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The Multifaceted Reactivity of *o*-Fluoranil

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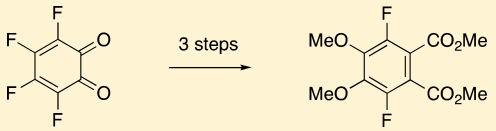
Supporting Information

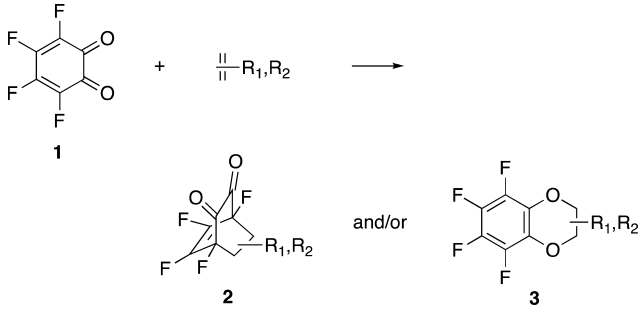
ABSTRACT: In addition to Diels–Alder and hetero-Diels–Alder reactions, tetrafluoro-*o*-benzoquinone (*o*-fluoranil) undergoes nucleophilic additions, addition–eliminations, dioxole formation, and charge-transfer complexation, reacting at every site on the molecular skeleton. It also effects dehydrogenations and other oxidations. The quinone can function as a $(CF)_4$ synthon.



INTRODUCTION

Previous publications have described [4 + 2] cycloadditions of *o*-fluoranil (**1**): Diels–Alder and hetero-Diels–Alder reactions.[1−3] To date, all acetylenic substrates have yielded exclusively Diels–Alder adducts, even though the alternative pathway is strongly favored thermodynamically. However, alkenes and dienes give either Diels–Alder (**2**) or hetero-Diels–Alder adducts (**3**), or both (Scheme 1).[4] Cycloaddition

Scheme 1

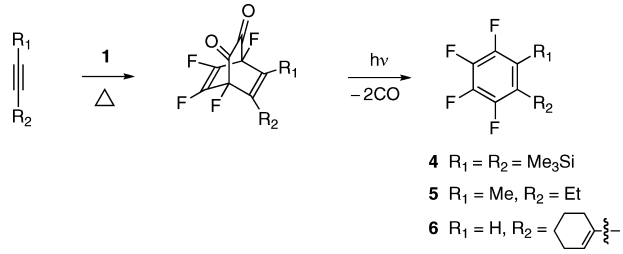


occurs with both electron-donating and electron-withdrawing substituents, under more vigorous conditions with the latter. Via its Diels–Alder adducts, *o*-fluoranil can serve as a $(CF)_4$ synthon, incorporating a (−CF=CF−CF=CF−) diene fragment into a variety of molecular frameworks, as described below. The present account then explores reaction types other than [4 + 2] cycloaddition in which the quinone engages.

RESULTS AND DISCUSSION

o-Fluoranil Diels–Alder adducts undergo extrusion of the dicarbonyl bridge under UV irradiation. Irradiation is generally carried out through Pyrex (λ > 280 nm), but if complications arise from a chromophore elsewhere in the molecule, a cutoff filter can be used that eliminates nearly all of the UV. In the case of alkyne adducts, the products are tetrafluorobenzenes. In addition to several known examples, new compounds **4**–**6** have been prepared by this method (Scheme 2). Kobrina obtained tetrafluorobenzenes by photoextrusion of the [−CClFCO−] bridge from alkyne adducts of 6-chloroperfluoro-2,4-cyclo-

Scheme 2



hexadienone.[5] Because the tetrafluorobenzene yields are typically better, that method is superior to ours.

Alkene adducts of the cyclohexadienone do not undergo photoextrusion of the bridge, as judged from the single example we tested, the norbornene adduct. However, alkene adducts of *o*-fluoranil do, yielding tetrafluoro-1,3-cyclohexadienes that can be aromatized by heating with DDQ. The photochemical step often proceeds in low yield, probably due to impurities introduced in the cycloaddition step. That step goes very well, though, in the case of cyclooctene, which yields benzocyclooctene **9** via adducts **7** (exo and endo) and cyclohexadiene **8** (Scheme 3).

o-Fluoranil undergoes another kind of cycloaddition, dioxole formation.[6] Treated with ethyl diazoacetate in refluxing benzene, for example, the quinone is transformed into dioxole **10** (Scheme 4).

Instead of cycloadding, some especially nucleophilic C=C double bonds add to a carbonyl group of *o*-fluoranil; for example, indole and *N*-alkylindoles give adducts **11** (Scheme 5). That the site of addition is a carbonyl and not a fluorinated carbon is clear from the ^{13}C NMR spectrum: the lone high-field (sp^3) skeletal carbon signal is not split by a one-bond C–F coupling, and four fluorinated carbons appear far downfield.

Two reports in the 1980s literature[7,8] that describe the interaction of indoles with *o*-chloranil claim a different mode of reaction, addition ortho to a carbonyl group to afford **12** (Scheme 6). This structure should lose HCl easily. By analogy to its fluorinated counterpart, *o*-chloranil would be expected to

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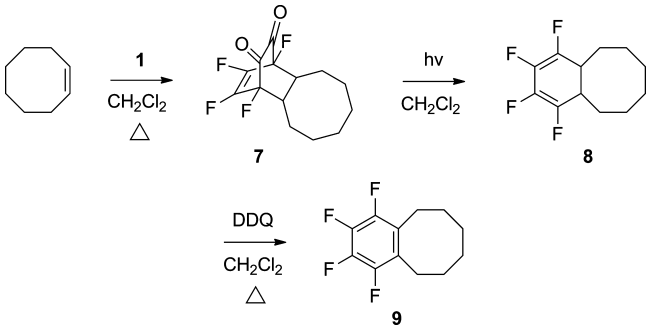
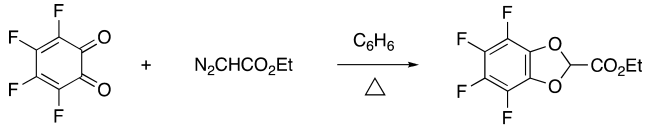
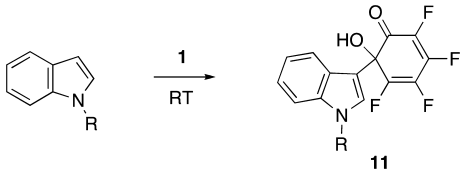
Scheme 3



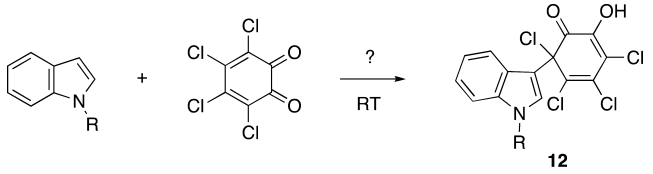
Scheme 4



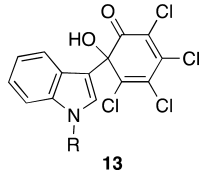
Scheme 5



Scheme 6



undergo addition at a carbonyl group, a surmise that is supported by the close similarity of the adducts' ^{13}C spectra. We prepared the *o*-fluoranil and *o*-chloranil adducts of *N*-hexylindole and found the high-field skeletal carbon peaks at δ 76.3 and δ 80.6, respectively. Thus, *o*-chloranil–indole adducts have the structure **13**, a conclusion reached long ago by Horner. He reported the adducts of indole and *N*-alkylindoles with *o*-chloranil in 1950[9] and, in 1955, without benefit of NMR, correctly assigned their structures primarily on the basis of their chemical reactivity.[10]



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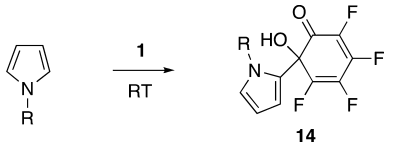
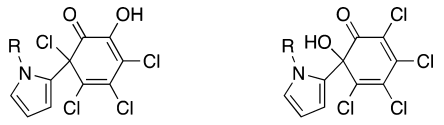
Pyrroles also add readily to *o*-fluoranil at a carbonyl carbon to give **14**, as evidenced in the ^{13}C spectrum again by the absence of a large CF coupling constant for the high-field (sp^2) skeletal carbon peak and by four fluorinated carbon signals at much lower field (Scheme 7). Assignments were confirmed with a fluorine-decoupled ^{13}C spectrum. The two 1980s reports alluded to above assigned the structures of pyrrole adducts of

Scheme 7



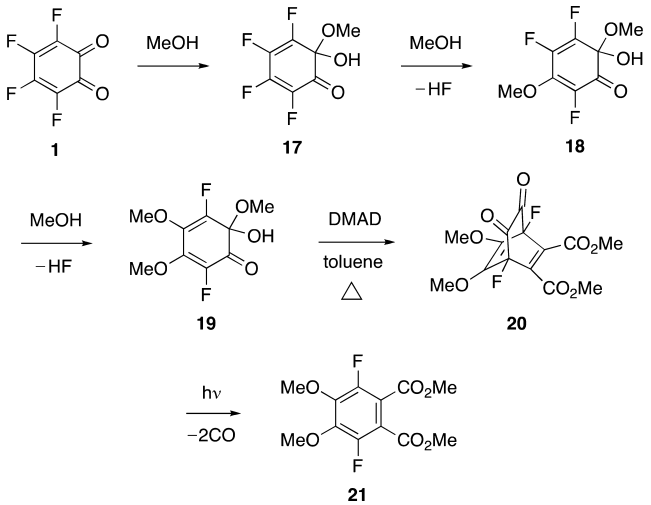
o-chloranil as **15**. However, we found the high-field skeletal carbon signal for the *N*-methylpyrrole adducts of *o*-fluoranil and *o*-chloranil at δ 76.1 and δ 80.7, respectively, similar to each other and almost identical with those found for the *N*-hexylindole adducts. We conclude that *o*-chloranil adducts actually have the structure **16**.



15 **16**

Saturated nucleophiles can also add to a carbonyl group of *o*-fluoranil. When excess methanol was added to a solution of the quinone in $CDCl_3$, four new signals corresponding to adduct **17** appeared quickly in the ^{19}F NMR spectrum (Scheme 8).

Scheme 8



The fluorine-decoupled ^{13}C spectrum obtained at 0 °C showed four CF carbons in the δ 132–150 region, establishing that methanol had added at a carbonyl carbon, which appeared at δ 90.6. At RT, this initial adduct soon diminished, giving way to three new signals that represented compound **18**, formed by addition–elimination. These peaks faded in turn, to be replaced by two signifying trimethoxy compound **19**. No further change occurred, even when the reaction was carried out in methanol as the solvent.

Formation of **19** from **18** presumably requires temporary loss of the hemiacetal methanol to activate the molecule for attack beta to the new carbonyl group. While catalysis by HF probably plays a role in this chemistry, similar results are obtained when the reaction mixture is stirred with a large excess of calcium carbonate.

The location of the remaining fluorine atoms in **19** was revealed when it was heated with dimethyl acetylenedicarboxylate in refluxing toluene, as the resulting Diels–Alder adduct

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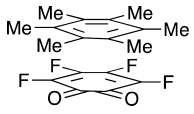
20 gave rise to a single resonance at δ −202.5 in the ^{19}F spectrum. Under the reaction conditions, the hemiketal methanol is expelled, making the two fluorines equivalent. The very high field location of the signal requires that they be located at the bridgehead positions in **20**; otherwise, they would appear at lower field by tens of parts per million.[11] The structure of **19** follows from that of **20**, and **18** is assigned on the basis that methanol would undergo conjugate addition to **17**. That is, it would attack at the carbon β, not γ, to the carbonyl group. The structure of **20** is further confirmed by photodecarbonylation to phthalate ester **21.**

As would be expected of a high-potential quinone,[12,13] *o*-fluoranil is a good dehydrogenating agent. It aromatizes 1,3-cyclohexadiene, 1,4-cyclohexadiene, and 1,2-dihydronaphthalene rapidly at RT in preference to undergoing cycloaddition. The quinone oxidizes electron-rich compounds, such as *o*-phenylenediamine and 2,5-dimethylpyrrole, to ill-defined products, forming tetrafluorocatechol in all of these reactions.

o-Fluoranil forms charge-transfer complexes with a wide variety of donor molecules as indicated, for example, by intense colors that commonly appear at the start of its Diels–Alder reactions. The 1:1 complex with hexamethylbenzene (**22**) was isolated as shiny brown needles; mp = 121–122 °C.



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In summary, the quinone is a versatile electrophile that undergoes reaction at every position on its skeleton, and it is also a building block that can provide a fluorinated diene fragment for the construction of more complex molecules.

EXPERIMENTAL SECTION

For some of the following experiments, the *o*-fluoranil was introduced as a readily synthesized 60:40 (o:p) mixture with its much less reactive para isomer, which was removed in the workup.[2,14] In other experiments, the ortho isomer alone was used. It was prepared by oxidation of tetrafluorocatechol as described below. ^{19}F NMR spectra were referenced to internal chlorotrifluoromethane, as ^{1}H and ^{13}C NMR spectra were referenced to TMS.

***o*-Fluoranil (1).**[1] A solution of tetrafluorocatechol (4.0 g, 22 mmol) in nitromethane (52 mL) was cooled to −30 °C in a bromobenzene slush bath. Concentrated nitric acid (16 mL) in nitromethane (5.2 mL) was added dropwise with stirring during 20 min. Cold water (52 mL) was added, stirring was continued for 2 min, then the mixture was extracted with benzene (22 mL). The aqueous layer was again extracted with benzene (2 × 15 mL), and the combined extract was dried over Na_2SO_4. Concentration of the solution below 30 °C gave 3.8 g of an orange semisolid product, 90% pure *o*-fluoranil (86% yield) that contains some nitromethane and benzene.[15] Pure quinone (mp 66.5–67.5 °C) can be obtained by sublimation, but the 90% material was used in the experiments described here. The specified amounts of quinone are corrected for the presence of impurity.

1,2,3,4-Tetrafluoro-5,6-bis(trimethylsilyl)benzene (4). In a 25 mL round-bottom flask were placed a 60:40 quinone mixture (1.00 g, 3.3 mmol ortho), 0.68 g (4 mmol) of bis(trimethylsilyl)acetylene, and 3 mL of toluene. The solution was refluxed until the *o*-fluoranil was consumed (2.5 h); then the solvent was evaporated. Tetrafluoro-5,6-bis(trimethylsilylbicyclo[2.2.2]octa-2,5-diene-7,8-dione: ^{1}H NMR ($CDCl_3$): δ 0.36 (s, 18H). ^{19}F NMR ($CDCl_3$): δ −153.2 (m, 2F), −193.3 (m, 2F). Unchanged *p*-fluoranil was observed at −142.0 ppm. This mixture dissolved in methylene chloride (25 mL) was placed in a cylindrical Pyrex tube and purged with a stream of nitrogen to remove oxygen. The tube was irradiated under nitrogen with a Hanovia 450 W medium pressure mercury lamp until decarbonylation was complete. The solvent was evaporated, and the product was chromatographed on 20 g of silica gel (200–400 mesh) with hexanes as the eluent. The yield of tetrafluorobenzene **4** was 48%; mp 35–36 °C. ^{1}H NMR ($CDCl_3$): δ 0.43 (s, 18H). ^{19}F NMR ($CDCl_3$): δ −120.3 (m, 2F), −155.1 (m, 2F). ^{13}C NMR ($CDCl_3$): δ 152.5 ($^{1}J_{CF}$ = 239 Hz), 140.3 ($^{1}J_{CF}$ = 261 Hz), 128.4, 2.6. HRMS Calcd for $C_{12}H_{18}F_4Si_2$: 294.0883. Found: 294.0866.

1-Ethyl-2,3,4,5-tetrafluoro-6-methylbenzene (5). The procedure used for **4** was followed with 0.27 g (4 mmol) of 2-pentyne and 5.5 h at reflux. 2-Ethyl-1,4,5,6-tetrafluoro-3-methylbicyclo[2.2.2]octa-2,5-diene-7,8-dione: ^{1}H NMR ($CDCl_3$): 2.44 (m, 2H), 2.00 (m, 3H), 1.05 (m, 3H). ^{19}F NMR ($CDCl_3$): δ −152.5 (m, 1F), −152.9 (m, 1F), −208.1(m, 1F), −209.4 (m, 1F). Tetrafluorobenzene **5** was obtained in 27% yield. ^{1}H NMR ($CDCl_3$): δ 2.67 (m, 2H), 2.21 (m, 3H), 1.14 (m, 3H). ^{19}F NMR ($CDCl_3$): δ −143.1 (m, 1F), −146.1 (m, 1F), −161.4 (m, 2F). ^{13}C NMR ($CDCl_3$): δ 146.5 ($^{1}J_{CF}$ = 242 Hz), 138.5 ($^{1}J_{CF}$ = 250 Hz), 126.0, 119.2, 18.7, 13.7, 9.8. HRMS Calcd for $C_9H_8F_4$: 192.0562. Found: 192.0551.

2′,3′,4′,5′-Tetrafluoro-2,3,4,5-tetrahydro-1,1′-biphenyl (6). The same procedure as used for **4** was employed with 0.42 g (4 mmol) of 1-ethynylcyclohexene, benzene as the solvent, and 0.5 h at reflux. 5-(Cyclohex-1-enyl)-1,2,3,4-tetrafluorobicyclo[2.2.2]octa-2,5-diene-7,8-dione: ^{19}F NMR ($CDCl_3$): δ −151.6 (m, 1F), −151.9 (m, 1F), −204.1 (m, 1F), −204.8 (m, 1F). Tetrafluorobenzene **6** was obtained in 21% yield. ^{1}H NMR ($CDCl_3$): δ 6.83 (s, 1H), 5.97 (s, 1H), 2.31–0.88 (m, 8H). ^{19}F NMR ($CDCl_3$): δ −140.9 (m, 1F), −142.3 (m, 1F), −156.6 (m, 1F), −159.3 (m, 1F). ^{13}C NMR ($CDCl_3$): δ 146.6 ($^{1}J_{CF}$ = 246 Hz), 145.0 ($^{1}J_{CF}$ = 247 Hz), 140.8 ($^{1}J_{CF}$ = 250 Hz), 139.0 ($^{1}J_{CF}$ = 248 Hz), 131.3, 130.4, 127.7, 109.7, 28.4, 25.7, 22.7, 21.7. ^{13}C NMR ($CDCl_3$, ^{19}F decoupled, ^{1}H coupled): δ 146.6 (d, J = 6.4 Hz), 145.0 (d, J = 12.3 Hz), 140.0 (s), 138.9 (d, J = 9.7 Hz), 131.3 (d, J = 6.0 Hz), 130.4 (d, J = 156 Hz), 127.7 (m), 109.7 (d, J = 167 Hz), 28.4 (t, J = 129 Hz), 25.7 (t, J = 127 Hz), 22.7 (t, J = 136 Hz), 21.7 (t, J = 136 Hz). HRMS Calcd for $C_{12}H_{10}F_4$: 230.0719. Found: 230.0720.

1,2,3,4-Tetrafluoro-5,6,7,8,9,10-hexahydrobenzo[8]-annulene (9).[16] A solution of *o*-fluoranil (225 mg, 1.25 mmol) and cyclooctene (229 mg, 2.08 mmol) in methylene chloride (10 mL) was refluxed for 12 h, forming *exo*- and *endo*-1,4,11,12-tetrafluorodecahydro-1,4-ethanobenzo[8]annulene-2,3-dione (**7**). ^{19}F NMR (CD_2Cl_2): δ −146.9 (m, 1F), −148.1 (m, 1F), −195.2 (m, 1F), −196.0 (m, 1F). Nitrogen was bubbled through the solution to remove oxygen; then the adducts were irradiated through Pyrex for 3 h under nitrogen with the 450 W Hanovia lamp to obtain 1,2,3,4-tetrafluoro-4a,5,6,7,8,9,10,10a-octahydrobenzo[8]annulene (**8**). ^{19}F NMR (CD_2Cl_2): δ −145.2 (m, 2F), −167.3 (m, 2F). The NMR yield, determined by integration against hexafluorobenzene, was 87%. DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 228 mg, 10.1 mmol) was added to the solution, which was then refluxed for 3.5 h. The solvent was evaporated, and chromatography of the residue on 10 g of silica gel with hexane as the eluent gave 131 mg of tetrafluorobenzene **9** (42% overall yield). ^{1}H NMR ($CDCl_3$): δ 2.78 (s, 4H), 1.67 (s, 4H), 1.4 (s, 4H). ^{19}F NMR ($CDCl_3$): δ −145.5 (m, 2F), −160.8 (m, 2F). ^{13}C NMR ($CDCl_3$): δ 144.9 ($^{1}J_{CF}$ = 245 Hz), 138.6 ($^{1}J_{CF}$ = 252 Hz), 124.6, 30.0, 25.8, 23.4. HRMS Calcd $C_{12}H_{12}F_4$: 232.0875. Found: 232.0877.

Ethyl 4,5,6,7-Tetrafluorobenzo[d]-1,3-dioxole-2-carboxylate (10). *o*-Fluoranil (0.264 g, 1.5 mmol) was refluxed with ethyl diazoacetate (0.335 g, 2.9 mmol) in benzene (10 mL) for 8 h. The solvent was evaporated under vacuum, and the crude product was taken up in diethyl ether (15 mL). To remove unreacted ethyl diazoacetate, the solution was washed with 1 M HCl (15 mL), then with saturated sodium bicarbonate solution (15 mL). Evaporation of the solvent left 263 mg (67% yield) of crude dioxole. This was chromatographed on 20 g of silica gel using 1% EtOAc/hexanes as the eluent. A colorless oily product was obtained: 0.154 g (40% yield). ^{1}H NMR ($CDCl_3$): δ 6.34 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{19}F NMR ($CDCl_3$): δ −162.4 (m, 2F), −164.6 (m, 2F).

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^{13}C NMR ($CDCl_3$): δ 163.4, 137.2 ($^1J_{CF}$ = 249 Hz), 132.8 ($^1J_{CF}$ = 251 Hz), 131.6, 105.8, 63.1, 13.7. HRMS Calcd for $C_{10}H_6F_4O_4$: 266.0202. Found: 266.0191.

2,3,4,5-Tetrafluoro-6-(1-hexyl-1*H*-indol-3-yl)-6-hydroxycyclohexa-2,4-dienone (11, R = *n*-hexyl). A mixture of *o*-fluoranil (360 mg, 2.0 mmol) and *N*-hexylindole (446 mg, 2.2 mmol) in benzene (10 mL) was stirred for 10 min. The solution was concentrated to 3 mL and chromatographed on silica gel (10 g, mesh size 200−400) with benzene. The resulting solid was dissolved in hot hexanes (30 mL), and the crystal crop obtained at RT was washed with hexanes (20 mL) and dried at room temperature to give the dienone as a yellowish solid: mp 86−87 °C (218 mg, 29% yield). ^{1}H NMR ($CDCl_3$): δ 7.83 (d, J = 7.5 Hz, 1H), 7.26 (m, 3H), 7.04 (s, 1H), 4.07 (t, J = 7.3 Hz, 2H), 3.53 (s, 1H), 1.83 (br s, 2H), 1.554 (s, 2H), 1.31 (br s, 4H), 0.88 (br s, 3H). ^{19}F NMR ($CDCl_3$): δ −132.6 (s, 1F), −132.8 (s, 1F), −161.3 (m, 1F), −165.8 (m, 1F). ^{13}C NMR ($CDCl_3$): δ 187.2, 150.8 ($^1J_{CF}$ = 268 Hz), 145.9 ($^1J_{CF}$ = 288 Hz), 137.4 ($^1J_{CF}$ = 269 Hz), 136.7, 131.6 ($^1J_{CF}$ = 259 Hz), 127.2, 124.9, 122.8, 120.8, 120.7, 110.2, 109.5, 76.3, 46.8, 31.2, 29.9, 26.5, 22.4, 13.9. Anal. Calcd for $C_{20}H_{19}F_4NO_2$: C, 62.99; H, 5.02; N, 3.67. Found: C, 62.74; H, 5.06; N, 3.63.

2,3,4,5-Tetrachloro-6-(1-hexyl-1*H*-indol-3-yl)-6-hydroxycyclohexa-2,4-dienone (13, R = *n*-hexyl). A mixture of *o*-chloranil (1000 mg, 4.1 mmol) and *N*-hexylindole (821 mg, 4.1 mmol) in benzene (15 mL) was stirred for 10 min. The solution was concentrated to 5 mL and chromatographed on silica gel (10 g, mesh size 200−400) with 5% EtOAc/hexanes. The resulting solid was dissolved in hexanes (30 mL), and the crystal crop obtained at −25 to −20 °C was washed with cold hexanes (10 mL) and dried at room temperature to give an orange solid: mp 102−103 °C (155 mg, 8.6% yield). ^{1}H NMR ($CDCl_3$): δ 7.70 (d, J = 7.5 Hz, 1H), 7.22 (m, 4H), 4.08 (m, 2H), 1.80 (s, 1H), 1.29 (m, 8H), 0.87 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 188.5, 143.8, 140.5, 136.6, 128.4, 127.3, 124.9, 124.6, 122.5, 120.7, 120.5, 110.3, 108.6, 80.6, 46.8, 31.2, 29.8, 26.5, 22.5, 14.0. Anal. Calcd for $C_{20}H_{19}Cl_4NO_2$: C, 53.72; H, 4.28; N, 3.13. Found: C, 53.90; H, 4.30; N, 3.22.

2,3,4,5-Tetrafluoro-6-hydroxy-6-(1-methyl-1*H*-pyrrol-2-yl)-cyclohexa-2,4-dienone (14, R = Me). A mixture of *o*-fluoranil (27 mg, 0.15 mmol) and *N*-methylpyrrole (13.5 mg, 0.16 mmol) in $CDCl_3$ (0.5 mL) was shaken for 2 min in an NMR tube. The orange quinone solution had turned dark brown upon addition of the pyrrole due to charge-transfer complexation, and addition followed rapidly. In our hands, the adduct was too labile to purify. ^{1}H NMR ($CDCl_3$): δ 6.68 (m, 1H), 6.03 (m, 2H), 3.85 (d, J = 1.2 Hz, 3H), 3.5 (br s, 1H). ^{19}F NMR ($CDCl_3$): δ −132.5 (m, 1F), −133.9 (m, 1F), −160.6 (m, 1F). −164.6 (m, 1F). ^{13}C NMR ($CDCl_3$): δ 186.7, 150.4 ($^1J_{CF}$ = 293 Hz), 144.9 ($^1J_{CF}$ = 282 Hz), 136.8 ($^1J_{CF}$ = 264 Hz), 131.9 ($^1J_{CF}$ = 260 Hz), 128.3, 123.8, 110.5, 107.2, 76.1, 36.3. ^{13}C NMR (CDCl3, ^{19}F decoupled, ^{1}H coupled): 186.7, 150.4, 144.9, 136.8, 131.9, 128.3 (d, J = 185 Hz), 123.8, 110.5 (d, J = 170 Hz), 107.2 (d, J = 174 Hz), 76.1, 36.3, (q, J = 140 Hz).

2,3,4,5-Tetrachloro-6-hydroxy-6-(1-methyl-1*H*-pyrrol-2-yl)-cyclohexa-2,4-dienone (16, R = Me).[7,8] *o*-Chloranil (30 mg, 0.12 mmol), *N*-methylpyrrole (9.9 mg, 0.12 mmol), and $CDCl_3$ (0.5 mL) were combined in an NMR tube. The orange quinone solution had turned dark brown upon addition of the pyrrole due to charge-transfer complexation. The tube was allowed to stand for 3 h to allow completion of the addition reaction. ^{13}C NMR ($CDCl_3$): δ 188.1, 143.7, 139.8, 128.3, 127.8, 125.6, 122.5, 110.8, 107.3, 80.7, 36.1.

Dimethyl-3,6-difluoro-4,5-dimethoxyphthalate (21). Methanol (4 drops) was added to a solution of 30 mg of *o*-fluoranil in 0.5 mL of $CDCl_3$ in an NMR tube cooled to 0 °C. The ^{19}F spectrum revealed the development of signals for adduct **17** at −132.1 (m, 1F), −141.1 (m, 1F), −162.2 (m, 1F), and −163.8 (m, 1F). ^{13}C NMR ($CDCl_3$, ^{19}F decoupled, ^{1}H coupled): 183.9, 150.1, 143.7, 136.6, 132.5, 90.6, 50.0 (q, J = 141 Hz). After the tube had warmed to RT, the ^{19}F signals faded and new peaks for compound **18** came to dominate the spectrum at −134.9 (1F), −140.9 (1F), and −156.5 (1F), all singlets under the measurement conditions. With the addition of more methanol, these peaks disappeared, replaced by two representing trimethoxy compound **19** at −144.4 (s, 1F) and −160.2 (q, J = 5.2 Hz, 1F, long-range coupled to a methyl group). To establish the structures of **18** and **19**, the reaction sequence was run on a larger scale in methanol as the solvent.

o-Fluoranil (0.450 g, 2.5 mmol) was dissolved in 5 mL of methanol. The solution was stirred for 13 h at room temperature to form trimethoxy compound **19**, NMR yield of 84%. The reaction mixture was cooled in ice and stirred with $NaHCO_3$ (2.25 g, to neutralize HF) until the pH reached ∼6. Methylene chloride (20 mL) was added, the mixture was filtered, and the solvent was evaporated to give compound **19**. ^{19}F NMR (toluene): δ −142.7 (s, 1F), −161.6 (s, 1F). A small amount of unreacted dimethoxy compound **18** was present: ^{19}F NMR (toluene): δ −135.3 (s, 1F), −140.4 (s, 1F), −157.7 (s, 1F). The product was dissolved in toluene (5 mL) containing dimethyl acetylenedicarboxylate (0.532 g, 3.75 mmol), and the solution was refluxed for 33 h, yielding Diels−Alder adduct **20**. ^{19}F NMR (toluene): δ −202.5 (s, 2F). The solvent was removed and replaced with methylene chloride. The solution was irradiated for 1 h through Pyrex with the 450 W Hanovia lamp. Evaporation of the solvent was followed by chromatography on silica gel with 5% EtOAc/hexanes as the eluent. The yield of phthalate ester **21** was 0.077 g (11% overall). ^{19}F NMR ($CDCl_3$): δ −133.4 (s, 2F). ^{1}H NMR ($CDCl_3$): δ 4.03 (s, 6H), 3.92 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 163.4, 150.0 ($^1J_{CF}$ = 254 Hz), 144.0, 115.5, 61.9, 53.0. HRMS Calcd for $C_{12}H_{12}F_2O_6$: 290.0602. Found: 290.0590.

Dehydrogenation of 1,3-Cyclohexadiene. *o*-Fluoranil (32 mg) was dissolved in $CDCl_3$ (0.5 mL) in an NMR tube, and 1,3-cyclohexadiene (12.8 mg, 0.9 equiv) was added. Within 10 min, the diene peaks in the ^{1}H spectrum had disappeared, replaced by a benzene peak at δ 7.37. The ^{19}F spectrum showed signals for tetrafluorocatechol at δ −165.3 (m, 2F) and −169.7 (m, 2F), and a small amount of residual quinone.

***o*-Fluoranil−Hexamethylbenzene Complex (22).** To a solution of *o*-fluoranil (0.204 g, 1.13 mmol) in chloroform (5 mL) was added hexamethylbenzene (0.183 g, 1.13 mmol). As the reaction mixture was stirred for 1 h, a brown solid precipitated. It was collected by filtration, dried on the filter, and recrystallized from hot hexanes (60 mL). Brown needles deposited at RT. The crystals were collected and washed with hexanes: mp 121−122 °C (0.137 g, 35% yield). ^{19}F NMR ($CDCl_3$): *o*-fluoranil signals were unperturbed by the benzene. Anal. Calcd for $C_{18}H_{18}F_4O_2$: C, 63.15; H, 5.30; F, 22.20. Found: C, 63.27; H, 5.25; F, 22.22.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

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■ NOTE ADDED AFTER ASAP PUBLICATION

Scheme 3 was published with errors on January 5, 2012; the corrected version was reposted on January 9, 2012.