Center, Indiana University, Bloomington, IN 47415, is thanked for the X-ray structure determination of compounds **14** and **36**.

Registry No. (±)-7, 137333-36-9; (±)-8, 137333-37-0; (±)-9, 137333-38-1; (±)-10, 137333-39-2; (±)-11, 137333-40-5; (±)-12, 137333-41-6; (±)-13, 137333-42-7; (±)-14, 137333-43-8; (±)-21, 137333-44-9; (±)-22, 137362-83-5; (±)-24, 137333-45-0; (±)-25, 137333-46-1; (±)-26, 137333-47-2; (±)-27, 137333-48-3; (±)-28 (isomer 1), 137333-49-4; (±)-28 (isomer 2), 137333-50-7; (±)-(*E*)-**29**, 137333-51-8; (±)-(*Z*)-**29**, 137333-52-9; (±)-**30**, 137333-53-0; (±)-**31**, 137333-54-1; (±)-**32**, 137333-55-2; (±)-**33**, 137333-56-3; (±)-**33** (deoxo derivative), 137333-57-4; (±)-**34**, 137333-58-5; (±)-**35**, 137333-59-6; (±)-**36**, 137333-60-9; (±)-**37**, 137333-61-0; (±)-**38**, 137333-62-1; (±)-**39**, 137333-63-2; (±)-**40**, 137333-64-3; (±)-**44**, 137333-65-4; PhNHNH$_2$·HCl, 59-88-1; PhSCH$_2$COCl, 7031-27-8; PhS(CH$_2$)$_2$NH$_2$, 2014-75-7; H$_2$NCH$_2$CH(OMe)$_2$, 22483-09-6; (±)-cyclohexanone-3-acetic acid, 62646-12-2; (+)-cyclohexanone-3-acetic acid, 137333-34-7; (−)-cyclohexanone-3-acetic acid, 137333-35-8.

Efficient Syntheses of Vinyl Ethers of Spiroquinol Ketals and Their High-Yield Photochemical Oxygen-to-Carbon [1,3]-Shift to Spiro-Fused 2,5-Cyclohexadienones

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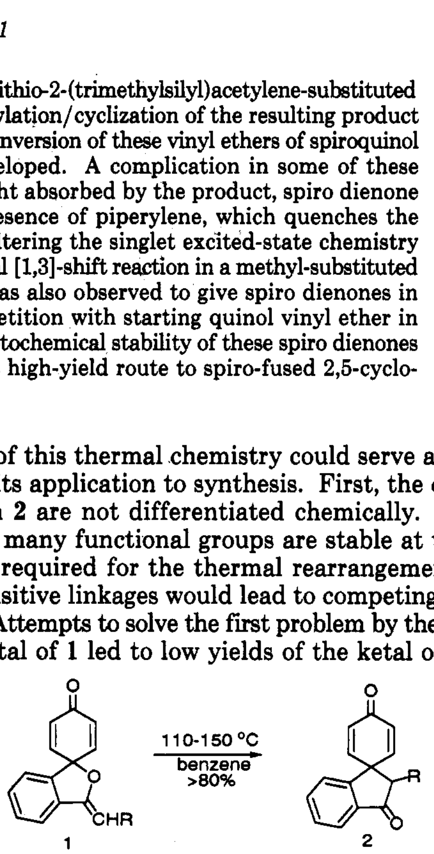
An efficient route to spiroquinol vinyl ethers involves addition of a 1-lithio-2-(trimethylsilyl)acetylene-substituted benzene to the monoethylene ketal of benzoquinone followed by desilylation/cyclization of the resulting product to give vinyl ethers of spiroquinol ketals. A high-yield photochemical conversion of these vinyl ethers of spiroquinol ketals to ketals of spiro-fused 2,5-cyclohexadienones has been developed. A complication in some of these photochemical reactions is formation of secondary products from light absorbed by the product, spiro dienone ketals. This has been solved by conducting the reaction in the presence of piperylene, which quenches the triplet-state chemistry of the product spiro dienone ketal without altering the singlet excited-state chemistry of the quinol ketal vinyl ether. The quantum yield for the photochemical [1,3]-shift reaction in a methyl-substituted vinyl ether is 0.4. Finally, irradiation of quinol spiro vinyl ethers was also observed to give spiro dienones in good yields. Although the spiro dienone is absorbing light in competition with starting quinol vinyl ether in this system, a high yield of product was obtained. The unexpected photochemical stability of these spiro dienones is discussed. The chemistry reported herein establishes an efficient high-yield route to spiro-fused 2,5-cyclohexadienones and their ketals under very mild conditions.

Introduction

Many methods for carbon–carbon bond formation are not applicable to the preparation of quaternary carbon–carbon centers.[1] Our interest in the functionalization chemistry of quinone monoketals[2] prompted investigation of the thermal [1,3] oxygen-to-carbon migration of quinol ethers such as **1**,[3] which are conveniently available from quinone monoketals. Indeed, heating **1** or its nonbenzenoid derivatives to 110–150 °C gives the respective dienones **2**.[3-5] Not only is a quaternary carbon–carbon center constructed in high yield but also further reactions of **2** could lead to derivatives of the spiro ring system. Two features of this thermal chemistry could serve as limitations on its application to synthesis. First, the carbonyl groups in **2** are not differentiated chemically. Second, although many functional groups are stable at the temperature required for the thermal rearrangement, thermally sensitive linkages would lead to competing side reactions. Attempts to solve the first problem by thermolysis of the ketal of **1** led to low yields of the ketal of **2**.



Photochemical activation could be an alternative method of effecting the [1,3] oxygen-to-carbon migration;[6] however, the published work did not suggest that a synthetically useful process would be likely via this method. The photochemistry of vinyl ethers has not been studied extensively. Excitation of ethyl vinyl ether **3** in the gas phase leads to two primary processes:[7] (1) cleavage to an ethyl and a vinyloxy radical and (2) concerted rearrangement to acetaldehyde and ethylene. The example most relevant to the present work is the photorearrangement of α-(benzyloxy)styrenes **4**, which affords β-phenylpropiophenones **5** with quantum yields from 0.04 to 0.11.[8]

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[1] Hendrickson, J. B. *J. Am. Chem. Soc.* **1971**, *93*, 6847. Hendrickson, J. B.; Bogard, T. L.; Fisch, M. E.; Grossert, S.; Yoshimura, N. *J. Am. Chem. Soc.* **1974**, *96*, 7781. Martin, S. F.; Phillips, G. W.; Puckette, T. A.; Colapret, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 5866. Martin, S. F. *Tetrahedron* **1980**, *36*, 419.

[2] For reviews and leading references, see the following. (a) Swenton, J. S. *Acc. Chem. Res.* **1983**, *16*, 74. (b) Swenton, J. S. *Chemistry of Quinones*, Part 2; Rappoport, Z., Patai, S., Eds.; John Wiley: New York, 1988; p 899.

[3] (a) Morrow, G. W., Wang, S.; Swenton, J. S. *Tetrahedron Lett.* **1988**, *29*, 3441–3444. (b) Wang, S.; Morrow, G. W.; Swenton, J. S. *J. Org. Chem.* **1989**, *54*, 5364–5371.

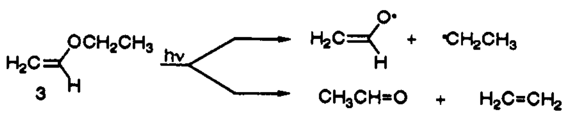
[4] Swenton, J. S.; Bradin, D.; Gates, B. D. *J. Org. Chem.* **1991**, *56*, 6156.

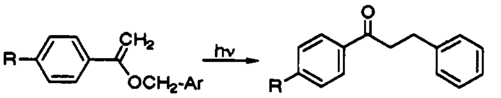
[5] For recent references to 2,5-cyclohexadienone preparations, see the following. Bentley, T.; Morris, S. J. *J. Org. Chem.* **1986**, *51*, 5005. Maity, S. K.; Bhattacharyya, S.; Mukherjee, D. *J. Chem. Soc., Chem. Commun.* **1986**, 481. Schultz, A. G.; Harrington, R.; Macielag, M.; Mehta, P.; Taveras, A. *J. Org. Chem.* **1987**, *52*, 5482. Kenny, M. J.; Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* **1986**, *27*, 3923. Schultz, A. G.; Taveras, R. E.; Harrington, R. *Tetrahedron Lett.* **1988**, *29*, 3907. Rishton, G. M.; Schwartz, M. A. *Tetrahedron Lett.* **1988**, *29*, 2643. Haack, R. A.; Beck, K. R. *Tetrahedron Lett.* **1989**, *30*, 1605. Maruoka, K.; Sato, J.; Banno, H.; Yamamoto, H. *Tetrahedron Lett.* **1990**, *31*, 377.

[6] A preliminary communication reported part of the work discussed herein: Wang, S.; Callinan, A.; Swenton, J. S. *J. Org. Chem.* **1990**, *55*, 2272.

[7] Murad, E. *J. Am. Chem. Soc.* **1961**, *83*, 1327.

0022-3263/92/1957-0078$03.00/0



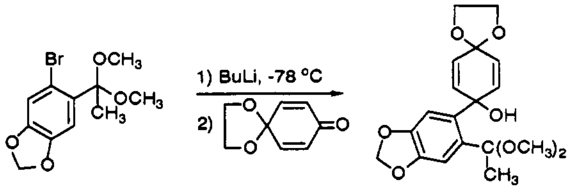


4 5

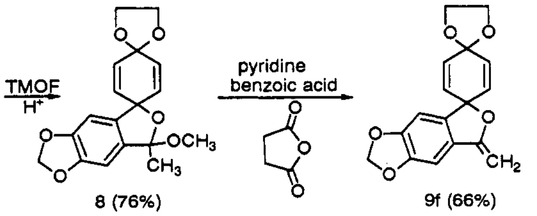
However, the isolated yield for the parent system (R = H) from a preparative irradiation was only 20% (40% when corrected for recovered starting material), making the reaction of questionable value. The rearrangement 4 → 5 was proposed to occur through the triplet state on the basis of the inhibition of the reaction by oxygen and the increase in the quantum yield of the reaction when *n*-propyl chloride was used as solvent.[9]

We report herein convenient routes to spiro vinyl ethers of type 1 and their photochemical [1,3]-shift chemistry.[6] The high-yield procedure for effecting photochemical [1,3]-shifts in these systems markedly expands the scope of the [1,3] oxygen-to-carbon shift reaction.

Synthesis of Vinyl Ethers. The first route employed for preparation of vinyl ethers is outlined below. Reaction of the lithio derivative of 6 with the benzoquinone ethylene ketal afforded 7, which was converted to the cyclic ketal 8. Elimination of MeOH then furnished the vinyl ether 9f. Chemistry similar to that outlined above gave the key intermediates for preparation of vinyl ethers 9a–e as described earlier.[3b]

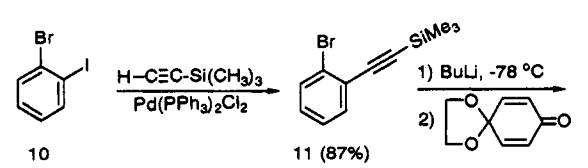


6 7 (67%)

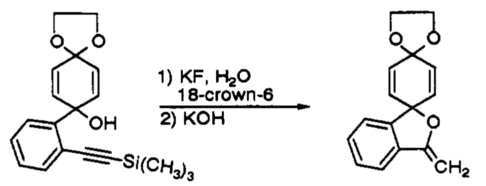


8 (76%) 9f (66%)

Although this short sequence was convenient, a better route is that outlined for the conversion of 10 to 9a. The usefulness of this route depends on the availability of the *o*-bromoacetylene derivative, i.e., 11. The palladium-catalyzed reaction of *o*-bromoiodobenzene with (trimethylsilyl)acetylene gave high yields of the monoacetylene 11.[10] The second key step in this route was the conversion of the hydroxy acetylene 12 to the vinyl ether 9a. The base-catalyzed addition of alcohols to unactivated acetylenes—the Favorskii–Shostakovskii reaction[11]—has not found much use in synthetic chemistry since a high temperature is required for the bimolecular version of the reaction. However, the intramolecular version of this reaction 12 → 9a occurs in excellent yield at room temperature. In some cases the addition of 18-crown-6 was found to further facilitate the cyclization chemistry.[4]

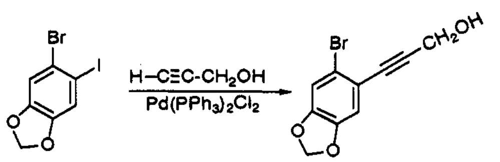


10 11 (87%)

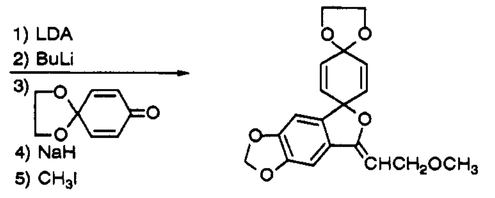


12 (82%) 9a (90%)

The versatility of the *o*-bromoacetylene/quinone monoketal strategy is illustrated by the preparation of 9g. The key intermediate 13, 5-bromo-6-iodo-1,3-benzodioxole, was prepared from the Sandmeyer reaction of 5-amino-6-bromo-1,3-benzodioxole. However, the scale-up of the reported zinc reduction of 5-bromo-6-nitro-1,3-benzodioxole to form this aniline derivative was inconvenient;[12] an improved procedure is the aluminum amalgam reduction of the nitro compound as described in the Experimental Section. Palladium-catalyzed coupling of 13 with propargyl alcohol gave 14, which was smoothly transformed into the functionalized vinyl ether 9g. In this synthesis, the cyclization of the hydroxy acetylene derivative analogous to 12 occurred with or without 18-crown-6 catalysis, but the latter procedure required overnight reaction with base at room temperature. The reaction sequence using the appropriate *o*-bromoiodobenzene derivative is probably the method of choice for preparation of all of the vinyl ethers studied herein.



13 14 (80%)



9g (58% from 14)

Photochemistry of Quinol Vinyl Ether Ketals. The results from initial photochemical studies modeled after the α-(benzyloxy)styrene chemistry noted earlier[8] were disappointing. Irradiation of 9b at 254 nm in degassed *tert*-butyl alcohol in a quartz tube led to a complicated reaction mixture with no major product. The UV absorption spectra of 9b and product 15b (Figure 1) indicate that both 9b and product 15b absorb light over the same wavelength range. Unless 15b is photochemically stable, secondary photochemical products could contribute to the

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[8] Izawa, Y.; Ogata, Y. *J. Org. Chem.* **1970**, *35*, 3192.

[9] Ordinarily, chlorinated solvents are not very effective at enhancing singlet-to-triplet intersystem crossing.

[10] The procedure was essentially that of Takahashi and Austin. Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627. Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. *J. Org. Chem.* **1981**, *46*, 2280.

[11] Shostakovskii, M. F.; Trofimov, B. A.; Atavin, A. S.; Lavrov, V. I. *Russ. Chem. Rev.* **1968**, *37*(11), 907. Venkataramani, P. S.; Saxena, N. K.; Tripathi, V. K. *The Chemistry of the Carbon–Carbon Triple Bond*, Patai, S., Ed.; John Wiley and Sons, Inc.: 1978; Part 2, Chapter 19, p 813.

[12] Jung, M. E.; Lam, P. Y.; Mansuri, M. M.; Speltz, L. M. *J. Org. Chem.* **1985**, *50*, 1087.

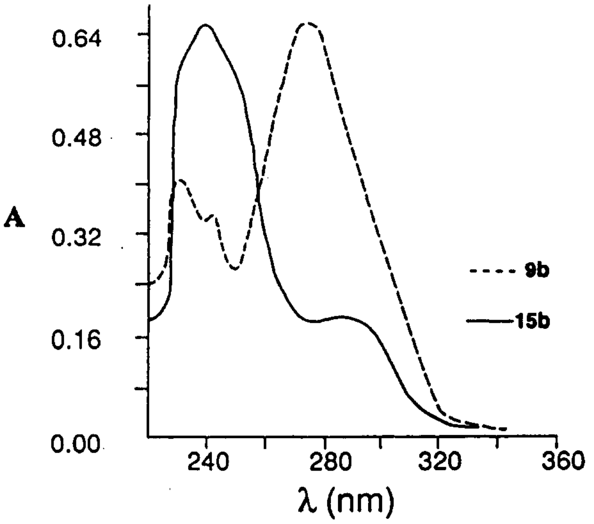
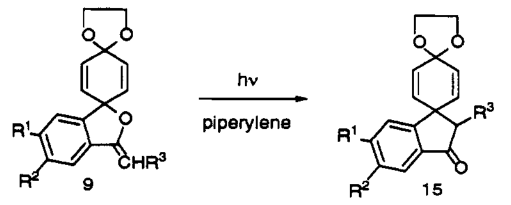


Figure 1. UV spectra of **9b** (5.9×10^{-5} M) and **15b** (4.9×10^{-5} M) in MeOH.

Table I. Photochemical 1,3 Oxygen-to-Carbon Rearrangements of Vinyl Ethers



entry	9	15 (%)
1[a]	**a**, $R^1, R^2, R^3 = H$	(82)
2[a]	**b**, $R^1, R^2 = H$; $R^3 = CH_3$	(96)
3[a]	**c**, $R^1, R^2 = H$; $R^3 = C_6H_5$	(96)
4[a]	**d**, $R^1, R^2 = H$; $R^3 = C_6H_4$-4-CH_3	(87)
5[a]	**e**, $R^1, R^2 = H$; $R^3 = C_6H_4$-4-OCH_3	(98)
6[b]	**f**, $R^1, R^2 = -OCH_2O-$; $R^3 = H$	(73)
7[b]	**g**, $R^1, R^2 = -OCH_2O-$; $R^3 = CH_2OCH_3$	(75)[c]
8[a]	**h**, $R^1, R^2 = -OCH_2O-$; $R^3 = CH_2OTBDMS$	(78)

[a] Irradiated with RPR 3000-Å lamps through Pyrex. [b] Irradiated with Corex-filtered light from a 450-W source. [c] Yield of **24** after elimination of MeOH.

Table II. Quantum Yields for 9b → 15b in Methylene Chloride

irradiation	quantum yield[a]
direct (300 nm)	0.40[b]
sensitized (350 nm)	<0.05[c]
quenched (0.42 M piperylene)	0.49[d]

[a] Average of two determinations for appearance of product at <10% conversion of starting material; estimated error ±10%. [b] [**9b**] = $3\text{–}4 \times 10^{-3}$ M. [c] [**9b**] = 5.4×10^{-3} M; [PhC_2O] = 1.8×10^{-2} M. [d] [**9b**] = 4.5×10^{-3} M; [piperylene] = 0.42 M.

complicated product mixture. Photoactivated aromatic ketones undergo rapid and efficient intersystem crossing to their respective triplet states (E_T = 65–68 kcal/mol),[13] suggesting that the photochemistry arising from **15b** was occurring from its triplet state. If the **9b** → **15b** transformation were a singlet-state reaction, addition of a triplet-state quencher would reduce the problem of secondary products from excitation of **15b** without affecting the **9b** → **15b** transformation.

Piperylene is inexpensive, easily separable from products, and is a known quencher of 2,5-cyclohexadienone triplet states.[14] Irradiation of **9b** at 254 nm in the presence of 0.4 M piperylene gave a much cleaner reaction mixture and a 50% isolated yield of **15b**. The yield of **15b** was still less than desirable for a synthetically useful process, and a further improvement was made. Although **9b** and **15b** absorb light over the same range of wavelengths, **9b** has approximately two times the extinction coefficient of **15b** near 300 nm. A RPR 3000-Å light source (maximum emission at 300 nm) and a Pyrex vessel to cut out wavelengths shorter than 280 nm were employed to minimize absorption of light by **15b** during the irradiation of **9b**. Using this light source and a Pyrex apparatus, irradiation of **9b** in the presence of 0.4 M piperylene gave **15b** in 96% yield.

Using the conditions developed for **9b**, the photochemical rearrangements of **9a,c–e** were conducted in excellent yield. Irradiations of the phenyl-substituted vinyl ethers **9c–e** afforded good yields of **15c–e** both with and without piperylene. For these aryl-substituted vinyl ethers, the starting material has a much more intense absorption than does the product in the irradiation region, and absorption of light by the product is not so important. The [1,3]-shift reactions can also be conducted in good yield by irradiation of vinyl ethers in the presence of piperylene using Corex-filtered light from a 450-W Hanovia medium-pressure source, Table I entries 6 and 7. This light source is much more convenient for larger scale irradiations. The identities of **15a–e** were established by acid hydrolysis to the known diene diketones.[3b] In every case clean ketal hydrolysis without competing dienone–phenol rearrangement was observed. For products **15f–h**, the structural assignment was based on ^1H NMR, IR, and HRMS data. Thus, by using an appropriate light source and piperylene concentration, excellent yields of the [1,3] oxygen-to-carbon migration product can be effected in these systems.

Mechanistic studies were conducted on the reaction **9b** → **15b** to establish the efficiency of these photochemical reactions and the multiplicity of the reacting state. For direct irradiations, quantum-yield measurements were conducted in CH_2Cl_2 using 300-nm light from a Bausch and Lomb monochrometer. All of these determinations were conducted at about 10% conversion of **9b** to **15b** to avoid complications from secondary reactions, and the product analysis was by HPLC (see Experimental Section). The quantum yields determined for the **9b** → **15b** reaction establish its high efficiency (Φ = 0.40).

The quantum yield for **9b** → **15b** was measured for reactions in the presence of a quencher and for reactions employing a sensitizer to obtain information on the multiplicity of the reactive state. As expected from the preparative studies, the reaction efficiency was not effected by the presence of 0.44 M piperylene (E_T = 59 kcal/mol).[15] Since the triplet-state energy of the styrene moiety in **9b** is not known, this experiment does not rigorously dismiss a triplet-state reactant for the **9b** → **15b** reaction. However, the quantum yield of <0.05 for the reaction sensitized by benzophenone (E_T = 68.6 kcal/mol)[15,16] unequivocally demonstrates that the triplet state of **9b** does not lead to efficient conversion to **15b**. In addition, attempts to conduct the **9b** → **15b** conversion preparatively using

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(13) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Company, Inc.: San Francisco, CA, 1978; pp 185–191.

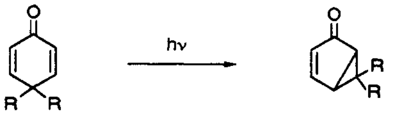
(14) Fisch, M. H.; Richards, J. H. *J. Am. Chem. Soc.* **1963**, *85*, 3029. Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 906.

(15) All triplet energies cited in this text are from Murov, S. L. *Handbook of Photochemistry*; Marcel Decker Inc.: New York, 1973; pp 3–27.

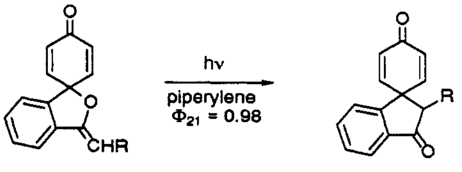
(16) At these concentrations of benzophenone and **9b**, the benzophenone captured >95% of the incident irradiation, and energy transfer from benzophenone triplet to **9b** was calculated to be >90% efficient.

benzophenone as sensitizer resulted in low conversion to product, even on extended irradiation. In contrast to the suggestion that α-(benzyloxy)styrenes undergoes rearrangement in the triplet state, these systems rearrange primarily via singlet states.

Photochemistry of Quinol Vinyl Ethers. We also briefly studied the photochemistry of quinol vinyl ethers **16** and **17** with surprising results. The rearrangement of 2,5-cyclohexadienones to form bicyclo[3.1.0]hexa-3-en-2-ones, **18** → **19**, is a classic photochemical conversion that often occurs with high quantum efficiency.[17-19] Thus, even if a quinol ether such as **16** did undergo the [1,3] oxygen-to-carbon migration in preference to processes known for quinol ethers, complications due to secondary photochemistry of **20** were expected to be factors in the chemistry. However, excitation of **16** and **17** in the presence of piperylene afforded the respective spirodienones **20** and **21** in good yield. Furthermore, irradiation of **16** at 350 nm without added piperylene gave **20** (80%). Since the presence of a quencher was not required to obtain a good yield of product, the products **20** and **21**, which are absorbing light during the reaction, must be reasonably photochemically stable. Indeed, irradiation of **20** for 8 h with light that effected the **16** → **20** reaction in 4 h led to only a small amount of decomposition of **20**. The quantum efficiencies for the direct and benzophenone-sensitized irradiation of **16** → **20** at 300 nm were found to be 0.98 and <0.02, respectively. Thus, this rearrangement involves the singlet excited state of **16**.



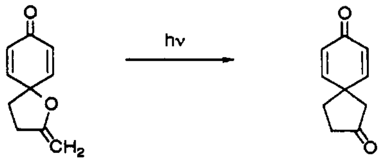
18 19



16, R = CH_3
17, R = C_6H_5

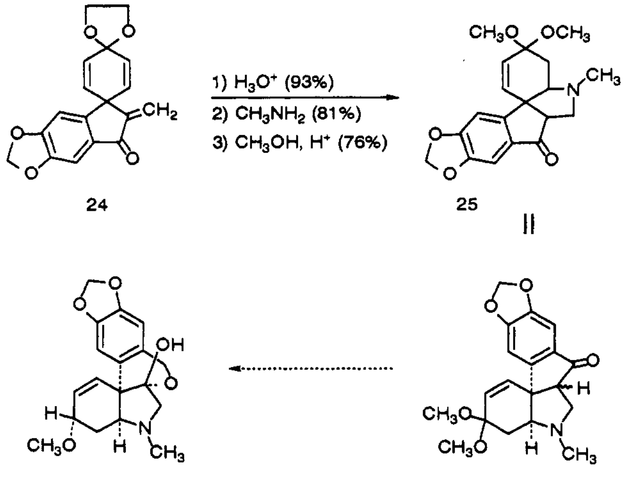
20 (80%)
21 (67%)

The relatively high stability of **20** and **21** is interesting. In both of these molecules, an aromatic ring is spiro-fused to a 2,5-cyclohexadienone. Since spiro conjugation is known to have profound effects on reactivity in some ground-state reactions,[20] perhaps this interaction leads to the relatively high photostability of these two 2,5-cyclohexadienones. However, irradiation of the quinol ether **22**[4] gives the respective dienone **23** in 75% yield. The reasonable stability of **23** to UV irradiation suggests that a spiro interaction of the benzene ring and the dienone is not responsible for the photostability observed for **20** and **21**. In addition, a 2,5-cyclohexadienone having a saturated five-membered ring at the 4-position shows normal dienone photochemistry,[21] ruling out some unusual effect on photochemical reactivity associated with the spiro-fused linkage in these molecules. The most reasonable explanation for the photostability of these dienones is the photochemical ring opening to form a phenoxyl- and acetonyl-type radical[22] pair in the excited state followed by ring closure back to the spiro-fused 2,5-cyclohexadienone (i.e., **20**). The photoracemization of dehydrogriseofulvin, a complex 2,5-cyclohexadienone natural product,[26] was explained by photochemical ring opening, followed by ring closure of the formed radical pair.



22 23

Selected Synthetic Transformations and Summary. The chemistry reported herein provides a rapid entry into highly functionalized spiro-fused 2,5-cyclohexadienones under mild conditions. Although the use of this chemistry in natural products synthesis awaits further study, the transformation **24** → **25** outlined below illustrates the synthetic potential of highly functionalized dienones. The ketal of the trienedione **24** available from **9g** in 75% yield (Table I) can be converted to the tetracyclic amine **25** in three steps. Thus, ketal hydrolysis of **24** to the trienedione followed by a double Michael addition of methylamine across the bis dienone and monoketalization gives **25**, which is one carbon–carbon bond cleavage removed from the ring structure of tazettine and related amaryllidacae alkaloids.[27] The selective ketalization of the enone car-



24 25

Tazettine 25

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[17] For a recent investigation of 2,5-cyclohexadienone photochemistry and a listing of quantum yields and rate constants for rearrangement of these compounds, see: Zimmerman, H. E.; Lamers, P. H. *J. Org. Chem.* **1989**, *54*, 5788.

[18] For 2,5-cyclohexadienone rearrangements of preparative value and references to related work, see: Schultz, A. G.; Lavieri, F. P.; Macielag, M.; Plummer, M. *J. Am. Chem. Soc.* **1987**, *109*, 3991.

[19] There are examples of 2,5-cyclohexadienones which have structural features which preclude the **18** → **19** rearrangement: Zimmerman, H. E.; Jones, G. *J. Am. Chem. Soc.* **1969**, *91*, 5678; **1970**, *92*, 2753.

[20] For a discussion and leading references, see the following. Simmons, H. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1967**, *89*, 5208. Hoffmann, R.; Imamura, A.; Zeiss, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5215.

[21] Griswold, A. A. Ph.D. Thesis, Iowa State University, 1963. Schuster, D. I.; Curran, W. V. *J. Org. Chem.* **1970**, *35*, 4192.

[22] Irraditions of 2,5-cyclohexadienones having 4-trichloromethyl,[23] acetoxy,[24] and methoxy[25] groups often give phenols formally derived from radical expulsion of this substituent. This reaction has been studied in detail for the trichloromethyl case; see ref 23 for details.

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bonyl to give **25** is supported by the IR absorption at 1700 cm^{-1} characteristic of the indanone carbonyl stretching in these systems and the ^{1}H NMR spectrum. The latter shows an upfield shift of the two vinyl hydrogens from δ 6.57 and 6.16 in the enedione to δ 5.96 and 5.65 in **25**. The double Michael addition described herein as well as Diels–Alder reactions across the cisoid enone of **24** should allow facile conversion of **24** to more complicated ring systems. Future reports will focus on the synthetic applications of the highly functionalized spirodienones.

Experimental Section[28]

5-Bromo-6-(1-hydroxyethyl)-1,3-benzodioxole. To a solution of 6-bromopiperonal[29] (20.02 g, 0.087 mol) in THF (200 mL) at 0 °C was added MeMgBr (31.9 mL, 3 M) dropwise over 10 min. The mixture was stirred for 1.5 h and then warmed at rt for 3 h. After addition of saturated NH_4Cl (300 mL) and extractive workup with Et_2O (2 × 750 mL), the alcohol was obtained as a yellow oil (20.23 g, 95%) which was suitable for the next step. A portion was distilled (bp 111–116 °C/0.05 mmHg) to yield a pale yellow oil that solidified upon standing: mp 48–50 °C. Recrystallization of this material from Et_2O/H gave white needles: mp 52–53 °C; IR (NaCl) 3360 (br), 1500, 1480, 1460, 1240, 1120, 1040, 920 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.02 (s, 1 H), 6.94 (s, 1 H), 5.96 (m, 2 H), 5.15 (m, 1 H), 2.14 (d, J = 3 Hz, 1 H), 1.41 (d, J = 6.3 Hz, 3 H); HRMS calcd for $C_9H_9O_3Br$ m/e 243.9735, obsd m/e 243.9717.

5-Bromo-6-(1-oxoethyl)-1,3-benzodioxole. To a solution of 5-bromo-6-(1-hydroxyethyl)-1,3-benzodioxole (3.0 g, 12.0 mmol) in dry DMF (50 mL) at 0 °C was added pyridinium dichromate (21.0 g, 86.0 mmol). The mixture was stirred for 5 h and then warmed to rt for 7 h. After adding H_2O (500 mL), extractive workup with Et_2O (3 × 400 mL) gave an off-white solid (2.42 g, mp 56–59 °C, 83%) which was suitable for the next step. A portion was recrystallized from Et_2O to give a white crystalline solid: mp 61–62 °C; IR (KBr) 1690, 1470, 1380, 1360, 1240, 1130, 1030 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.04 (s, 1 H), 7.02 (s, 1 H), 6.04 (s, 2 H), 2.61 (s, 3 H); HRMS calcd for $C_9H_7O_3Br$ m/e 241.9578, obsd m/e 241.9579.

7″-Methoxy-7″-methyldispiro[1,3-dioxolane-2,1′-[2,5]-cyclohexadiene-4′,5″(7″*H*)-furo[3,4-*f*][1,3]benzodioxole] (8). To a solution of 5-bromo-6-(1-oxoethyl)-1,3-benzodioxole (2.35 g, 9.70 mmol) in MeOH (25 mL, 0.62 mol) were added trimethyl orthoformate (10 mL, 91.4 mmol) and *p*-TsOH (50 mg, 0.26 mmol). After 6 h, TLC analysis (50% EtOAc/H) indicated that the reaction was complete. The mixture was added to a 1% KOH/MeOH solution and concd in vacuo. Extractive workup with CH_2Cl_2 (100 mL) gave an orange oil (2.35 g). Kugelrohr distillation (110 °C/0.70 mmHg) yielded pure **6** as an oil (2.17 g, 77%): IR (NaCl) 1470, 1240, 1220, 1140, 1120, 1100, 1030 cm^{-1}; ^{1}H NMR δ 7.30 (s, 1 H), 7.03 (s, 1 H), 5.96 (s, 2 H), 3.17 (s, 6 H), 1.64 (s, 3 H); HRMS calcd for $C_{11}H_{13}O_4Br$ m/e 287.9997, obsd a fragment corresponding to M − 31.0183 (CH_3O) = 256.9814, m/e 256.9772.

To a solution of **6** from above (5.0 g, 0.017 mol) in THF (30 mL) at −78 °C was added *n*-BuLi (8.24 mL, 2.3 M) dropwise over 3 min. The mixture was stirred for 45 min and then *p*-benzoquinone monoethylene ketal[30] (2.59 g, 0.017 mol) in THF (10 mL) was added dropwise over 5 min. The mixture was stirred for 2 h and then warmed to rt for 30 min. Extractive workup with EtOAc (2 × 100 mL) gave an oily white solid which was triturated with cold Et_2O (25 mL) to yield the alcohol diketal **7** as a white powder (4.15 g, 67%, mp 157–159 °C). This compound was unstable and decomposed upon storage at 0 °C; thus, HRMS/combustion analysis was not attempted: IR (KBr) 3330 (br), 1500, 1480, 1240, 1180, 1140, 1110, 1030, 960, 940 cm^{-1}; ^{1}H NMR δ 6.95 (s, 1 H), 6.85 (s, 1 H), 6.60 (s, 1 H), 6.21 (d, J = 10.2 Hz, 2 H), 5.84 (s, 2 H), 5.73 (d, J = 10.2 Hz, 2 H), 4.00 (s, 4 H), 3.20 (s, 6 H), 1.67 (s, 3 H).

To **7** from above (0.50 g, 1.38 mmol) in CH_2Cl_2 (200 mL) and trimethyl orthoformate (5 mL) at 0 °C was added a slurry of powdered PPTS (10.0 mg, 0.04 mmol) in trimethyl orthoformate (5 mL). After 30 min, TLC analysis (50% EtOAc/H) indicated that the reaction was complete, and the mixture was poured into saturated $NaHCO_3$ (100 mL). Extractive workup gave a white foam (0.450 g). Crystallization from Et_2O/H yielded compound **8** as a chunky white solid (0.345 g, 76%, mp 106–108 °C) which was deemed suitable for use in the next step. Recrystallization from Et_2O/H yielded the analytical sample as a white crystalline solid: mp 109–110 °C; IR (KBr), 1480, 1380, 1300, 1110 (br), 1030, 1000, 960, 880 cm^{-1}; ^{1}H NMR (200 MHz) δ 6.66 (s, 1 H), 6.52 (s, 1 H), 6.12–5.86 (m, 4 H), 5.98 (s, 2 H), 4.10 (s, 4 H), 3.17 (s, 3 H), 1.72 (s, 3 H); HRMS calcd for $C_{18}H_{18}O_6$ m/e 330.1103, obsd m/e 330.1098.

7″-Methylenedispiro[1,3-dioxolane-2,1′-[2,5]cyclohexadiene-4′,5″(7″*H*)-furo[3,4-*f*][1,3]benzodioxole] (9f). To a solution of **8** (300 mg, 0.91 mmol) and succinic anhydride (194 mg, 1.81 mmol) in diglyme (2 mL) and pyridine (2 mL) at rt was added benzoic acid (5.60 mg, 0.046 mmol). The mixture was heated to 110 °C for 2 h and after cooling to rt the dark orange mixture was poured into saturated $NaHCO_3$ (30 mL). Extractive workup with Et_2O (2 × 40 mL) gave a brown solid (243 mg). Trituration with cold Et_2O (5 mL) afforded **9f** as a tan crystalline solid (180 mg, 66%): mp 131–133 °C; IR (KBr) 1660 (m), 1470, 1300, 1110, 1010, 970 cm^{-1}; ^{1}H NMR δ 6.63 (s, 1 H), 6.55 (s, 1 H), 5.98 (s, 2 H), 5.92 (s, 4 H), 4.35 (dd, J = 5.7, 2.4 Hz, 2 H), 4.10 (s, 4 H); HRMS calcd for $C_{17}H_{14}O_5$ m/e 298.0837, obsd m/e 298.0857.

[(*o*-Bromophenyl)ethynyl]trimethylsilane (11). To a solution of *o*-bromoiodobenzene[31] (10 g, 35 mmol) in Et_3N (110 mL) were added $Pd(PPh_3)_2Cl_2$ (100 mg), CuI (0.13 g), and (trimethylsilyl)acetylene (4.13 g, 42 mmol) at rt, and the reaction mixture was stirred for 68 h.[32] The heterogeneous solution was then filtered through Celite, and the filter cake was washed with Et_3N (50 mL). The solvent was removed in vacuo, and the residue was dissolved in Et_2O (50 mL). Extractive workup gave a dark oil (9.41 g) which was purified by Kugelrohr distillation (bath 60–80 °C/1–2 mmHg) to give 8.50 g (87%) of **11** as a light yellow liquid: IR (NaCl) 2960 (m), 2080 (m), 1465 (m), 1255 (m), 865, 845, 755 (m) cm^{-1}; ^{1}H NMR δ 7.65–7.40 (str m, 2 H), 7.30–7.15 (str m, 2 H), 0.2 (s, 9 H); HRMS calcd for $C_{11}H_{13}BrSi$ m/e 251.9970, obsd m/e 251.9994.

8-[*o*-[(Trimethylsilyl)ethynyl]phenyl]-1,4-dioxaspiro[4.5]deca-6,7-dien-8-ol (12). To a solution of **11** (3.9 g, 16.3 mmol) in THF (15 mL) at −78 °C was added *n*-BuLi (9.8 mL of a 2.0 M solution, 1.2 equiv) dropwise, and the resulting mixture was

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(28) **General Procedures.** Melting points were determined in capillaries and are uncorrected. Only strong absorptions are reported for IR spectra unless otherwise noted. ^{1}H NMR spectra were measured at 80 MHz in $CDCl_3$ unless noted otherwise. All reagents or compounds not explicitly referenced were obtained from the Aldrich Chemical Co. Alumina and silica gel (kieselgel 60, 230–400 mesh) were obtained from E. Merck Co. TLC was done using Merck silica gel 60 F_{254} pre-coated Al-backed plates, 0.2-mm thickness. All organometallic reactions were done under N_2 or Ar. Visualization was by UV or by spraying with 5% ethanolic phosphomolybdic acid and then heating. THF was purified by distillation from benzophenone ketyl. Throughout the Experimental Section the following abbreviations are used: petroleum ether, bp 35–60 °C (H), *p*-toluenesulfonic acid (*p*-TsOH). Extractive workup refers to extraction of the material into the indicated solvent, washing the organic layer with brine solution, drying over Drierite ($CaSO_4$), concentration in vacuo, and drying to constant weight under vacuum (1–2 Torr). All quinone monoketals were handled in glassware washed with 5% NH_4OH.

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(30) Dolson, M. G.; Swenton, J. S. *J. Org. Chem.* **1981**, *46*, 177.

(31) Millar, I. T.; Heaney, H. *Org. Synth.* **1960**, *40*, 105.

(32) This method was developed by the following. Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, *627*. Austin, W. B.; Bilow, N.; Kellghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280. If more catalyst is used the reaction is completed in a shorter time.

stirred at this temperature for 2 h. A solution of benzoquinone monoethylene ketal[30] (3.0 g, 1.2 equiv) in THF (10 mL) was added to the above reaction mixture, and the resulting mixture was stirred at −78 °C for 1 h. The reaction mixture was then warmed to rt over a period of 0.5 h before being quenched with H_2O (20 mL). Extractive workup (Et_2O, 3 × 30 mL) gave a slightly yellow solid which was purified by column chromatography (silica gel, 2.5 × 12 cm column, 10% Et_2O/H as eluant) to give 12 (4.0 g, 82%) as a white crystalline solid, mp 92–94 °C. A small portion of the product was recrystallized from Et_2O/H to give white needles, mp 98–99 °C: IR (KBr) 3400 (br), 2150 (m), 1245, 1115, 1005, 950, 855, 840, 755 cm^{-1}; ^{1}H NMR (250 MHz) δ 7.50 (dd, *J* = 8, 2 Hz, 1 H), 7.35 (dd, *J* = 7, 2 Hz, 1 H), 6.44 (d, *J* = 7 Hz, 2 H), 5.91 (d, *J* = 7 Hz, 2 H), 4.6 (s, 1 H), 4.1–4.0 (str m, 4 H), 0.3 (s, 9 H); HRMS calcd for $C_{19}H_{22}O_3Si$ *m/e* 326.1339, obsd *m/e* 326.1332.

3″-Methylenedispiro[1,3-dioxolane-2,1′-[2,5]cyclohexadiene-4′,1″(3″*H*)-isobenzofuran] (9a). To a solution of 12 (2.4 g, 8.05 mmol) in THF (50 mL) and H_2O (2 mL) were added KF·H_2O (0.91 g, 1.2 equiv) and 18-crown-6 (80 mg) at rt, and the resulting mixture was stirred for 40 min (TLC analysis with 40% Et_2O/H as eluant indicated that a slower moving product was formed). To the reaction mixture was added KOH (1 crushed pellet), and the resulting mixture was stirred for 20 min at rt. Extractive workup (Et_2O, 100 mL) gave **9a** as a white solid (1.89 g, 97%). This material was >95% pure on the basis of its ^{1}H NMR spectrum and could be used directly in the photochemical step. This crude product can be further purified by column chromatography (silica gel, 2.5 × 12 cm column, 30% Et_2O/H as eluant) to give **9a** (1.76 g, 90%) as a white crystalline solid, mp 88–90 °C (lit.[3b] mp 89–91 °C) with spectral properties identical to those previously described.[3b]

5-Bromo-6-iodo-1,3-benzodioxole (13). A 1% HgCl/H_2O (750 mL) solution was poured over Al foil cut into ≤1 in. squares (52.4 g, 1.94 mol) in a 3-L three-necked round-bottomed flask. The contents were swirled for 5 s, the solution was decanted, THF (1.5 L) was added, and the flask was fitted with a mechanical stirrer, condenser, and addition funnel (*Note*: *These operations must be done rapidly because the activated Al is very reactive.*) Next, the 5-bromo-6-nitro-1,3-benzodioxole[33] (24.0 g, 0.097 mol) in THF (100 mL) was added immediately over 15 min with vigorous stirring, and the exothermic reaction was controlled by the occasional application of an ice bath. When the refluxing subsided (approximately 1 h), the *still hot* grey suspension was filtered through Celite, and the Al salts were washed with *hot* THF (3 × 500 mL). The solvent was removed in vacuo to give a dark green oil that solidified upon standing. This solid was used directly in the next step.

The crude amine was placed in a 1-L three-necked round-bottomed flask fitted with a mechanical stirrer, H_2O (200 mL) and concd H_2SO_4 (50 mL) were added, and the solution was cooled to 0 °C. Next, $NaNO_2$ (8.03 g, 0.12 mol) was added in small portions over 20 min, and the mixture was stirred for 45 min and then poured into a solution of KI (56.0 g, 0.34 mol) in H_2O (200 mL). The dark black precipitate was collected by vacuum filtration, washed with H_2O (2 × 100 mL), and partitioned between saturated $NaHSO_3$ (300 mL) and CH_2Cl_2 (300 mL). Passage of the CH_2Cl_2 solution through a short column of alumina gave an orange solid (16.4 g, 52% over two steps), mp 62–65 °C (lit.[12] no mp given), which was used directly in the next step.

5-Bromo-6-(3-hydroxy-1-propynyl)-1,3-benzodioxole (14). To a solution of 5-bromo-6-iodo-1,3-benzodioxole (14.2 g, 0.043 mol), bis(triphenylphosphine)palladium(II) dichloride (604 mg, 0.860 mmol), and copper(I) iodide (164 mg, 0.860 mmol) in Et_3N (175 mL) at rt was added propargyl alcohol (4.25 mL, 0.075 mol), and the mixture was stirred overnight.[32] The TLC analysis (50% EtOAc/H) of the resulting dark brown suspension indicated that the starting material was consumed, and the solvent was removed in vacuo to yield a dark brown residue which was chromatographed on silica gel [5 × 17 cm column, 15% Et_2O/H (500 mL), then 50% Et_2O/H (1000 mL) as eluant] to yield a light tan solid that was recrystallized from CH_2Cl_2/H to give 14 as a fluffy white solid (8.86 g, 80%): mp 90–91 °C; IR (KBr) 3300 (br), 2110 (w), 1490, 1480, 1040; ^{1}H NMR (200 MHz) δ 7.00 (s, 1 H), 6.89 (s, 1 H), 5.99 (s, 2 H), 4.51 (d, *J* = 6.1 Hz, 2 H), 2.22 (t, *J* = 6.1 Hz, 1 H); HRMS calcd for $C_{10}H_7O_3Br$ *m/e* 253.9578, obsd *m/e* 253.9603.

7″-(2-Methoxyethylidene)dispiro[1,3-dioxolane-2,1′-[2,5]-cyclohexadiene-4′,5″(7″*H*)-furo[3,4-*f*][1,3]benzodioxole] (9g). To a solution of diisopropylamine (2.87 mL, 21 mmol) in THF (15 mL) at −78 °C was added *n*-BuLi (10.5 mL of a 2.0 M solution), and the mixture was stirred for 1 h. Next, 5-bromo-6-(3-hydroxypropynyl)-1,3-benzodioxole (5.0 g, 20 mmol) in THF (10 mL) was added, and the mixture, which turned orange, was stirred for 1 h. After warming to rt, the solvent along with the last traces of diisopropylamine was removed in vacuo by gentle heating. The resulting salts were dissolved in THF (50 mL), the solution was cooled to −78 °C, and *n*-BuLi (10.5 mL of a 2.0 M solution) was added. After stirring for 1.5 h, *p*-benzoquinone monoethylene ketal (3.18 g, 21 mmol) in THF (10 mL) was added to the deep red solution, which was stirred for 1 h and then gradually warmed to rt for 15 min. After the reaction mixture was poured into saturated NH_4Cl (150 mL), extractive workup with CH_2Cl_2 (2 × 100 mL) gave an orange oil which contained mostly the uncyclized addition product. To complete cyclization, the residue was dissolved in THF (100 mL), KOH (1.12 g, 20 mmol) and 18-crown-6 (528 mg, 2.0 mmol) were added, and the mixture was stirred for 15 min. The TLC analysis (50% EtOAc/H as eluant) indicated that the *p*-quinol had fully cyclized, and the mixture was worked up as above to yield the crude alcohol as a dark orange oil (8.3 g). Alternatively, stirring the mixture overnight with gradual warming to rt completes the cyclization; thus, this last step can be omitted.

To a solution of crude alcohol (8.3 g) in THF (75 mL) at rt was added NaH [1.82 g, 76 mmol, from a suspension of 60% w/w in mineral oil washed with hexane (2 × 5 mL)], and the mixture was stirred for 30 min. After cooling to 0 °C, methyl iodide (4.73 mL, 76 mmol) was added, and the mixture was stirred for 1 h. The TLC analysis (50% EtOAc/H as eluant) indicated that the reaction was complete, the reaction was carefully quenched by adding H_2O (10 mL), and the mixture was poured into saturated NH_4Cl (150 mL). Extractive workup with CH_2Cl_2 (2 × 100 mL) yielded a dark orange oil (8.5 g) which was chromatographed (activity III neutral alumina, 4.5 × 18 cm column, 10% EtOAc/H, then 50% EtOAc/H as eluant) to yield a pale yellow oil which solified upon standing (3.85 g, 58% over three steps, mp 79–86 °C). Analytically pure **9g** was obtained after two recrystallizations from EtOAc/Et_2O/H to yield white crystals: mp 95–97 °C; IR (NaCl) 1470, 1300, 1110, 1030, 960 cm^{-1}; ^{1}H NMR (200 MHz) δ 6.81 (s, 1 H), 6.54 (s, 1 H), 5.99 (s, 2 H), 5.92 (s, 4 H), 4.92 (t, *J* = 7.5 Hz, 1 H), 4.17 (d, *J* = 7.5 Hz, 2 H), 4.12 (s, 4 H), 3.35 (s, 3 H); HRMS calcd for $C_{19}H_{18}O_6$ *m/e* 342.1103, obsd *m/e* 342.1108. Anal. Calcd for $C_{19}H_{18}O_6$: C, 66.64; H, 5.30. Found: C, 66.44; H, 5.37.

7″-[2-[(*tert*-Butyldimethylsilyl)oxy]ethylidene]dispiro-[1,3-dioxolane-2,1′-[2,5]cyclohexadiene-4′,5″(7*H*)-furo[3,4-*f*][1,3]benzodioxole] (9h). To a solution of the crude vinyl ether alcohol from the **9g** preparation (1.0 g, 3.04 mmol) were added imidazole (724 mg, 10.6 mmol) and TBDMS chloride (1.14 g, 7.59 mmol). The TLC analysis (25% EtOAc/H) after 4 h indicated that the reaction was complete, and the mixture was poured into H_2O (100 mL). Extractive workup with EtOAc (2 × 100 mL) gave a yellow oil (1.45 g) that was passed through a column of activity III neutral alumina (1.5 × 17 cm column, 10% Et_2O/H as eluant) to yield **9h** as an off-white solid [675 mg, 50% over three steps from 5-bromo-6-(3-hydroxpropynyl)-1,3-benzodioxole, mp 71–75 °C]. Two recrystallizations from Et_2O/H gave the analytical sample as a white solid, mp 78–80 °C: IR (KBr) 1680 (m), 1470, 1290, 1110, 1030, 960, 830 cm^{-1}; ^{1}H NMR (200 MHz) δ 6.80 (s, 1 H), 6.53 (s, 1 H), 5.98 (s, 2 H), 5.91 (s, 4 H), 4.92 (t, *J* = 7.0 Hz, 1 H), 4.44 (d, *J* = 7.0 Hz, 2 H), 4.12 (m, 4 H), 0.91 (s, 9 H), 0.09 (s, 6 H). Anal. Calcd for $C_{24}H_{30}O_6Si$: C, 65.13; H, 6.84. Found: C, 64.98; H, 6.88.

Photochemical Rearrangements. The small-scale photochemical reactions were conducted in Pyrex vessels at 25–35 °C using a Rayonet photochemical reactor available from New England Ultraviolet Company with lamps having emissions centered at 300 nm (RPR 3000 Å) or 350 nm (RPR 3500 Å). Some of the larger preparative runs used Corex-filtered light from a 450-W Hanovia medium-pressure source at 10–15 °C. In all cases

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degassing of the solvent was performed prior to irradiation by slowly bubbling N$_2$ through the solutions for 5 min. Detailed procedures are given for the irradiation of **9a,c**. The structures of the photoproducts **15a–e** were confirmed by hydrolysis of the ketal to give the known diketones.[3b]

Spiro[2,5-cyclohexadiene-1,1′-[1*H*]indene]-3′(2′*H*),4-dione 4-Ethylene Acetal (15a). A solution of **9a** (100 mg, 0.39 mmol) in CH$_2$Cl$_2$ (6 mL) and piperylene (1 mL) in a Pyrex test tube was irradiated with 6 RPR 3000-Å lamps in a merry-go-round apparatus for 52 h. The reaction mixture was concd in vacuo to give a slightly yellow oil which was chromatographed (silica gel, 1 × 10 cm column, 100% H and then 10% Et$_2$O/H as eluant) to obtain **15a** as a colorless oil (82 mg, 82%): IR (NaCl) 1715, 1118, 1100, 962 cm^{-1}; ^{1}H NMR δ 7.7–7.2 (str m, 4 H), 5.8 (s, 4 H), 4.0 (s, 4 H), 2.7 (s, 2 H); HRMS calcd for C$_{16}$H$_{14}$O$_3$ m/e 254.0943, obsd m/e 254.0934.

The structural assignment for **15a** was confirmed by hydrolysis to the known diketone.[3b] The photoproduct **15a** (50 mg, 0.20 mmol) was dissolved in THF (10 mL), 5% HCl (1 mL) was added, and the mixture was allowed to stand at rt for 0.5 h. Standard workup gave the ketone as a white solid (41 mg, 100%) with spectral properties identical to those previously described.

2′-Methylspiro[2,5-cyclohexadiene-1,1′-[1*H*]indene]-3′-(2′*H*),4-dione 4-Ethylene Acetal (15b). A solution of **9b** (1.0 g , 3.94 mmol) in benzene (60 mL) and piperylene (16 mL) in eight Pyrex test tubes was irradiated with 12 RPR 3000-Å lamps in a merry-go-round apparatus for 2.5 h. The reaction mixture was then concd in vacuo, and the crude product was chromatographed (silica gel, 1 × 12 cm column, 100% H and then 20% Et$_2$O/H as eluant) to give **15b** as a clear liquid (970 mg, 97%) with spectral properties identical to those previous described.[3b]

2′-Phenylspiro[2,5-cyclohexadiene-1,1′-[1*H*]indene]-3′-(2′*H*),4-dione 4-Ethylene Acetal (15c). A solution of **9c** (50 mg, 0.15 mmol) in benzene (8 mL) and piperylene (2 mL) was irradiated with 12 RPR 3000-Å lamps for 1.5 h. The reaction mixture was concd in vacuo, and the crude product was chromatographed (silica gel, 1 × 10 cm column, 100% H first and then 20% Et$_2$O/H as eluant) to obtain **15c** as a white solid (48 mg, 96%). A small portion was recrystallized in Et$_2$O/H to give crystals: mp 111–112 °C; IR (KBr) 1720 (vs), 1115, 1110, 961 cm^{-1}; ^{1}H NMR δ 7.8–6.9 (str m, 9 H), 6.1–5.8 (m, 2 H), 5.4 (m, 2 H), 4.0 (s, 1 H), 3.9 (s, 4 H); HRMS calcd for C$_{22}$H$_{18}$O$_3$ m/e 330.1256, obsd m/e 330.1263.

Hydrolysis of **9c** (15 mg, 0.045 mmol) in THF (10 mL) and 5% HCl (1 mL) at rt for 0.5 h and workup gave a slightly yellow solid (14 mg, 94%) which was recrystallized in MeOH to give a white solid, mp 149–151 °C (lit.[3b] mp 152–155 °C) with spectral properties identical to those previously described.[3b]

2′-(4-Methylphenyl)spiro[2,5-cyclohexadiene-1,1′-[1*H*]-indene]-3′(2′*H*),4-dione 4-Ethylene Acetal (15d). The crude product obtained from the photochemical reaction was triturated in Et$_2$O and hexane to obtain **15d** as a white solid (26 mg, 87%). A small portion was recrystallized in Et$_2$O/H to give white crystals: mp 97–99 °C; IR (KBr) 1720, 1115, 1100, 960, 955 cm^{-1}; ^{1}H NMR δ 8.0–7.0 (str m, 8 H), 6.2–5.8 (m, 2 H), 5.6 (s, 2 H), 4.1–4.0 (br s, 5 H), 2.4 (s, 3 H); HRMS calcd for C$_{23}$H$_{20}$O$_3$ m/e 344.1412, obsd m/e 344.1407.

2′-(4-Methoxyphenyl)spiro[2,5-cyclohexadiene-1,1′-[1*H*]-indene]-3′(2′*H*),4-dione 4-Ethylene Acetal (15e). The crude white solid obtained from the reaction mixture was recrystallized from Et$_2$O/H to give a white crystalline solid: mp 113–116 °C; IR (KBr) 1712, 1518, 1252, 1186, 1120, 1110, 961 cm^{-1}; ^{1}H NMR δ 7.8–7.1 (str m, 4 H), 6.8 (q, J = 9 Hz, 4 H), 6.1–5.8 (m, 2 H), 5.4 (s, 2 H), 4.0 (br s, 5 H), 3.7 (s, 3 H); HRMS calcd for C$_{23}$H$_{20}$O$_4$ m/e 360.1362, obsd m/e 360.1349.

Dispiro[1,3-dioxolane-2,1′-[2,5]cyclohexadiene-4′,5″-[5*H*]indeno[5,6-*d*][1,3]dioxol]-7″(6″*H*)-one (15f). The vinyl ether **9f** (150 mg, 0.50 mmol) was dissolved in a mixture of dry CH$_2$Cl$_2$ (8 mL), dry benzene (8 mL), and piperylene (2 mL) and was irradiated through Pyrex with 12 RPR 3000-Å lamps for 16 h. The TLC analysis (50% EtOAc/H) indicated that the reaction was complete, and the mixture was concd in vacuo to yield an oily yellow solid (155 mg). Trituration with cold Et$_2$O (3 × 2 mL) afforded **15f** as a light yellow powder (110 mg, 73%, mp 185–188 °C), showing an ^{1}H NMR spectrum identical to analytically pure material. A portion was recrystallized twice from Et$_2$OAc/H to yield clear needles: mp 190–191.5 °C; IR (KBr) 1700, 1290, 1120 cm^{-1}; ^{1}H NMR δ 7.06 (s, 1 H), 6.72 (s, 1 H), 6.06 (s, 2 H), 5.88 (s, 4 H), 4.12 (s, 4 H), 2.78 (s 2 H); mass spectrum, exact mass calcd for C$_{17}$H$_{14}$O$_5$ m/e 298.0841, obsd m/e 298.0853.

6″-Methylenedispiro[1,3-dioxolane-2,1′-[2,5]cyclohexadiene-4′,5″-[5*H*]indeno[5,6-*d*][1,3]dioxo]-7″(6″*H*)-one (24). The vinyl ether **9g** (3.5 g, 10.2 mmol) was dissolved in a mixture of dry benzene (200 mL) and piperylene (20 mL) and irradiated with Corex-filtered light from a 450-W Hanovia medium pressure source for 8 h. Removal of the solvent in vacuo afforded crude **15g** as a yellow oil (3.75 g), which was dissolved in EtOAc (100 mL), Florisil (40 g) was added, and the slurry was heated at 70 °C for 16 h. After cooling to rt the slurry was vacuum filtered, and the Florisil was washed with EtOAc (2 × 75 mL). Removal of the solvent in vacuo yielded an oily yellow solid (3.20 g), which was triturated with cold acetone, affording **24** as a white solid (2.37 g, 75% over two steps, mp 178–181 °C). Recrystallization of a small portion with EtOAc/H yielded an analytical sample as white crystals, mp 188–189 °C: IR (KBr) 1700, 1480, 1460, 1290, 1110, 960 cm^{-1}; ^{1}H NMR δ 7.19 (s, 1 H), 6.74 (s, 1 H), 6.29 (s, 1 H), 6.07 (s, 2 H), 5.86 (q, $\Delta\nu$ = 14.4 Hz, J = 10.2 Hz, 4 H), 5.49 (s, 1 H), 4.13 (s, 4 H), ^{13}C NMR and DEPT (62.5 MHz) δ 189.9 (s), 154.7 (s), 150.8 (s), 149.3 (s), 148.8 (s), 134.7 (d), 131.8 (s), 125.7 (d), 120.4 (t), 105.1 (d), 102.8 (d), 102.4 (t), 99.3 (s), 65.3 (t), 65.2 (t); mass spectrum, exact mass calcd for C$_{18}$H$_{14}$O$_5$ m/e 310.0841, obsd m/e 310.0836.

6″-[2-[(*tert*-Butyldimethylsilyl)oxy]ethyl]dispiro[1,3-dioxolane-2,1′-[2,5]cyclohexadiene-4′,5″-[5*H*]indeno[5,6-*d*]-[1,3]dioxol]-7″(6″*H*)-one (15h). The silyl derivative **9h** (450 mg, 1.01 mmol) in a mixture of dry benzene (45 mL) and piperylene (5 mL) was irradiated using 18 RPR 3000-Å lamps for 5.5 h. Concentration of the reaction mixture in vacuo and rapid elution of the residue through a column of base-washed silica gel (1 × 12 cm column, 25% EtOAc/H as eluant) gave **15h** as a pale yellow oil (350 mg, 78%): IR (NaCl) 1700, 1460, 1450, 1270, 1250, 1110, 1030, 950, 930, 830 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.02 (s, 1 H), 6.65 (s, 1 H), 6.23 (dd, J = 10.3, 1.9 Hz, 1 H), 6.00 (s, 2 H), 5.90 (dd, J = 10.3, 1.9 Hz, 1 H), 5.78 (m, 2 H), 4.07 (s, 4 H), 4.06 (obscurred dd, 1 H), 3.85 (dd, J = 10.4, 2.6 Hz, 1 H), 2.68 (m, 1 H), 0.7 (s, 9 H), −0.04 (s, 3 H), −0.07 (s, 3 H); mass spectrum, exact mass calcd for C$_{24}$H$_{30}$O$_6$Si m/e 442.1803, obsd a fragment corresponding to M − 57.0702 [C$_4$H$_9$ (t-Bu)] = 385.1101, m/e 385.1157.

2′-Methylspiro[2,5-cyclohexadiene-1,1′-[1*H*]indene]-3′-(2′*H*),4-dione (20). A solution of **16** (110 mg, 0.49 mmol) in CH$_2$Cl$_2$ (10 mL) and piperylene (2 mL) was irradiated with 12 RPR 3000-Å lamps for 1.5 h. The resulting yellow solution was concd in vacuo, and the crude product was triturated with Et$_2$O/H to give **20** as a light yellow solid (88 mg, 80% pure by ^{1}H NMR analysis). A small portion was recrystallized in Et$_2$O/H to give a white solid, mp 147–149 °C (lit.[3b] mp 149–150 °C), showing spectroscopic properties identical to an authentic sample.

The irradiation of **16** (80 mg, 0.36 mmol) in benzene (10 mL) was also performed in a Pyrex test tube using 8 RPR 3500-Å lamps for 4 h without added piperylene. Workup and trituration of the crude product mixture with Et$_2$O/H gave **20** (61 mg, 76%)

2′-Phenylspiro[2,5-cyclohexadiene-1,1′-[1*H*]indene]-3′-(2′*H*),4-dione (21). A solution of **17** (30 mg) in benzene (10 mL) and piperylene (2 mL) was irradiated with 12 RPR 3000-Å lamps for 14 min. The reaction mixture was concd in vacuo to yield a light yellow solid which was triturated with cold MeOH to give **21** as a white solid (20 mg, 67%), mp 150–152 °C (lit.[3b] mp 152–155 °C), showing spectroscopic properties identical to the authentic sample.

Spiro[4.5]deca-6,9-diene-2,8-dione (23). A solution of **22** (40 mg, 0.25 mmol) in benzene (2 mL) in a Pyrex test tube was irradiated with eight 3500-Å lamps for 20 min. The resulting solution was concd, and the crude product was purified by column chromatography (silica gel, 1.5 × 10 cm column, 50% Et$_2$O/H as eluant) to yield **23** as a white solid (30 mg, 75%) identical in all respects with the known compound.

Quantum Yield Determinations. Two light sources were used in this study. The first light source was a Bausch and Lomb Model 5 high-intensity monochronometer, equipped with a UV–vis grating, variable entrance and exit slits, and an Osiam HBO 200-W superpressure mercury lamp. This light source was used for the absolute quantum yield determinations. The front and back slits were set at 6 nm. The cell and the details of these measurements are given in detail elsewhere.[34] The cylindrical irradiation cell contained two identical compartments, each 1.5 cm in diameter with a 4.8-cm optical path length. The cell was constructed from 1.5-cm Pyrex tubing and had flat quartz faces and a quartz spacer which separated the two compartments. Each cell was equipped with a 14/20 male joint and the back cell also had a 7/25 female joint. Conversions to product were <10% in all quantum yield determinations. The results for these determinations are reported in Table II.

The second light source was a Rayonet Model RPR-100 photochemical reactor equipped with 12 RPR 3000-Å lamps. A merry-go-round apparatus, which could be inserted into the reactor, held a maximum of eight test tubes. Using this light source, the normal operating temperature was about 35 °C with the cooling fan in operation. This light source was used for relative quantum yield measurements for irradiations containing a quencher.

Quantitative HPLC was used to analyze the amount of starting material **9b** and the rearrangement product **15b**. The HPLC was calibrated using solutions having known amounts of **9b**, **15b**, and **16** using an analyzing wavelength of 260 nm. For the quantum yield determinations on the **16** → **20** reaction, the analysis was done by ^{1}H NMR spectroscopy. The quantity of the product was calculated from the ^{1}H NMR spectrum of the concd reaction mixture was an added amount of the internal standard (*o*-xylylene dibromide). The integrations of the peaks at δ 4.6 (methylene protons of the standard) and 2.9 (methylene protons of the product) were used for the analysis.

Sensitized Irradiations. Similar procedures were used in the quantum yield measurements of the sensitized reactions of **9b**. These studies were conducted at 350 nm in benzene, and the benzophenone was calculated to capture >95% of the incident irradiation. The stability of the product **15b** under sensitization conditions was established as follows. A solution of **15b** (7.9 mg, 0.031 mmol) and benzophenone (42.4 mg) was dissolved in benzene (12 mL) and irradiated at 350 nm for 20 min. HPLC analysis indicated no decomposition of **15b**; 10% would have been easily detected. In addition, a preparative run of the sensitization was conducted as follows. A solution of **15b** (25 mg, 0.098 mmol) and benzophenone (120 mg, 0.659 mmol) was irradiated for 4 h at 350 nm with a monochronometer. TLC analysis (40% Et_2O/H as eluant) showed primarily starting material with the formation of a small amount of unknown product.

Attempted Quenching Irradiations. A solution of **9b** (13.0 mg, 0.051 mmol) in CH_2Cl_2 (11.5 mL) and piperylene (0.5 mL) and a second solution of **9b** (14.3 mg, 0.056 mmol) in CH_2Cl_2 (12.0 mL) were put into two matched Pyrex test tubes. The solutions were irradiated for 1.5 min. The HPLC analysis of these two solutions at this low conversion (<10%) showed no detectable difference in the amount of **15b** formed.

4a,5,6,6a-Tetrahydro-5-methyl-3*H*-[1,3]dioxolo[5,6]-indeno[2,1-*c*]indole-3,7(4*H*)-dione 3-Dimethyl Acetal (25). To a solution of compound **24** (690 mg, 2.22 mmol) in THF (25 mL) at rt was added 5% aqueous HCl (10 mL) dropwise with vigorous stirring. After 1 h the reaction was quenched by adding saturated $NaHCO_3$ (25 mL) and then concd in vacuo. Extractive workup with CH_2Cl_2 (2 × 30 mL) gave the trienedione (550 mg, 93%, mp 190–192 °C), which was suitable for the next step. The analytical sample was obtained by recrystallization from EtOAc/H to give white crystals, mp 210–211 °C: IR (KBr) 1700, 1670, 1480, 1460, 1290 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.28 (s, 1 H), 6.66 (s, 1 H), 6.55 (AB q, $\Delta\nu$ = 60.5 Hz, J = 10.1 Hz, 4 H), 6.39 (s, 1 H), 6.14 (s, 2 H), 5.52 (s, 1 H). Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.16; H, 3.79. Found: C, 72.22; H, 3.55.

To a solution of the trienedione from above (100 mg, 0.376 mmol) in THF (20 mL) was added an aqueous buffered solution of NaOAc/HOAc/H_2O (154 mg, 1.88 mmol/108 μL, 1.88 mmol in 5 mL of H_2O). Next, methylamine (1.75 mL, 1.43 M in EtOH) was added dropwise to the solution over 15 min, and the mixture was stored immediately in the freezer overnight. The color of the mixture turned from light yellow to orange, then red, and finally dark purple over the course of the reaction. Extractive workup with $CHCl_3$ (20 mL) gave a dark purple solid that was passed through a short alumina column ($CHCl_3$ as eluant) to yield the amine enedione as a tan solid (90 mg, 81%, mp 201–204 °C) that was >95% pure by ^{1}H NMR. Two recrystallizations from $CHCl_3$/H gave the analytically pure sample as a white fluffy solid, mp 219–220 °C: IR (KBr) 2800, 1690–1670, 1480, 1310, 1300, 1030 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.13 (s, 1 H), 6.80 (s, 1 H), 6.57 (dd, J = 10.1, 1.5 Hz, 1 H), 6.16 (partially obscured d, 1 H), 6.13 (s, 2 H), 3.54 (t, J = 9.7 Hz, 1 H), 3.20 (dd, J = 9.7, 7.0 Hz, 1 H), 2.76 (d, J = 4.0 Hz, 2 H), 2.63 (m, 1 H), 2.44 (dd, J = 9.7, 7.0 Hz, 1 H), 2.25 (s, 3 H); ^{13}C NMR and DEPT (62.5 MHz) δ 202.6 (s), 196.2 (s), 155.0 (s), 151.9 (s), 149.7 (s), 149.5 (d), 130.2 (s), 128.0 (d), 104.5 (d), 103.3 (d), 102.8 (t), 69.2 (d), 57.7 (d), 56.5 (t), 54.9 (s), 38.9 (q), 35.9 (t). Anal. Calcd for $C_{17}H_{15}O_4N$: C, 68.66; H, 5.09. Found: C, 68.83; H, 5.08.

To a solution of the above amino enedione (810 mg, 2.72 mmol) in MeOH (35 mL) and trimethyl orthoformate (5 mL) at rt was added *p*-TsOH (620 mg, 3.26 mmol), and the solution was stirred for 15 min. Then the reaction mixture was dripped into a 1% KOH/MeOH (15 mL) solution. Extractive workup with $CHCl_3$ (50 mL) gave a brown oil which was eluted down a column of base-washed silica gel (EtOAc as eluant) to yield a tan solid (704 mg, 76%, mp 165–169 °C). Recrystallization twice from EtOAc/H gave the analytically pure **25** as clear crystals, mp 175–176 °C: IR (KBr) 1700, 1470, 1460, 1300, 1290 (sh), 1120, 1090, 1030 cm^{-1}; H^1 NMR (200 MHz) δ 7.04 (s, 1 H), 6.71 (s, 1 H), 6.08–6.05 (m, 2 H), 5.96 (dd, J = 10.1, 1.1 Hz, 1 H), 5.65 (d, J = 10.1 Hz, 1 H), 3.47 (dd, J = 12.0, 5.1 Hz, 1 H), 3.35 (s, 3 H), 3.34 (s, 3 H), 3.10 (dd, J = 9.5, 1.5 Hz, 1 H), 2.96 (pseudo t, J = 9.5, 8.0 Hz, 1 H), 2.77 (dd, J = 8.0, 1.5 Hz, 1 H), 2.27 (s, 3 H), 2.23 (partially obscurred ddd, J = 5.1, 1.1 Hz, 1 H), 1.62 (t, J = 12.0 Hz, 1 H). Anal. Calcd for $C_{19}H_{21}O_5N$: C, 66.44; H, 6.17. Found: C, 66.80; H, 6.28.

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Registry No. **6**, 87850-46-2; **7**, 137256-59-8; **8**, 137256-60-1; **9a**, 120254-85-5; **9b**, 120254-93-5; **9c**, 120254-91-3; **9e**, 126084-13-7; **9f**, 126084-14-8; **9g**, 126084-20-6; **9g** free alcohol, 137256-58-7; **9h**, 137256-63-4; **10**, 583-55-1; **11**, 38274-16-7; **12**, 137256-61-2; **13**, 94670-76-5; **14**, 137256-62-3; **15a**, 126084-15-9; **15b**, 120254-86-6; **15c**, 126084-16-0; **15d**, 126084-17-1; **15e**, 126084-18-2; **15f**, 126084-19-3; **15h**, 137256-67-8; **16**, 120254-88-8; **17**, 120291-92-1; **20**, 120254-89-9; **21**, 120254-92-4; **22**, 135614-74-3; **23**, 52727-26-1; **24**, 126084-21-7; **24** trienedione deriv., 137256-64-5; **24** amino deriv., 137256-66-7; **25**, 137256-65-6; 5-bromo-6-(1-hydroxyethyl)-1,3-benzodioxole, 71095-27-7; 5-bromo-6-(1-oxoethyl)-1,3-benzodioxole, 71095-26-6; 6-bromopiperonal, 15930-53-7; 5-bromo-6-nitro-1,3-benzodioxole, 7748-58-5; propargyl alcohol, 107-19-7; *p*-benzoquinone monoethylene ketal, 35357-34-7.

Supplementary Material Available: ^{1}H NMR spectra for all new compounds reported (22 pages). Ordering information is given on any current masthead page.

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