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Cyclopentadiene Bisadduct of Tetrafluoro-*p*-benzoquinone: Its Stereochemistry, Reactivity toward Nucleophiles, and Photochemistry

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The stereochemistry of the cyclopentadiene bisadduct of tetrafluoro-*p*-benzoquinone (**3**) is proposed to be endo-trans-exo. This adduct is observed to undergo a facile addition of oxygen nucleophiles to one of the carbonyl groups with subsequent addition of the carbonyl adduct to the double bond of the *endo*-bicycloheptene moiety. Both **3** and the cyclopentadiene bisadduct of *p*-benzoquinone (**5**) are observed to undergo photochemical intramolecular oxetane formation. The extremely facile oxetane formation observed with **3** is discussed.

Intramolecular oxetane formation in 5-acylbicyclo[2.2.1]hept-2-enes and -[2.2.2]oct-2-enes has been extensively studied by Sauers.[2] Recently he has concluded that this type of oxetane formation proceeds through an intermediate carbonyl–olefin exciplex[2a,b] and that this exciplex formation is sensitive to the geometric constraints imposed upon the carbonyl and olefin moieties by the rigid framework of the bicyclic skeleton.[2d]

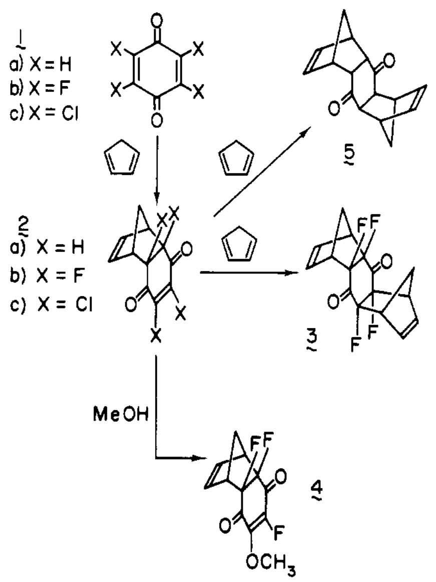
Before the role of exciplexes in oxetane formation was appreciated, it had been observed that intermolecular oxetane formation was greatly facilitated when α-fluoroaldehydes and ketones were used in place of the unfluorinated carbonyl compounds.[3] In the framework of present-day knowledge of carbonyl–olefin photochemistry, this observation indicates that excited α-fluoro carbonyl compounds are better electron acceptors in the formation of preoxetane charge-transfer (C-T) exciplexes than their hydrocarbon analogues. Indeed Wagner has recently shown that C-T exciplexes between α-fluoroketones and substituted benzenes play an important role in the photoreduction of these fluoro ketones.[4]

Some years ago we observed but did not report a bisadduct in the Diels–Alder reaction between tetrafluoro-*p*-benzoquinone (**1b**) and cyclopentadiene. More recently this same bisadduct has been reported by Hudlicky and Bell.[5] We are prompted to report our work with this bisadduct at this time due to its enhanced significance arising from the current interest in the intermediary of C-T exciplexes in carbonyl–olefin photochemistry.

Bisadduct 3: Structure and Stereochemistry

Hudlicky and Bell[5] used elevated temperature (98 °C for 1.5 h) and observed only the cyclopentadiene bisadduct of tetrafluoro-*p*-benzoquinone (**1b**; **3** in Scheme I). At ambient temperature, we have observed that this reaction is complete in about 60 h. If products are isolated after shorter reaction times, it is possible to isolate the intermediate monoadduct **2b** as well as **3**. Care must be exercised in manipulating **2b** as it is extremely susceptible to attack by nucleophiles. Attempts to recrystallize **2b** from hot methanol resulted in the isolation of the methoxy analogue **4** in good yield.

Scheme I



The monoadduct **2b** exhibits a normal olefinic proton signal at δ 6.18 in its ^{1}H NMR spectrum. This lack of fluorine deshielding indicates that **2b** has the usual endoconfiguration with exo fluorine atoms (vide infra). This assignment is supported by the appreciable fluorine coupling (J = 2 Hz) with the bridgehead protons which only would be expected for exo fluorine atoms.[6]

The ^{1}H NMR spectrum of the bisadduct **3** is shown in Figure 1 and clearly indicates that the second cyclopentadiene unit has added in an exo geometry. The olefinic protons of the endo moiety (exo fluorine atoms) display a chemical shift of δ 5.99 and those of the exo moiety (endo fluorine atoms) are shifted downfield to δ 6.54 due to deshielding by the endo fluorine atoms. This unequivocal assignment is based upon the chemistry of this molecule, which is described in later sections. The only other assignment that can be made is that of the unique bridge proton signal centered at δ 1.68. Heteronuclear decoupling experiments demonstrate that this pattern contains the largest proton–fluorine coupling constant in the spectrum (J = 8.0 Hz). A *W* configuration between

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[1] This work was initiated in the laboratories of the late Professor R. B. Woodward at Harvard University and completed at the University of Cincinnati.

[2] (a) Sauers, R. R.; Lynch, D. C. *J. Org. Chem.* **1980**, *45*, 1286. (b) Sauers, R. R.; Bierenbaum, R.; Johnson, R. J.; Thich, J. A.; Potenza, J.; Schugar, H. J. *Ibid.* **1976**, *41*, 2943. (c) Sauers, R. R.; Rousseau, A. D.; Byrne, B. *J. Am. Chem. Soc.* **1975**, *97*, 4947. (d) Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* **1974**, *39*, 1850. (e) Sauers, R. R.; Rousseau, A. D. *J. Am. Chem. Soc.* **1972**, *94*, 1776. (f) Sauers, R. R.; Kelly, K. W. *J. Org. Chem.* **1970**, *35*, 498. (g) Sauers, R. R.; Whittle, J. A. *Ibid.* **1969**, *34*, 3579. (h) Sauers, R. R.; Schinski, W.; Mason, M. M. *Tetrahedron Lett.* **1969**, 79.

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[4] Wagner, P. J.; Puchalski, A. E. *J. Am. Chem. Soc.* **1980**, *102*, 6177. Wagner, P. J.; Thomas, M. J. *Ibid.* **1980**, *102*, 4173. Wagner, P. J.; Lam, H. M. H. *Ibid.* **1980**, *102*, 4167. Wagner, P. J.; Leavitt, R. A. *Ibid.* **1973**, *95*, 3669. Wagner, P. J.; Leavitt, R. A. *Ibid.* **1970**, *92*, 5806.

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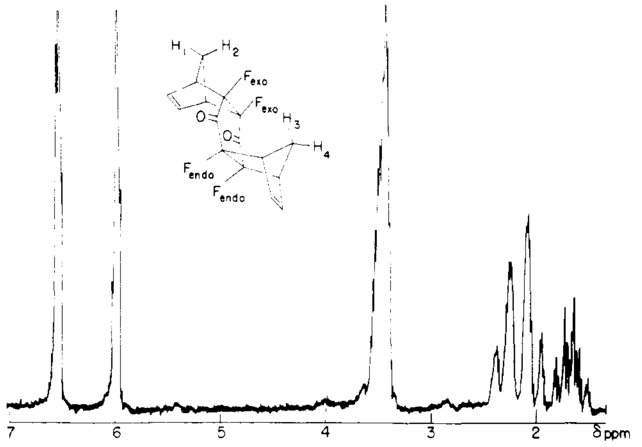
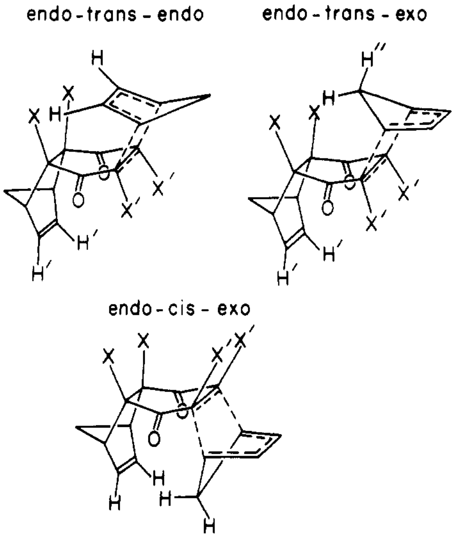


Figure 1. ^1H NMR (90-MHz) spectrum of the cyclopentadiene bisadduct of tetrafluoro-*p*-benzoquinone (**3**).

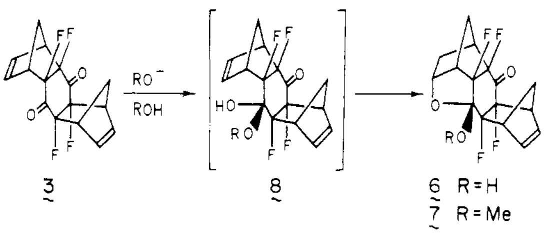
Scheme II



the coupled nuclei would be required for such a strong long-range coupling.[7] The only such arrangement of nuclei in **3** is between H_4 and the endo fluorine atoms.

We are in agreement with the previous workers[5] that these NMR data do not permit an unequivocal distinction to be made between the endo-trans-exo and the endo-cis-exo geometries for the bisadduct **3**. However, the endo-trans-exo stereochemistry, depicted in Scheme I and Figure 1, seems much more likely for the following reasons. The Diels–Alder reaction is known to be most sensitive to steric crowding in the transition state. The room-temperature reaction between *p*-benzoquinone and cyclopentadiene produces the endo-trans-endo bisadduct **5** exclusively.[8] Thus, when X is small, X = H, the steric repulsion between X and H in the endo-trans-endo transition state (Scheme II) is not prohibitive. Clearly when X is larger, X = F, this interaction does become prohibitive and the endo-trans-endo bisadduct is not formed. In related moderately congested systems, the alternative endo-trans-exo transition state assumes control in the second addition step.[9] This is probably due to the reduced steric crowding of the configuration in which H is directed between the X groups. This model accounts for the behavior of the fluorine system most satisfactorily. Indeed, if congestion is increased still further by replacing the fluorines by chlorine, even this transition state becomes sterically prohibitive and only the monoadduct **2c** can be formed (Scheme I).[10] Finally, *cis*-cyclopentadiene bisadducts are known not to be formed in related Diels–Alder reactions.[11] The reason for this can be understood by examination of the only sterically acceptable transition state for formation of the endo-cis-exo bisadduct (Scheme II). As adduct formation proceeds in this configuration, the incipient σ bonds become oriented so that they can no longer overlap with the π orbitals of the carbonyl groups, and a serious loss in stabilization should result. Thus, the transition state for this endo-cis-exo bisadduct would be expected to occur at significantly higher energy than that of the endo-trans-exo bisadduct where this type of stabilization is not lost. A possible mechanism for lowering this cis transition state energy would be for the X′ groups to provide the stabilization for the incipient σ bonds, but it is very doubtful that inductive groups like fluorine could provide the necessary stabilization.

Scheme III



Attack by Nucleophiles

The susceptibility of carbonyl groups to nucleophilic attack is enhanced significantly by substitution of the α protons with fluorines.[12] Even though the carbonyls in bisadduct **3** are activated by only two such fluorine atoms, they are very labile to attack by nucleophiles. Thus, hydroxide and methoxide ions add to these carbonyl groups in facile reactions (Scheme III).

The elemental compositions of these nucleophile adducts exclude the possibility that they are Favorskii rearrangement products. The ^1H NMR spectra of both of these adducts do not exhibit the high-field olefinic signal associated with the *endo*-bicycloheptene moiety of **3**. A new >CHO triplet appears in the spectra of both adducts, δ 4.60 for **6** and δ 4.55 for **7**. These data indicate that the double bond of the *endo*-bicycloheptene has participated in the reaction and that a new carbon–oxygen bond has been formed at this site. The hydroxide adduct **6** contains a hydroxyl group, δ 3.81, which is moderately acidic, as this substance is soluble in aqueous sodium hydroxide. The methoxide adduct **7** contains a methoxy group, δ 3.55 (d, J = 4.0 Hz), which is coupled to a single fluorine atom. While an assignment of this fluorine–methoxy coupling cannot be made from the data available, a similar long-range fluorine–methoxy coupling was observed in the methoxy-substituted monoadduct **4**, δ 4.21 (d, J = 5 Hz). Aside from these features, the NMR spectra of **6** and **7** are

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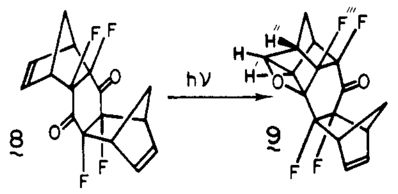
Scheme IV



virtually identical and consistent with the structures proposed in Scheme III.

These structures can be derived by a straightforward mechanistic pathway. Initial attack of the oxygen nucleophile upon the electron-deficient carbonyl groups should lead to the tetrahedral intermediate **8** (Scheme III). It should be noted that due to the conformation of the 1,4-cyclohexandione ring of **3** (see Figure 1), attack by methoxide from the most accessible carbonyl face will lead to the stereochemistry shown in which the hydroxy group is in close proximity to the double bond of *endo*-bicycloheptene moiety. The enhanced acidity of this hydroxy group should facilitate the hydration of this proximate double bond to form **6** and **7**. Finally, the same type of tricyclic ether skeleton is formed upon treatment of chlorinated *endo*-bicycloheptene-5-carbinols with methoxide.[13]

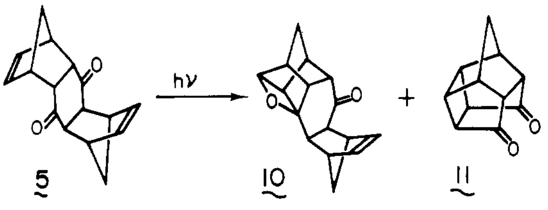
When the bisadduct **5** (Scheme I) is treated with hydroxide under similar conditions, the analogous tricyclic ethers are not observed. Instead epimerization at the carbon atoms α to the carbonyl groups occurs.[11c] Therefore, the transformations described above would seem to provide a good qualitative measure of the electron-deficient nature of the carbonyl groups in the bisadduct **3**.

Photochemistry

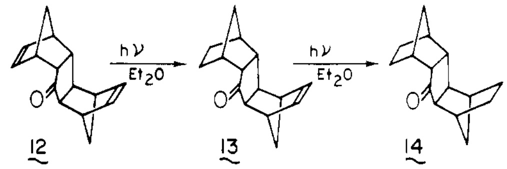
The bisadduct **3** is transformed in good yield to a single product **9** (Scheme IV) upon irradiation with ultraviolet light for a few hours. That this substance is an oxetane related to those described by Sauers[2] is indicated by its ^{1}H NMR spectrum. This spectrum exhibits a single olefinic proton signal at δ 6.47, which corresponds to the low-field olefinic proton signal in the spectrum of **3** and the olefinic proton signals in the spectra of **6** and **7**. Therefore, all of these signals are assigned to the olefinic protons in the *exo*-bicycloheptene moiety in which these olefinic protons are deshielded by the endo fluorine atoms. In place of the olefinic proton signal associated with the *endo*-bicycloheptene moiety an oxetane >CHO signal appears at δ 5.01. This signal is a triple doublet in which the coupling constants have been established by double resonance experiments to be two proton–proton doublets, J' = 1 Hz and J'' = 1 Hz, and a proton–fluorine doublet, J''' = 3 Hz. The nuclei leading to these couplings are the two protons H′ and H″ and the fluorine F‴ indicated in Scheme IV. The regiochemistry of the carbonyl addition to the endo olefin is assigned by analogy to the many examples that Sauers has observed.[2]

It is interesting to compare the aforementioned photochemistry of **3** with that of the well-known bisadduct **5** (Scheme V). Irradiation of **5** under conditions similar to those used for **3** produced a reaction mixture complicated by extensive polymer formation on the surface of the immersion well. Only after extremely long irradiation times (10–20 days) was it possible to accumulate isolable quantities of the oxetane **10** along with the cage diketone **11**. The diketone **11** is an artifact of a slow retrograde Diels–Alder reaction to produce the cyclopentadiene monoadduct of *p*-benzoquinone followed by the well-known intramolecular photocycloaddition of this monoadduct.[14] The formation of **11** is certainly a consequence of the extremely long irradiation times necessary to accumulate significant quantities of **10**.

Scheme V



Scheme VI



The oxetane **10** had a ^{1}H NMR spectrum that exhibited an olefinic proton AB pattern centered at δ 6.19, which is characteristic of endo unsymmetrically disubstituted bicycloheptene systems. In addition the oxetane >CHO proton signal appears as a broad unresolved multiplet at δ 4.87.

The photochemistry of the bisadduct **12** was also examined (Scheme VI) and found to afford isolable products only in solvents with abstractable hydrogen atoms. This system produced no oxetane products. Instead the sequential reduction of the bicycloheptene double bonds was observed to take place. The structure of the tetrahydro ketone **14** was confirmed by hydrogenation of **12**.

These photochemical results are in accord with those of Sauer's who found that intramolecular oxetane formation proceeds through an unquenchable short-lived triplet or singlet n,π^* state,[2c,e] and that cyclopentanone systems related to **12** undergo bicycloheptene double bond reduction via the olefin π,π^* triplet state.[2d] He ascribes this lack of oxetane formation in the cyclopentanone systems to steric inhibition to overlap between the carbonyl nonbonding orbitals and the p orbitals of the bicycloheptene double bond. Overlap of this type is thought to be necessary for the formation of exciplexes, which in turn are thought to be precursors of many oxetanes,[15] including those formed in the intramolecular reactions under discussion here.[2d] Failure to achieve exciplex stabilization in these cyclopentanone systems apparently leads to energy transfer to the olefin and the subsequent reduction of its π,π^* state by hydrogen atom abstraction.

The most interesting question arising from these results is why oxetane formation is so very much more efficient with the fluoro ketone **3** than with the unsubstituted ketone **5**. This difference cannot be due to steric inhibition to exciplex formation, since both **3** and **5** have about the same degree of conformational mobility. Therefore, the enhanced cyclization efficiency of **3** must be due to electronic factors.

Arnold has found that excited carbonyl compounds with triplet energies above 72 kcal/mol form very little oxetane

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(13) Hoch, P. E.; Stratton, G. B.; Colson, J. G. *J. Org. Chem.* **1969**, *34*, 1912.

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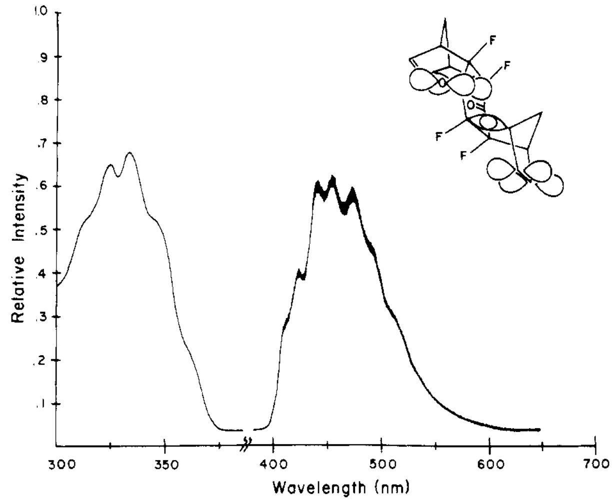

Figure 2. Absorption and phosphorescence spectra of bisadduct **3** in 2-methyltetrahydrofuran. The orbitals of the extended chromophore are indicated in the structure. It should be noted that both carbonyls are part of the same extended chromophore. For the sake of clarity, the orbitals of only one of the carbonyl systems have been represented in the drawing.

with norbornene; instead they undergo energy transfer to the norbornene double bond and polymerization results. When the carbonyl triplet energy falls below 72 kcal/mol, oxetane formation becomes the predominant process. The threshold of this change in mechanism is very narrow, only about 1 kcal/mol.[16] Therefore, it is possible that the fluoro ketone **3** has a triplet energy below 72 kcal/mol and does not undergo energy transfer but forms oxetane instead. The unsubstituted ketone **5** exhibits the usual aliphatic ketone n,π^* transition, λ_{max}(2-methyltetrahydrofuran) 305 nm (ϵ 32).[17] This would correspond to an n,π^* triplet energy of about 81–82 kcal/mol.[18] Therefore, **5** would be expected to undergo very inefficient oxetane formation. In contrast, the fluoro ketone **3** exhibits a surprisingly intense low-energy n,π^* transition, λ_{max}(2-methyltetrahydrofuran) 334 nm (ϵ 187) (Figure 2). Judging from the band structure in this transition, the n,π^* 0–0 band should fall in the region of 375–380 nm, which corresponds to an n,π^* singlet energy of about 75–76 kcal/mol, which would indicate that the triplet energy is about 73 kcal/mol. This estimate of the triplet energy for **3** is very close to the triplet energy of norbornene, 72 kcal/mol.

The emission properties of both **3** and **5** were examined in order to more firmly establish these triplet energies. As expected the unsubstituted ketone **5** exhibits no emission. However, as indicated by the aforementioned absorption properties, the fluoro ketone **3** does exhibit moderately intense n,π^* phosphorescence in 2-methyltetrahydrofuran glass at 77 K (Figure 2). On the basis of this phosphorescence spectrum, the n,π^* triplet energy of **3** can be set at 70.5–72.5 kcal/mol, depending upon whether the 0–0 band is weakly or strongly forbidden, respectively. The observation of this spectrum confirms that the carbonyl n,π^* triplet of **3** is at lower energy than the olefin π,π^* triplet and that the energy of the n,π^* triplet is very close to or below the threshold for energy transfer established by Arnold.[16] While these observations do not rigorously exclude the possibility of some fluorooxetane formation via the fluorocarbonyl singlet state, they do provide good evidence for oxetane formation via an unusually low-energy fluorocarbonyl triplet state.

The question remains as to why the n,π^* singlet and triplet states of **3** are so low in energy. Fluorine substitution can lower the energy of the n,π^* state. A similar very strong bathochromic shift has been reported for perfluorocyclobutanone, n,π^* 0–0 band = 410 nm, relative to cyclobutanone, n,π^* 0–0 band = 340 nm.[19] Alternatively, **3** does contain the extended chromophore indicated in Figure 2. This extended chromophore incorporates the aligned π orbitals of the carbonyl, the σ orbitals of the exo-substituted bicycloheptene moiety, and the π orbitals of its double bond. The characteristics of closely related extended chromophores are an intensification and small bathochromic shift of the n,π^* band system.[20] These characteristics are similar to those observed for **3** (Figure 2) except that the bathochromic shift in the spectrum of **3** is much larger than that observed for other related extended chromophores. Apparently, a combination of the effect of the fluorine substitution and the extended chromophore are reinforcing each other to produce this very large shift to lower energy, which brings the energies of the n,π^* states of **3** to low levels typical of aryl ketones.

Finally, it must be mentioned that while an exciplex between the excited carbonyl and the endo-substituted bicycloheptene system of **3** may well be involved in the formation of oxetane **9**, no direct evidence for such a species has been observed in this work.

In conclusion, the results related here indicate the photochemistry of olefins with fluoro ketones can provide access to unusual ring systems that are not readily accessible with the unsubstituted ketones. They further indicate that the photochemistry of α-fluoro ketones should provide a most profitable area for more quantitative studies.

Experimental Section

General Procedures. Tetrafluoro-*p*-benzoquinone was obtained from K & K Laboratories. Melting points are uncorrected and were determined with a Mettler FP-2 hot stage apparatus with a polarizing microscope. Nuclear magnetic resonance spectra were recorded with a Varian Associates A-60 or a Bruker HFX-90 instrument. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane for ^{1}H and hexafluorobenzene for ^{19}F. Infrared spectra were recorded with a Perkin-Elmer Model 337 spectrophotometer. Ultraviolet spectra were recorded with a Cary Model 14 spectrophotometer and emission spectra with an Aminco-Bowman spectrophotofluorometer. Mass spectra were determined with a Hitachi RMU-7 spectrometer at an ionizing voltage of 70 eV. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Photochemical reactions were conducted in Pyrex with a Rayonet photochemical reactor and 360-nm lamps.

Reaction of Tetrafluoro-*p*-benzoquinone (1b) with Cyclopentadiene: Formation of Bisadduct 3. To a solution of 0.492 g (2.74 mmol) of **1b** in 10 mL of benzene was added 1.6 g (24.2 mmol) of freshly distilled cyclopentadiene. The reaction was difficult to follow by TLC as no definite spots could be detected until the reaction neared completion. After standing 60 h at room temperature, the reaction mixture was passed through Celite and evaporated to dryness. The semisolid residue was dissolved in a minimum amount of methylene chloride and mixed with about 10 volumes of *n*-pentane. The oily hydrocarbon polymer that separated was removed by passing the solution through Celite and the filtrate evaporated to dryness. The resulting oily, pale-yellow crystals were triturated twice with 2-mL

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portions of *n*-pentane and recrystallized from ether to yield 0.583 g (68%) of **3**: mp 153–155 °C; IR (CCl_4) ν_{max} 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.68 (dtt, $J_{H,H}$ (bridge proton) = 12 Hz, $J_{H,F}$ (endo fluorines) = 8 Hz, $J_{H,H}$ (bridgehead protons) = 2 Hz, 1 H), 2.18 (AB, J = 12 Hz, 3 H), 3.44 (br s, 4 H), 5.99 (s, 2 H), 6.54 (s, 2 H); ^{19}F NMR ($CDCl_3$, 84.66 MHz) δ 2.76 (br d, $J_{H,F}$ (bridge proton) = 8 Hz, 2 F), 9.99 (br s, $J_{H,F}$ (bridgehead protons) = 4 Hz, 2 F); UV (*n*-pentane) λ_{max} 252 nm (4950), 314 (s, 170), 326 (218), 337 (228), 347 (s, 174), 360 (s, ϵ 72); mass spectrum, *m/e* 312 (M$^+$). Anal. Calcd for $C_{16}H_{12}F_4O_2$: C, 61.53; H, 3.88. Found: C, 61.76; H, 3.84.

Formation of Monoadducts 2b and 4. Monoadducts **2b** and **4** were isolated during the course of the development of the above procedure. No effort was devoted to increasing the yields. If the aforementioned procedure was modified by reducing the ratio of cyclopentadiene:**1b** to about 2:1, and by reducing the reaction time to several hours, then extensive recrystallization of the product from methylene chloride–ether yielded **2b**: mp 126.5–127.5 °C; IR (CCl_4) ν_{max} 1710, 1660 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (AB, J = 11 Hz, 2 H), 3.51 (ddd, J = 7 Hz, J = 4 Hz, J = 2 Hz, 2 H), 6.18 (br s, 2 H); mass spectrum, *m/e* 246 (M$^+$). Anal. Calcd for $C_{11}H_6F_4O_2$: C, 53.66; H, 2.46. Found: C, 53.78; H, 2.44.

If the same crude reaction mixture containing **2b** was treated with hot methanol in a recrystallization operation, the methoxy-substituted monoadduct **4** was obtained: mp 96–98 °C; IR (CCl_4) ν_{max} 1690, 1610 cm^{-1}; NMR ($CDCl_3$) δ 2.28 (AB, J = 10 Hz, 2 H), 3.43 (br, 2 H), 4.21 (d, J = 5 Hz, 3 H), 6.15 (br s, 2 H); mass spectrum, *m/e* 258 (M$^+$). Anal. Calcd for $C_{12}H_9F_3O_3$: C, 55.81; H, 3.52. Found: C, 55.67; H, 3.54.

Addition of Water to the Bisadduct 3: Formation of Hemiketal 6. A solution of 0.117 g (0.375 mmol) of **3** and 0.112 g (2.78 mmol) of sodium hydroxide in dioxane:water (15 mL:5 mL) was refluxed at 102 °C for 1 h. The residue remaining upon evaporation to dryness was distributed between methylene chloride and water. The aqueous layer was acidified with hydrochloric acid and extracted with methylene chloride. After drying over magnesium sulfate, the organic layer was evaporated to dryness to yield 0.103 g (83%) of crude **6**. Purification by filtration through silica gel, and recrystallization from methylene chloride–ligroin afforded **6**: mp 173–175 °C; IR ($CHCl_3$) ν_{max} 3580, 3300, 1736 cm^{-1}; NMR ($CDCl_3$) δ 1.3–2.45 (c, 6 H), 2.87 and 3.14 (br s, 2 H), 3.51 (br s, 2 H), 3.81 (br s, 1 H, OH), 4.60 (dd, J = 5 Hz, J = 5 Hz, 1 H), 6.49 (br s, 2 H); mass spectrum, *m/e* 330 (M$^+$), 312 (M$^+$ – H_2O). Anal. Calcd for $C_{16}H_{14}F_4O_3$: C, 58.17; H, 4.28. Found: C, 58.37; H, 4.23.

Addition of Methanol to the Bisadduct 3: Formation of Ketal 7. A solution of 0.102 g (0.328 mmol) of **3** and 0.0922 g (2.30 mmol) of sodium hydroxide in 50 mL of methanol underwent complete reaction at room temperature within 24 h. The residue remaining upon evaporation to dryness was dissolved in methylene chloride and extracted with water. The organic layer was dried over magnesium sulfate and evaporated to dryness to yield 0.1073 g (95%) of colorless crystals. A single recrystallization from methylene chloride–methanol yielded **7**: mp 144–145.5 °C; IR (CCl_4) ν_{max} 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.3–2.45 (c, 6 H), 2.82 and 3.13 (br s, 2 H), 3.48 (br, 2 H), 3.55 (d, J = 4 Hz, 3 H), 4.55 (dd, J = 5 Hz, J = 5 Hz, 1 H), 6.48 (br s, 2 H); mass spectrum, *m/e* 349 (M$^+$), 312 (M$^+$ – CH_3OH). Anal. Calcd for $C_{17}H_{16}F_4O_3$: C, 59.29; H, 4.69. Found: C, 59.44; H, 4.67.

Photocyclization of Bisadduct 3: Formation of Oxetane 9. A solution of 0.119 g (0.381 mmol) of **3** in 30 mL of benzene was irradiated at 360 nm for 5 h under nitrogen. The residue obtained upon evaporation of the solvent was purified by thick-layer chromatography, eluting with *n*-pentane:methanol (95:5). The oxetane **9** was slightly more polar than the starting diketone **3**. Recrystallization from ether yielded 0.076 g (64%) of **9**: mp 154–157 °C; IR (CCl_4) ν_{max} 1750 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.70 (br s, 2 H), 1.92 (ddd, J = 12 Hz, J = 5 Hz, J = 2 Hz, 1 H), 2.30 (c, 1 H), 2.82 (ddd, J = 12 Hz, J = 3.5 Hz, J = 3.5 Hz, 1 H), 3.08 (br d, J = 11 Hz, 1 H), 3.40 (br s, 2 H), 3.56 (br, 1 H), 5.01 (ddd, J = 1 Hz, J = 1 Hz, J = 3 Hz, 1 H), 6.47 (br s, 2 H); mass spectrum, *m/e* 312 (M$^+$). Anal. Calcd for $C_{16}H_{12}F_4O_2$: C, 61.53; H, 3.88. Found: C, 61.62; H, 3.81.

Photocyclization of Bisadduct 5: Formation of Oxetane 10. A solution of 5.02 g (20.9 mmole) of **5** in 800 mL of benzene was stirred magnetically under nitrogen and irradiated at 360 nm. At intervals of about 48 h the reaction mixture was filtered through Celite to remove the copious orange polymer that was produced. After a total of 19 days irradiation the reaction was concluded, even though TLC showed a great deal of unreacted starting material to be present. The residue (3.7 g) remaining upon evaporation of the solvent was recrystallized from hot benzene to yield 1.3 g of recovered **5**. The mother liquor was chromatographed on 50 g of silica gel, eluting with benzene:chloroform (50:1). The fractions containing the photoproducts were purified further by thick-layer chromatography, eluting four times with benzene:methanol (99:1) to obtain crude **11** (0.337 g) and **10** (0.302 g) in 15% and 10% yield, respectively (based on 3.06 g of reacted starting material). The structure of **11** was confirmed by comparison with an authentic sample.[14] After recrystallizations from hot methanol and from methanol–methylene chloride, **10** had the following: mp 136–139 °C; IR (CCl_4) ν_{max} 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.45 (c, 2 H), 1.69 (br s, 2 H), 2.11 (br, 1 H), 2.91, 2.78, and 2.54 (c, 6 H), 3.21 (br, 1 H), 3.40 (br, 1 H), 4.87 (br, 1 H), 6.19 (br AB, 2 H); mass spectrum, *m/e* 240 (M$^+$). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.72. Found: C, 79.91; H, 6.77.

Photoreduction of Bisadduct 12: Formation of 14. A solution of 0.054 g (0.256 mmol) of **12** in 20 mL of ether under nitrogen was irradiated at 360 nm for 29 h. Aliquots were analyzed periodically by VPC, using a 0.25 in. × 12 ft 5% SE-30 on 60–80 Chromosorb W column at 150 °C (isothermal). Two products were detected with retention times **13**/**12** = 1.24 and **14**/**12** = 1.54. The 1.24 peak (**13**) appeared during the initial stages of the reaction. The 1.54 peak (**14**) appeared later in the reaction, and increased in size while the 1.24 peak diminished until at 29 h only the 1.54 peak remained. This product was collected by preparative VPC and without further purification had the following: mp 172–173 °C; IR (CCl_4) ν_{max} 1715 cm^{-1}; mass spectrum, *m/e* 216 (M$^+$).

Comparison of this material with authentic **14** prepared by reduction of **12** with hydrogen at atmospheric pressure in ethanol using 10% Pd/C as the catalyst proved them to be identical. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.34. Found: C, 83.25; H, 9.24.

The photolysis of **12** was also examined in cyclohexane, benzene, and perfluoromethylcyclohexane. Photoreduction was observed in cyclohexane albeit with lower efficiency than in ether, whereas only polymer formation was observed in the latter two solvents.

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Registry No. **1b**, 527-21-9; **2b**, 84500-37-8; **3**, 56298-31-8; **4**, 84520-48-9; **5**, 78548-82-0; **6**, 84520-49-0; **7**, 84500-38-9; **9**, 84500-39-0; **10**, 84500-40-3; **11**, 2958-72-7; **12**, 5019-95-4; **13**, 5019-99-8; **14**, 35121-30-3; cyclopentadiene, 542-92-7.