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Photochemistry of *o*-Fluoranil

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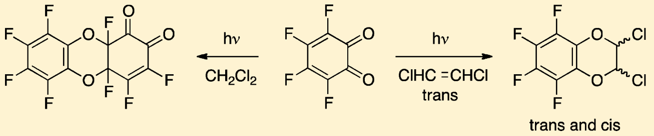
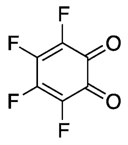
Supporting Information

ABSTRACT: Initial exploration of the photochemical behavior of *o*-fluoranil has revealed dimer formation, cycloaddition to alkenes, and hydrogen abstraction from hydrocarbons, aldehydes, and ethers.



INTRODUCTION

Thermal chemistry of *o*-fluoranil (tetrafluoro-*o*-benzoquinone, **1**) has been described in several publications,[1−4] but this account represents the first foray into its photochemistry. Benzoquinones in general undergo photodimerization, cycloadditions to alkenes and alkynes, and hydrogen abstraction reactions.[5] These transformations of *o*-chloranil (**2**), *o*-fluoranil's closest relative, have been well studied. Not surprisingly, the photochemistry of the fluoroquinone has been found to display strong similarities to that of its much better known chloro counterpart.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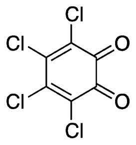
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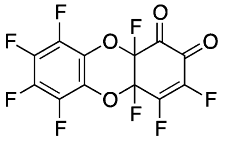
RESULTS AND DISCUSSION

The lowest singlet excited state of both *o*-quinones is n, π*, with the maximum of the first π, π* state lying at considerably shorter wavelengths (Table 1). However, the latter transition is far more intense than the former, and its broad band partially overlaps the n → π* band in the case of both quinones.[8] Thus, the π→ π* 0−0 transition energy is not far greater than that of the corresponding n→ π* transition. Since the singlet−triplet gap is typically much larger for π, π* than for n, π* states,[9a] it is not certain a priori which triplet lies lower.

Following UV/visible excitation of *o*-fluoranil, very rapid internal conversion should ensure efficient population of the n, π* singlet state. Intersystem crossing would lead to the n, π* triplet state, which would quickly undergo internal conversion to the π, π* triplet if that should lie lower in energy. Because intersystem crossing in n, π* singlet states is typically as slow or slower than diffusional rates,[9b] photoreactions could originate from this state. Thus, three states, two n, π*, and one π, π*, are candidates for the reacting species responsible for most of the quinone's photoreactions. Evidence relating to the choice among them is discussed below.

When a solution of *o*-fluoranil in methylene chloride is irradiated through Pyrex with a medium pressure mercury arc ($\lambda > 280$ nm), it undergoes cycloaddition to give the dioxene-containing dimer **3**. This α-diketone hydrates voraciously, and is isolated as its hydrate **4**. Treatment with P_2O_5 is necessary to obtain the free dimer. To confirm its structure, the dimer was derivatized as quinoxaline **5** by condensation with *o*-phenylenediamine. *o*-Chloranil (**2**) also photodimerizes, yielding a structure analogous to **3**.[6] Surprisingly, *o*-fluoranil's tendency to photodimerize is so great that a substantial amount of dimer is often formed even in the presence of a very large excess of a trapping agent for the excited state. This suggested that the excited state might be nucleophilic, as the site(s) that are attacked in the ground state molecule are strongly electrophilic. Representations of the n orbital (the NHOMO) and the π-type HOMO and LUMO of *o*-fluoranil are shown in Figure 1. In the n, π* state, an electron belonging primarily to oxygen has been delocalized over the molecule, leaving the oxygens relatively electron deficient. However, in the π, π* state the oxygens have gained electron density, as a π electron has been promoted into an orbital with a larger coefficient at oxygen. These considerations suggested that the attacking species might be the π, π* state, but see below.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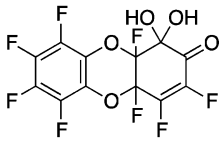
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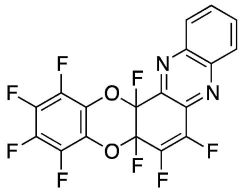
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Irradiation of a solution of *o*-fluoranil in vinyl acetate gives dioxene **6**, and the isomeric dioxene **7** is obtained similarly from methyl acrylate (Scheme 1). Formation of the dioxenes complements the thermal reactions of the quinone with these

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Table 1. Electronic Spectra of *o*-Fluoranil and *o*-Chloranil

compd	solvent	λ_{max} (π, π^*) (nm)	ε_{max} (1 mol^{-1} cm^{-1})	λ_{max} (n, π^*) (nm)	ε_{max} (1 mol^{-1} cm^{-1})
o-fluoranil	CCl_4	407	1080	547.5 (510 sh)[a]	18 (25 sh)
o-chloranil[6]	CCl_4	445	1900	537	55

[a] Both maximum and shoulder are ascribed to the same n,π^* state because transition from the lower lying antisymmetric n orbital (B_1) is symmetry forbidden. CIS calculations also find a single n → π^* transition (B3LYP/6-311 G**+).[7]

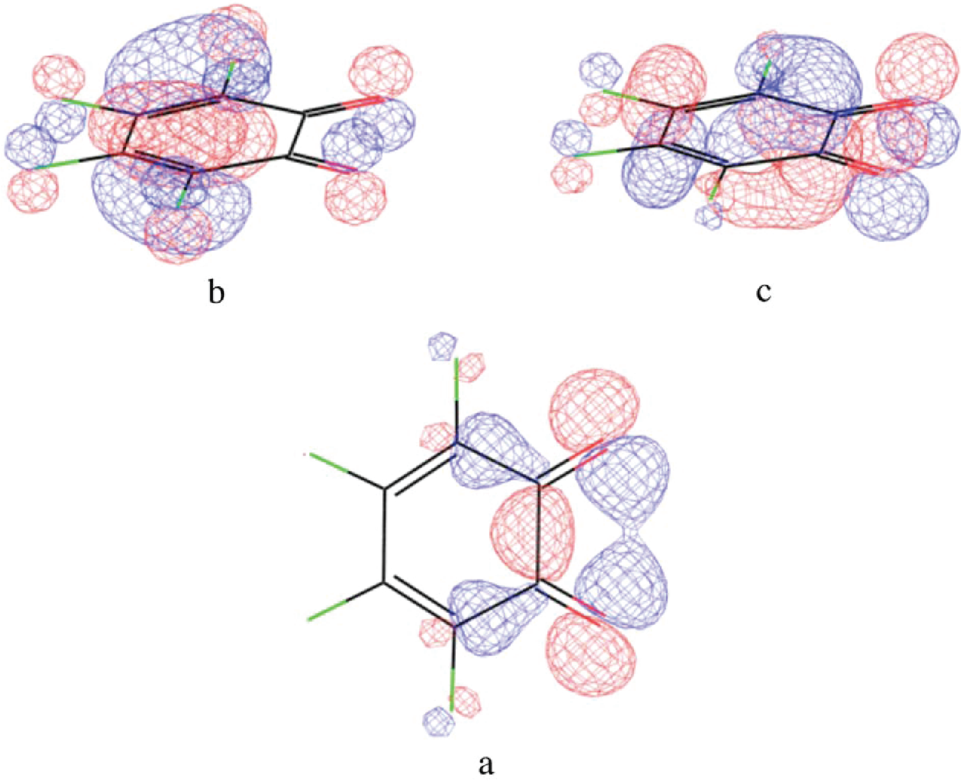
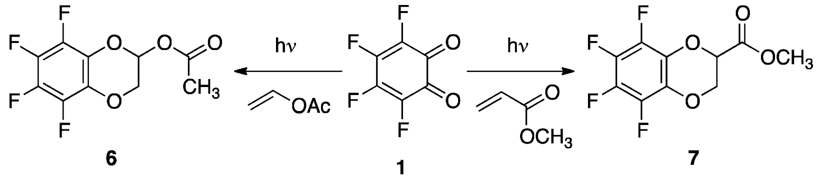
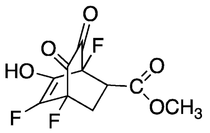


Figure 1. *o*-Fluoranil molecular orbitals: (a) n, (b) π, (c) π^* at the B3LYP/6-311G**+ level of theory.[7]

Scheme 1



alkenes, which afford Diels–Alder adducts; e.g., **8** from methyl acrylate.



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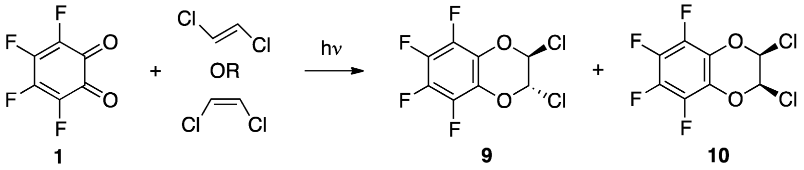
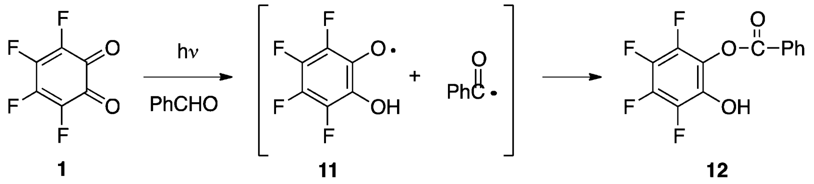
When *o*-fluoranil is irradiated in a 1:1 mixture of vinyl acetate and methyl acrylate, adducts **6** and **7** are formed in a ratio of 3:1, respectively. For both alkenes, the expected site of attack is the terminal carbon, electron-rich in the case of vinyl acetate and electron poor in methyl acrylate. The preponderance of the vinyl acetate adduct in the photoproduct, albeit modest, thus argues for an electron-deficient attacking species, thereby implicating an n, π^* state.[10] In the quinone's ground state,

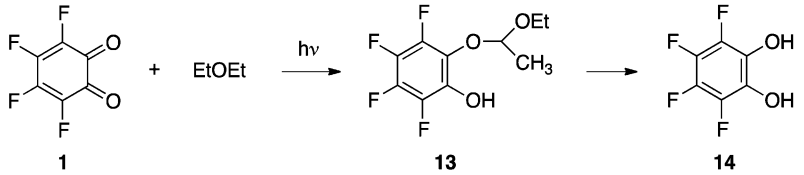
Scheme 2



Scheme 3



Scheme 4



the oxygens bear considerable negative charge (0.40)[11] that would be enhanced in the π, π^* state, a further reason to favor an n, π^* state as the reacting species. The great tendency of the quinone toward photodimerization may reflect not so much the character of the excited state as the high reactivity of the ground state. It is also possible that the quinone associates in the ground state, resulting upon excitation in the formation of an excimer that evolves into the dimer.

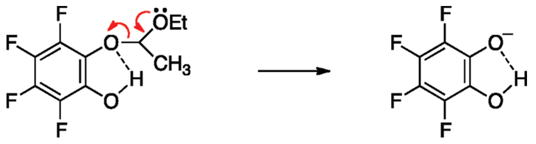
To address the question of stepwise versus concerted photocycloaddition, *trans*-1,2-dichloroethylene was chosen as the substrate because alkenes such as the 2-butenes are subject to attack at allylic hydrogens. Both trans (**9**) and cis (**10**) adducts were obtained in the ratio ∼8:1, demonstrating that reaction occurred stepwise (Scheme 2). Irradiation of the quinone in *cis*-1,2-dichloroethylene again gave both **9** and **10**, now in the ratio ∼1:10. Since loss of configuration was rather slight in both experiments, either intersystem crossing in intermediate triplet diradicals is considerably faster than rotation about the bond between the chlorine-bearing carbons, or the intermediate diradicals are singlets arising from the quinone's n, π^* singlet state. Concerted [4 + 2] photocycloaddition would be forbidden according to the Woodward−Hoffmann rules.[12]

Attempts to obtain photoadducts with norbornene and phenylacetylene resulted in complex mixtures, as was the case with styrene containing a little 2,5-di-*tert*-butylhydroquinone as a polymerization inhibitor. Irradiation of methylene chloride solutions of diphenylacetylene and each of the stilbenes through a 400 nm cutoff filter (to ensure selective excitation of the quinone) gave no reaction. Further investigation with these substrates is probably worthwhile, as *o*-chloranil (**2**) has yielded photoadducts with styrene,[13] the stilbenes,[14,15] and several with diphenylacetylene.[15−18]

Photoexcited *o*-fluoranil abstracts hydrogen from a variety of substrates. Like *o*-chloranil,[19] it reacts with benzaldehyde to give catechol ester **12**, presumably via the benzoyl radical and phenoxy radical **11** (Scheme 3).

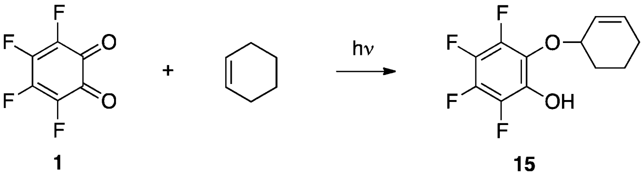
Ethers such as tetrahydrofuran and diethyl ether undergo α-hydrogen abstraction, resulting in the formation of labile catechol acetals that spontaneously cleave to tetrafluorocatechol (**14**). For example, acetal **13** formed from diethyl ether (Scheme 4) decomposes completely in a few hours even in the presence of calcium carbonate, introduced to ensure the absence of any HF that might have been generated during the irradiation. The hydroxyl group in **13** may catalyze cleavage of the acetal, generating a very stable anion[20] (Scheme 5).

Scheme 5



Upon irradiation, *o*-fluoranil reacts with cyclohexene to afford allylic ether **15** (Scheme 6). Thus, abstraction of allylic hydrogen occurs in preference to cycloaddition to the double bond. This selectivity is unsurprising in light of the thermodynamics of the initial step of the reaction. For an oxygen atom, abstraction of an allylic hydrogen is more exothermic than addition to a C═C bond, and entropy favors formation of two species over one (Figure 2).

Scheme 6



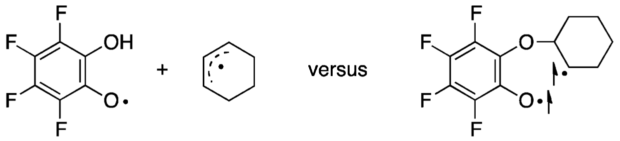
■ SUMMARY

A first sampling of the photoreactions of *o*-fluoranil has been presented, together with a brief discussion of the quinone's excited states and reaction mechanisms.

■ EXPERIMENTAL SECTION

NMR spectra were measured on 300 and 500 MHz spectrometers. ^{19}F NMR spectra were referenced to internal chlorotrifluoromethane, as ^{1}H and ^{13}C NMR spectra were referenced to TMS. *o*-Fluoranil was prepared by oxidation of tetrafluorocatechol.[1,4] Irradiations were performed with a 450 W Hanovia medium pressure mercury arc housed in a water-cooled quartz well. Reactants were placed in a glass-stoppered Pyrex test tube with a side arm, and the tube was purged of oxygen by bubbling a stream of nitrogen through the liquid. A nitrogen atmosphere was maintained via the side arm. For cooling, the tube was immersed in a beaker of running tap water and placed close to the quartz well.

3,4,4a,6,7,8,9,10a-Octafluorodibenzo[*b*,*e*][1,4]dioxine-1,2-(4a*H*,10a*H*)-dione (3) and Its Hydrate (4). A solution of *o*-fluoranil (1.19 g, 6.59 mmol) in methylene chloride (25 mL) was irradiated until all quinone was consumed (4.5 h). Chromatography on silica gel



S_{rel} (cal/mol K)	41.0	0.0
H_{rel} (kcal/mol)	0.0	12.2
G_{rel} (kcal/mol, 25 °C)	0.0	24.5

Figure 2. Calculated thermodynamic differences between intermediates along alternative pathways for the *o*-fluoranil−cyclohexene photoreaction (B3LYP/6-311G**+).[7]

(15 g) with 10% EtOAc/hexanes as eluent yielded 1.2 g of pale yellow solid, the dimer hydrate (**4**). Recrystallization from hexane gave 374 mg (31.5% yield) of white crystals of the hydrate, mp 129−130 °C. ^{1}H NMR (CD_3CN): *δ* 6.23 (s, 2H), 2.38 (s, ∼4H). [This *gem*-diol binds additional water that is not observed in the mass spectrum.] ^{19}F NMR (CD_3CN): *δ* −139.2 (narrow "d", 2F), −145.6 (s, 2F), −160.5 (br s, 1F), −160.8 (d, *J* = 20 Hz), 1F), −162.8 (t, *J* = 20 Hz), 1F), −163.4 (m, 1F). The two lowest field signals each integrated for 1F even with allowance for long relaxation times, but actually represented 2F, as shown below. ^{13}C NMR (CD_3CN, ^{19}F-decoupled, ^{1}H-coupled): *δ* 183.4, 149.1, 142.1, 138.9, 138.3, 138.2, 137.9, 127.8, 125.5, 103.0, 101.0, 93.4. MS *m*/*z*: 378 (M^+), 360 ($M^+ - H_2O$), 332 ($M^+ - CH_2O_2$), 294, 257, 210, 152, 124 (base), 93, 69. HRMS calcd for $C_{12}H_2O_5F_8$ 377.9774, found 377.9758; calcd for $C_{12}O_4F_8$ 359.9669, found 359.9665.

The hydrate (100 mg) was dissolved in methylene chloride (5 mL) and stirred with P_4O_{10} for 4 h. Filtration to remove the partially hydrated P_4O_{10} and evaporation gave anhydrous dimer. However, the dimer absorbs water so voraciously that it became contaminated with hydrate formed during the filtration. To obtain a spectrum of pure dimer, hydrate was dissolved in CD_3CN in an NMR tube, P_4O_{10} was added, and the mixture was allowed to stand overnight. ^{19}F NMR (CD_3CN): *δ* −117.3 (m, 1F), −132.9 (d, *J* = 18.6 Hz, 1F), −133.2 (d, *J* = 25 Hz, 1F), −141.1 (s, 1F), −160.0 (d, *J* = 18.9 Hz, 1F), −160.6 (d, *J* = 18.9 Hz, 1F), −162.0 to −162.3 (m, 2F). The four low field resonances were derived from the two low field signals of the hydrate.

1,2,3,4,5a,6,7,13b-Octafluoro-5a,13b-dihydrobenzo[5,6]-[1,4]dioxino[2,3-*a*]phenazine (5). Dimer hydrate (330 mg, 0.873 mmol) was dissolved in 10 mL of a 1:1 MeOH/HOAc mixture and a solution of *o*-phenylenediamine (91 mg, 0.84 mmol) in methanol (5 mL) was added. The reaction mixture was refluxed for 2 h. After cooling, it was diluted with water (45 mL) and extracted with CH_2Cl_2 (3 × 15 mL). Organic layer was washed with saturated $NaHCO_3$ solution (45 mL), then dried over Na_2SO_4. The crude product was chromatographed on 15 g of silica gel using 1% EtOAc/hexanes as eluent. Recrystallization from hexanes gave 213 mg (58.7% yield) of the phenazine, mp 105−107 °C. ^{1}H NMR ($CDCl_3$): *δ* 8.25 (s, 2H), 7.95 (s, 2H). ^{19}F NMR ($CDCl_3$): *δ* −126.0 (s, 1F), −133.5 (s, 1F), −146.0 (s, 1F), −149.8 (s, 1F), −159.7 (s, 1F), −160.1 (s, 1F), −162.1 (s, 1F) −162.4 (s, 2F). ^{13}C NMR ($CDCl_3$, ^{19}F-decoupled, ^{1}H-coupled): *δ* 143.2, 142.7, 140.9, 140.6, 140.3, 138.7, 137.9, 137.8, 137.2, 137.0, 133.2 (dd, J_{CH} = 163, 9.2 Hz), 132.4 (dd, J_{CH} = 163, 8.7 Hz), 130.2 (dm, J_{CH} = 166 Hz), 129.7 (dm, J_{CH} = 167 Hz), 125.6, 125.4, 101.7, 100.7. Anal. Calcd for $C_{18}H_4F_8N_2O_2$: C, 50.02; H, 0.93; N, 6.48. Found: C, 49.84; H, 0.90; N, 6.58.

5,6,7,8-Tetrafluoro-2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl Acetate (6). A solution of *o*-fluoranil (436 mg, 2.42 mmol) in vinyl acetate (5 mL) was irradiated until the quinone was completely consumed (0.5 h). Solvent was evaporated, and the crude product was chromatographed on 20 g of silica gel (200−400) using 4% EtOAc/hexanes as eluent. Pale yellow oily adduct was obtained, 260 mg (40.4% yield). ^{1}H NMR ($CDCl_3$): *δ* 6.55 (s, 1H), 4.40 (d, *J* = 12 Hz, 1H), 4.17 (d, *J* = 12 Hz, 1H), 2.11 (s, 3H). ^{19}F NMR ($CDCl_3$): *δ* −163.3 (d, *J* = 25 Hz, 1F), −164.1 (d, *J* = 25 Hz, 1F), −167.8 (m, 1F), −168.1 (m, 1F). ^{13}C NMR ($CDCl_3$): *δ* 168.8, 137.4 ($^{1}J_{CF}$ = 247 Hz), 137.1 ($^{1}J_{CF}$ = 247 Hz), 136.3 ($^{1}J_{CF}$ ∼ 245 Hz), 136.0 ($^{1}J_{CF}$ = 244 Hz), 129.6, 127.3, 86.0, 65.1, 20.4. Anal. Calcd for $C_{10}H_6F_4O_4$: C, 45.13; H, 2.27; F, 28.55. Found: C, 45.19; H, 2.19; F, 28.80.

Methyl 5,6,7,8-Tetrafluoro-2,3-dihydrobenzo[*b*][1,4]dioxine-2-carboxylate (7). *o*-Fluoranil (457 mg, 2.54 mmol) dissolved in methyl acrylate (5 mL) was irradiated until the *o*-fluoranil got consumed (1.5 h). After evaporation of the solvent, crude product was chromatographed on 20 g of silica gel (200−400 mesh) using 3% EtOAc/hexanes as eluent. The white crystalline adduct obtained weighed 305 mg (45.2% yield). Mp: 87−88 °C. ^{1}H NMR ($CDCl_3$): *δ* 4.96 (m, 1H), 4.58 (dd, *J* = 11.7, 3.6 Hz, 1H), 4.40 (dd, *J* = 11.7, 2.7 Hz, 1H), 3.83 (s, 3H). ^{19}F NMR ($CDCl_3$): *δ* −164.0 (m, 2F), −168.4 (m, 1F), −168.9 (m, 1F). ^{13}C NMR ($CDCl_3$): *δ* 166.9, 137.2 ($^{1}J_{CF}$ = 247 Hz, 2C), 135.9 ($^{1}J_{CF}$ = 244 Hz, 2C), 129.7, 129.1, 71.5, 65.0, 52.8. Anal. Calcd for $C_{10}H_6F_4O_4$: C, 45.13; H, 2.27; F, 28.55. Found: C, 44.89; H, 2.13; F, 28.83.

2,3-Dichloro-5,6,7,8-tetrafluoro-2,3-dihydrobenzo[*b*][1,4]-dioxine (9, 10). *o*-Fluoranil (460 mg, 2.55 mmol) dissolved in *trans*-1,2-dichloroethylene (5 mL) was irradiated until it had reacted completely (1.5 h). After evaporation of the solvent, the residue was chromatographed on 20 g of silica gel using 1% EtOAc/hexanes as eluent. The pale yellow oily product was a ∼8:1 trans/cis mixture of adducts, 241 mg (34.0% yield). ^{1}H NMR ($CDCl_3$): trans (**10**), *δ* 6.29 (s, 2H); cis (**9**), 6.15 (s, 2H). ^{19}F NMR ($CDCl_3$): trans, *δ* −161.8 (m, 2F), −163.8 (m, 2F); cis, *δ* −161.4 (m, 2F), −164.2 (m, 2F). ^{13}C NMR ($CDCl_3$, F-decoupled, ^{1}H-coupled): trans, *δ* 137.9, 137.5, 124.7, 83.2 (J_{CH} = 189 Hz); cis, 137.4, 137.3, 126.7, 84.1 (J_{CH} = 182 Hz). MS *m*/*z*: 276, 278, 280 (M^+), 241, 243 ($M^+ - Cl$), 206 ($M^+ - 2Cl$), 193 ($M^+ - CHCl_2$, base). HRMS calcd for $C_8H_2Cl_2F_4O_2$ 275.9368, found 275.9370.

In an NMR tube were placed 20 mg of *o*-fluoranil and 0.5 mL of *cis*-1,2-dichloroethylene. After irradiation for 30 min, the solution yielded a ∼10:1 cis/trans mixture of the adducts described above.

2,3,4,5-Tetrafluoro-6-hydroxyphenyl Benzoate (12). *o*-Fluoranil (425 mg, 2.36 mmol) dissolved in benzaldehyde (5 mL) was irradiated until the quinone was gone (1.5 h). Unreacted benzaldehyde was distilled under vacuum and the product was dissolved in methylene chloride (25 mL). The solution was stirred with saturated aqueous sodium bisulfite (50 mL) in two portions to remove residual aldehyde, then washed with water (25 mL). Crude product was chromatographed on 20 g of silica gel using 3% EtOAc/hexanes as eluent. The solid that precipitated upon concentration was collected by filtration and recrystallized from hexanes. Yield: 102 mg (15.1%). Mp: 166−167 °C. ^{1}H NMR ($CDCl_3$): *δ* 8.21 (m, 2H), 7.70 (m, 1H), 7.52 (m, 2H), 5.48 (s, 1H). ^{19}F NMR ($CDCl_3$): *δ* −154.3 (dd, *J* = 21.7, 5.9 Hz, 1F), −160.2 (t, *J* = 21.7 Hz, 1F), −163.5 (dd, *J* = 21.7, 5.93 Hz, 1F), −168.6 (m, 1F). ^{13}C NMR (CD_3CN): *δ* 164.3, 142.3 ($^{1}J_{CF}$ = 245 Hz), 140.5 ($^{1}J_{CF}$ = 244 Hz), 139.3 ($^{1}J_{CF}$ = 244 Hz), 136.8, 135.7 ($^{1}J_{CF}$ = 245 Hz), 135.7, 131.4, 130.1, 128.7, 125.8. Anal. Calcd for $C_{13}H_6F_4O_3$: 54.56; H, 2.11; F, 26.55. Found: C, 54.30; H, 1.99; F, 26.82.

2-(1-Ethoxyethoxy)-3,4,5,6-tetrafluorophenol (13). A solution of *o*-fluoranil (460 mg, 2.55 mmol) in diethyl ether (20 mL) was irradiated until the quinone was consumed (30 min). The acetal product, which contained a comparable amount of tetrafluorocatechol (**14**), was too unstable to isolate on silica gel or florisil. ^{19}F NMR ($C_2H_5OC_2H_5$): *δ* −158.2 (d, *J* = 18.6 Hz, 1F), −164.7 (d, *J* = 18.9 Hz), 1F), −166.2 (m, 1F, merged with catechol signal), −172.7 (m, 1F), −173.8 (m, catechol). The product from another photolysis run was stirred with a large excess of finely divided calcium carbonate to ensure the absence of HF, but complete cleavage to tetrafluorocatechol occurred within a few hours.

A solution of *o*-fluoranil (20 mg, 0.11 mmol) in 0.5 mL of tetrahydrofuran was irradiated for 30 min. The ^{19}F NMR spectrum (THF) showed the presence of the hydroxyacetal analogous to that from diethyl ether, together with tetrafluorocatechol: δ −158.5 (d, J = 25 Hz, 1F), −165.5 (d, J = 25 Hz, 1F), −166.3 (m, catechol), −166.7 (m, 1F), −173.3 (m, 1F) −174.2 (m, catechol). After another 1.5 h conversion to catechol was complete.

2-(Cyclohex-2-en-1-yloxy)-3,4,5,6-tetrafluorophenol (15). A solution of *o*-fluoranil (800 mg, 4.44 mmol) in CH_2Cl_2 (5 mL) was diluted with cyclohexene (20 mL) and irradiated for 30 min, completing consumption of the quinone. Solvents were evaporated under vacuum to afford crude adduct in 25% yield by NMR. This was chromatographed on 15 g of silica gel with 1% EtOAc/hexanes as eluent, affording 110 mg of the adduct (9.5% yield). Recrystallization from hexanes gave white needles, mp 63−64 °C. ^{1}H NMR ($CDCl_3$): δ 6.05 (m, 1H), 5.81 (d, J = 8.5 Hz, 1H), 5.48 (s, 1H), 4.72 (s, 1H), 1.67−2.18 (m, 6H). ^{19}F NMR ($CDCl_3$): δ −157.1 (m, 1F), −164.2 (m, 1F), −164.6 (m, 1F), −170.3 (m, 1F). ^{13}C NMR ($CDCl_3$, ^{19}F-decoupled, ^{1}H-coupled): δ 141.5, 137.8, 136.9, 135.3, 135.1, 134.3 (d, J = 159 Hz), 130.2, 125.0 (d, J = 159 Hz), 78.6, 28.7 (t, J = 132 Hz), 25.0 (t, J = 126 Hz), 18.5 (t, J = 128 Hz). HRMS: calcd for $C_{12}H_{10}F_4O_2$ 261.0539, found 261.0534.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{19}F, and ^{13}C NMR spectra plus computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(20) At the B3LYP/6-311G**+ level, the anion is predicted to be unsymmetrical, with 0.99 and 1.89 Å bonds to hydrogen.[7]