the same as 4 but with an additional broad band at 3250 cm^{-1}. NMR of the mixture (benzene-d_6): δ 7.92 (s, 1), 7.78 (s, 2), 7.38 (s, 1), 8.00 (s, 2). The hydroxyl proton NMR resonances were *not* present.

(5) 2-Hydroxy-4,6-dinitrobenzonitrile (8) (R_f 0.00, yellow turns green with EDA/Me$_2$SO) formed slowly from 6 in solution or on the TLC plate. It was isolated as a yellow acidic solid by preparative TLC [IR 3525 (OH), 2250 cm^{-1} (CN); MS (M$^+$, 209); NMR (acetone-d_6) pair of meta coupled doublets with 10-Hz couplings at δ 8.24 and 8.48]. Treatment of 8 with diazomethane gave 2-methoxy-4,6-dinitrobenzonitrile which was independently synthesized from reaction of 2,4,6-trinitrobenzonitrile with sodium methoxide. These two methoxy compounds had identical TLC, NMR, and MS data. The structural assignments for 6 and 8 are also supported by the reported[23] chemistry of substituted benzisoxazole formation and subsequent ring opening to the corresponding ortho cyanophenol.

(6) Reaction of 2,4,6-Trinitrobenzonitrile with Sodium Methoxide: 2-Methoxy-4,6-dinitrobenzonitrile, 4-Methoxy-2,6-dinitrobenzonitrile, and 2,4-Dimethoxy-6-nitrobenzonitrile. Sodium metal (0.6 g) was dissolved in 15 mL of methanol. A 5.5-mL aliquot of this solution was added dropwise, with stirring, to a boiling solution of 3.0 g (0.0125 mol) of 2,4,6-trinitrobenzonitrile in 30 mL of methanol. The red reaction mixture was allowed to cool and evaporate to half its original volume. Crystals formed and were isolated and recrystallized from benzene. TLC (in benzene) indicated mainly two compounds, one at R_f 0.35 and one at R_f 0.30. These were separated by column chromatography on silica gel-60 using benzene/hexane (1:1) at the start and gradually changing to benzene/hexane (3:1).

The component with an R_f value of 0.35 was found to be 2-methoxy-4,6-dinitrobenzonitrile: mp 120–121 °C (0.75 g isolated); NMR (acetone-d_6) δ 4.30 (s, 3), 8.58 (d, 1), 8.40 (d, 1); MS (M$^+$, 223). Anal. Calcd for C$_8$H$_5$N$_3$O$_5$: C, 43.06; H, 2.26; N, 18.83. Found: C, 42.92; H, 2.21; N, 18.74.

The component at R_f 0.30 (0.5 g isolated) was 4-methoxy-2,6-nitrobenzonitrile: mp 133–134 °C; NMR (acetone-d_6) δ 8.10 (s, 2), 4.12 (s, 3); MS (M$^+$, 223). Anal. Calcd for C$_8$H$_5$N$_3$O$_5$: C, 43.06; H, 2.26; N, 18.83. Found: C, 43.00; H, 2.21; N, 18.76.

When the mother liquor from the above monomethoxy compounds was further concentrated, a third compound, 2,4-dimethoxy-6-nitrobenzonitrile, crystallized out (yellow needles): mp 142–143 °C; NMR (acetone-d_6) δ 3.96 (s, 3), 4.01 (s, 3), 7.32 (d, 1), 7.07 (d, 1); MS (M$^+$, 208). Anal. Calcd for C$_9$H$_8$N$_2$O$_4$: C, 51.93; H, 3.87; N, 13.46. Found: C, 51.88; H, 3.88; N, 13.34.

(7) Preparation of *syn*-2,4,6-Trinitrobenzaldoxime. To a solution of 14.4 g (0.06 mol) of the aldehyde in 300 mL of boiling ethanol was added 12.4 g of NH$_2$OH·HCl (0.18 mol) in 60 mL of water, followed by 120 mL of 5% NaHCO$_3$ added dropwise with stirring. Water was added until the solution became cloudy, then it was cooled to give 10.0 g of white solid, mp 156–157.6 °C (lit. 158 °C).[23] Upon concentrating the filtrate, another 3.3 g (mp 155.7 °C) was obtained to give a total yield of 88%. Determination of the structure to be the syn form was done by X-ray crystallography of a single crystal.

Reactions of o-Xylylenes Produced Photochemically from o-Alkylstyrenes[1a]

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The potential synthetic utility of o-xylylenes generated photochemically from o-alkylstyrenes has been investigated. The o-xylylenes produced from 3a, 3b, and 3c were trapped with cyclohexene to yield octahydroanthracene derivatives in good yields (94, 86, and 63%, respectively). In the absence of cyclohexene, the o-xylylene from 3a dimerized to produce 8. Irradiation of 16 gave an o-xylylene which is an enol and which subsequently tautomerized to aldehyde 9. Deuterium-labeling studies supported this mechanism. The quantum yield for formation of 9 upon direct irradiation of 16 was 0.085, and that for the xanthone photosensitized process was 0.027.

Because of their high reactivity as dienes in the Diels–Alder reaction, o-xylylenes (or o-quinodimethanes) are showing considerable promise as intermediates in organic synthesis.[2] Among the many methods for generating o-xylylenes, the one most used in synthesis is the thermolysis of benzocyclobutenes. Another method for generating o-xylylenes that has been used synthetically is

the photoenolization of o-alkylphenyl ketones, such as 1.[3] The resulting photoenols 2 are readily trapped with reactive dienophiles. However, it has been reported[4] that

1   2
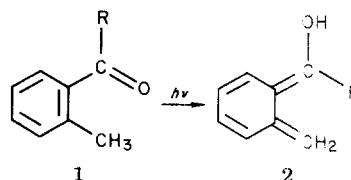
the photoenol derived from 2,4-dimethylbenzophenone cannot be trapped with weaker dienophiles such as cyclohexene. Presumably the proton tautomerization of 2

(1) (a) For a preliminary communication of part of this work see J. M. Hornback, *Tetrahedron Lett.*, 3389 (1976); (b) NSF Undergraduate Research Participant, Summer 1976; (c) NSF Undergraduate Research Participant, Summer, 1978.

(2) For a few leading references see (a) T. Kametani et al., *J. Am. Chem. Soc.*, 100, 6218 (1978); (b) T. Kametani and K. Fukumoto, *Acc. Chem. Res.*, 9, 319 (1976); (c) R. L. Funk and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 99, 5483 (1977); (d) K. P. C. Vollhardt, *Acc. Chem. Res.*, 10, 1 (1977); (e) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, 16, 10 (1977); (f) W. Oppolzer, *Synthesis*, 793 (1978); (g) J. R. Wiseman, N. I. French, R. K. Hallmark, and K. G. Chiong, *Tetrahedron Lett.*, 3765 (1978).

(3) For a recent review see P. G. Sammes, *Tetrahedron*, 32, 405 (1976).

(4) N. D. Heindel, E. W. Sarver, and M. A. Pfau, *Tetrahedron Lett.*, 3579 (1968).
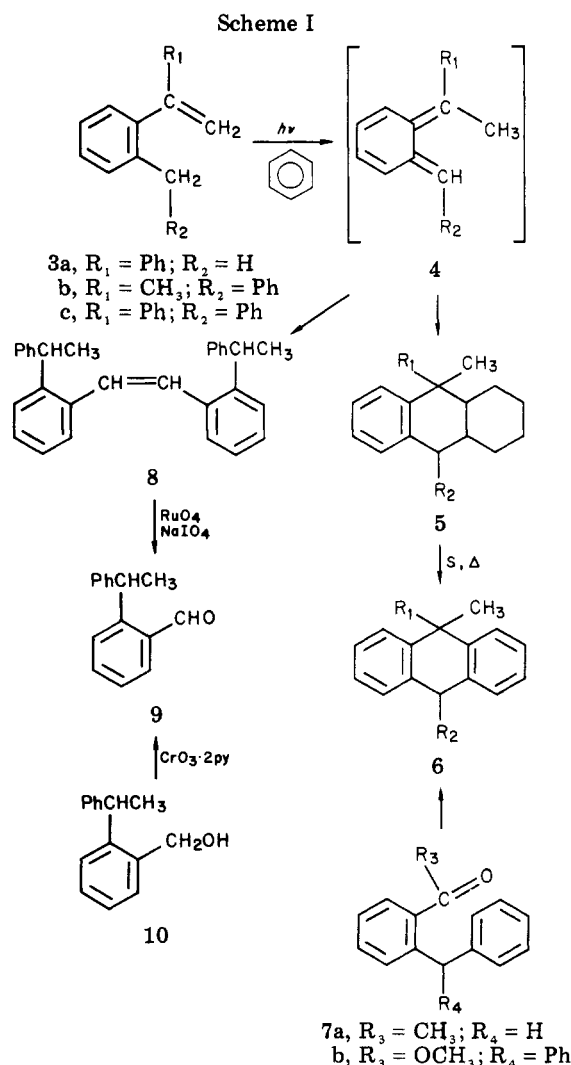
to regenerate 1 is too fast for the reaction of 2 with weak dienophiles to be competitive. o-Xylylenes can also be generated by irradiation of o-alkylstyrene derivatives, a reaction that is the carbon analogue of the photoenolization of 1. Morrison and Scully[5] used deuterium labeling to show that 4a was produced photochemically from 3a and Pratt[6] has shown that 4a can be trapped as a Diels–Alder adduct when 3a is irradiated in the presence of maleic anhydride. We became interested in using this reaction as a method for generating o-xylylenes for use in synthesis since we felt that 4a should be longer lived and, therefore, more readily trapped than photoenols such as 2. We report here our initial studies which demonstrate that the o-xylylenes produced photochemically from 3a and related compounds are trapped in good yields with cyclohexene to give octahydroanthracene derivatives.

Results and Discussion

Our studies began with an attempt to determine if o-xylylene 4a, the known photochemical product of 3a,[5,6] could be trapped with a weak dienophile such as cyclohexene. Irradiation of 3a[7] in a mixture of benzene and cyclohexene gave a 94% yield of 5a (Scheme I). The mass spectrum of 5a indicated that it was a 1:1 adduct of 3a and cyclohexene. The NMR spectrum of the adduct was consistent with its proposed structure, and the presence of two signals for the methyl group indicated that 5a was a mixture of stereoisomers. To confirm this structural assignment, we dehydrogenated 5a by heating it with sulfur to produce 6a. This material was identical in all respects with a sample of 6a prepared by a Grignard reaction of 7a[8] with phenylmagnesium bromide followed by Friedel–Crafts cyclization of the resulting crude alcohol in the presence of 85% sulfuric acid.

The formation of 5a upon irradiation of 3a in the presence of cyclohexene can be explained by an initial hydrogen transfer to give 4a as proposed by previous workers.[5,6] o-Xylylene 4a can potentially exist as either of two geometrical isomers (only the E isomer is shown in Scheme I). Although the evidence is not conclusive, the observation that 5a is formed as a mixture of stereoisomers seems most consistent with the presence of both geometrical isomers of 4a. Both isomers of 4a could be formed directly from 3a or the mixture could result from photochemical cis–trans isomerization of the initially produced isomer. The Diels–Alder reaction of 4a and cyclohexene would then be expected[9] to give 5a with cis stereochemistry at the ring junctions. However, the methyl group can be either cis or trans to the bridgehead hydrogens. If the Diels–Alder reaction proceeds with endo addition,[9] then both geometrical isomers of 4a are required to produce two stereoisomers of 5a.

When 3a was irradiated in benzene in the absence of cyclohexene, an interesting dimerization resulted. Thus, prolonged irradiation of 3a gave a new photoproduct in quantitative yield based on unrecovered 3a. The mass spectrum of this product showed it to be a dimer of 3a, and the NMR spectrum suggested that it was stilbene 8, of unknown stereochemistry (Scheme I). The structure of 8 was confirmed by oxidative cleavage of the ethylenic double bond with ruthenium tetraoxide and sodium periodate[10] to give aldehyde 9. The sample of 9 thus

Scheme I

3a, R_1 = Ph; R_2 = H
b, R_1 = CH$_3$; R_2 = Ph
c, R_1 = Ph; R_2 = Ph

7a, R_3 = CH$_3$; R_4 = H
b, R_3 = OCH$_3$; R_4 = Ph

obtained was identical with a sample prepared by oxidation of 10[11] with chromium trioxide–pyridine complex.[12]

A possible mechanism for the formation of 8 is the reaction of two molecules of 4a to give biradical 11. Two intramolecular hydrogen migrations would then produce 8. A similar biradical may be involved in the dimerization
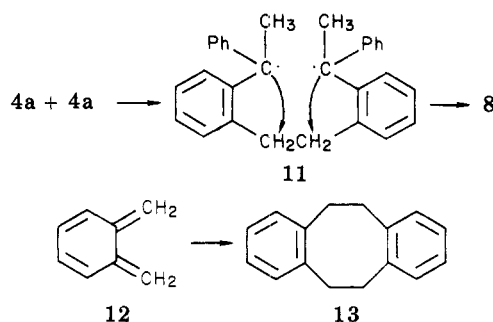
of 12 to give 13,[13] since concerted 4s + 4s cycloadditions are thermally forbidden.[14] In this case, the intermediate biradical would couple to give 13. In the case of biradical

(5) F. Scully and H. Morrison, *J. Chem. Soc., Chem. Commun.*, 529 (1973).
(6) A. C. Pratt, *J. Chem. Soc., Chem. Commun.*, 183 (1974).
(7) E. Bergmann and A. Bondi, *Chem. Ber.*, 66, 286 (1933).
(8) C. K. Bradsher and S. T. Webster, *J. Am. Chem. Soc.*, 79, 393 (1957).
(9) J. G. Martin and R. K. Hill, *Chem. Rev.*, 61, 537 (1961).

(10) L. M. Berkowitz and P. N. Rylander, *J. Am. Chem. Soc.*, 80, 6682 (1958).
(11) N. J. Leonard, A. J. Kreske, and M. Oki, *J. Am. Chem. Soc.*, 77, 5078 (1955).
(12) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, 35, 4000 (1970).
(13) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, 81, 4266 (1959).
(14) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970, p 70. H. E. Zimmerman, *Acc. Chem. Res.*, 4, 272 (1971). Of course, if the reaction were to proceed by a 4s + 4a pathway, it would be thermally allowed.

11, the coupling reaction is slowed by steric factors, and the hydrogen migrations occur instead.

Irradiation of a solution of **3a** with benzophenone as a photosensitizer did not produce **8**, nor was **5a** produced in a similar irradiation conducted in the presence of cyclohexene. However, these results do not necessarily imply that **4a** is a product of the singlet excited state of **3a**. It is also possible that the lifetime of **4a** is decreased by photosensitized conversion back to **3a** so that the Diels–Alder reaction and the dimerization can no longer compete.

The photochemical behavior of two other *o*-alkylstyrene derivatives was also investigated to provide some indication of the generality and efficiency of the reaction. Alkene **3b** was prepared by a Grignard reaction of methyl 2-(phenylmethyl)benzoate with excess methylmagnesium iodide. Careful acid-catalyzed elimination of water from the resulting crude alcohol gave **3b** contaminated by a small amount of the intramolecular Friedel–Crafts product, 9,9-dimethyl-9,10-dihydroanthracene.[15] After purification by chromatography, **3b** was irradiated in a mixture of benzene and cyclohexene to give an 86% yield of **5b**. The mass spectrum of the photoproduct indicated that it was a 1:1 adduct of **3b** and cyclohexene. The NMR spectrum was consistent with the assigned structure and showed two sets of two singlets each for the methyl groups, indicating that **5b** was a mixture of two stereoisomers. The structure of **5b** was confirmed by dehydrogenation to **6b**[16] by heating with sulfur. This sample of **6b** was identical with a sample obtained from a Grignard reaction of ester **7b**[17] with excess methylmagnesium iodide followed by an intramolecular Friedel–Crafts cyclization of the crude alcohol in sulfuric acid.

Alkene **3c** was prepared by a Grignard reaction of *o*-benzylacetophenone (**7a**)[8] and phenylmagnesium bromide followed by careful elimination of water from the resulting alcohol. Irradiation of **3c** in the presence of cyclohexene gave a 63% yield of **5c**. Adduct **5c** was identified on the basis of its mass spectrum and a comparison of its NMR spectrum with those of **5a** and **5b**. The NMR spectrum of **5c** indicated that it was a mixture of at least three stereoisomers (three different signals for the methyl groups).

We were also interested in the efficiency of formation of the *o*-xylylenes in these reactions. However, the quantum yield of formation of the adducts is not a measure of the quantum yield of *o*-xylylene formation; rather, it is a product of the quantum yield for *o*-xylylene formation and the fraction of *o*-xylylene that is trapped before it returns to the starting alkene. To avoid this complication and to provide additional mechanistic information, we investigated the photochemical behavior of **16**. Irradiation of **16** was expected to produce *o*-xylylene **17** (Scheme II). Because **17** is an enol, it was expected to undergo a rapid proton tautomerization to produce **9**. Thus, the quantum yield for the formation of **9** from **16** should be the same as the quantum yield for the formation of **17**. Of course, this would give only an approximate idea of the quantum yields for *o*-xylylene formation from **3** since the substituents are different in each case.

The synthesis of **16** appeared to be straightforward. Reduction of known acid **14** gave a 73% yield of product. However, NMR analysis showed this product to be a mixture of **16** and **10** in a 7:3 ratio.[19] Normal techniques

Scheme II
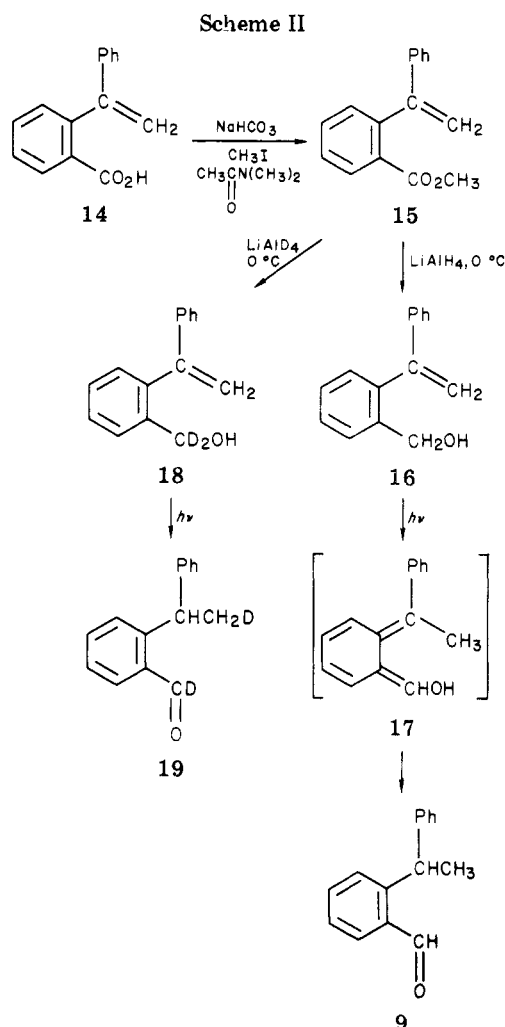
failed to separate this mixture, so an alternative synthesis was developed. Acid **14** was esterified, under nonacidic conditions, by treatment with sodium bicarbonate and methyl iodide in *N,N*-dimethylacetamide[20] to give **15**. Reduction of ester **15** with lithium aluminum hydride at low temperature gave **16** uncontaminated with **10**.

Irradiation of **16** in benzene or hexane gave aldehyde **9** (30% yield at 21% conversion of **16**). Aldehyde **9** was also produced from **16** (42% yield at 36% conversion of **16**) when xanthone was used as a photosensitizer. In order to establish that *o*-xylylene **17** was an intermediate in this reaction, we employed deuterium labeling. Reduction of **15** with lithium aluminum deuteride gave deuterated alcohol **18**. Irradiation of **18** gave aldehyde **19**. The positions of the deuterium were established by NMR. Furthermore, **9** was produced from **16** about 4 times more rapidly than **19** was produced from **18**, indicating a substantial primary deuterium isotope effect on the reaction.

The quantum yield for the formation of **9** from **16** upon direct irradiation in hexane was 0.085, and that upon xanthone-sensitized irradiation in benzene was 0.027. To establish that these values accurately reflect the quantum yields for *o*-xylylene formation, we found it necessary to demonstrate that *o*-xylylene **17** did not revert to alcohol **16**. Mellows and Sammes[21] have shown that *o*-tolu-

(15) A. Hafelinger and A. Streitwieser, Jr., *Chem. Ber.*, **101**, 657 (1968).
(16) A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *J. Am. Chem. Soc.*, **89**, 59 (1967).
(17) R. E. Lovins and L. J. Andrews, *J. Org. Chem.*, **29**, 478 (1964).
(18) E. Bergmann, *J. Org. Chem.*, **4**, 1 (1939).

(19) Lithium aluminum hydride is known to occasionally reduce carbon–carbon double bonds. See H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, CA, 1972, pp 89 ff.
(20) F. S. Alvarez and A. N. Watt, *J. Org. Chem.*, **33**, 2143 (1968).
(21) S. M. Mellows and P. G. Sammes, *J. Chem. Soc., Chem. Commun.*, 21 (1971).

aldehyde gives an o-xylylene upon irradiation. Therefore, irradiation of aldehyde **9** should produce **17**. However, when **9** was irradiated in benzene, no **16** was detected by GC analysis, indicating that **17** does not produce **16**. Thus, the quantum yields reported above for the formation of aldehyde **9** are fairly accurate values for the formation of **17** and **16** and indicate that o-xylylene formation is a moderately efficient photochemical reaction of o-alkylstyrenes.[22]

The observation that **16** produces **9** upon sensitized irradiation indicates that the triplet excited state of **16** produces o-xylylene **17** under these conditions. Since it is reasonable to assume that **3** should behave similarly to **16**, the failure to trap the o-xylylenes produced from these alkenes upon sensitized irradiation must be due to a decreased lifetime for the o-xylylenes under these conditions. The higher quantum yield for formation of **9** upon direct irradiation of **16** supports the conclusion that at least part of the reaction is proceeding via the singlet excited state of **16**.[23]

In summary, this study has shown that o-xylylenes are produced upon irradiation of a variety of o-alkylstyrene derivatives. The fact that these o-xylylenes can be trapped in good yields by a Diels–Alder reaction with a poor dienophile like cyclohexene indicates that this reaction is potentially useful in synthesis.

Experimental Section

General Methods. Boiling points are uncorrected; melting points are corrected. NMR spectra were obtained on a Varian EM-360 or a Varian HA-100 spectrometer. IR spectra were obtained with a Perkin-Elmer 337 spectrophotometer. UV spectra were obtained on a Beckman Acta V spectrophotometer. Mass spectra were obtained with an AEI MS-12 spectrometer. Elemental analyses were obtained from Atlantic Microlab, Inc., Atlanta, GA. GC analyses employed a Hewlett-Packard 5750 chromatograph coupled to a Columbia Scientific Industries CSI 38 digital integrator. Unless otherwise specified the column employed was a 1.8 m × 3.2 mm column with 10% Silicone Gum Rubber UCW-982 on 60/80 Chromsorb W. Preparative GC employed an Aerograph A-700 chromatograph.

Photochemical Apparatus. Preparative irradiations employed a quartz immersion well and a Hanovia 450-W medium-pressure mercury-vapor lamp. Water-jacketed vessels of 250 or 500 mL were used, and the solutions were purged continuously with a stream of oxygen-free nitrogen.[24]

Analytical irradiations employed the same light source and immersion well, combined with a "merry-go-round" type apparatus with quartz or Pyrex photolysis tubes of ca. 15-mL capacity. Solutions (10–15 mL, ca. 10^{-2} M in compound to be studied) were degassed with oxygen-free nitrogen[24] prior to irradiation.

Preparative Irradiation of 1-(2-Methylphenyl)-1-phenylethene (3a) in the Presence of Cyclohexene. A solution of 1.057 g (5.44 mmol) of **3a**[7] and 50 mL of cyclohexene in 250 mL of benzene was irradiated for 6.5 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel, with hexane as eluant, to give 1.41 g (94%) of **5a** (mixture of stereoisomers). Distillation gave 0.84 g (56%) of viscous liquid: bp 146–150 °C (0.1 mm); NMR (CDCl₃) τ 2.9 (m, 9 H, aromatics), 7.3 (m, 2 H, benzylics), 7.9–9.2 (m with two singlets superimosed at 8.27 and 8.50, 13 H, remaining protons); λ$_{max}$ (cyclohexane)

256 nm (ε 626), 262 (690), 266 (621), 269 (536), 273 (425); molecular ion at m/e 276 in the mass spectrum. An analytical sample was obtained by preparative GC on a 1.5 m × 0.64 cm, 3% SE-30 column at 217 °C, followed by short-path distillation.

Anal. Calcd for C₂₁H₂₄: C, 91.25; H, 8.75. Found: C, 91.31; H, 8.62.

Dehydrogenation of 9-Methyl-9-phenyl-1,2,3,4,4a,9,9a,-10-octahydroanthracene (5a). A mixture of 0.516 g (1.87 mmol) of **5a** and 0.240 g (7.5 mmol) of sulfur was heated to 230–240 °C for 3 h. The black, tarry residue was chromatographed on aluminum oxide, with hexane as eluant, to give 0.126 g (25%) of **6a**. This material crystallized on standing, and two recrystallizations from hexane gave a white solid, mp 112–113 °C. The NMR and IR spectra of this material were identical with an independently synthesized sample of **6a**, and a mixture of this material and authentic **6a** melted at 112–113 °C.

9-Methyl-9-phenyl-9,10-dihydroanthracene (6a). A solution of 2.788 g (0.0133 mmol) of o-benzylacetophenone (7a)[8] in 25 mL of anhydrous ether was added dropwise over a period of 10 min to a solution of Grignard reagent prepared from 0.394 g (0.016 mol) of magnesium and 2.750 g (0.0175 mol) of bromobenzene in 30 mL of anhydrous ether. The solution was heated to reflux for 2 h. Saturated NH₄Cl solution (ca. 3 mL) was added until the solids precipitated, and a clear solution resulted. The solid was removed by filtration and washed well with ether. The combined ether solutions were concentrated in vacuo to leave 3.44 g of yellow oil.

This oil was added to 20 mL of 85% H₂SO₄ at 0 °C. This slurry was stirred at room temperature for 20 min and then poured into 200 mL of cold water and extracted with ether. The extracts were washed with water, saturated NaHCO₃ solution, and again with water and dried. After removal of the solvent in vacuo the residue crystallized to give 1.25 g (38%) of **6a**. Two recrystallizations from hexane gave an analytical sample: mp 112.5–113 °C; NMR (CDCl₃) τ 2.84 (m, 13 H, aromatics), 6.08 and 6.28 (AB quartet, J = 18 Hz, 2 H, benzylics), 8.07 (s, 3 H, methyl); λ$_{max}$ (cyclohexane) 263 nm (ε 1700), 271 (1550).

Anal. Calcd for C₂₁H₁₈: C, 93.29; H, 6.71. Found: C, 93.41; H, 6.59.

Preparative Irradiation of 1-(2-Methylphenyl)-1-phenylethene (3a) in Benzene. A solution of 3.0 g (0.016 mol) of **3a**[7] in 500 mL of benzene was irradiated for 162 h. At this point, GC analysis (218 °C) showed ca. 50% of **3a** had reacted. After the solvent had been removed in vacuo, the residue was chromatographed on silica gel, with 1% ether in hexane as eluant, to give 1.4 g of **3a** and 1.6 g of **8** (100% based on unrecovered starting material).

Dimer **8** gave the following spectral data: a molecular ion at m/e 388; NMR (CDCl₃) τ 2.92 (m, 18 H, aromatics), 3.36 (br s, 2 H, vinylics), 5.64 (br q, J = 7 Hz, 2 H, methines), 8.44 (br d, J = 7 Hz, 6 H, methyls); λ$_{max}$ (cyclohexane) 256 nm (ε 10600). An analytical sample was obtained by rechromatography followed by molecular distillation at 220 °C and 0.1 mm.

Anal. Calcd for C₃₀H₂₈: C, 92.74; H, 7.26. Found: C, 92.48; H, 7.43.

Oxidative Cleavage of 2,2'-Bis(1-phenylethyl)stilbene (8). A solution of 0.020 g of ruthenium trichloride hydrate (37% ruthenium, 0.073 mmol) and 0.20 g of NaIO₄ in 8 mL of water was added to a solution of 0.39 g (1.0 mmol) of **8** in 50 mL of acetone. An additional 0.82 g of NaIO₄ was added in several portions over the course of 6 h. At this point, 2 mL of 2-propanol was added and the solution stirred for an additional 15 min. The solution was filtered, and the solvent was removed in vacuo. The residue was dissolved in ether, and the ether solution was washed twice with water, twice with 10% NaOH solution, and again with water and dried. Removal of the solvent in vacuo gave 0.226 g of oil which was chromatographed on silica gel with 5% ether in hexane as eluant to give 0.072 g (17%) of aldehyde **9**. The NMR and IR spectra of the aldehyde were identical with those of an independently synthesized sample. The 2,4-dinitrophenylhydrazone derivative melted at 142–143 °C, and the melting point was not depressed upon admixture with an authentic sample.

2-(1-Phenylethyl)benzaldehyde (9). To a stirring solution of 11.5 g (0.145 mol) of pyridine in 200 mL of dichloromethane was added 7.26 g (0.0726 mol) of CrO₃. After this solution was stirred for 15 min at room temperature, a solution of 2.56 g (0.0121

(22) The quantum yields for the formation of **9** from **16** are actually minimum values for the quantum yields for the formation of **17** from **16**, since **9** is unstable to the photolysis conditions. Since the quantum yields were measured at low conversions of **16**, this problem should be minimized. In any case, the quantum yields could be larger only by a factor of 2–3, based on the chemical yields of **9**.

(23) An alternative explanation for the higher quantum yield for the production of **9** upon direct irradiation of **16** is that **17** is selectively converted back to **16** by the photosensitizer. We feel that this explanation is less probable due to the short lifetime expected for **17**.

(24) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

mol) of o-(α-methylbenzyl)benzyl alcohol[11] (10) in 20 mL of dichloromethane was added. After this solution was stirred for 15 min, the solvent was decanted, and the tarry residue was washed with 400 mL of ether. The combined organic layers were washed three times with 5% NaOH solution, once with 5% HCl solution, and once with saturated NaCl solution and dried. Distillation gave 1.622 g (64%) of 9: bp 123–125 °C (0.4 mm); IR (neat) 1690 cm^{-1}; NMR (CDCl$_3$) τ –0.23 (s, 1 H, aldehyde), 2.23 (m, 1 H, aromatic ortho to carbonyl), 2.74 (m, 8 H, aromatics), 4.78 (q, 1 H, J = 7.2 Hz, methine), 8.40 (d, 3 H, J = 7.2 Hz, methyl).

Anal. Calcd for C$_{15}$H$_{14}$O: C, 85.68; H, 6.71. Found: C, 85.72; H, 6.72.

The 2,4-dinitrophenylhydrazone derivative melted at 143–144 °C (from absolute ethanol).

Anal. Calcd for C$_{21}$H$_{18}$N$_4$O$_4$: C, 64.60; H, 4.65; N, 14.35. Found: C, 64.63; H, 4.68; N, 14.39.

2-[2-(Phenylmethyl)phenyl]propene (3b). To a solution of methylmagnesium iodide, prepared from 2.13 g (0.088 mol) of magnesium turnings and 12.45 g (0.088 mol) of methyl iodide in 100 mL of anhydrous ether, was added dropwise a solution of 6.07 g (0.022 mol) of methyl 2-(phenylmethyl)benzoate (prepared by Fisher esterification of commercial α-phenyl-o-toluic acid) in 20 mL of anhydrous ether. The solution was heated to reflux for 2 h, followed by addition of saturated NH$_4$Cl solution. The ether was decanted from the precipitate, the precipitate was washed well with ether, and the combined ether solutions were dried. The solvent was removed in vacuo to leave 6.0 g of crude alcohol, which was dehydrated without further purification.

A solution of 6.0 g of the crude alcohol and 2 drops of concentrated H$_2$SO$_4$ in 60 mL of glacial acetic acid was stirred at room temperature for 4 h. The reaction mixture was poured into 600 mL of water and extracted with ether. The combined extracts were washed four times with 10% NaHCO$_3$ solution, once with 10% NaHSO$_3$ solution, and once with saturated NaCl solution and dried. Distillation yielded 4.33 g (78%) of 3b, bp 96–100 °C (0.20 mm). NMR analysis showed that 3b was contaminated with ca. 4% of 9,9-dimethyl-9,10-dihydroanthracene.[15] The impurity was removed by chromatography on silica gel with hexane as eluant. Distillation yielded an analytical sample: bp 87.5–88 °C (0.1 mm); NMR (CDCl$_3$) τ 2.97 (m, 9 H, aromatics), 4.93 (d of q, 1 H, vinylic, J$_{vinylic}$ = 2.2 Hz, J$_{methyl}$ = 1.6 Hz), 5.20 (d of q, 1 H, vinylic, J$_{vinylic}$ = 2.2 Hz, J$_{methyl}$ = 1.0 Hz), 6.03 (s, 2 H, methylenes), 8.10 (d of d, 3 H, methyl, J = 1.6 and 1.0 Hz); λ$_{max}$ (cyclohexane) 268 nm (ε 500), 261 (635), 254 (903).

Anal. Calcd for C$_{16}$H$_{16}$: C, 92.26; H, 7.74. Found: C, 92.31; H, 7.67.

Preparative Irradiation of 2-[2-(Phenylmethyl)phenyl]propene (3b) in the Presence of Cyclohexene. A solution of 2.0 g (0.0096 mol) of 3b and 30 mL of cyclohexene in 450 mL of benzene was irradiated for 12 h. The solvent was removed in vacuo to leave 3.0 g of dark oil. Chromatography of this material on silica gel with hexane as eluant gave 2.4 g (86%) of 5b (mixture of stereoisomers) which crystallized on standing. Two recrystallizations from pentane gave an analytical sample (mixture of stereoisomers): mp 126–139 °C; NMR (CDCl$_3$) τ 2.4–3.6 (m, 9 H, aromatics), 6.03 and 6.47 (two br d, J = 5.2 and 8.6 Hz, respectively, total area 1 H, H on C-10 of two different stereoisomers), 7.7–9.3 (m with two singlets of approximately equal area superimposed at τ 8.53 and 8.83 and two other singlets of approximately equal area, but larger than the former pair, superimposed at τ 8.60 and 8.73, total area of 16 H, methyls of two diastereomers and remaining protons); molecular ion at m/e 290 in the mass spectrum.

Anal. Calcd for C$_{22}$H$_{26}$: C, 90.98; H, 7.02. Found: C, 90.74; H, 7.19.

Dehydrogenation of 9,9-Dimethyl-10-phenyl-1,2,3,4,4a,-9,9a,10-octahydroanthracene (5b). A mixture of 0.40 g (0.0014 mol) of 5b and 0.18 g (0.0056 mol) of sulfur flowers was heated to 240 °C for 3 h. Chromatography of the tarry residue on silica gel with hexane as eluant gave 0.087 g (22%) of 6b, which crystallized on standing. After recrystallization from hexane the material melted at 144–146 °C. The NMR spectrum of this material was identical with that of an independently prepared sample, mp 144–146 °C, and a mixture melting point was not depressed.

9,10-Dihydro-9,9-dimethyl-10-phenylanthracene (6b). A solution of 2.5 g (0.008 mol) of methyl 2-(diphenylmethyl)benzoate (7b)[17] in 50 mL of anhydrous ether was added dropwise to a solution of methylmagnesium iodide, prepared from 0.58 g (0.024 mol) of magnesium and 3.41 g (0.024 mol) of methyl iodide in 40 mL of anhydrous ether. After the solution had been heated at reflux overnight, 35 mL of saturated NH$_4$Cl solution was added. The layers were separated, and the aqueous layer was extracted with ether. After the combined organic layers had been dried, the solvent was removed in vacuo to leave 2.3 g of oil.

This oil was added to 100 mL of ice-cold 85% H$_2$SO$_4$, and the resulting solution was stirred at room temperature for 1 h. The solution was poured into 500 mL of ice–water and extracted with ether. The combined extracts were washed twice with saturated NaHSO$_3$ solution, twice with saturated NaHCO$_3$ solution, and three times with water and dried. Removal of the solvent gave a solid which was recrystallized from hexane to give 0.8 g (34%) of 6b: mp 144–146 °C (lit.[16] mp 147.5–148.5 °C); NMR (CDCl$_3$) τ 2.3–3.1 (m, 14 H, aromatics), 4.70 (s, 1 H, methine), 8.27 (s, 3 H, methyl), 8.32 (s, 3 H, methyl).

1-Phenyl-1-[2-(phenylmethyl)phenyl]ethene (3c). A solution of 5.37 g (0.0255 mol) of 7a[8] in 30 mL of anhydrous ether was added dropwise to a solution of phenylmagnesium bromide, prepared from 1.24 g (0.051 mol) of magnesium and 7.00 g (0.051 mol) of bromobenzene in 45 mL of anhydrous ether. The resulting solution was heated to reflux for 20 h, and then 9.5 mL of saturated NH$_4$Cl solution was added dropwise. The ether solution was decanted from precipitated solids, and the solids were washed well with ether. The combined ether solutions were concentrated in vacuo, and the residue was added to a solution of 6 drops of H$_2$SO$_4$ in 150 mL of glacial acetic acid and stirred at room temperature for 3 h. The solution was poured into 1 L of water and extracted with ether. The combined extracts were washed twice with water, three times with saturated NaHCO$_3$ solution, and again with water and dried. The solvent was removed in vacuo, the residue was chromatographed on silica gel with hexane as eluant, and the fractions containing 3c were distilled to give 2.15 g (31%) of 3c, bp 180–182 °C (1.2 mm), which slowly crystallized to give a solid: mp 63.5–65.5 °C; NMR (CDCl$_3$) τ 2.4–3.2 (m, 14 H, aromatics), 4.32 (d, J = 1.4 Hz, 1 H, vinylic), 4.93 (d, J = 1.4 Hz, 1 H, vinylic), 6.27 (s, 2 H, methylene).

Anal. Calcd for C$_{21}$H$_{18}$: C, 93.29; H, 6.71. Found: C, 93.47; H, 6.52.

Preparative Irradiation of 1-Phenyl-1-[2-(phenylmethyl)phenyl]ethene (3c) in the Presence of Cyclohexene. A solution of 1.00 g (0.0037 mol) of 3c and 50 mL of cyclohexene in 225 mL of benzene was irradiated for 6.25 h. Chromatography on silica gel with hexane as eluant gave 0.82 g (63%) of 5c. This material consisted of at least three stereoisomers as indicated by the presence of three different singlets (at τ 7.95, 8.09, and 8.32) for the methyl group in the NMR spectrum. The adduct partially crystallized on standing, and one stereoisomer could be obtained pure by several recrystallizations from pentane to give 5c: mp 157.5–158 °C; NMR (CDCl$_3$) τ 1.9–3.4 (m, 14 H, aromatic), 6.57 (d, J = 9 Hz, 1 H, H on C-10), 7.95 (s, 3 H, methyl) 8.3–9.7 (m, 10 H, remaining protons); molecular ion at m/e 352 in the mass spectrum.

Anal. Calcd for C$_{27}$H$_{28}$: C, 91.99; H, 8.01. Found: C, 91.84; H, 8.13.

Methyl 2-(1-Phenylethenyl)benzoate (15). A solution of 6.5 g (0.029 mol) of 14,[18] 30 g of NaHCO$_3$, and 25 g (0.18 mol) of methyl iodide in 125 mL of dry N,N-dimethylacetamide was stirred at room temperature for 96 h. The solids were removed by filtration, and the solution was poured into 200 mL of 10% NaCl solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers were washed several times with 10% NaCl solution and dried. Distillation yielded 3.2 g (54%) of 15: bp 134–135 °C (0.75 mm); NMR (CDCl$_3$) τ 2.06–2.33 (m, 1 H, aromatic ortho to carbonyl), 2.53–3.0 (m, 8 H, aromatics), 4.38 (d, J = 1.5 Hz, 1 H, vinylic), 4.80 (d, J = 1.5 Hz, 1 H, vinylic), 6.57 (s, 3 H, methyls).

Anal. Calcd for C$_{16}$H$_{14}$O$_2$: C, 80.65; H, 5.92. Found: C, 80.58; H, 5.97.

1-[2-(Hydroxymethyl)phenyl]-1-phenylethene (16). A solution of 4.58 g (0.0193 mol) of 15 in 200 mL of anhydrous ether was added dropwise to a slurry of 2.43 g (0.064 mol) of LiAlH$_4$

in 100 mL of anhydrous ether under a nitrogen atmosphere. The solution was cooled in an ice bath during the addition, and cooling was continued while the solution was stirred for 2.5 h after the addition. To this was added carefully 9.75 mL of water, and the solution was then allowed to warm to room temperature. The solids were removed by filtration and washed well with ether. The combined ether solutions were dried. Distillation yielded 3.08 g (76%) of **16**: bp 163–164 °C (1.5 mm); NMR (CDCl$_3$) τ 2.7 (m, 9 H, aromatics) 4.27 (d, J = 1.2 Hz, 1 H, vinylic), 4.80 (d, J = 1.2 Hz, 1 H, vinylic), 5.64 (s, 2 H, methylenes), 8.20 (s, 1 H, OH); λ_{max} (hexane) 257 nm (ϵ 9080).

Anal. Calcd for C$_{15}$H$_{14}$O: C, 85.68; H, 6.71. Found: C, 85.57; H, 6.71.

Preparative Irradiation of 1-[2-(Hydroxymethyl)-phenyl]-1-phenylethene (16). A solution of 0.500 g (0.002 38 mol) of **16** in 284 mL of benzene was irradiated for 2.75 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel with 3% ether in hexane as eluant to give 0.09 g (18%) of **9**. This sample of **9** had IR and NMR spectra identical with those of authentic **9**. Furthermore, this sample gave a 2,4-dinitrophenylhydrazone derivative which had the same melting point as an authentic sample and which gave an undepressed mixture melting point.

An analytical photolysis of 10 mL of 5 × 10^{-3} M **16** in hexane showed, by GC analysis (190 °C) using benzophenone as an internal standard, that 21% of **16** had reacted to produce a 30% yield of **9** after 10 min of irradiation. An analytical photolysis of 5 × 10^{-3} M **16** and 7 × 10^{-2} M xanthone as photosensitizer showed 36% of **16** had reacted to produce a 42% yield of **9** after 10 min of irradiation through Pyrex.

1-[2-(Hydroxydideuteriomethyl)phenyl]-1-phenylethene (18). A solution of 1.77 g (0.0074 mol) of **15** in 50 mL of anhydrous ether was added dropwise over a period of 40 min to a slurry of 0.600 g (0.014 mol) of LiAlD$_4$ in 50 mL of anhydrous ether. The addition was conducted under a nitrogen atmosphere with cooling in an ice bath, and cooling was continued while the solution was stirred for an additional 1.25 h. Then 2.4 mL of water was carefully added, and the mixture was stirred for 50 min as it was allowed to warm to room temperature. The solids were removed by filtration and washed well with ether. The combined ether solutions were dried. Distillation gave 1.05 g (59%) of **18**: bp 191–195 °C (1.65 mm); NMR (CDCl$_3$) τ 2.75 (m, 9 H, aromatics), 4.24 (d, J = 1.2 Hz, 1 H, vinylic), 4.80 (d, J = 1.2 Hz, vinylic), 8.44 (br s, 1 H, OH).

Preparative Irradiation of 1-[2-(Hydroxydideuterio-methyl)phenyl]-1-phenylethene (18). A solution of 0.803 g (0.003 78 mol) of **18** in 290 mL of benzene was irradiated for 2.75 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel to give 0.18 g (22%) of **19**: NMR

(CDCl$_3$) τ 2.1–3.1 (m, 9 H, aromatics), 4.84 (t, J = 7.2 Hz, 1 H, methine), 8.44 (br d, J = 7.2 Hz, 2 H, CH$_2$D).

The effect of the deuteriums on the efficiency of the reaction was determined in the following manner. Equimolar solutions (10 mL, 0.0100 M) of **16** and **18** were irradiated in parallel in the "merry-go-round" apparatus for 30 min. GC analysis (200 °C), using benzophenone as internal standard, showed that **16** had produced 1.3 mg of **9**, and **18** had produced 0.3 mg of **19** (Φ_H/Φ_D = 4).

Quantum Yields. Quantum yields were measured with an apparatus similar to the "Wisconsin Black Box"[25] by using potassium ferrioxalate actinometry.[26]

For direct quantum yields, 2 cm each of 2 M NiSO$_4$ in 5% H$_2$SO$_4$, 0.38 M CoSO$_4$ in 5% H$_2$SO$_4$, and 1.9 × 10^{-4} M BiCl$_3$ in 10% HCl were used as filter solutions to isolate a window from 260–300 nm. Conversions were less than 15% for three runs using ca. 0.0015 M **16** in hexane, and the average quantum yield was 0.085 ± 0.006.

For the sensitized quantum yield, 2 cm each of the Ni and Co filter solutions described above and 2 cm of 0.02 M SnCl$_2$ in 40% HCl were used to isolate a window from 300–350 nm. A solution containing approximately 0.05 M xanthone and 0.003 M **16** in benzene was irradiated for a period of time so that conversions were less than 15%. For two runs the average quantum yield was 0.027 ± 0.001.

An analytical photolysis of 3.85 × 10^{-2} M **9** in benzene showed no detectable **16** by GC analysis (SE-30 column at 185 °C) after irradiation for 2 h (30% of **9** had disappeared), showing that o-xylylene **17** does not produce **16**.

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Thermal and Photochemical Reactions of Sodium Salts of β-Phosphono Tosylhydrazones

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Thermal and photochemical reactions of sodium salts of β-phosphono tosylhydrazones have been investigated. When the sodium salt of dimethyl α-acetylmethylphosphonate tosylhydrazone is heated, the dimethoxyphosphonyl anion, though a relatively strong base, was eliminated. On the other hand, ultraviolet irradiation of the sodium salts of β-phosphono tosylhydrazones leads to dimethoxyphosphonyl-substituted olefins, presumably via the carbene intermediate. Some of the products result from a previously unreported phosphonyl group migration to a carbene.

The migration of phosphonyl groups to electron-deficient centers has been intensively investigated for carbonium ion,[1-3] oxygen,[4] and nitrogen.[5] In the migration

to the carbonium ion center the preference order was Ph > PO(OR)$_2$ > H > R, while in the case of the oxygen center

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