 CO), 136 (14). Structures 3 and 4 cannot be distinguished on the basis of the first three mass numbers, these being analogous to those obtained from 2. However, the *m/e* 136 could in our opinion be ascribed to structure 3.

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