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Improved Methodology for Photocyclization Reactions[†]

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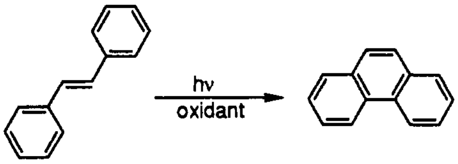
To photocyclize stilbenes, a stoichiometric amount of iodine plus propylene oxide in the absence of air is superior to a catalytic amount of iodine in the air. The propylene oxide prevents HI from photoreducing double bonds. The absence of air prevents photooxidative side reactions, shown in one case to be caused by a photogenerated oxidant, possibly hydrogen peroxide.

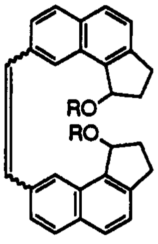
Introduction

Reported here is a procedure that greatly improves the yields and purities in photocyclizations of stilbenes, exemplified by eq 1, transformations widely used to prepare complex ring systems.[1] The generally accepted procedure, developed by Mallory et al. in 1964, uses air plus catalytic amounts of iodine to effect the oxidation,[2] and the many reported photocyclizations that use it testify to its effectiveness.[1] Nevertheless, we find that when the amount of iodine in the reaction mixtures is raised to that required to effect the oxidation, excess propylene oxide is added to consume the HI formed, and air is excluded, in every one of a large number of examples both the amounts of the products and their purities are increased.



(1)

We made this discovery after developing the procedure to solve a problem that arises when molecules like 1, having ether functions in benzylic positions, are cyclized.[3] The problem was that the conventional procedure eliminates these ethers, forming alkenes, undoubtedly because of the HI generated. The solution was to add propylene oxide to consume the acid, which prevents the elimination. However, the removal of the HI requires the addition of 1 full equiv of iodine, for air alone is less effective as an oxidant[2a,b,4] and air cannot regenerate iodine when HI is absent. In turn, since air is not needed, the reactions can be carried out in an inert atmosphere.



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Results and Discussion

It is remarkable that even for molecules without benzylic ether functions, this recipe greatly improves the effectiveness of photocyclizations. Table I compares the yields obtained in a number of such reactions carried out by the two procedures: the one using catalytic amounts of iodine plus air as the oxidant, the other using stoichiometric amounts of iodine as the oxidant plus propylene oxide to consume the HI formed. For the latter procedure, the yields recorded are those of products isolated. For the former, the yields of purified products could be measured in only three experiments (entries 1, 3, and 8). In the others the products were complex, and the ones desired were barely recognizable (by ^{1}H NMR spectroscopy) only after short periods of irradiation.

When the irradiations were conducted in air with catalytic amounts of iodine, precipitates were commonly seen and the products usually displayed proton magnetic resonances characteristic of aldehydes. When the irradiations were conducted in the absence of air, neither precipitates nor, of course, aldehyde resonances were observed.

The essential observations in Table I are that in each case the yields in the procedure using propylene oxide exceed those in the procedure using catalytic amounts of iodine and when methoxyls are on the aromatic rings, the improvements are immense.

It is not just the oxidizing power of the iodine that accounts for this improvement, but also the presence of propylene oxide. Thus, if the amount of iodine is raised to the stoichiometric figure, but propylene oxide is omitted, the products obtained from the reactants in entries 1, 3, and 4 are shown by their ^{1}H NMR spectra to be grossly impure, exhibiting prominent superfluous resonances around δ 3.2, as well as elsewhere. This can be seen in Figure 1, which compares the ^{1}H NMR spectra of the products (purified by a simple chromatography) after the photocyclization of **6** had been carried out under two conditions: (a) with 2 mol of iodine plus propylene oxide and (b) with 2 mol of iodine alone. In the latter spectrum, the presence of the helicene **7** is barely recognizable.

The reason is that the oxidizing agent iodine *reduces* the various organic substances present in solution, and it does so by generating the reducing agent HI. Therefore, unless the HI is removed, as in our procedure, iodine alone is an ineffective oxidant for photocyclizations.[6]

Photoreduction by HI. That HI photoreduces alkene linkages is shown by the data in Table II. This table

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[†] Dedicated to Harry H. Wasserman on his 70th birthday.

[1] (a) Mallory, F. B.; Mallory, C. W. *Organic Reactions*; Wiley & Sons: New York, 1984; Vol. 30, p 1. (b) Laarhoven, W. H. In *Organic Photochemistry*; Padwa, A., Ed; Marcel Dekker: New York, 1989; Vol. 10, p 163. (c) Floyd, A. J.; Dyke, S. F.; Ward, S. E. *Chem. Rev.* **1976**, *76*, 509. (d) Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 185. (e) Laarhoven, W. H. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 241.

[2] (a) Wood, C. S.; Mallory, F. B. *J. Org. Chem.* **1964**, *29*, 3373. (b) Mallory, F. B.; Wood, C. S.; Gordon, J. T. *J. Am. Chem. Soc.* **1964**, *86*, 3094.

[3] (a) Sudhakar, A.; Katz, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 179. (b) Sudhakar, A.; Katz, T. J.; Yang, B.-W. *J. Am. Chem. Soc.* **1986**, *108*, 2790.

[4] Sato, T.; Shimada, S.; Hata, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2484.

[5] Scholz, M.; Mühlstädt, M.; Dietz, F. *Tetrahedron Lett.* **1967**, 665.

[6] Mallory et al. reported[2b] that when I_2 is the only oxidant the yield and purity of the phenanthrene decreases. That iodine suppresses photocyclizations is also reported in refs 7a and b. Sato et al.,[4] however, obtained a good yield of triphenylene from *o*-terphenyl only when 1 full equiv of iodine was used as the oxidant.

[7] (a) Grellmann, K.-H.; Hentzschell, P.; Wismontski-Knittel, T.; Fischer, E. *J. Photochem.* **1979**, *11*, 197. (b) Collins, D. J.; Hobbs, J. J. *Aust. J. Chem.* **1967**, *20*, 1905.

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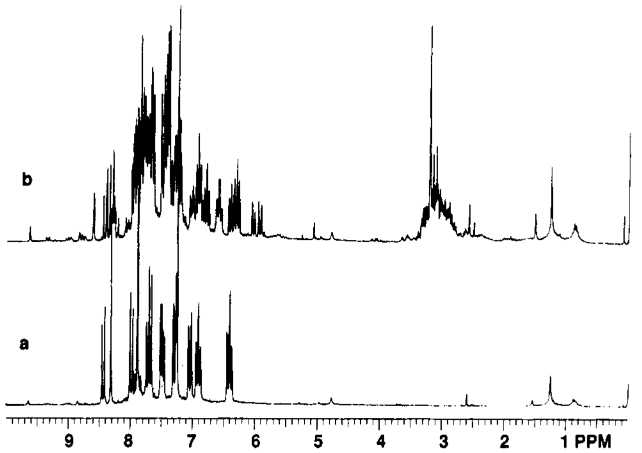
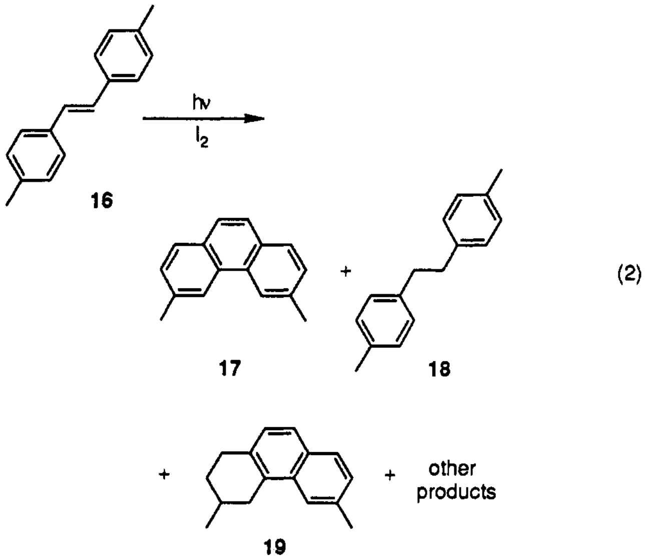
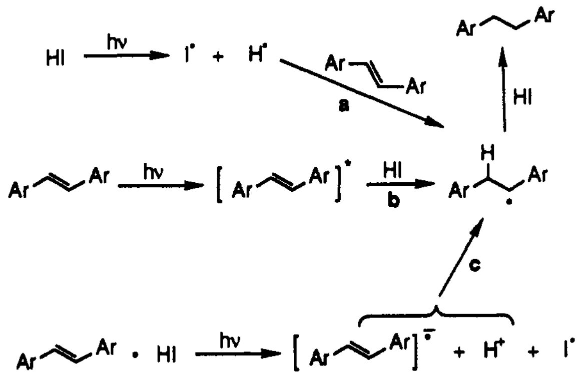


Figure 1. ^{1}H NMR spectrum of the product formed by irradiating 6 (0.6 mM, in benzene) plus 2 mol of iodine through Pyrex for 1.2 h and then removing polar materials by chromatography: (a) with 713 mol of propylene oxide present per mole of bisstilbene 2; (b) without added propylene oxide.

records the amounts of the products formed after *p,p'*-dimethylstilbene (**16**)[8] is irradiated (eq 2) in the presence and absence of various combinations of air, iodine, propylene oxide, and hydrogen iodide.[9] It shows that the reduction product **18**[10] (and also some **19**[11]) is produced in appreciable amounts if 1 equiv of iodine is present (entry 2). Absorbing generated HI with propylene oxide (entry 1) or diminishing its amount by using only traces of iodine (entry 3) suppresses the products of reduction, whereas adding HI to the reaction mixture enhances them (entry 4). When as much as 20 equiv of HI are added, the only products are reduced materials (entry 6). None of the phenanthrene is then recognizable by ^{1}H NMR spectroscopy. Notice that neither HI in the absence of light (entry 5) nor light in the absence of HI (entries 7 and 8) reduces the double bond in **16**. HI in the presence of light does reduce the phenanthrene (entry 9).



Scheme I



Effect of Increased Iodine Concentration. We could imagine that large amounts of iodine might oxidize the dihydrophenanthrenes to the phenanthrenes before hydrogen iodide can reduce them. Under these circumstances there would be no need for propylene oxide. Indeed, one experiment using **2**, a large amount of iodine (20 equiv), no propylene oxide, and a low concentration of the stilbene (0.43 mM) did give the phenanthrene in essentially quantitative yield and with a purity as high as that obtained in the procedure using only 1 equiv of iodine and a large excess of propylene oxide.

However, experiments to test the generality of this idea reveal a flaw. As Table III shows in entries 1–3, when **16** (rather than **2**) was irradiated under argon in the presence of increasing amounts of iodine, the yield of phenanthrene **17**, instead of rising, fell significantly. Decreasing the concentration of **16**, while keeping that of iodine high (entry 4), did not appreciably improve the yield of **17**, as it had in the experiments with **2**.

A comparison of entries 6 and 7 shows that increasing the concentration of iodine (the concentration of **16** was also increased) had the same effect when propylene oxide was present as when it was absent: the yield of **17** decreased. Incidentally, these experiments and those compared in entries 4 and 5 confirm the observations summarized in Table II, that propylene oxide suppresses the formation of reduction-product **18**.

Table III also shows that larger concentrations of iodine, as they decrease the yields of phenathrene, increase the amounts of the stilbene **16** recovered. The reason may be that iodine either catalyzes the photoisomerization of the *cis*-stilbene to the trans isomer[13] or quenches the excited state of the stilbene, presumably the singlet,[1a,14] that undergoes the cyclization. With respect to the latter point, it is known that iodine is a superb quencher of fluorescence from aromatic hydrocarbons[7a,15] and of other oxidative photocyclizations.[7a] Moreover, since it should complex only a small fraction of the stilbene present,[16] its effect should increase with its concentration.

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[8] This material was chosen because it gives relatively simple products and the *p*-methyls give distinct ^{1}H NMR signals.

[9] Previously reported photocyclizations of *p,p'*-dimethylstilbene in the presence of 4–10 mol % iodine in cyclohexane, hexane, or cyclohexane–benzene gave 46–81% yields of 3,6-dimethylphenanthrene. (a) Buquet, A.; Couture, A.; Lablache-Combier, A. *J. Org. Chem.* **1979**, *44*, 2300. (b) Laarhoven, W. H.; Peters, W. H. M.; Tinnemans, A. H. A. *Tetrahedron* **1978**, *34*, 769. (c) Staab, H. A.; Meissner, U. E.; Meissner, B. *Chem. Ber.* **1976**, *109*, 3875. (d) Davy, J. R.; Jessup, P. J.; Reiss, J. A. *J. Chem. Educ.* **1975**, *52*, 747.

[10] Prepared by hydrogenating **16** (PtO_2, 2.5:1 ethyl acetate–benzene): Cram, D. J.; Bauer, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 5983.

[11] The ^{1}H NMR, ^{13}C NMR, IR, and high-resolution mass spectra were all appropriate. The COSY ^{1}H NMR spectrum shows the coupling pattern required. The UV spectrum in petroleum ether—λ_{max} (log ϵ) 283 (3.75), 229 nm (4.75)—was like that of 1,2,7-trimethylnaphthalene in petroleum ether:[12] λ_{max} (log ϵ) 287 (3.76), 230 nm (4.96).

[12] Heilbronner, E.; Fröhlicher, U.; Plattner, Pl. A. *Helv. Chim. Acta* **1949**, *32*, 2479.

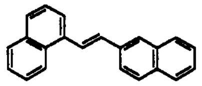
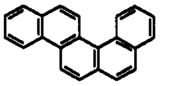
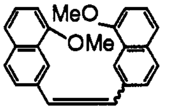
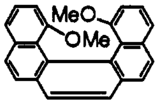
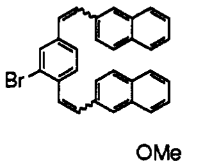
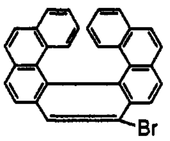
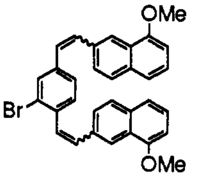
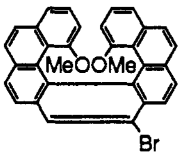
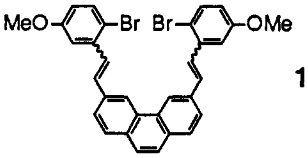
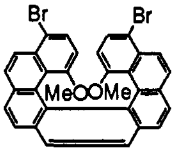
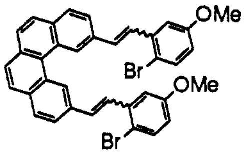
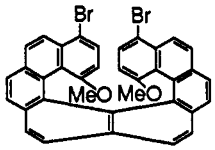
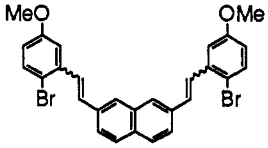
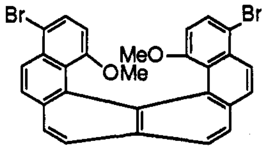
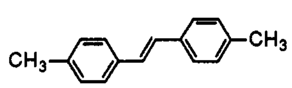
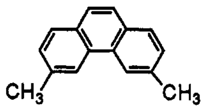
[13] Yamashita, S. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 972.

[14] Muszkat, K. A. *Top. Curr. Chem.* **1980**, *88*, 89.

[15] Martinho, J. M. G. *J. Phys. Chem.* **1989**, *93*, 6687.

[16] For the parent *cis*- and *trans*-stilbenes the complexation constants at 25 °C in *n*-hexane are 5.10 and 1.97 M^{-1} (Yamashita, S. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1212), which would cause only a small amount of stilbene to be complexed when the iodine concentration is only millimolar.

Table I. Yields and Purities in Photocyclizations. Catalytic I$_2$ in Air Compared to Stoichiometric I$_2$ under Argon with Propylene Oxide[a]

			Purities and Yields[b]	
Entry	Starting Material	Product	Catalytic amounts of I$_2$ in air (reaction time)[c]	Stoichiometric amounts of I$_2$ plus propylene oxide (reaction time)
1	 2	 3	61% yield[d] (4 h)	100% yield (1 h)
2	 4	 5	<8% yield[e] (3.5 h)	61% yield (13 h)
3	 6	 7	66% yield (1.2 h)	87% yield (1.2 h)
4	 8	 9	<20% yield[e] (3 h)	87% yield (8-12 h)
5	 10	 11	<18% yield[e] (2.5 h)	75% yield (6-8 h)
6	 12	 13	<17% yield[e] (2 h)	91% yield (9-13 h)
7	 14	 15	< 4% yield[e] (4.5 h)	71% yield (4.5 h)
8	 16	 17	51% yield (8 h)	95% yield (8 h)

[a] The starting materials were dissolved in benzene (0.43–0.625 mM, except for entry 8, for which the concentration was 1.25 mM) and the light, from a Hanovia high-pressure mercury lamp, was filtered through Pyrex. Propylene oxide was used in great excess (ranging from 110 to 550 equiv). [b] The yields are those of products isolated and purified, except for the experiments in entry 8, in which the yields were measured by gas chromatography. [c] For entries 2 and 4–6, when the irradiation times were comparable to those used in the experiments in the last column, the reaction products were complex and no signals attributable to those desired were recognizable in the ^{1}H NMR spectra. [d] Reported by Scholz et al. in ref 5 for a cyclization in air with *no* iodine. [e] The ^{1}H NMR spectrum showed the reaction product, isolated in the yield indicated by the numerical figure, to be grossly impure. Pure product was not isolated.

These experiments also reveal a serious limitation to the procedure using a full stoichiometric amount of iodine plus propylene oxide. It requires the solutions of the stilbenes to be much more dilute than when the amount of iodine is only catalytic.

Mechanism of Reduction by HI. Scheme I shows three mechanisms by which HI might photoreduce alkenes, and while we do not know which, if any, of these is correct, analogies for the third seem strongest. That mechanism, involving electron transfer followed by proton transfer, is patterned on the mechanism suggested for the light-induced reductions of anthracene and stilbene by secondary amines.[17] For the other mechanisms in Scheme I the analogies are weaker: for a, a gas-phase photoreduction of 1-butene by HI,[18] and for b, photoreductions of phenyl-*tert*-butylacetylene by 2-propanol,[19] of α,β-unsaturated

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[17] (a) Yang, N. C.; Libman, J. *J. Am. Chem. Soc.* **1973**, *95*, 5783. (b) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1977**, *99*, 7991. (c) Kubota, T.; Sakurai, H. *Chem. Lett.* **1972**, 923. See also: (d) Barltrop, J. A. *Pure Appl. Chem.* **1973**, *33*, 179. (e) Reference 9a. (f) Kawanishi, M.; Matsunaga, K. *Chem. Commun.* **1972**, 313. (g) Perkins, M. J.; Smith, B. V.; Turner, E. S. *Chem. Commun.* **1980**, 977.

[18] Gawlowski, J.; Gierczak, T.; Niedzielski, J. *J. Photochem.* **1980**, *13*, 335. HI absorbs UV light weakly at wavelengths Pyrex transmits (>ca. 300 nm; Ninomiya, I.; Naito, T. *Photochemical Synthesis*; Academic: New York, 1989, p 214). See: Ogilvie, J. F. *Trans. Faraday Soc.* **1971**, *67*, 2205.

Table II. Products and Yields Obtained When 16 or 17 Was Irradiated with UV Light in the Presence of Various Combinations of Iodine, Air, Propylene Oxide, and Hydrogen Iodide[a]

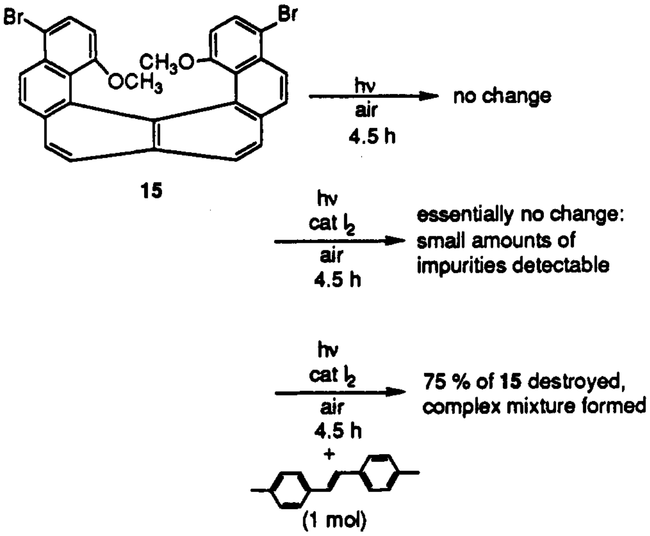
entry	substrate	reagents	yields (%) 17	18	19	other
1	**16**	1 equiv of I_2 + PO[b]	95[c]	0	0	
2	**16**	1 equiv of I_2	76	19	3.5	
3	**16**	cat. I_2 + air	51	0	0	
4	**16**	4 equiv of HI, no I_2	24	36	39	
5	**16**	4 equiv of HI, no light	0	0	0	only **16** recovered
6	**16**	20 equiv of DI	0	85[d]		5 X[f]
7[e]	**16**	none	3.4	0	0	15.8 **16**, 80.7 *cis*-**16**
8	**16**	0.05 equiv of I_2, degassed	41	2.8	4.6	22 **16**, 23 *cis*-**16**, 7 Y[f]
9	**17**	4 equiv of HI	70	0	ca. 15[g]	ca. 15 X;[f,g] some Y[f]

[a] Except for entries 3 and 8, all reactions were effected under argon. Solutions in benzene (1.25 mM for entries 1–3, 6, and 8, 0.6 mM for entries 4, 5, 7, and 9) were irradiated for 8 h with light, filtered through Pyrex, from a medium-pressure mercury lamp. After having been washed (aqueous $Na_2S_2O_3$), dried ($MgSO_4$), and concentrated, the products were analyzed by gas chromatography on D-5-30N Durabond using pyrene (except for entry 7) as an internal standard. [b] PO is propylene oxide (ca. 20 mL, 550 equiv in 320 mL benzene). [c] The yield of **17** isolated was >90%. [d] 80 ± 8% dideuterated on the double bond. [e] The irradiation time was 6 h, and since no internal standard was used, for this experiment, the yields are relative, no absolute. [f] The structures of X and Y were not analyzed. [g] The chromatographic peaks for **19** and X overlap and seem similar in size.

ketones by alcohols[20] and hydrocarbons[21] and of norbornene by various solvents.[22] In addition, three experiments suggested by mechanisms a and b failed. Thus, attempts to see whether the mild reductants benzhydrol or methanol would reduce **16**, experiments suggested by mechanism b, resulted in no **18**. After 1.5 mM solutions of **16** in 4:1 cyclohexane/benzene plus 10 equiv of benzhydrol had been photoirradiated for 8 h, the product was analyzed to contain **16**, *cis*-**16**, and **17** in ratios 5:1:2.2 and no **18** was seen. After 1.5 mM solutions of **16** in benzene plus 100 equiv of methanol were photoirradiated for 8 h, **17** was formed in 43% yield, but if it was accompanied by any of the other products in Table II, their amounts must have been minute. Attempts to photoreduce 7-tetradecene with 12.5 equiv of HI in benzene during 8 h under argon, an experiment suggested by mechanism a, also failed. Only 7-tetradecene was recovered. Accordingly, mechanism c seems most likely to be responsible for the photoreductions.

Photooxidative Degradations. The reason the procedure using stoichiometric amounts of iodine plus propylene oxide is superior to the procedure using catalytic amounts of iodine and air may be that oxygen brings about undesired oxidations. Evidence includes the formation of aldehydes, noted above,[23] as well descriptions by others of products resulting from oxidative cleavages of double bonds.[7b,24] That oxidations are responsible for the low yields recorded in Table I when photocyclizations are carried out in air is also suggested by the observation that methoxylated derivatives are the ones whose yields are most diminished when air is the oxidant.

Scheme II



However, air itself appears not to be the destructive agent. It seems rather to be a substance formed from air during the photocyclizations. Evidence for this hypothesis is outlined in Scheme II. The experiments summarized therein show that while photoirradiation in air in the presence of catalytic amounts of iodine has almost no effect on the derivative of hexahelicene **15**—and in the absence of the trace of iodine no effect at all—the same photoirradiation in the presence of 1 mol of *p,p'*-dimethylstilbene destroys most of the helicene. The only plausible explanation we see is that the destructive substance is generated by reaction of the stilbene. A likely culprit is hydrogen peroxide, for it is known to form in stoichiometric amounts when dihydrophenanthrenes[14] that intervene in the photocyclizations react with oxygen.[25] And although in the dark this reagent did not react with one dihydrophenanthrene tested,[25b] in the light we found (using large amounts) that it does. In one experiment in which 275 equiv of hydrogen peroxide were substituted for the stilbene in Scheme II, ca 89% of **15** was destroyed.[26,27]

The mechanism envisioned for generating hydrogen peroxide is shown in Scheme III, where ArH_2 is the dihydroaromatic structure formed when a stilbene cyclizes. In accord with this scheme, cyclohexadienyl radicals are known to transfer a hydrogen atom to O_2, giving the aromatic compound and $HO_2\bullet$,[28] and the reaction of $HO_2\bullet$ with HI (in the gas phase) is (at 25 °C) exothermic by 15.9 kcal/mol.[2b,29] This also agrees with the observation by

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(19) Zimmerman, H. E.; Pincock, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3246.

(20) Chan, A. C.; Schuster, D. I. *J. Am. Chem. Soc.* **1986**, *108*, 4561.

(21) Byrne, B.; Wilson, C. A., II; Wolff, S.; Agosta, W. C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1550.

(22) Sauers, R. R.; Schinski, W.; Mason, M. M. *Tetrahedron Lett.* **1967**, 4763.

(23) Laarhoven also saw these.[1b] Also, when oxygen rather than air was used as the oxidant in one series of studies, significantly more oxygen was absorbed than was required for the desired reaction. Hugelshofer, P.; Kalvoda, J.; Schaffner, K. *Helv. Chim. Acta* **1960**, *43*, 1322.

(24) Tsuge, O.; Oe, K.; Ueyama, Y. *Chem. Lett.* **1976**, 425.

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(26) A similar experiment, performed using **15** from which the bromines had been removed, 200 equiv of H_2O_2, and no I_2, destroyed >95% of the helicene (^1H NMR analysis) and gave material with a complex ^1H NMR spectrum and prominent IR absorption (KBr) at 1735 cm^{-1}.

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Table III. Photochemistry of 16. How the Yields of 17, 18, and Recovered 16 Vary with the Amount of Iodine Present[a]

entry	$[I_2]$ (mM)	[16] (mM)	[propylene oxide] (M)	yield (%)			mass balance[b] (%)
				17	18	16	
1	1.67	1.67		64	30	ca. 2 (16 + 19)	96
2	6.68	1.67		42	17[c]	29 (+ 8% *cis*-16)[c]	95
3	33.4	1.67		38	22	16	76
4	8.6	0.43		41	13	23	77
5	8.6	0.43	0.24	40	1	54 + (2% *cis*-16)	96
6	1.67	1.67	0.9	97			97
7	4.7	4.7	1.1	23	0	59	82

[a] Benzene solutions under argon were irradiated for 8 h. The yields are those measured by gas chromatography with pyrene as an internal standard. [b] The sum of the yields in the three columns to the left. [c] Measured by combining integrals under gas chromatograms and those under the ^{1}H NMR's of the olefinic and benzylic protons.

Collins and Hobbs[7b] that cupric chloride prevents oxidative side reactions in iodine-catalyzed oxidative photocyclizations, for cupric ions are noted for their ability to oxidize carbon radicals.[30] They would therefore be expected to transform the cyclohexadienyl radical directly into the product.

Scheme III

$$ArH_2 + I\bullet \rightarrow ArH\bullet + HI$$

$$ArH\bullet + O_2 \rightarrow Ar + HO_2\bullet$$

$$HO_2\bullet + HI \rightarrow H_2O_2 + I\bullet$$

Conclusions

Iodine is superior to oxygen for oxidizing the dihydrophenanthrenes that intervene in photocyclizations. Unlike oxygen, it does not oxidatively degrade the substrates and products. However, to be effective it cannot be used in large concentration, and since HI in the light reduces double bonds, the iodine must be used with a reagent, like propylene oxide, that quickly removes the HI generated.

Experimental Section

The following instruments were used: IR, Perkin-Elmer 1600 FTIR; NMR, Varian XL series; capillary GLC, Varian Model 3700 (FI Detector), with a Hewlett-Packard HP-3396A integrator; preparative GLC, Aerograph Autoprep Model A-700 equipped with a thermal conductivity detector; low-resolution MS, DELSI-NERMAG R10-10, interfaced with a DELSI-DI200 GC, on which GC-MS analyses were performed; high-resolution MS (HRMS), JEOL JMS-DX303HF mass spectrometer; UV-vis, Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer.

The term "chromatography" specifies flash column chromatography on silica, 32–62 mm, from Woelm. TLC plates were silica gel 60 F-254, 0.25 μm, from E. Merck.

Unless otherwise noted, solvents from commercial sources were used without purification. THF was distilled from potassium–benzophenone ketyl. Benzene was Fisher Certified ACS Grade, propylene oxide was 99%+ from Aldrich Chemical Co., Inc., and argon was labeled as high purity, 99.995%, from Matheson. All title compounds were judjed to be appropriately pure by ^{13}C and ^{1}H NMR spectroscopic determinations.

Bisstilbenes 4, 8, 10, 12, and 14 are described in the dissertation of B. V. Yang.[31] Stilbenes 16[32] and 6[33] were synthesized using published procedures.

1,2'-(1,2-Ethenediyl)bisnaphthalene (2). 2-Naphthaldehyde (0.56 g, 3.59 mmol), diethyl (1-naphthylmethyl)phosphonate[34] (1 g, 3.60 mmol, prepared in 64% yield from 1-bromonaphthalene[35]), 25 mL of benzene, 25 mL of HMPA, and 95 mg (3.96 mmol) of NaH (washed with pentane) were added sequentially to a 100-mL round-bottomed flask equipped with a magnetic stirring bar and septum, which had been flamed and purged with argon. Since after the reactants had been stirred at room temperature for 2 h TLC revealed that some naphthaldehyde remained, 5 mg more of NaH was added, and the mixture was stirred for another 12 h. Water (150 mL) was used to quench the reaction, and the mixture was extracted with ether (1 × 50 mL, 3 × 25 mL) followed by 2 × 200 mL of half-saturated brine, with each washing back-extracted (4 × 30 mL ether). The combined organics were dried with $MgSO_4$, filtered, and concentrated to a yellow-green solid, which was fairly insoluble in ether, CH_2Cl_2, $CHCl_3$, or benzene. It was dissolved in a minimal amount of hot CH_2Cl_2–benzene and chromatographed (1:3 hexanes–CH_2Cl_2) to give a light yellow-green solid (R_f = 0.49 in 2:1 hexanes–CH_2Cl_2), 0.85 g (85%): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.29 (d, J = 9.0 Hz, 1 H), 8.02 (d, J = 15.9 Hz, 1 H, *trans*-olefinic), 7.87 (m, 8 H), 7.52 (m, 5 H), 7.32 (d, J = 16.0 Hz, 1 H, *trans*-olefinic); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.09, 135.00, 133.75, 133.72, 133.10, 131.79, 131.40, 128.63, 128.37, 128.08, 128.04, 127.71, 126.78, 126.38, 126.11, 126.05, 125.97, 125.84, 125.71, 123.77, 123.67, 123.59. These spectra are displayed in the supplementary material.

General Procedure for Photocyclizations. The photoreactor was a cylindrical glass vessel with an immersion well connected through a standard taper 60/50 ground glass joint. Attached to the upper part of the reaction vessel was a gas-inlet tube leading to a sintered glass frit at the bottom of the vessel and two standard tapered joints, one vertical (standard taper 24/40), attached to a condenser (with a gas outlet leading to a mercury bubbler), and one angled (standard taper 10/30), for withdrawal or addition of samples. The vessel was flat-bottomed to allow a magnetic stirring bar to rotate. The vessels ranged in volume from 0.3 to 2 L. The immersion well was a double-walled Pyrex tube cooled by water and containing a Hanovia 450-W high-pressure quartz Hg-vapor lamp (Englehard-Hanovia, Inc. catalog No. 679A-0360).

Procedure for Photoirradiation in the Presence of Propylene Oxide (PO). Argon was bubbled through the stirred solution of stilbene and iodine in benzene for 20–30 min before excess PO was added through the angled joint, and the lamp was turned on. The argon flow was maintained throughout the procedure. The photoirradiation was monitored by either NMR (aliquots taken via the angled joint) or the disappearance of the iodine color. When excess iodine was present at the end, workup included washing with 15% $Na_2S_2O_3$, H_2O, and saturated brine, drying with $MgSO_4$, filtering, and concentrating to dryness on a rotary evaporator. Otherwise, the solutions (which did not have an iodine color) were evaporated directly. ^{1}H NMR analyses of the crude materials (often yellow-brown solids) showed peaks characteristic of the photocyclization product(s) plus small ones attributable to the HI adducts of PO: δ 3.60–3.80 (m), 3.20–3.45 (m), 1.95 (d), 1.30 (d). The integrals of the first multiplets, the second multiplets, and the doublets were ca. 1:2:3, suggesting that this is a mixture of vicinal hydroxyiodopropanes. Washing the material through a short column of silica gel provided the pure product.

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(33) Sudhakar, A.; Katz, T. J. *Tetrahedron Lett.* **1986**, *27*, 2231.

(34) Poindexter, M. K. Ph.D. Dissertation, Columbia University, 1988.

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Procedure for Photoirradiation in the Presence of Large Amounts of Iodine and No Propylene Oxide. The procedure was the same as in the previous text except that no PO was used. The products of the reactions, often highly colored, were washed as described previously.

Procedure for Photoirradiation in the Presence of Catalytic Amounts of I_2. A crystal of iodine was added to the stirred stilbene solution in the photoreactor. The condenser was left open to the atmosphere. The solution often turned cloudy after the photoirradiation. Evaporation gave materials that were only partially soluble in $CDCl_3$, but completely soluble in acetone-d_6. The NMR spectra of the solutions in $CDCl_3$ were, however, the same.

Benzo[*c*]chrysene (3). 1,2′-(1,2-Ethenediyl)bisnaphthalene (**2**; 58 mg, 0.21 mmol) in 480 mL of benzene was irradiated in the presence of I_2 (55 mg, 0.22 mmol) and PO (2.6 mL, 37 mmol) for 1 h. Workup and chromatography (1:1 hexanes–CH_2Cl_2, $R_f = 0.6$) gave 58 mg of a yellow crystalline solid with an ^{1}H NMR spectrum identical with that reported.[36] When the reaction was performed similarly, but without PO, the ^{1}H NMR spectrum showed many extraneous resonances at both high and low fields. The mass recovery after chromatography was excellent. TLC (1:1 hexanes–CH_2Cl_2) showed faint spots slightly leading and trailing the main one at $R_f = 0.6$.

1,1′-Dimethoxy[5]helicene (5).[31] A solution of 1,1′-dimethoxy-7,7′-(1,2-ethenediyl)bisnaphthalene (**4**; 82 mg, 0.24 mmol), I_2 (31 mg, 0.24 mmol), and PO (4 mL, 57 mmol) in 400 mL of benzene was irradiated for 13 h. Evaporation and chromatography (1:5 CH_2Cl_2–petroleum ether) afforded 50 mg (61%) of **5**. ^{1}H NMR ($CDCl_3$, 200 MHz, displayed in the supplemantary material) δ 7.96 (br s, 2 H), 7.89 (br s, 4 H), 7.60 (dd, J = 7.7, 1.6 Hz, 2 H), 7.47 (t, J = 7.8 Hz, 2 H), 6.71 (dd, J = 8.0, 0.8 Hz, 2 H), 2.85 (s, 6 H); MS (EI) *m/e* 338 (M^+, 100), 276 (73); HRMS calcd for $C_{24}H_{18}O_2$ 338.1302, found 338.1309.

9-Bromo[7]helicene (7).[33] Irradiation of **6** (93 mg, 0.2 mmol), I_2 (103 mg, 0.41 mmol), and PO (10 mL, 143 mmol) in 320 mL of benzene for 70 min gave a bright yellow solution, which after workup (with aqueous washings) gave a brown solid. Filtering through a short column of silica with 1:1 CH_2Cl_2–CCl_4 yielded a yellow solid: mp 254–6 °C; 80 mg (87%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.43 (d, J = 8.5 Hz, 1 H), 8.31 (s, 1 H), 7.98 (d, J = 8.5 Hz, 1 H), 7.90 (d, J = 8.3 Hz, 1 H), 7.85 (d, J = 8.3 Hz, 1 H), 7.69 (m, 2 H), 7.48 (m, 2 H), 7.28 (br d, J = 7.7 Hz, 2 H), 7.03 (br d, J = 8.5 Hz, 2 H), 6.90 (m, 2 H), 6.39 (m, 2 H); see Figure 1a; HRMS calcd for $C_{30}H_{17}Br$ 456.0514, found 456.0489. When the previous procedure was repeated in the absence of PO, the product of the photoirradiation was a dirty red mixture. Aqueous workup gave 107 mg of black residue (ca. 116% recovery). Purification by chromatography, collecting the nonpolar fractions, yielded an orange oil with the ^{1}H NMR spectrum displayed in Figure 1b. The structure is proven by removal of the bromine giving [7]-helicene.[33] Photoirradiation using the same amounts of **6** and benzene, but only a trace of iodine, gave a yellow suspension, which after aqueous workup and purification gave 61 mg (66%) of product ^{1}H NMR analysis showed this to be somewhat impure **7**.

1,1′-Dimethoxy-9-bromo[7]helicene (9). A solution of **8** (130 mg, 0.25 mmol) and I_2 (127 mg, 0.5 mmol) in the presence of PO (4.5 mL, 64 mmol) in 400 mL of benzene was irradiated for 8 h. After 18 runs (with irradiation times ranging from 8 to 12 h), the combined crude material was chromatographed with 1:1 CH_2Cl_2–petroleum ether. The resulting yellow solid was debrominated (*n*-BuLi–THF, −78 °C, 30 min, then H_2O), giving 1.8 g (91% overall) of 1,1′-dimethoxy[7]helicene, which decomposes at 239 °C; ^{1}H NMR ($CDCl_3$, 200 MHz, displayed in the supplementary material) δ 7.98 (d, J = 8.1 Hz, 2 H), 7.95 (s, 2 H), 7.84 (d, J = 8.1 Hz, 2 H), 7.65 (d, J = 8.4 Hz, 2 H), 7.34 (d, J = 8.4 Hz, 2 H), 6.87 (d, J = 5.1 Hz, 2 H), 6.86 (d, J = 3.9 Hz, 2 H), 5.96 (dd, J = 5.1, 3.9 Hz, 2 H), 2.63 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.40, 133.11, 131.29, 129.46, 129.08, 126.82, 126.38, 125.88, 125.63, 125.49, 124.82, 123.41, 121.76, 119.39, 104.56, 53.92; MS (EI) *m/e* 438 (M^+, 100), 375 (10); HRMS calcd for $C_{32}H_{21}BrO_2$ 438.1614, found 438.1629. The same conditions, but with no PO added, gave after chromatography 50 mg (38%) of material showing very complicated ^{1}H NMR resonances between δ 8.5–6.8 and 4.0–1.0.[37]

1,1′-Dimethoxy-4,4′-dibromo[7]helicene (11). A solution of **10** (180 mg, 0.30 mmol), I_2 (152 mg, 0.6 mmol), and PO (4.5 mL, 60 mmol) in 400 mL of benzene was irradiated for 6 h. After several runs (with irradiation times ranging from 6 to 8 h), the combined material was passed through a column of silica gel with 1:3 CH_2Cl_2–petroleum ether as eluent. The amount of yellow solid obtained from 620 mg of starting material was 470 mg (75%): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.00 (d, J = 8.2 Hz, 2 H), 7.93 (s, 2 H), 7.82 (d, J = 8.2 Hz, 2 H), 7.75 (d, J = 8.7 Hz, 2 H), 7.69 (d, J = 8.7 Hz, 2 H), 7.26 (d, J = 8.4 Hz, 2 H), 5.79 (d, J = 8.4 Hz, 2 H), 2.58 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.77, 131.36, 130.69, 129.44, 129.06, 127.98, 127.29, 127.12, 126.31, 125.69, 125.36, 122.86, 122.74, 113.27, 105.29, 54.05. These spectra are displayed in the supplementary material. HRMS calcd for $C_{32}H_{20}O_2Br_2$ 593.9830, found 593.9829.[37]

1,1′-Dimethoxy-4,4′-dibromo[8]helicene (13). A solution of bisstilbene **12** (162.5 mg, 0.25 mmol), I_2 (133 mg, 0.52 mmol), and PO (6 mL, 85 mmol) in 400 mL of benzene was irradiated for 9 h. Ten batches (with irradiation times ranging from 9 to 13 h), consuming 1.42 g of **12**, gave, after chromatography using 1:3 CH_2Cl_2–petroleum ether, 1.3 g (91%) of yellow solid, which decomposes at 295 °C: ^{1}H NMR ($CDCl_3$, 200 MHz, displayed in the supplementary material) δ 7.95 (d, J = 8.2 Hz, 2 H), 7.84 (d, J = 8.2 Hz, 2 H), 7.78 (d, J = 8.1 Hz, 2 H), 7.77 (d, J = 8.8 Hz, 2 H), 7.37 (d, J = 8.1 Hz, 2 H), 7.23 (d, J = 8.5 Hz, 2 H), 7.22 (d, J = 8.8 Hz, 2 H), 5.74 (d, J = 8.5 Hz, 2 H), 2.63 (s, 6 H); HRMS calcd for $C_{36}H_{22}O_2Br_2$ 643.9987, found 643.9970.[37]

1,1′-Dimethoxy-4,4′-dibromo[6]helicene (15). A solution of **14** (165 mg, 0.3 mmol), I_2 (152 mg, 0.6 mmol), and PO (4 mL, 57 mmol) in 400 mL of benzene was irradiated for 4.5 h and worked up as before. Ten batches, consuming 1.62 g of **14**, gave, after chromatography with 1:5 CH_2Cl_2–petroleum ether, 1.15 g (71%) of **15**, a yellow solid, which decomposes at 267 °C: ^{1}H NMR ($CDCl_3$, 200 MHz, displayed in the supplementary material) δ 8.25 (d, J = 8.8 Hz, 2 H), 8.06 (d, J = 8.2 Hz, 2 H), 8.00 (d, J = 8.8 Hz, 2 H), 7.97 (d, J = 8.2 Hz, 2 H), 7.49 (d, J = 8.5 Hz, 2 H), 5.90 (d, J = 8.5 Hz, 2 H), 2.56 (s, 6 H); HRMS calcd for $C_{28}H_{18}O_2Br_2$ 543.9673, found 543.9672.[37]

Photoirradiations Summarized in Table II. The following conditions were used for GLC analyses: column DB-5-30N Durabond; T_{inj} 270 °C, T_{fid} 350 °C; temperature program 180 °C (1 min)–5 °C/min–250 °C (10 min); carrier gas He (30 cc/min), H_2 (30 cc/min), air (300 cc/min). *cis*-**16** was prepared by photoisomerizing **16** (Table II, entry 7) in benzene for 6 h. The ^{1}H NMR spectrum of the major product (ca. 81%, relative) was identical with that reported.[9a] For **18**, see ref 10 (^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.08 (s), 2.85 (s), 2.31 (s); intensities 2:1:1.5). The retention times (in minutes) were for **17** 12.82, for **16** 11.55, for **19** 11.13, for **18** (and *cis*-**16**) 8.18, for X 11.00, and for Y <9.00. Mixtures of **16** and pyrene (retention time 14.86 min) were prepared in ratios varying from 1:2 to 3:2, and a calibration curve was constructed by plotting the ratios of the GLC areas against ratios of the weights of **16** and pyrene (slope 0.992). This calibration curve was used to analyze all the products of the photoirradiations, under the assumption that all elicit the same response from the flame ionization detector.

3,6-Dimethylphenanthrene (17; Table II). The procedure for entry 1 was as follows. After an argon stream had been passed for 20 min through a solution of **16** (105 mg, 0.5 mmol) in 400 mL of benzene, I_2 (130 mg, 0.51 mmol) and PO (20 mL, 285 mmol) were added. After photoirradiation for 8 h (GLC analyses showed that this reaction and the one in entry 3 were complete after 7 h), the resulting colorless solution was evaporated, leaving a light yellow solid, which showed the following ^{1}H NMR ($CDCl_3$, 200 MHz) in agreement with the spectrum reported:[9a] δ 8.44 (s, 2 H), 7.74 (d, J = 8.2 Hz, 2 H), 7.60 (s, 2 H), 7.38 (d, J = 8.2 Hz, 2 H), 2.59 (s, 6 H). The GLC showed only one peak, at 12.82 min. A mixture of pyrene (101 mg) and this material, dissolved in benzene, was analyzed by GLC. The ratio of the two peaks observed showed the yield to be 95%. A similar reaction, carried out with 105 mg

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(36) Bax, A.; Ferretti, J. A.; Nashed, N.; Jerina, D. M. *J. Org. Chem.* **1985**, *50*, 3029.

(37) Removal of bromine and oxidation to the quinone further confirms the structure.[31]

of **16** in 300 mL benzene, gave a yield of 97%.

The procedures for entries 2 and 3 in Table II were similar.

Photoirradiation Using HI (Table II, Entries 4, 5, and 9). HI gas, prepared from I_2 and tetralin,[38] was transferred in an argon stream to benzene in the photoreactor, and the concentration was analyzed by titration. Either **16** or **17** (51 mg, 0.245 mmol) was then added, and the solutions were irradiated. The usual workup included one wash with water. Except when no light was used (Table II, entry 5), iodine was formed during the photoirradiation. The solutions turned a deep red, which was bleached by $Na_2S_2O_3$. They colored starch solutions blue.

Formation of X and Y. The reaction product from the photoirradiation of **17** plus HI (Table II, entry 9), when subjected to GCMS (EI) analysis, showed a parent peak at *m/e* 208 for X and parent peaks at *m/e* 210 and 214 for Y. (GLC analysis showed Y to be a mixture of several compounds.)

3,6-Dimethyl-1,2,3,4-tetrahydrophenanthrene (19). A solution of the product of the photoirradiation of **16** with HI (Table II, entry 4) and 50 mg of pyrene (the internal standard for GLC analysis) in 400 μL of benzene was injected (in four 100-μL portions) onto a $^1/_4$ in. × 10 ft column (from Alltech Associates) of 5% SE-30 on 80/100 mesh Chromosorb W-HP. Helium was the carrier gas, and the temperatures of the injector, column, and detector were 200, 200, and 250 °C, respectively. The second fraction (elution starting at 40 min) was collected in a U-tube cooled with liquid nitrogen. The collected material was rechromatographed under the same conditions, giving a white, low-melting solid, which showed only one peak (retention time 11.13 min) on analysis by GLC: ^{1}H NMR ($CDCl_3$, 400 MHz, displayed in the supplementary material) δ 1.19 (d, J = 6.4 Hz, 3-CH_3), 1.46 (m, 2-H), 1.95 (m, 3-H, 2′-H), 2.53 (s, 6-CH_3), 2.56 (dd, J = 16.3, 10.08 Hz, 4-H), 2.95 (m, 1-H, 1′-H), 3.27 (dd, J = 16.6, 5.1 Hz, 4′-H), 7.14 (d, J = 8.2 Hz, 10-H), 7.26 (dd, J = 8.2, 1.7 Hz, 7-H), 7.56 (d, J = 8.4 Hz, 9-H), 7.68 (d, J = 8.2 Hz, 8-H), 7.74 (br s, 5-H); the structure is proved by the {^{1}H, ^{1}H COSY} 2D NMR spectrum shown in the supplementary material; ^{13}C NMR ($CDCl_3$, 75 MHz, displayed in the supplementary material) δ 135.28, 133.90, 132.52, 130.64, 130.18, 128.17, 127.06, 126.77, 125.33, 122.04, 34.43, 31.19, 30.43, 29.34, 22.37, 22.14; HRMS calcd for $C_{16}H_{18}$ 210.1409, found 210.1427; UV (petroleum ether), λ_{max} (log ϵ) 283 (3.75), 229 nm (4.75); FTIR (neat) 2919 (vs), 2848 (vs), 1507 (w), 1454 (s), 1372 (w), 826 (s) cm^{-1}.

Photoirradiation Using DI (Table II, Entry 6). The glassware was dried in an oven, rinsed with D_2O, and dried again in an oven before being quickly assembled and purged with argon (dried by passage through 3-Å molecular sieves). The photoreactor was then rinsed with benzene saturated with D_2O, as were the short pieces of Tygon tubing used for connections. DI was prepared[39] by stirring and shaking 4 g of I_2 and 2.5 g of red phosphorus (dried previously in a vacuum over P_2O_5) in a three-necked round-bottomed flask until I_2 lost its luster (ca. 10 min). D_2O (99.8% D, 1.5 mL) was then added cautiously (exothermic), and with the aid of gentle heat and an argon stream, DI was carried to 400 mL of benzene (distilled from K) in the photoreactor. An aliquot of the benzene solution was then titrated. Stilbene **16** (98 mg, 0.47 mmol) was added and irradiated for 8 h. The resulting deep red solution was concentrated in vacuo and the ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) determined. The material was then dissolved in CH_2Cl_2 and freed of iodine as described previously. The ^{1}H NMR showed that **18** was the major product and that the benzylic protons had not exchanged D for H during the workup. The ratio of methyl and methylene proton resonances (there was a 5-s delay between NMR pulses) and the MS (EI) analysis both showed that 80 ± 8% of the **18** was dideuterated. The result was similar when cyclohexane was used in place of benzene: ^{2}H NMR ($CHCl_3$, 46.04 MHz) δ 2.53 (br s).

Photoirradiation of 16 with Catalytic Amounts of I_2 in the Absence of Air (Table II, Entry 8). A solution of **16** (27 mg, 0.125 mmol) and iodine (1.6 mg, 0.0125 mmol) in 100 mL of benzene was placed in a 150-mL pear-shaped flask with a Teflon valve and a standard taper 19/38 ground glass joint. The solution was frozen, pumped (at 10^{-5} Torr), and thawed three times, then placed next to the immersion well and irradiated for 8 H. The solvent was evaporated, and the GLC analysis was performed.

Photoirradiation of 15 (Scheme II). An open solution of **15** (9 mg, 0.016 mmol), **16** (4 mg, 0.019 mmol), and a trace of iodine in benzene (15 mL) was placed near the water-jacketted lamp and irradiated for 4.5 h. The resulting deep yellow solution was concentrated to an oily solid, which showed complex ^{1}H NMR's in both the aromatic and aliphatic regions, between δ 9.84 and 10.18 (m, aldehydes), and at δ 11.05 (s). The adduct of maleic anhydride and furan was used as an internal standard. Thus, 17 mg of the adduct was added to the product and, in a separate experiment, also to 9 mg of pure **15**. ^{1}H NMR analyses ($CDCl_3$, 300 MHz) of the doublet resonance at δ 5.9 in **16** and the singlet at δ 5.45 in the reference compound, using a 10-s pulse delay, showed the recovery of **15** to be ca. 25%. A similar experiment using 1 mol% of I_2 returned 40% of **15**.

Photooxidation of 15 by H_2O_2. A solution of **15** (7 mg, 0.013 mmol) and I_2 (1 mol%) in benzene (15 mL) was stirred vigorously with 90% H_2O_2 (0.1 mL, 3.6 mmol) and irradiated for 4.5 h. The solvent was stripped, and the yellow residue was analyzed as in the experiment in the previous text. The ^{1}H NMR spectrum was even more complex than the one described there (although there were no appreciable resonances above δ 8.5), and the recovery of **15** was ca. 15%.

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Supplementary Material Available: ^{1}H NMR COSY spectra of **19**, ^{1}H NMR spectra of **2**, **5**, **9**, **11**, **13**, **15**, and **19**, and ^{13}C NMR spectra of **2**, **11**, and **19** (12 pages). Ordering information is given on any current masthead page.

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