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**Supplementary Material Available:** Experimental proce-

dures and analytical data for all new compounds reported in this manuscript and a reproduction of the 400-MHz  $^1\text{H}$  NMR spectrum of synthetic 7 (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

## Articles

### Thermal and Photochemical Rearrangements of Cyclopropyl Ethers of *p*-Quinols. Competing Reaction Pathways Leading to Five- and Six-Membered Ring Spirocyclic Ketones

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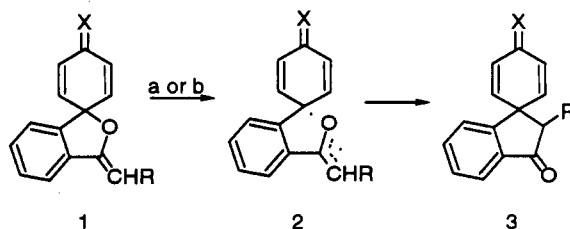
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Cyclopropyl ethers of *p*-quinols were prepared by reaction of 3''-methylenedispiro[1,3-dioxolone-2,1'-[2,5]-cyclohexadiene-4',1''(3''*H*)-isobenzofuran] and the associated ketone with ethyl diazoacetate/rhodium(II) acetate and diethylzinc/methylene iodide, respectively, and their thermal and photochemical rearrangements were studied. One major process at 180–200 °C is cleavage of the carbon–oxygen bond at the spiro center of the quinol to give a phenoxy and cyclopropoxy radical pair. A cyclopropylcarbinyl-like opening of the latter radical followed by recombination of the ring-opened radical with the phenoxy radical resulted in formation of a six-membered ring spirocyclic ketone. The other major thermal process for the cyclopropyl ether is conveniently viewed as ring-opening of the cyclopropane ring without breakage of the quinol carbon–oxygen bond followed by a hydrogen shift to afford a functionalized vinyl ether. This compound reacts under the thermal conditions to afford as the final product the five-membered ring spirocyclic ketone. Interestingly, the importance of these two competing pathways is influenced by the stereochemistry of ester substituents on the cyclopropane ring. Two major processes have been established in the photochemistry of these cyclopropyl ethers of *p*-quinols. One is rearrangement to the same six-membered ring spirocyclic ketone as discussed above. The second process is photolysis to a styrene derivative and a carbene.

**Introduction.** The thermal<sup>1</sup> and photochemical<sup>2</sup> [1,3]-oxygen-to-carbon migrations of vinyl ethers of *p*-quinols lead to spirocyclic ketones in high yield, Scheme I. Since the starting vinyl ethers are readily available from quinone monoketals,<sup>3</sup> this serves as a useful route to these spiro-fused compounds containing the cyclopentanone moiety. The reaction is most conveniently viewed as involving homolytic cleavage of the carbon–oxygen bond of the *p*-quinol followed by reclosure of the phenoxy–allyloxy biradical, 2, at the carbon of the latter radical, Scheme I. If a similar bond homolysis occurs for cyclopropyl ethers of *p*-quinols, then a convenient route to spiro-fused dienones containing a six-membered ring could result. We report here the preparation of cyclopropyl ethers of *p*-quinols and a study of their thermal and photochemical rearrangements.

**Synthesis and Rearrangement Studies.** The most direct route to the cyclopropyl ethers required for study would be reaction of carbenoid reagents with the readily available vinyl ether 4.<sup>2b</sup> There are two different types of

Scheme I. [1,3]-Oxygen-to-Carbon Migrations in Spirocyclic Vinyl Ethers<sup>a</sup>



<sup>a</sup> Key: (a) X = O, 120–160 °C; (b) X = (OR)<sub>2</sub>, *hν*.

double bonds available for cyclopropanation in 4 in addition to a vinyl ether and ketal function which could be unstable in the presence of Lewis acid catalysts. Thus, we first investigated the rhodium(II)<sup>4</sup>-catalyzed reaction of ethyl diazoacetate with 4. The mild conditions for the reaction together with the selectivity of the carbenoid species for an electron-rich double bond offered the best chance for a high-yield cyclopropanation reaction. As shown below, reaction of 4 under these conditions gave in 63% yield a ca. 1:1 mixture of 5a and 5b.<sup>5</sup> These compounds could be separated by chromatography, but hy-

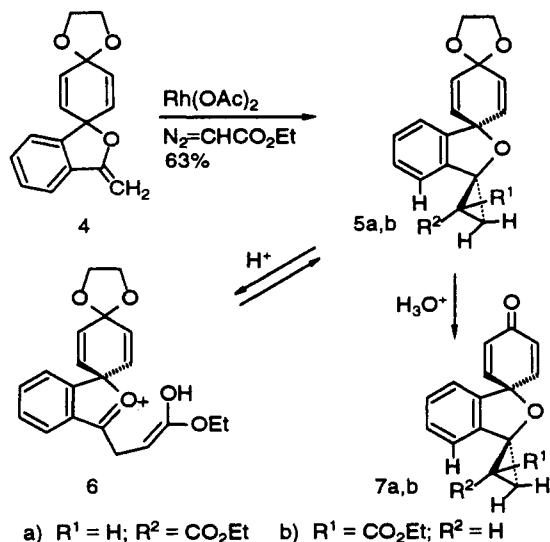
(1) (a) Morrow, G. W.; Wang, S.; Swenton, J. S. *Tetrahedron Lett.* 1988, 29, 3441. (b) Wang, S.; Morrow, G.; Swenton, J. S. *J. Org. Chem.* 1989, 54, 5364.

(2) (a) Wang, S.; Callinan, A.; Swenton, J. S. *J. Org. Chem.* 1990, 55, 2272. (b) Swenton, J. S.; Callinan, A. C.; Wang, S. *J. Org. Chem.* 1992, 57, 78.

(3) For reviews and leading references, see: Swenton, J. S. *Acc. Chem. Res.* 1983, 16, 74. Swenton, J. S. In *Chemistry of Quinonoid Compounds, Part 2*; Rappoport, Z., Patai, S., Eds.; John Wiley: New York, 1988; p 899.

(4) For a review, see: Doyle, M. *Chem. Rev.* 1986, 86, 919.

(5) The cyclopropyl hydrogens in both 5a and 5b showed nearly identical patterns to those of 7a and 7b, so the stereochemistries for 5a and 5b were assigned based on this similarity (see supplementary material for spectra).

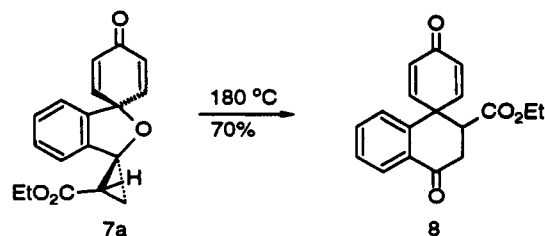


drolysis of pure 5a or 5b led to formation of the same mixture of 7a and 7b. Thus, under acidic conditions, *cis*-*trans* isomerism is occurring, perhaps via the intermediate 6 shown below. However, 7a and 7b could again be separated by silica gel chromatography.

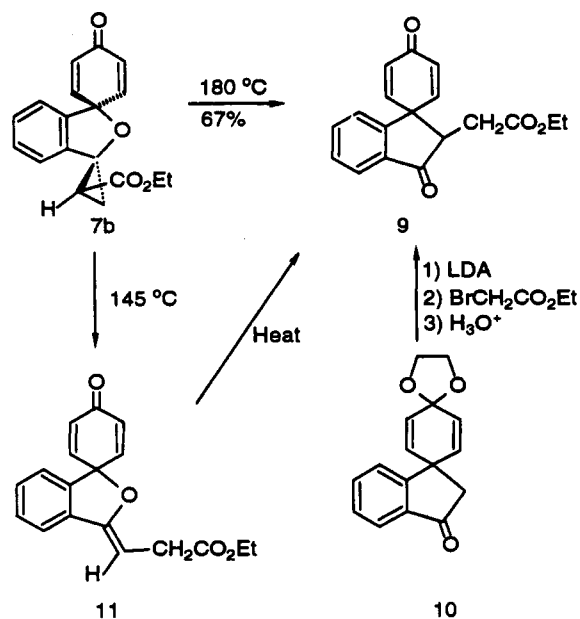
Because the thermal chemistry of these compounds is dramatically dependent on the stereochemistry of the ester group (see below), the stereochemical assignments for 7a and 7b will be discussed first. A key feature to interpretation of the NOE studies was the chemical shifts of the cyclopropyl methine hydrogen in 7a and 7b. This point was established by preparation of the deuterated compounds 7a-*d*<sub>1</sub> and 7b-*d*<sub>1</sub> from 4 and ethyl diazoacetate-*d*<sub>1</sub>.<sup>6</sup> The most informative NOE experiments arose from irradiation of the cyclopropyl methine protons, H<sub>d</sub>, in these isomeric esters as shown graphically in Table I. For 7a, the NOE enhancement observed at H<sub>e</sub> when H<sub>d</sub> is irradiated is only consistent with the structure wherein the ester group is *syn* to the aromatic ring. Likewise, in 7b the enhancement of H<sub>e</sub> when H<sub>d</sub> is irradiated is only consistent with an ester group which is *syn* to the oxygen function. Other NOE results for 7a and 7b are summarized in Table I and detailed in the Supplementary Section.

With the structure assignments for the isomeric esters 7a,b secure, the thermal isomerization studies of 7a,b were initiated. The thermolyses were first investigated at 180 °C, a higher temperature than that used for the analogous vinyl ether systems.<sup>1</sup> The stabilization of the cyclopropalkoxy radical was expected to be substantially less than that of the oxyallyl radical, and this difference would be reflected in the ease of homolysis of the carbon-oxygen bond. The thermal rearrangement of 7a produced a major product in 70% yield to which the structure 8 was assigned. This compound showed carbonyl stretchings in the IR at 1731, 1689, and 1666 cm<sup>-1</sup> characteristic of ester,  $\alpha$ -tetralone, and dienone moieties, respectively. The aliphatic region of the <sup>1</sup>H NMR spectrum of 8 was especially informative, showing three one-proton signals:  $\delta$  3.50 (dd,  $J = 4.6, 13$  Hz), 3.20 (dd,  $J = 13, 18$  Hz), 2.95 (dd,  $J = 4.6, 18$  Hz).

The thermolysis of 7b was then studied at 180 °C with the expectation that 8 would also be formed. Instead, there was formed a different major product, 9, in 67% yield. The <sup>1</sup>H NMR spectrum of 9 showed three one-proton signals in the aliphatic region:  $\delta$  3.55 (dd,  $J = 5.3, 8$  Hz), 2.92 (dd,  $J = 5.3, 17$  Hz), and 2.38 (dd,  $J = 8, 17$  Hz). Moreover, the carbonyl region in the IR spectrum showed strong



absorptions at 1735, 1715, and 1660 cm<sup>-1</sup>. The replacement of the absorption at 1689 cm<sup>-1</sup> in 8 by an absorption at 1715 cm<sup>-1</sup> in 9 suggested that the ketone carbonyl group in 9 was not in a six-membered ring, but rather in a five-membered ring. The supposition was verified when an authentic sample of 9 was prepared by alkylation of 10.<sup>2b</sup> The product prepared from alkylation of 10 was identical in all respects with 9 obtained from the thermal reaction of 7b.

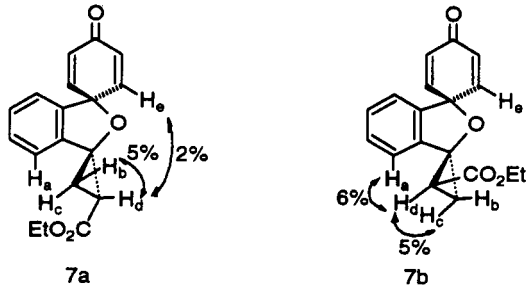


It seemed that the formation of 9 involved intermediates which could be isolated if the reaction were done at a lower temperature. Indeed, conducting the reaction of 7b at a lower temperature led to the detection of an intermediate. Unfortunately, the intermediate formed was more reactive than starting 7b, making it difficult to obtain isolable amounts of the compound. However, by heating 7b at 145 °C for 3 h, a separable mixture of starting material (33%), 9 (20%), and the intermediate (25%) was obtained. The intermediate was isolated and assigned structure 11; however, the stereochemistry shown was not unequivocally established. The IR spectrum of 11 showed both ester and dienone carbonyl absorptions at 1738 and 1674 cm<sup>-1</sup>. However, the <sup>1</sup>H NMR spectrum was most informative, showing the vinyl hydrogen as a triplet,  $\delta$  5.3 ( $J = 7.3$  Hz) and the methylene hydrogens as a doublet at  $\delta$  3.3 ( $J = 7.3$  Hz). The thermal reaction of 11 resulted in formation of 9 via a process analogous to previously studied vinyl ethers.<sup>1</sup>

Photochemical activation in previously studied vinyl ethers<sup>2</sup> led to spirocyclic ketones in excellent yields, Scheme I. The lower temperature employed for the photochemical reactions would decrease the likelihood of a 7b  $\rightarrow$  11 conversion and could lead exclusively to the six-membered ring spirocyclic ketone. The ketals 5a,b were reasonably stable under a variety of irradiation conditions. However, irradiation of 7a and 7b gave 8 as the major characterized product, but only in 25% yield. All attempts

(6) Swenton, J. S.; Madigan, D. M. *Tetrahedron* 1972, 28, 2703.

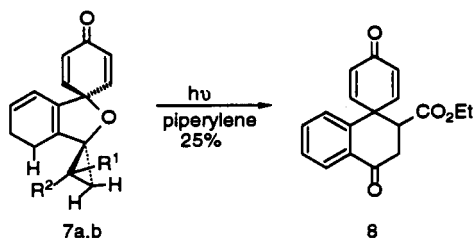
Table I. NOE Data for 7a and 7b. NOE Enhancements when H<sub>d</sub> Is Irradiated



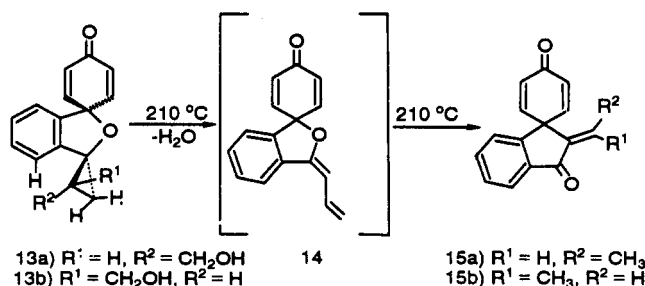
7a		7b	
proton irradiated	signal enhanced	proton irradiated	signal enhanced
H <sub>b</sub>	H <sub>c</sub> <sup>a</sup> , H <sub>d</sub> <sup>a</sup>	H <sub>b</sub>	H <sub>c</sub> (28%)
H <sub>c</sub>	H <sub>a</sub> (~5%), H <sub>b</sub> <sup>a</sup>	H <sub>c</sub>	H <sub>a</sub> (4%), H <sub>b</sub> (13%), H <sub>d</sub> (4%)
H <sub>d</sub>	H <sub>b</sub> (~5%), H <sub>e</sub> (2%)	H <sub>d</sub>	H <sub>a</sub> (6%), H <sub>c</sub> (5%)

<sup>a</sup>An NOE enhancement was observed, but the difference in chemical shifts of H<sub>b</sub> and H<sub>c</sub> is not sufficient to assign a reliable percent enhancement.

to improve the yield of the reaction were unsuccessful. Work discussed later suggests that photolysis of the cyclopropane ring in 7a and 7b to an alkene and a carbene may contribute to the low yield of 8.



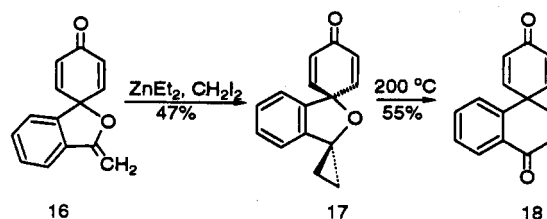
Another strategy to avoid the thermal isomerization of the cyclopropyl ether to a vinyl ether followed by rearrangement to a five-membered ring spirocyclic ketone, 7b → 11 → 9, would be to raise the energy of the cyclopropane ring-opening reaction relative to energy for carbon-oxygen bond cleavage in the quinol. Thus, the thermal chemistry of the alcohols, 13a,b, was studied. Thermolysis of each of these epimeric alcohols gave a mixture of 15a and 15b in about 60% yield. The two structures were supported



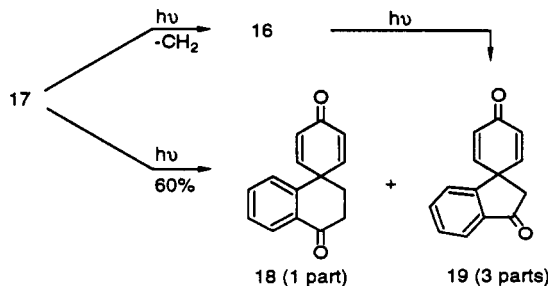
by spectroscopic data, and the stereochemistry was tentatively assigned on the basis of the known shielding of groups cisoid to a carbonyl moiety.<sup>7</sup> Thus, for 15a (R<sup>1</sup> = H), the vinyl hydrogen occurred at δ 7.15 (q, *J* = 7.5 Hz) and the methyl resonance at δ 1.81 (*J* = 7.5 Hz). For the isomer assigned as 15b (R<sup>2</sup> = H), the vinyl hydrogen appeared at δ 6.28 (*J* = 7.5 Hz) and the methyl group ap-

peared at δ 2.4 (*J* = 7.5 Hz). These products most reasonably arise from dehydration/isomerization of the alcohols to the vinyl ether 14, [1,3]-oxygen-to-carbon migration, and then double-bond isomerization. The cyclopropyl carbonyl system is again rearranging to an isomeric vinyl ether before the desired rearrangement can take place.

The work thus far has demonstrated that substituted cyclopropyl quinol ethers often prefer a pathway involving isomerization to a vinyl ether which subsequently undergoes a [1,3]-oxygen-to-carbon shift leading to spirocyclic ring systems containing a five-membered ring. This pathway could not operate for a simple unsubstituted system. However, some difficulty was initially experienced in preparing the unsubstituted cyclopropane 17. Under Simmons-Smith<sup>8</sup>-type conditions, the synthetic difficulties probably relate to acid sensitivity of this phenyl vinyl ether linkage to the zinc iodide generated in the cyclopropanation step. However, conditions were developed<sup>9</sup> which allowed preparation of 17 reproducibly in 47% yield. At 200 °C this compound rearranged in 55% yield to the six-membered spirocyclic ketone 18. Thus, when a pathway for isomerization of the cyclopropyl ether to a vinyl ether is absent, the desired rearrangement is the major reaction pathway.



The photochemistry of 17 was also studied with the hope of increasing the yield and lowering the temperature of the 17 → 18 conversion. Irradiation of 17 with 3000-Å light led to 1:3 mixture of 18 and 19 in 60% yield. The major product 19 presumably arises via photolysis of the cyclopropane ring to yield the vinyl ether 16 and methylene. Although the photofragmentation of 17 to 16 and a carbene has not been unequivocally established here, the photolysis of simple aryl cyclopropanes to give styrenes and methylene is well-documented.<sup>10</sup> Previous research has shown that irradiation of 16 gives 19 in high yield.<sup>2</sup> Unfortunately, the minor product in the photochemical reaction is the desired ring expansion compound 18.



**Discussion and Summary.** The research described herein has established that cyclopropyl ethers of quinols

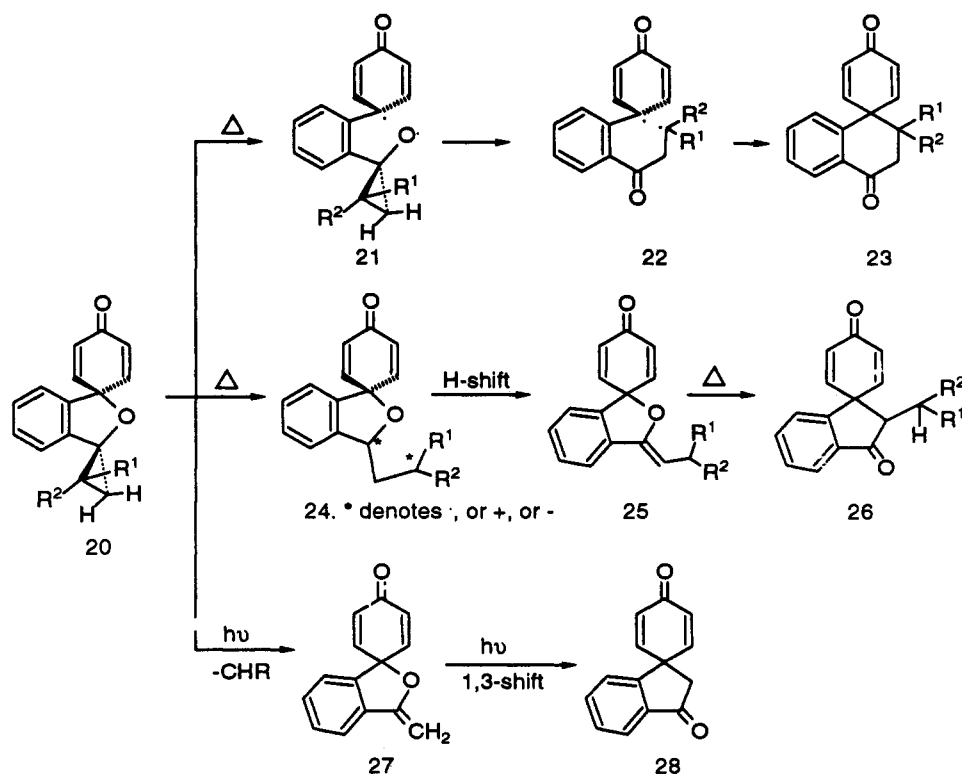
(8) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React.* 1973, 20, 1.

(9) Swada, S.; Inouye, Y. *Bull. Chem. Soc. Jpn.* 1969, 42, 2669. For a recent study of this chemistry and leading references see: Friedrich, E. C.; Niyati-Shirkhodaee, F. *J. Org. Chem.* 1991, 56, 2202.

(10) Richardson, D. B.; Durrett, L. R.; Martin, J. M., Jr.; Putnam, W. E.; Slaymaker, S. C.; Dvoretzky, I. *J. Am. Chem. Soc.* 1965, 87, 2763. Pomerantz, M.; Gruber, G. W. *Ibid.* 1967, 87, 2763; 1967, 89, 6799. Ciganek, E. *Ibid.* 1967, 89, 1458. Swenton, J. S.; Krubsack, A. J. *Ibid.* 1969, 91, 786.

(7) Dyke, S. F.; Floyd, A. J.; Sainsbury, M.; Theobald, R. S. *Organic Spectroscopy, An Introduction, 2nd ed.*; Longman: New York, 1978; pp 110-111.

Scheme II. Probable Reaction Pathways in the Thermal and Photochemical Reactions of Cyclopropyl Quinol Ethers



are capable of affording six-membered spirocyclic compounds, i.e., 7a → 8 and 17 → 18, both thermally and photochemically. In the thermal reaction, a second isomerization pathway can effectively compete with the desired rearrangement. Scheme II shows probable steps involved in the thermal and photochemical reactions of cyclopropyl quinol ethers. The reaction pathway leading to the six-membered spirocyclic ketones, 20 → 21 → 22 → 23, involves as the high-energy step formation of a phenoxy-cyclopropoxy radical pair. The low stability of this particular alkoxy radical is responsible for the high temperature required for the reaction. For compounds which can undergo facile opening of the cyclopropyl ring prior to carbon-oxygen bond cleavage, this ring opening followed by a hydrogen shift reaction yields a substituted vinyl ether which then leads to the five-membered ring spirocyclic ketone, 20 → 24 → 26. The hydrogen shift process could be occurring from either a dipolar or diradical species.

An interesting aspect of the 7a,b thermolysis is the dramatic dependence of the course of the thermal reaction on the stereochemistry of the ester. Whereas the thermal reaction of 7a follows the first pathway, giving a six-membered spirocyclic ketone, 7b follows the second pathway, affording the five-membered spirocyclic ketone. Models suggest that in 7a the ester group, due to steric interactions with the aromatic ring, cannot be oriented so as to conjugate with the cyclopropane bond and thus stabilize the transition state for the cyclopropane ring opening, 20 → 24. This then slows down the 20 → 24 → 25 → 26 reaction and allows the higher energy process, 20 → 21 → 22 → 23, to occur. While accurate kinetic studies were not conducted, preparative runs established with certainty that 7a reacts much more slowly than does 7b. The minimum temperature noted for the former reaction is about 180 °C, while the 7b → 9 conversion can be effected at temperatures as low as 110 °C. In fact, for cyclopropyl ether 17, wherein the pathway 20 → 24 → 25 → 26 cannot operate, the six-membered ring spirocyclic ketone is formed in good yield but at a relatively high temperature.

Finally, the photochemical version of this reaction, which works so well for the vinyl ether analogue<sup>2</sup> (Scheme I), is complicated by photolysis of the cyclopropane ring to give a styrene derivative and a carbene. Although the formation of the six-membered ring spirocyclic ketone can be performed under mild conditions, the yields are not attractive for synthetic purposes.

### Experimental Section<sup>11</sup>

**Ethylene Ketal of Benzoquinone.** The following is an improved procedure to the title compound. To a solution of *p*-methoxyphenol (25.02 g, 201 mmol) and ethylene carbonate (24.78 g, 251 mmol) in DMF (25 mL) was added tetraethylammonium bromide (4.39 g, 20 mmol), and the solution was heated at 140 °C for 7 h. Fractional distillation under reduced pressure was used to remove the DMF and to give 2-(4-methoxyphenoxy)ethanol as a liquid which solidified to a white solid (bp ≈ 155 °C (0.6 Torr)). This solid was recrystallized from Et<sub>2</sub>O/H to afford 2-(4-methoxyphenoxy)ethanol (29.1 g, 86%), mp 64–66 °C (lit.<sup>12</sup> mp 63–65 °C).

A stirred solution of 2-(4-methoxyphenoxy)ethanol (64.01 g, 0.38 mol) and 1% KOH/MeOH (500 mL) at 20 °C was anodically oxidized using a circular platinum mesh anode (45 mesh, 1.5-in.

(11) Routine <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were taken on a Bruker AC 200-MHz spectrometer using CDCl<sub>3</sub> and (CD<sub>3</sub>)<sub>2</sub>CO as solvents unless noted otherwise. Infrared (IR) spectra were taken on a Perkin-Elmer Model 283B spectrometer in KBr pellets or neat using NaCl plates, with strong (s) bands being reported. Melting points were determined with a Thomas-Hoover "Unimelt" apparatus and are uncorrected. Silica gel (Kieselgel 60, 230–400 mesh) was obtained from E. Merck Co. Thin-layer chromatography was done using Merck silica gel 60 F254 precoated aluminum-backed plates, 0.2-mm thickness. Visualization was done by UV or spraying with 5% ethanolic phosphomolybdic acid and then heating. THF was purified by distillation from benzophenone ketyl. Benzene and toluene were distilled from CaH<sub>2</sub> and stored over molecular sieves under nitrogen. All organometallic reactions were done under an argon or nitrogen atmosphere. For chromatography and recrystallization, H refers to distilled hexanes, bp 68–70 °C. The term *extractive workup* refers to extraction with the indicated solvent, washing the organic layer with brine, drying over Drierite (CaSO<sub>4</sub>), concentration in vacuo, and drying at <5 Torr until a constant weight was obtained.

(12) Yoshino, T.; Inaba, S.; Ishido, Y. *Bull. Chem. Soc. Jpn.* 1973, 46, 553–557.

diameter  $\times$  2-in. height) and a platinum sheet cathode (0.5 in.  $\times$  0.5 in.) at a current of 2.0 amp for 12 h. The reaction was monitored by UV spectroscopy with the starting material showing a maximum at 290 nm which decreased to 5% of its initial value at the completion of the electrolysis. The reaction mixture was concd in vacuo, and the residue was treated with ice (30 g) to give a mushy solid, which was filtered, washed with water (100 mL), and vacuum dried for 2 h to yield a yellow solid. This solid was recrystallized from Et<sub>2</sub>O/H to yield the ethylene dimethyl bisketal of benzoquinone (64 g, 85%), mp 61–62 °C (lit.<sup>13</sup> mp 62–63 °C).

The pH of a solution of the above bisketal (16 g, 0.08 mol) in THF (60 mL) and H<sub>2</sub>O (15 mL) was adjusted to 5.00 by adding glacial acetic acid (4 mL), and this solution was stirred for 5 h. The progress of the hydrolysis was monitored via gas chromatography (5% OV-101 Chromosorb G-HP 100/112, 20 in.  $\times$  1/8 in. at 120 °C) and judged to be complete after 5 h. Potassium bicarbonate was then added to neutralize the excess acetic acid, the THF layer was decanted off, and the remaining salt was washed with THF (40 mL). The THF fractions were collected and concd in vacuo to give an oil which crystallized upon addition of H<sub>2</sub>O (30 mL). The crystals were washed with cold H<sub>2</sub>O (20 mL) and dried in a vacuum desiccator to give a semi-white solid, which was recrystallized from Et<sub>2</sub>O/H to give the ethylene ketal of benzoquinone (8.6 g, 71%); mp 47–49 °C (lit.<sup>13</sup> mp 50–51 °C).

**Ethyl ( $\pm$ )-(1*R*\*,2*R*\*)-Trispiro[cyclopropane-1,1'-phthalan-3',1'-[2,5]cyclohexadiene-4'',2''-[1,3]dioxolane]-2-carboxylate, 5a, and Ethyl ( $\pm$ )-(1*R*\*,2*S*\*)-Trispiro[cyclopropane-1,1'-phthalan-3',1'-[2,5]cyclohexadiene-4'',2''-[1,3]dioxolane]-2-carboxylate, 5b.** To a solution of 4<sup>2</sup> (1.41 g, 5.6 mmol) in Et<sub>2</sub>O/THF (10:5 mL) was added Rh(OAc)<sub>2</sub> dimer (52 mg, 2 mol %) with subsequent addition of N<sub>2</sub>CHCO<sub>2</sub>Et (1.12 g, 9.8 mmol) in Et<sub>2</sub>O (4 mL) via a syringe pump (2.4 mL/h). The catalyst was removed by filtration of the material through a short column of alumina (3.5  $\times$  3 cm), and the crude oil was chromatographed (2.5 cm  $\times$  19 cm, silica gel, 15% Et<sub>2</sub>O/H as eluant) to yield isomer 5b (710 mg) and then isomer 5a (670 mg) as oils. Crystallization from Et<sub>2</sub>O/H (25%) gave crystalline isomer 5b (610 mg, 32%), mp 113–115 °C: IR (KBr) 1718, 1175, 1160, 1115, 1005, 955 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.25–7.35 (m, 3 H), 7.1 (m, 1 H), 6.2 (dd,  $J$  = 8, 2 Hz, 1 H), 6.0 (m, 2 H), 5.8 (dd,  $J$  = 10, 2 Hz, 1 H), 4.2–4.0 (m, 6 H), 2.4 (dd,  $J$  = 9.5, 7 Hz, 1 H), 1.9 (m, 2 H), 1.15 (t,  $J$  = 7.1 Hz, 3 H). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>O<sub>5</sub>: C, 70.58; H, 5.92. Found: C, 70.14; H, 6.03.

Recrystallization from Et<sub>2</sub>O/H gave 5a (590 mg, 31%) which showed mp 94–95 °C: IR (KBr) 1720, 1170 (br), 1110 (br), 1005, 950 (br) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.2–7.3 (m, 2 H), 7.0–7.15 (m, 1 H), 6.9–6.8 (m, 1 H), 6.1 (dd,  $J$  = 10, 2 Hz, 1 H), 5.85–6.05 (m, 2 H), 5.76 (dd,  $J$  = 10, 2 Hz, 1 H), 4.3–4.1 (m, 6 H), 2.26 (t,  $J$  = 7 Hz, 1 H), 2.05 (dd,  $J$  = 7, 6.8 Hz, 1 H), 1.6 (dd,  $J$  = 7.2, 6.8 Hz, 1 H), 1.25 (t,  $J$  = 7.1 Hz, 3 H). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>O<sub>5</sub>: C, 70.58; H, 5.92. Found: C, 70.25; H, 6.10.

**Ethyl ( $\pm$ )-(1'*R*\*,2'*R*\*)-4-Oxodispiro[2,5-cyclohexadiene-1,1'-phthalan-3',1'-cyclopropane]-2''-carboxylate, 7a, and Ethyl ( $\pm$ )-(1'*R*\*,2'*S*\*)-4-Oxodispiro[2,5-cyclohexadiene-1,1'-phthalan-3',1'-cyclopropane]-2''-carboxylate, 7b.** To a solution of 5b (610 mg, 1.8 mmol) in (CH<sub>3</sub>)<sub>2</sub>CO (50 mL) was added *p*-TsOH·H<sub>2</sub>O (120 mg), and the mixture was stirred for 1 h. The reaction was quenched by adding saturated NaHCO<sub>3</sub> (2 mL), and the (CH<sub>3</sub>)<sub>2</sub>CO was removed in vacuo. Extractive workup with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  10 mL) gave an oil which was chromatographed (2.5 cm  $\times$  12.5 cm, silica gel, 10% Et<sub>2</sub>O/H as eluant) to give crystalline isomer 7b. This material was recrystallized from Et<sub>2</sub>O/H to yield analytically pure 7b (210 mg, 40%), mp 128–129 °C: IR (KBr) 1718, 1670, 1630, 1210, 1175, 1160 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.4–7.2 (m, 3 H), 7.05–6.95 (m, 2 H), 6.80 (dd,  $J$  = 10, 3 Hz, 1 H), 6.35 (dd,  $J$  = 10, 2 Hz, 1 H), 6.2 (dd,  $J$  = 10, 2 Hz, 1 H), 4.0–4.2 (m, 2 H), 2.5 (dd,  $J$  = 9, 2 Hz, 1 H), 1.9–2.1 (m, 2 H), 1.26 (t,  $J$  = 7 Hz, 3 H). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>: C, 72.95; H, 5.45. Found: C, 73.15; H, 5.45.

Eluting second was isomer 7a which was recrystallized from Et<sub>2</sub>O/H to give analytically pure 7a (230 mg, 43%), mp 96–97 °C: IR (KBr) 1722, 1675, 1180, 1160, 850 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.4–7.2 (str m, 2 H), 7.0–6.7 (str m, 4 H), 6.3 (dd,  $J$  = 10.0 Hz, 2 Hz, 1

H), 6.1 (dd,  $J$  = 10, 2 Hz, 1 H), 4.2–4.1 (str m, 2 H), 2.3 (t,  $J$  = 7.2 Hz, 1 H), 2.1 (pseudo, t,  $J$  = 7 Hz, 1 H), 1.6 (dd,  $J$  = 8, 7 Hz, 1 H), 1.26 (t,  $J$  = 7.2 Hz, 3 H). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>: C, 72.95; H, 5.45. Found: C, 72.94; H, 5.78.

**Ethyl ( $\pm$ )-3',4'-Dihydro-4,4'-dioxospiro[2,5-cyclohexadiene-1,1'-(2'*H*)-naphthalene]-2'-carboxylate, 8.** A solution of 7a (80 mg) in benzene (3 mL) was placed in a glass tube (prewashed with saturated NaHCO<sub>3</sub>, water, and (CH<sub>3</sub>)<sub>2</sub>CO), degassed by three freeze–thaw cycles, and then sealed under vacuum. The glass tube was heated in an oil bath at 180 °C for 17 h, removed from the oil bath, cooled to rt, and then opened. The reaction mixture was concd in vacuo to give the crude product as a slightly dark oily solid, which was purified by column chromatography (1 cm  $\times$  12 cm, silica gel, 10% Et<sub>2</sub>O/H as eluant) to give a white solid. Recrystallization from Et<sub>2</sub>O/H afforded 8 (56 mg, 70%), mp 110–111 °C: IR (KBr) 1731, 1689, 1666 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  8.1 (dd,  $J$  = 2, 8 Hz, 1 H), 7.6–7.4 (m, 2 H), 7.2–6.9 (m, 3 H), 6.54 (dd,  $J$  = 10, 2 Hz, 1 H), 6.29 (dd,  $J$  = 10, 2 Hz, 1 H), 4.1 (m, 2 H), 3.50 (dd,  $J$  = 4.6, 13 Hz, 1 H), 3.20 (dd,  $J$  = 13, 8 Hz, 1 H), 2.95 (dd,  $J$  = 18, 5 Hz, 1 H), 1.1 (t,  $J$  = 7.1 Hz, 3 H). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>: C, 72.95; H, 5.45. Found: C, 72.81; H, 5.54.

**Ethyl ( $\pm$ )-3',4'-Dioxospiro[2,5-cyclohexadiene-1,1'-indan]-2'-acetate, 9.** A solution of 7b (105 mg) in benzene (3 mL) was added to a glass tube (prewashed with saturated NaHCO<sub>3</sub>, water, and (CH<sub>3</sub>)<sub>2</sub>CO), degassed by three freeze–thaw cycles, and then sealed under vacuum. The glass tube was placed in an oil bath at 180 °C for 17 h and then removed, cooled to rt, and opened. The reaction mixture was concd in vacuo to give the crude product as a slightly dark oily solid, which was purified by column chromatography (1 cm  $\times$  12 cm, silica gel, 10% Et<sub>2</sub>O/H as eluant) to give 9 (80 mg, 76%) as a white solid. Recrystallization in Et<sub>2</sub>O/H afforded an analytically pure product (70 mg, 67%) which was identical in all respects with synthesized material.

**9 via Synthesis from 10.** To a solution of diisopropylamine (51 mg, 0.53 mmol) in THF (5 mL) at 0 °C was added dropwise *n*-BuLi (2.4 M, 0.21 mL). After being stirred for 30 min, the solution was cooled to –78 °C, 10 (100 mg, 0.39 mmol) in THF (5 mL) was added dropwise, and stirring was continued for 1 h. Ethyl bromoacetate (250  $\mu$ L, 2.1 mmol) was then added at –78 °C over a period of 10 min, and the reaction mixture was allowed to warm to rt with stirring. After H<sub>2</sub>O (10 mL) was added to the reaction mixture, extractive workup with Et<sub>2</sub>O (2  $\times$  20 mL) gave an oil which was chromatographed (1  $\times$  22 cm column silica gel, 5% Et<sub>2</sub>O/H 10% Et<sub>2</sub>O/H, and 20% Et<sub>2</sub>O/H as eluant) to afford a solid. Recrystallization of this material from Et<sub>2</sub>O/H gave the alkylated ketal (90 mg, 70%), mp 95–96 °C: IR (KBr) 1723, 1668 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.75 (d,  $J$  = 7.1 Hz, 1 H), 7.55 (dd,  $J$  = 1.4, 7.5 Hz, 1 H), 7.40 (dd,  $J$  = 1.4, 7.5 Hz, 1 H), 7.30 (dd,  $J$  = 1.4, 7.5 Hz, 1 H), 6.05 (m, 2 H), 5.85 (dd,  $J$  = 2, 10 Hz, 1 H), 5.55 (dd,  $J$  = 2, 10 Hz, 1 H), 4.2–4.0 (m, 6 H), 3.45 (t,  $J$  = 7 Hz, 1 H), 2.78 (dd,  $J$  = 7, 16.8 Hz, 1 H), 2.38 (dd,  $J$  = 7, 16.8 Hz, 1 H), 1.25 (t,  $J$  = 7 Hz, 3 H). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>O<sub>5</sub>: C, 70.58; H, 5.92. Found: C, 70.64; H, 5.84.

To a solution of the above compound (30 mg, 0.09 mmol) in (CH<sub>3</sub>)<sub>2</sub>CO (10 mL) was added *p*-TsOH (20 mg), and the solution was stirred for 2 h. The reaction was quenched by adding saturated NaHCO<sub>3</sub> (20 mL), and the (CH<sub>3</sub>)<sub>2</sub>CO was removed in vacuo. Extractive workup with Et<sub>2</sub>O (2  $\times$  50 mL) gave a slightly yellow solid, which was recrystallized from Et<sub>2</sub>O/H to give 9 (25 mg, 100%), mp 106–107 °C: IR (KBr) 1735, 1715, 1660, 1623, 1285 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.88 (d,  $J$  = 7.5 Hz, 1 H), 7.63 (t,  $J$  = 7.4 Hz, 1 H), 7.52 (t,  $J$  = 7.48 Hz, 1 H), 7.25 (d,  $J$  = 7.5 Hz, 1 H), 6.97 (dd,  $J$  = 2.9, 10.0 Hz, 1 H), 6.6–6.4 (m, 2 H), 6.35 (dd,  $J$  = 10, 1.6 Hz, 1 H), 4.10 (q,  $J$  = 7.1 Hz, 2 H), 3.55 (dd,  $J$  = 5.3, 8 Hz, 1 H), 2.92 (dd,  $J$  = 5.3, 17 Hz, 1 H), 2.38 (dd,  $J$  = 8, 17 Hz, 1 H), 1.20 (t,  $J$  = 7.1 Hz, 3 H); <sup>13</sup>C NMR (DEPT, 62.9 MHz)  $\delta$  201.7 (s), 185.1 (s), 171.1 (s), 151.9 (s), 150.6 (d), 148.8 (d), 135.7 (d), 134.7 (s), 129.9 (d), 129.6 (d), 129.2 (d), 125.1 (d), 61.2 (t), 54.3 (d), 51.5 (s), 30.9 (t), 14.1 (q). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>: C, 72.95; H, 5.45. Found: C, 72.53; H, 5.50.

**Isolation of Ethyl (*Z*)-4-Oxospiro[2,5-cyclohexadiene-1,1'-phthalan]- $\Delta^{\beta,\delta}$ -propionate, 11.** A solution of 7b (12 mg), which had been purified with Florisil (micropipet), in benzene (3 mL) was added to a glass tube (prewashed with saturated NaHCO<sub>3</sub>, water, and (CH<sub>3</sub>)<sub>2</sub>CO), degassed by three freeze–thaw

cycles, and then sealed under vacuum. The glass tube was placed in an oil bath at 145 °C for 3 h and then removed, cooled to rt, and opened. The reaction mixture consisted of compounds **7b**, **9**, and the vinyl ether **11**. After concentration in vacuo, the mixture was chromatographed (1 cm × 16 cm, neutral alumina Activity III, 10% Et<sub>2</sub>O/H as eluant) to afford **7b** (4 mg, 33%), **9** (2.5 mg, 20%) and crystalline **11** (3 mg, 25%). Recrystallization of **11** from Et<sub>2</sub>O/H afforded an analytical sample, which was very sensitive to trace acid, mp 83–85 °C: IR (KBr) 1738, 1674, 1243 cm<sup>-1</sup>; <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO) δ 7.72 (dd, *J* = 2, 6 Hz, 1 H), 7.43 (m, 2 H), 7.18 (dd, *J* = 2, 6 Hz, 1 H), 6.85 (d, *J* = 10 Hz, 2 H), 6.28 (d, *J* = 10 Hz, 2 H), 5.31 (t, *J* = 7.3 Hz, 1 H), 4.12 (q, *J* = 7.1 Hz, 2 H), 3.30 (d, *J* = 7.3 Hz, 2 H), 1.2 (t, *J* = 7.1 Hz, 3 H); HRMS calcd for C<sub>18</sub>H<sub>16</sub>O<sub>4</sub> *m/e* 296.1044, obsd *m/e* 296.1046.

**Irradiation of 7a.** A solution of **7a** (30 mg, 0.1 mmol) in benzene (9 mL) with piperylene (1.2 g) was added to a quartz tube, and the solution was degassed with nitrogen. The solution was irradiated in a Rayonet photochemical reactor with 16 RPR-3000-Å bulbs for 2 h and then concd in vacuo and chromatographed (1 cm × 18 cm, silica gel, 15% Et<sub>2</sub>O/H eluant) to give **8** (14 mg, 46%). The crude product was recrystallized from Et<sub>2</sub>O/H to afford **8** (7.2 mg, 24%) as a crystalline solid.

**Irradiation of 7b.** A solution of **7b** (25 mg, 0.09 mmol) in benzene (9 mL) with piperylene (1.2 g) was added to a quartz tube, and the solution was degassed with nitrogen. The solution was irradiated in a Rayonet photochemical reactor with 16 RPR 3000-Å bulbs for 2 h. The solution was concd in vacuo and chromatographed (1 cm × 18 cm, silica gel, 10% Et<sub>2</sub>O/H as eluant) to afford **8** (9.3 mg, 37%). Compound **8** was recrystallized from Et<sub>2</sub>O/H to give white crystals (5 mg, 20%).

(±)-(1'*R*\*,2'*R*\*)-2''-(Hydroxymethyl)dispiro[2,5-cyclohexadiene-1,1'-phthalan-3',1''-cyclopropan]-4-one, **13b**. To a stirred solution of lithium aluminum hydride (150 mg, 3.9 mmol) at 85 °C in THF (5 mL) was added **5b** (220 mg, 0.65 mmol) in THF (3 mL). After 1 h the cooled reaction was quenched by carefully adding H<sub>2</sub>O (20 mL), and the solution was poured into H<sub>2</sub>O (50 mL) and 10% H<sub>2</sub>SO<sub>4</sub> (10 mL). Extractive workup with Et<sub>2</sub>O (3 × 50 mL) gave an oil which was chromatographed (1 cm × 15 cm, silica gel, 40% Et<sub>2</sub>O/H as eluant) to give a translucent oil. The oil was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/H to yield crystalline **13b** (133 mg, 78%), mp 97–99 °C: IR (KBr) 3424, 1668 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.4–7.2 (m, 2 H), 7.04 (m, 3 H), 6.85 (dd, *J* = 10, 3 Hz, 1 H), 6.27 (dd, *J* = 10, 2 Hz, 1 H), 6.15 (dd, *J* = 10, 2 Hz, 1 H), 3.87 (dd, *J* = 12, 6 Hz, 1 H), 3.65 (dd, *J* = 12, 8 Hz, 1 H), 2.01–1.8 (m, 1 H), 1.64 (dd, *J* = 10, 8 Hz, 1 H), 1.1 (t, *J* = 8 Hz, 1 H), OH resonance missing. Anal. Calcd for C<sub>16</sub>H<sub>14</sub>O<sub>3</sub>: C, 75.58; H, 5.55. Found: C, 75.61; H, 5.56.

(±)-(1'*R*\*,2'*S*\*)-2''-(Hydroxymethyl)dispiro[2,5-cyclohexadiene-1,1'-phthalan-3',1''-cyclopropan]-4-one, **13a**. To a stirred solution of lithium aluminum hydride (450 mg, 11.8 mmol) at 85 °C in THF (20 mL) was added **5a** (700 mg, 2.1 mmol) in THF (5 mL). After 2 h the cooled reaction was quenched by carefully adding H<sub>2</sub>O (100 mL) and 10% H<sub>2</sub>SO<sub>4</sub> (70 mL). Extractive workup with Et<sub>2</sub>O (3 × 75 mL) and chromatography and crystallization as for **13b** gave **13a** (430 mg, 80%), mp 104–106 °C: IR (KBr) 3459, 1662 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.4–7.2 (m, 2 H), 7.0–6.8 (m, 4 H), 6.25–6.15 (m, 2 H), 4.08 (dd, *J* = 12.5, 5.2 Hz, 1 H), 3.77 (dd, *J* = 12.5, 8 Hz, 1 H), 1.65–1.50 (m, 1 H), 1.36–1.23 (m, 2 H), OH resonance missing; HRMS calcd for C<sub>16</sub>H<sub>14</sub>O<sub>3</sub> *m/e* 254.0943, obsd *m/e* 254.0942.

**Preparation of 2'(E)-Ethylidenespiro[2,5-cyclohexadiene-1,1'-indan]-3',4-dione, 15a, and 2'(Z)-Ethylidenespiro[2,5-cyclohexadiene-1,1'-indan]-3',4-dione, 15b.** The thermolyses of **13a** and **13b** were performed individually and shown in each case to produce a mixture of **15a** and **15b** (<sup>1</sup>H NMR). For isolation, a mixture was thermalized as described herein. A solution of **13a** and **13b** (150 mg, 0.6 mmol) in distilled benzene (5 mL) was added to a tube (prewashed with saturated NaHCO<sub>3</sub>, H<sub>2</sub>O, and (CH<sub>3</sub>)<sub>2</sub>CO). The solution was degassed with

three freeze-thaw cycles and sealed under vacuum. The tube was placed in a silicone oil bath at 210 °C for 22 h. After the tube was opened, the solvent was removed in vacuo, and the crude products (dark oil) were chromatographed to afford **15a** and **15b** as solids. The stereochemical assignments for **15a** and **15b** should be considered tentative. The current structure assignments are based on the deshielding of the exocyclic vinyl proton in **15a**. The solids were each recrystallized from Et<sub>2</sub>O/H to give **15a** (45 mg, 32%), mp 173–175 °C: IR (KBr) 1702, 1668, 1647 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.92 (d, *J* = 7 Hz, 1 H), 7.7–7.5 (m, 2 H), 7.15 (q, *J* = 7.5 Hz, 1 H), 6.70 (d, *J* = 10 Hz, 2 H), 6.48 (d, *J* = 10 Hz, 2 H), 1.81 (d, *J* = 7.5 Hz, 3 H); HRMS calcd for C<sub>16</sub>H<sub>11</sub>O<sub>2</sub> *m/e* 236.0834, obsd *m/e* 236.0837.

Compound **15b** (39 mg, 28%), mp 176–178 °C: IR (KBr) 1692, 1669, 1648 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.90 (d, *J* = 7 Hz, 1 H), 7.6–7.4 (m, 2 H), 6.70 (d, *J* = 10 Hz, 2 H), 6.38 (d, *J* = 10 Hz, 2 H), 6.28 (q, *J* = 7.5 Hz, 1 H), 2.4 (d, *J* = 7.5 Hz, 3 H); HRMS calcd for C<sub>16</sub>H<sub>11</sub>O<sub>2</sub> *m/e* 236.0834, obsd *m/e* 236.0839.

**Dispiro[2,5-cyclohexadiene-1,1'-phthalan-3',1''-cyclopropan]-4-one, 17.** A solution of diethylzinc (1.0 M, 2 equiv, 1.77 mL) and methylene iodide (1.77 mmol, 143 mL) in anhydrous Et<sub>2</sub>O (2 mL) was heated to reflux for 1 h. To this solution was then added dropwise vinyl ether **15** (200 mg, 0.89 mmol) in Et<sub>2</sub>O (2 mL), and the reaction mixture was stirred at reflux for 15 min. The reaction was quenched by adding saturated NH<sub>4</sub>Cl (50 mL). Extractive workup with Et<sub>2</sub>O (3 × 50 mL) gave an oil which was chromatographed (1 cm × 15 cm, silica gel, 40% Et<sub>2</sub>O/H as eluant) to give white crystals. Recrystallization from Et<sub>2</sub>O/H gave **17** (100 mg, 47%), mp 136–138 °C: IR (KBr) 1671, 1626, 1605 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.5–7.2 (m, 2 H), 7.1–6.8 (m, 4 H), 6.18 (d, *J* = 10 Hz, 2 H), 1.4 (m, 2 H), 1.04 (m, 2 H); HRMS calcd for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub> *m/e* 224.0837, obsd *m/e* 224.0837.

**2',3'-Dihydrospiro[2,5-cyclohexadiene-1,1'(4'H)-naphthalene]-4,4'-dione, 18.** A solution of **17** (80 mg, 0.36 mmol) in benzene (3 mL) was placed in a glass tube (prewashed with saturated NaHCO<sub>3</sub>, water, and (CH<sub>3</sub>)<sub>2</sub>CO), degassed by three freeze-thaw cycles, and then sealed under vacuum. The glass tube was placed in an oil bath at 200 °C for 17 h and then removed, cooled to rt, and opened. The reaction mixture was concd in vacuo to give the crude product as a slightly dark oily solid, which was purified by column chromatography (1 cm × 12 cm, silica gel, 30% Et<sub>2</sub>O/H as eluant) to give an oil. This oil was crystallized from Et<sub>2</sub>O/H to afford crystalline **18** (44 mg, 55%), mp 127–129 °C: IR (KBr) 1685, 1663 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 8.14 (dd, *J* = 10, 2 Hz, 1 H), 7.55–7.35 (m, 2 H), 7.2–7.0 (m, 3 H), 6.40 (d, *J* = 10 Hz, 2 H), 2.85 (t, *J* = 7.2 Hz, 2 H), 2.33 (t, *J* = 7.2 Hz, 2 H); HRMS calcd for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub> *m/e* 224.0834, obsd 224.0835.

**Irradiation of 17 To Give 18 and 19.** A solution of **17** (40 mg, 0.28 mmol) in benzene (3 mL) and piperylene (200 mg) was degassed by bubbling nitrogen through the solution for 5 min. The solution in a Pyrex tube was then irradiated for 2.5 h with light from 16 RPR-3000-Å lamps. The solution was concd in vacuo and chromatographed (1 cm × 18 cm, silica gel, 10% Et<sub>2</sub>O/H as eluant) to afford **18** (6 mg, 15%) and **19** (18 mg, 45%) as solids. The spectral properties of **19** are identical to those previously described.<sup>1</sup>

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**Supplementary Material Available:** NOE experiments as well as <sup>1</sup>H NMR spectra of all compounds reported in the paper (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.