

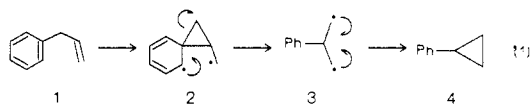
Diradical Rearrangements: An Unusual 1,2-Shift in a Photochemically Generated 1,3-Diradical. Mechanistic and Exploratory Organic Photochemistry^{1,2}

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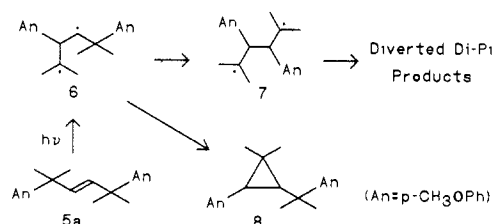
Abstract: The triplet photochemistry of 2,5-dianisyl-2,5-dimethyl-hex-3-ene was explored in a study of the behavior of diradical species occurring in the di- π -methane rearrangement. It was observed that the penultimate species, the 1,3-diradical, crosses more rapidly to cyclopropane product than the latter rearranges further. The photoproduct, 1-anisyl-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane, was observed to undergo a novel singlet rearrangement resulting from three-ring opening to a 1,3-diradical, followed by a 1,2-shift of the *p*-methoxycumenyl moiety. The diradical, 1-anisyl-2-(*p*-methoxycumenyl)-3,3-dimethylpropane-1,3-diyl, was also observed to undergo fragmentation to *p*-methoxycumenyl and 1-anisyl-3,3-dimethylallyl radicals as a minor process constituting ca. 12%. Most interesting was the observation of the two products of the 1,2-shift of the *p*-methoxycumenyl group in the 1,3-diyl to afford 1,4-dianisyl-3,3,4-trimethylpent-1-ene and 4,5-dianisyl-2,5-dimethylhex-2-ene. This unusual diradical rearrangement was the major reaction course of the singlet 1,3-diyl. Crossover experiments were run using the bis(deuteriomethoxy)-labeled cyclopropane. Four percent crossover, resulting from disengagement of a *p*-methoxycumenyl radical and recombination, was observed. The mechanism of the 1,3-diyl 1,2-shift is discussed. Finally, the quantum yield for the diyl rearrangement was determined as $\phi = 0.11$.

Background to the Problem. Our present study began with two objectives in mind. The first was the investigation of a di- π -methane^{3a-d,f-h,4} system having the possibility of diverting a reaction intermediate from undergoing the normal reaction. The second was the study of the potential di- π -methane product. In the aryl-vinyl version of the di- π -methane mechanism, depicted in eq 1,^{3e,i} one intriguing possibility was that the 1,3-diradical 3

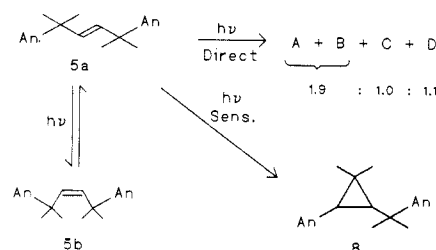


occurring in triplet examples of the reaction might be diverted in some fashion. In the present instance we selected 2,5-dianisyl-2,5-dimethylhex-3-ene (**5**), whose di- π -methane rear-

Scheme I. Two Possible Courses of Rearrangement of Dianisyl Reactant **5**



Scheme II. Exploratory Photochemistry of Dianisylhexene **5a**

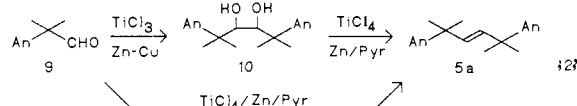


angement mechanism leads to the 1,3-diradical **6**. Note Scheme I. The interception of 1,3-diradical **6** appeared possible in view of evidence indicating that this triplet species has finite existence in the di- π -methane rearrangement^{3a,b,4} (vide infra).

Indeed, our study did result in information on this point. Additionally, some new molecular rearrangements were encountered and became the major focus of our study.

Results

Synthesis of Photochemical Reactant. The synthesis of the reactant 2,5-dianisyl-2,5-dimethyl-hex-3-ene (**5**) is outlined in eq 2. This used the McMurry^{5a} and Lenoir reagents.^{5b} Isolation



of intermediate pinacol **10** proved advantageous, and only one

(5) (a) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* 1978, 43, 3255-3266. (b) Lenoir, D. *Synthesis* 1977, 553-554.

(1) This is publication 151 of our photochemical series and 211 of the general papers.

(2) For photochemical publication 150, see: Zimmerman, H. E.; Nuss, J. M. *J. Org. Chem.* 1986, 51, 4604-4617. For papers 209 and 210 of the general series, see: Randic, M.; Zimmerman, H. E. *Int. J. Quantum Chem.* 1986, *Symp. No. 20*, 185-201; Zimmerman, H. E. *Acc. Chem. Res.* 1987, 20, 263-268.

(3) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* 1967, 89, 3932-3933. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* 1969, 91, 3316-3323. (c) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* 1969, 91, 1718-1727. (d) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* 1968, 90, 4191-4193. (e) It should be recognized that the notation defined by the author^{3f-h,4} and used in eq 1 provides structures such as **2** as conveniences in organic chemical notation without implication whether these are intermediates or just points on an excited-state hypersurface; this point is made at the request of a referee. (f) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* 1970, 92, 1409-1410. (g) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* 1970, 92, 6259-6267. (h) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* 1973, 73, 531-551. (i) However, whether or not a diradical such as **2** is an energy minimum seems to be somewhat controversial.³ⁱ⁻¹ (j) Paquette, L. A.; Varadarajan, A.; Burke, L. D. *J. Am. Chem. Soc.* 1986, 108, 8032-8039 and references cited therein have argued for a "direct 1,2-shift" of a π -group. (k) Quenemoen, K.; Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* 1985, 107, 5054-5059 have presented theoretical evidence in favor of a triplet minimum for a cyclopropylidene diradical. (l) Early spin-free extended-Hückel calculations^{3a,b} for the barrelene to semibullvalene rearrangement revealed an energy minimum in agreement with ref 3k, and more recent SCF-CI calculations^{3m} indicate this also. (m) Zimmerman, H. E.; Moore, J., to be published.

(4) (a) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980. (b) Zimmerman, H. E. *Top. Curr. Chem.* 1982, 100, 45-73. (c) Zimmerman, H. E. *Acc. Chem. Res.* 1982, 10, 312-317.

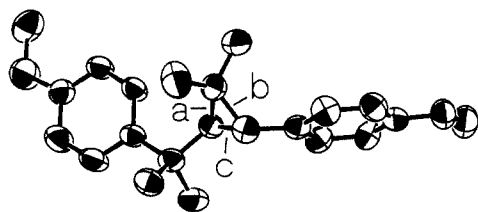
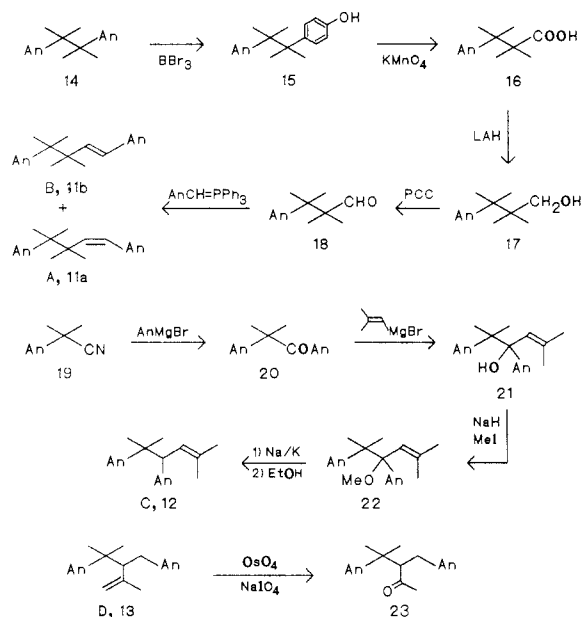


Figure 1. ORTEP drawing of photoproduct 8.

Scheme III. Structure Proofs for Photoproducts A, B, C, and D



diastereomer of 10 was observed. X-ray analysis⁶ showed dianisylhexene 5a to be the *trans* stereoisomer.

Photochemistry of Dianisylhexene 5. Sensitized irradiation of dianisylhexene 5a using acetone gave rapid *cis*-*trans* isomerization along with a photoproduct (8), mp 60–61 °C. The structure of this photoproduct was established as 1-anisyl-2,2-dimethyl-3-(*p*-methoxycumenyl)cyclopropane by X-ray analysis.⁶ Note the ORTEP drawing in Figure 1.

In contrast, the direct irradiation of dianisylhexene 5a led to entirely different photochemistry with formation of photoproducts A, B, C, and D. These results are outlined in Scheme II.

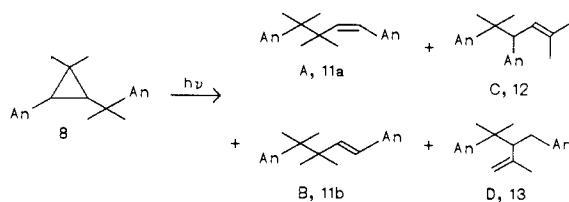
Elucidation of the Four Direct Photoproduct Structures. The four photoproducts were separated by preparative HPLC, and their structures were suggested by proton NMR analysis. With tentative structures in hand, we proceeded to synthesize A, B, and C, as outlined in Scheme III. In the case of photoproducts A and B, which proved to be *cis* and *trans* stereoisomers, the assignment of configuration was made on the basis of vinyl coupling constants. The *cis* isomer A had the smaller coupling constant of $J = 12.7$ Hz compared with the *trans* isomer B, the coupling constant of which was 16.4 Hz.

The structure of photoproduct D was established by Johnson-Lemieux⁷ oxidation to dianisyl ketone 23, whose structure was established by X-ray analysis. This conversion is included in

(6) (a) Since the advent of powerful direct-methods programs^{6c,d} we have utilized X-ray analysis, rather than degradation and synthesis, for final structure proofs of our photoproducts. (b) We have made use of a VAX/750 along with the MULTAN⁸⁰ and SHELXS⁸⁶ programs imbedded in a series of command procedures^{6e} automating parameter and data input as well as running of the programs. (c) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* 1971, 27, 368–376. (d) Sheldrick, G. M. *Crystallographic Computing*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985, Vol. 3, pp 175–189. (e) The VAX procedures used were patterned after those supplied to us by Prof. C. Strouse of UCLA. The modification and expansion were by J. Moore, A. M. Weber, and H. E. Zimmerman.

(7) Pappo, R.; Allen, D. S., Jr.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem.* 1956, 21, 478–479.

Scheme IV. Photochemistry of Anisylcyclopropane 8

Table I. Quantum Yields for the Anisylcyclopropane Rearrangement^a

run	extent conv, %	quantum yield of photoproduct			
		<i>cis</i> -styrene 11a (A)	<i>trans</i> -styrene 11b (B)	isobutylene 12 (C)	isobutylene 13 (D)
1	5.5	0.063	0.028	0.040	0.050
2	6.9	0.091	0.011	0.040	0.055
3	7.5	0.048	0.025	0.038	0.040
4	9.9	0.055	0.025	0.040	0.043
5	13.3	0.058	0.017	0.041	0.041
6	17.3	0.063	0.014	0.037	0.043
E ^b	0	0.070	0.027	0.040	0.052

^aAll runs in *t*-BuOH. Irradiations at 289 nm. ^bZero percent conversion extrapolated values.

Scheme III, and the ORTEP drawing may be obtained as supplementary material.

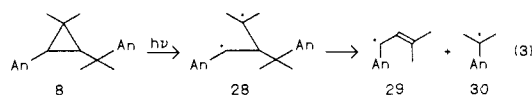
Hence, the structures assigned to the four photoproducts are (*Z*)-1,4-dianisyl-3,3,4-trimethylpent-1-ene (11a) for A, (*E*)-1,4-dianisyl-3,3,4-trimethylpent-1-ene (11b) for B, 4,5-dianisyl-2,5-dimethylhexene (12) for C, and 4-anisyl-2,4-dimethyl-3-(*p*-anisylmethyl)pent-1-ene (13) for D.

Exploratory Photochemistry of Anisylcyclopropane 8. We next turned our attention to the photochemistry of anisylcyclopropane 8. Interestingly, on direct irradiation, the same four photoproducts A (i.e., 11a), B (11b), C (12), and D (13) were formed and in the same distribution as in the direct irradiation of dianisylhexene 5. We therefore concluded that the formation of photoproducts A, B, C, and D in the direct irradiation of 8 derives from secondary photochemistry of anisylcyclopropane 8. Since the unusual rearrangements actually originated with anisylcyclopropane 8, its photochemistry became the focus of our study. The photochemistry of anisylcyclopropane 8 is outlined in Scheme IV.

In contrast, sensitized irradiation of anisylcyclopropane 8 using acetone revealed a total lack of reactivity. This is consonant with the high-yield formation, without further reaction, of anisylcyclopropane 8 from dianisylhexene 5 under sensitized conditions.

Quantum Yield Determination. Quantum yields were determined by using the microbench apparatus⁸ and the electronic actinometer⁹ described by us previously. The results are summarized in Table I. The quantum efficiency was extrapolated to zero percent conversion, giving a value of $\phi = 0.19$ as a total for formation of the four products.

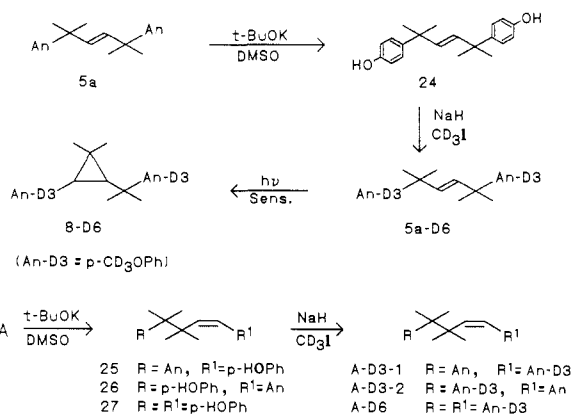
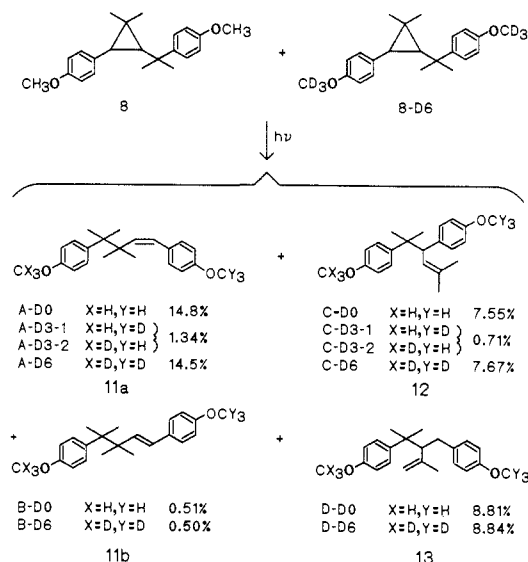
Question of Intramolecularity and the Need for Crossover Experiments. Synthetic Aspects. One other observation was the formation of trace amounts of *p,p'*-dimethoxybicumanyl (14) in the anisylcyclopropane photochemistry, thus suggesting the possibility of dissociation-recombination mechanisms involving a *p*-methoxycumenyl group. It was realized that products A, B, and C (i.e., 11a, 11b, and 12) result from photoreactant 1-anisyl-2,2-dimethyl-3-(*p*-methoxycumenyl)cyclopropane (8) undergoing fission of bond 1,2, as in eq 3, along with a formal



1,2-shift of a *p*-methoxycumenyl group. Initial fragmentation to radicals 29 and 30 seemed possible and led us to devise a crossover

(8) Zimmerman, H. E. *Mol. Photochem.* 1971, 3, 281–292.

(9) (a) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. *J. Mol. Photochem.* 1977, 8, 379–385. (b) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* 1956, 235, 518–536.

Scheme V. Preparation of Hexadeuterated (*p*-Methoxycumenyl)cyclopropane **8-D6** and Potential Crossover d_3 Photoproducts**Scheme VI.** Crossover Photolysis Experiment

experiment utilizing the hexadeuterated dianisylcyclopropane **8** having the two methoxyl groups labeled. The synthesis used was identical with that outlined in Scheme II for the unlabeled cyclopropane except for using hexadeuterated dianisylhexene **5a-D6**. The preparation of **5a-D6** is shown in Scheme V. Also included in Scheme V is the synthesis of potential crossover (i.e., d_3) products.

Crossover Experiments. The photolysis was run with equimolar amounts of the unlabeled and hexadeuterated (*p*-methoxycumenyl)cyclopropane **8** as depicted in Scheme VI. The percent of each photoproduct observed is listed in Scheme VI. Interestingly, there was relatively little crossover. However, crossover was definitely detected in photoproducts **A** (i.e., **11a**) and **C** (i.e., **12**), this to an extent of 5%. Since the crossover experiment was run to relatively high conversion, *cis*-*trans* steady-state isomerization led to such a predominance of *cis* isomer **A** that analysis for **B** did not prove practical. In the case of photoproduct **D** (i.e., **13**) only d_0 and d_6 products were detected. Finally, in recovered reactant **8**, only the original d_0 and d_6 compounds were found to be present.

Thus, ca. 95% of the reaction proceeded without, and 5% with, crossover. Making the reasonable assumption of negligible secondary isotope effects, we realize that for every two molecules of crossover products formed (i.e., **A-D3-1** and **A-D3-2**), four product molecules (i.e., **A-D3-1**, **A-D3-2**, **A-D0**, and **A-D6**) resulting from dissociation-recombination outside the solvent cage are actually formed. Hence, the fraction of the rearrangement proceeding via a cage escape path is twice the amount of the crossover product divided by the total amount of d_0 , d_3 , and d_6 product. This corresponds to 9% for the present rearrangement,

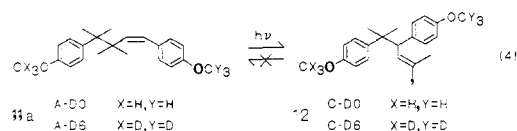
Table II. 1,2-Rearrangements of Photochemically Generated 1,3-Diradicals

reactant	putative 1,3-diradical	product	ref
			11a-d
			11e
			11f
			11g,h
			11i
			11j

whether the calculations are based upon product **A** or **C**. This does not include any dissociation-recombination within the cage.

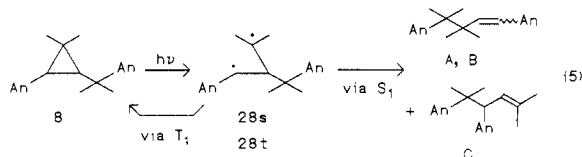
One further point is that in all of these high-conversion photolyses of the anisylcyclopropane **8** the small quantities of *p,p'*-dimethoxybicycmenyl (**14**) encountered were in amounts of the same order as the crossover products noted above. Note the Experimental Section for details.

Interconversion of Photoproducts A and C. Control Runs. It seemed not only of intrinsic interest, but also necessary, to determine product stability. Indeed, it was observed that *cis*-styrene **A** (**11a**) was very slowly converted to isobutylene **C** (i.e., **12**) along with the rapid *cis*-*trans* isomerization noted earlier. When the reaction was run with d_0 - and d_6 -labeled **A** under conditions used in the anisylcyclopropane crossover experiments, the recovered reactant was devoid of d_3 material within experimental error. These results are given in eq 4. In contrast, photoproducts **C** and **D** proved unreactive.

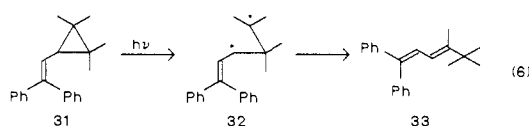


Interpretative Discussion

Observed Photochemical Rearrangements. The most novel results encountered are the rearrangements leading to photoproducts **A**, **B**, and **C** as outlined in Scheme IV. The overall mechanism of these rearrangements can be envisaged as proceeding via a 1,2-shift of a *p*-methoxycumenyl group in a singlet 1,3-diradical arising from three-ring opening. This is depicted in eq 5.

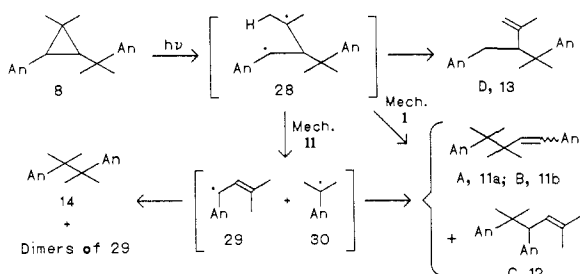


Such 1,2-rearrangements of 1,3-diradicals in photochemistry are rare. The first such example was the excited singlet rearrangement of 1-(2,2-diphenylvinyl)-2,2,3,3-tetramethylcyclopropane,¹⁰ which we observed to undergo a methyl migration as depicted in eq 6. Table II lists several further photochemical examples; in these loss of nitrogen affords a 1,3-diradical, which then rearranges.



(10) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6259-6267.

Scheme VII. Two Alternative Mechanisms for the Photochemical Rearrangements of 1-Anisyl-2,2-dimethyl-3-(*p*-methoxycumenyl)cyclopropane **8**



Also, a limited number of related ground-state diradical rearrangements has been reported.^{11a,12}

One mechanism for the rearrangement of the dianisyl diradical **28** is outlined in Scheme VII. The 1,2-shift of the *p*-methoxycumenyl moiety is seen to proceed in both directions to afford two of the photoproducts, namely, the stereoisomers **11a,b** (i.e., **A** and **B**) and **12** (i.e., **C**).

An alternative mechanism also needs consideration. Thus, the dissociation of diradical **28** to afford the *p*-anisylidimethylallyl radical **29** and the *p*-methoxycumenyl radical **30**, followed by recombination to afford photoproducts **A**, **B**, and **C**, is included in Scheme VII.

The formation of photoproduct **D** is included in Scheme VII. This, too, proceeds via 1,3-diradical **28**, but by a more classical, hydrogen-transfer route.

A point relevant to all of the observed cyclopropane reactions is the regioselectivity of three-ring opening. As seen in Scheme VII, biradical **28** is the most stable of three alternatives if one considers only electronic factors, since the odd-electron centers are benzylic and tertiary. The ORTEP drawing for cyclopropane **8** (note Figure 1) permits one to gauge the steric factors involved. Bond *c* is the least strained, having trans substituents. Bond *a* is most susceptible to fission on a steric basis, since a methyl group is cis to a large, quaternary center. Bond *b* is intermediate in strain, and yet it is this bond which is severed. Hence we can conclude that electronic, rather than steric, factors dominate.

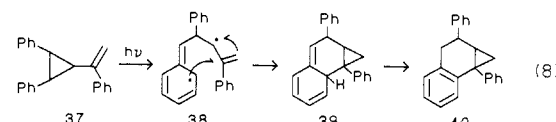
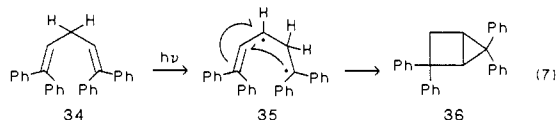
Alternative Rearrangement Mechanisms. Turning to consideration of the two mechanisms giving rise to photoproducts **A**, **B**, and **C**, we recognize that the crossover experiments demonstrate that minimally 9% of the reaction product occurs by the dissociation–recombination mechanism shown in Scheme VII. In principle, the extent of this mechanism should be greater, since the crossover experiments detect only radical pairs that escape from the solvent cage. The formation of dimethoxybicumenyl (**14**) confirms formation of these radicals and escape from the cage.

We now need to consider whether or not the remaining 90% of rearrangement occurs by way of the dissociation–recombination mechanism or, instead, by a direct 1,2-*p*-methoxycumenyl shift. Reference to the literature^{13a–d} of cage effects on radical pair

dissociation reveals that for cumenyl and other highly stabilized radical pairs, the extent of escape from the solvent cage is greater than the extent of recombination within the cage, although the converse is true for poorly stabilized radical pairs, and indeed for the overwhelming majority of known examples. Table III summarizes the behavior of some cumenyl and benzylic radical pairs, as well as some less stabilized cases. The most stabilized radicals in Table III exhibit ca. 20–35% intracage reaction. In the case of the present *p*-methoxycumenyl radical **30** and the anisylidimethylallyl radical **29**, the two radicals are subject to even greater delocalization. Hence we anticipate even less than the 20–35% reaction of radical pairs within the cage.

With 9% observed radical pair recombination outside the solvent cage in the present study, we can set a reasonable limit of ca. 3% of product formed by radical pair recombination within the cage, and thus a total of ca. 12% of the reaction resulting from the dissociation–recombination mechanism. We conclude, then, that the major reaction course is a 1,2-sigmatropic intramolecular rearrangement of diradical **28** as shown in Scheme VII.

The process by which 1,3-diradical **28** expels an odd-electron species from the central carbon to afford an allylic radical (here **29**) is unusual and of interest. This is the formal microscopic reverse of a known, but equally unusual, photochemical process. Thus, in both eq 7¹⁴ and 8¹⁵ a singlet diradical possessing an odd-electron center and a separate allylic radical moiety undergoes a reaction involving attack of the odd-electron center on the central carbon of the allylic system with concomitant 1,3-bonding in the latter.



A further noteworthy point is that this unusual dissociation occurs only from the singlet excited state and not the triplet. Indeed, ring opening is expected of triplet arylcyclopropanes,¹⁶ and it seems that by far the most rapid process available to the triplet diradical **28t** is reclosure to the cyclopropane.

Proclivity of Triplet 1,3-Diradicals To Close and Excited Singlet Diradicals To Rearrange. There is the related point that in the triplet di- π -methane rearrangement the penultimate species, a 1,3-diradical, undergoes three-ring closure. In the present study triplet 1,3-diradical **6** closes to cyclopropane product as the only reaction.

More generally, it is often observed that the most facile process available to triplet 1,3-diradicals is closure to the corresponding cyclopropane. This seems to derive from the availability of conformations having a very near degeneracy of the diradical triplets (i.e., T_1) with their ground states (S_0).¹⁷ Hence one can

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understand the rapid intersystem crossing and ring closure of the triplet diradicals and the potential for further reactions of S_1 .

Regioselectivity of the 1,2-Migration. A final result requiring comment is the regioselectivity encountered wherein singlet 1,3-diradical **28** rearranges to styryl photoproduct **11** in preference to the isobutylene **12**. A simplistic, but nevertheless revealing, rationale is seen in a comparison of the two transition-state orbital arrays in a 1-electron (i.e., Hückel) approximation. Thus the Hückel energy is lower for the orbital array I having the aryl



substitution on the developing π bond rather than for the alternative II, in agreement with observation. Although Hückel calculations are only first-order approximations which ignore electron-electron repulsion and exchange, they do correlate exactly with molecular topology, as in graph theory.

Conclusion. Perhaps the most obvious result of the present studies, in addition to delineation of new photochemistry, is further evidence that the framework of known photochemical transformations is limited. While one often can predict what some potential photoproducts may be, we still have not accumulated sufficient photochemistry to permit prediction of photoproducts with certainty. It also is clear that a multitude of unknown photochemical rearrangements remain awaiting discovery.

Experimental Section¹⁸

2,5-Di(*p*-anisyl)-3,4-dihydroxy-2,5-dimethylhexane (10). A modification of the general method of McMurry^{3a} was used. A slurry of 1.38 g (8.93 mmol) of titanium trichloride and 1.33 g (65.0 mmol) of zinc-copper couple in 50 mL of dimethoxyethane was refluxed for 2 h. A

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(18) Melting points were determined by means of a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc. Unless otherwise specified, reactions were run under an atmosphere of dry nitrogen, and anhydrous magnesium sulfate was utilized as the standard drying agent in reaction workups. The *tert*-butyl alcohol used for direct irradiations and pentane for HPLC separations were distilled from calcium hydride immediately before use. Acetone for sensitized photolyses was distilled prior to use. Tetrahydrofuran and dimethoxyethane were stored over potassium hydroxide, followed by successive distillations under a nitrogen atmosphere from calcium hydride, lithium aluminum hydride, and sodium-benzophenone ketyl. High-purity benzene was prepared by washing reagent grade benzene successively with 10% sulfuric acid saturated with potassium permanganate, water, concentrated sulfuric acid, and aqueous sodium carbonate, followed by drying over magnesium sulfate and distillation from calcium hydride. High-purity hexane was prepared by washing reagent hexane with 1:1 concentrated nitric and sulfuric acids, water, and aqueous saturated sodium carbonate, followed by passage through alumina and distillation from calcium hydride.

Exploratory photolyses were done with a Hanovia 450-W medium-pressure mercury lamp enclosed in either a Corex ($\lambda > 270$ nm) or Pyrex ($\lambda > 300$ nm) cylindrical filter of 2-mm thickness, and all solutions for photolysis were purged with dry, doxygenated nitrogen¹⁹ for 1 h before and during irradiation.

Column chromatography was performed with silica gel (Matheson Coleman and Bell, grade 62, 60-200 mesh) mixed with Sylvania 2282 phosphor and slurry-packed into Vycor columns, permitting monitoring by a hand-held UV lamp. Preparative thick-layer chromatography was carried out on 20 cm \times 20 cm plates of MN-Kieselgel G/UV 254 silica gel and monitored by a hand-held UV lamp. High-performance liquid chromatography (HPLC) was effected by means of a liquid chromatograph with an LDC 254-nm detector and an LDC 5000-psi minipump, with recycling capabilities. Preparative HPLC separations were performed with a 50 cm \times 9.5 mm polished stainless steel column packed with 6-10- μ m-diameter porous silica beads.²⁰

Proton nuclear magnetic resonance spectra were recorded on either a Bruker WP-270SY or WP-200SY spectrometer, and data are reported in ppm downfield from tetramethylsilane (δ). Infrared spectra were measured on a Mattson Polaris FT-IR spectrometer, and UV spectra were obtained with a Varian Cary 118 spectrophotometer.

HPLC relative retention times are given as RRT values.

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Table III. Cage Effects in Radical Pair Dissociation-Recombination

radical pair ^a	% cage reaction	% escape	ref
2 PhC(CH ₃) ₂	26-29 ^{a,d,e}	71-74	13a
2 <i>p</i> -CH ₂ C ₆ H ₄ C(CH ₃) ₂	22-36 ^{a,d}	70-78	13b
2 PhCH(CH ₃) + 2 PhCH(CD ₃)	29-32 ^{a,b,d,c}	68-71	13c,d
PhCH(CH ₃) + PhCH ₂	25-35 ^{a,c,d}	65-75	13e
2 (CH ₃) ₂ C(CN)	34-45 ^{a,d}	55-66	13f
2 CH ₃	63-83 ^{a,c-e}	17-37	13g,h
2 CH ₃ + 2 CD ₃	91 ^{b,e}	9	13i
2 ethyl	58-76 ^{a,e}	24-42	13j
2 <i>tert</i> -butyl	50-65 ^{a,e}	35-50	13k
2 CH ₂ =CHC(CH ₃) ₂ + 2 CD ₂ =CDC(CH ₃) ₂	40-65 ^{a-e}	35-60	13l

^aGenerated from the corresponding azo compound. ^bScavenging method. ^cCrossover method. ^dThermal. ^ePhotochemical.

solution of 3.00 g (16.8 mmol) of 2-(*p*-anisyl)-2-methylpropanal²¹ in 40 mL of dimethoxyethane was added over 8 h to the refluxing slurry, and reflux was continued for 23 h. The cooled mixture was filtered and the solids were rinsed successively with dry ether and dichloromethane. The filtrate was chromatographed on a silica gel column (13 cm \times 0.35 cm, packed with hexane), eluting with 8 L of hexane to afford 0.20 g of a partially crystallized oil; recrystallization from methanol afforded 65 mg (0.20 mmol, 2.4%) of (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene (**5a**) as a colorless solid, mp 78.0-79.0 °C. The stereochemistry was established (vide infra) by single-crystal X-ray diffraction analysis.^{6,22} Further elution with 4 L of ether gave 3.0 g of a pasty solid; recrystallization from ether afforded 2.50 g (6.97 mmol, 83.0%) of 2,5-di(*p*-anisyl)-3,4-dihydroxy-2,5-dimethylhexane (**10**) as a white solid, mp 108-109 °C.

The spectral data for (*E*)-2,5-dianisyl-2,5-dimethylhexene(**5a**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.262 (d, *J* = 8.9 Hz, 4 H, arom), 6.842 (d, *J* = 8.9 Hz, 4 H, arom), 5.625 (s, 2 H, vinyl), 3.794 (s, 6 H, arom OCH₃), 1.377 (s, 12 H, CH₃); IR (CHCl₃) 2967, 1611, 1511, 1466, 1300, 1251, 1183, 1035, 833 cm⁻¹; MS *m/e* 324.2074 (calcd for C₂₂H₂₈O₂, *m/e* 324.2089); UV (EtOH) λ_{\max} (nm) 226.5 (ϵ 22800), 279 (ϵ 3980), 286 (ϵ 3460).

Anal. Calcd for C₂₂H₂₈O₂: C, 81.43; H, 8.70. Found: C, 81.10; H, 8.77.

The spectral data for 2,5-di(*p*-anisyl)-3,4-dihydroxy-2,5-dimethylhexane (**10**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.194 (d, *J* = 8.9 Hz, 4 H, arom), 6.817 (d, *J* = 8.9 Hz, 4 H, arom), 3.797 (s, 6 H, arom OCH₃), 3.500 (d, *J* = 6.2 Hz, 2 H, CHOH), 1.897 (d, *J* = 6.2 Hz, 2 H, CHOH), 1.197 (s, 6 H, CH₃), 1.185 (s, 6 H, CH₃); IR (CHCl₃) 3548, 2969, 1611, 1513, 1468, 1296, 1252, 1189, 1074, 1035, 832 cm⁻¹; MS *m/e* 358.2143 (calcd for C₂₂H₃₀O₄, *m/e* 358.2144).

Anal. Calcd for C₂₂H₃₀O₄: C, 73.71; H, 8.44. Found: C, 74.11; H, 8.61.

(*E*)-2,5-Di(*p*-anisyl)-2,5-dimethylhexene (5a).^{5b} Titanium tetrachloride (10.8 mL, 18.0 g, 98.0 mmol) was added cautiously to 250 mL of rapidly stirred tetrahydrofuran at 0 °C. Zinc dust (13.4 g, 205 mmol) was added, followed after 5 min by 8.00 mL (7.82 g, 98.9 mmol) of dry pyridine. The slurry was refluxed for 30 min, a solution of 8.70 g (24.3 mmol) of 2,5-di(*p*-anisyl)-3,4-dihydroxy-2,5-dimethylhexane in 30 mL of tetrahydrofuran was added over 10 min, refluxing was continued for 39 h, and the cooled mixture was quenched with 150 mL of 10% aqueous potassium carbonate. Filtration left a black cake, which was rinsed with water and ether. The aqueous layer of the filtrate was extracted with ether, and the combined extracts were washed with brine, dried, and concentrated to give 11 g of a yellow paste.

Chromatography of the product (silica gel column, 50 cm \times 0.37 cm, packed with 2.5% ether in hexane), eluting with 3 L of 2.5% ether in hexane, 1 L of 20% ether, and 2 L of pure ether and collecting 200-mL fractions, gave fractions 3-10 (5.2 g of (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene) and fractions 21-31 (3.1 g of yellow recovered 2,5-di(*p*-anisyl)-3,4-dihydroxy-2,5-dimethylhexane). The pinacol was recrystallized from ether to afford 2.52 g (7.04 mmol, 29.0% recovery) of pure material, mp 107-109 °C.

The (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene was recrystallized from hexane, affording 4.96 g (15.3 mmol, 89.0% based on unrecovered starting material) as a white solid, mp 78-79 °C.

(*E*)-2,5-Di(*p*-anisyl)-2,5-dimethylhexene (5a). One-Step Procedure.^{5b} A 10.9-mL (19.0 g, 100 mmol) portion of titanium tetrachloride was added over 5 min to 200 mL of tetrahydrofuran at 0 °C with rapid

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(22) A complete listing of atomic coordinates, selected bond angles and distances, and isotropic and anisotropic thermal parameters are provided as supplementary material.

stirring. Zinc dust (12.7 g, 190 mmol) was added to the bright yellow slurry, followed after 10 min by 7.70 mL (7.53 g, 95.2 mmol) of dry pyridine. The brown mixture was refluxed for 1 h. Then a solution of 15.0 g (84.3 mmol) of 2-(*p*-anisyl)-2-methylpropanal²¹ in 25 mL of tetrahydrofuran was added over 2 h, followed by refluxing for 40 h, cooling in ice, and quenching with 200 mL of 75% saturated aqueous sodium carbonate. The slurry was filtered, and the residue was rinsed with water and ether. The aqueous layer of the filtrate was extracted with ether again, and the extracts were dried and concentrated to give 22 g of a dark oil. Chromatography on a silica gel column (100 cm × 0.37 cm, packed with hexane), eluting with 7 L of 0.5% ether in hexane, 7 L of 0.8% ether, 10 L of 5% ether, and 2 L of 7.5% ether and collecting 1-L fractions, gave fractions 7–10 (3.3 g of a pasty yellow solid, (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene) and fraction 26 (7.8 g of 2,5-di(*p*-anisyl)-3,4-dihydroxy-2,5-dimethylhexane, an oily yellow solid, mp 90–105 °C). The crude (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene was recrystallized from hexane to give 3.04 g (9.38 mmol, 22.0%) of white crystals, mp 78.5–79.0 °C. The 2,5-di(*p*-anisyl)-3,4-dihydroxy-2,5-dimethylhexane was recrystallized from 10% ether in hexane to give 5.40 g (15.1 mmol, 36.0%) of pure white crystals, mp 108–109 °C.

Low-Conversion Acetone-Sensitized Photolysis of (*E*)-2,5-Di(*p*-anisyl)-2,5-dimethylhexene (5a). A solution of 102 mg (315 μmol) of (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene in 250 mL of acetone was irradiated with a 450-W Hanovia lamp through Pyrex for 3 h and concentrated to afford 123 mg of a pungent, yellow oil, which was separated by thick-layer chromatography, eluting once with 20% ether in hexane, giving one band, 103 mg of a cloudy oil. Separation by recycling HPLC, eluting with 0.5% ethyl acetate in pentane, gave three peaks: (1) 43.0 mg of *trans*-1-(*p*-anisyl)-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane (**8**), HPLC relative retention time (RRT) 1.00,¹⁸ as a white solid, mp 59–61 °C; (2) 32.0 mg of pure (*Z*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene, RRT 1.17, as a white solid, mp 93–94 °C; (3) 24.1 mg of pure recovered (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene, RRT 1.23, as a white solid, mp 78–79 °C. The combined recovered yield of (*E*)- and (*Z*)-2,5-di(*p*-anisyl)-2,5-dimethylhexenes (**5a** and **5b**) was 56.1 mg (173 μmol, 55.0%).

The *trans*-1-(*p*-anisyl)-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane was recrystallized once from pentane (–20 °C) to afford 41.5 mg (128 μmol, 90.5% yield based on unrecovered **5**) of pure material as white crystals, mp 60–61 °C. The stereochemistry was established as *trans* by single-crystal X-ray diffraction analysis (vide infra).^{6,22}

The spectral data for *trans*-1-(*p*-anisyl)-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane (**8**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.341 (d, *J* = 8.9 Hz, 2 H, arom), 7.083 (d, *J* = 8.6 Hz, 2 H, arom), 6.845 (d, *J* = 8.9 Hz, 2 H, arom), 6.809 (d, *J* = 8.6 Hz, 2 H, arom), 3.803 (s, 3 H, arom OCH₃), 3.787 (s, 3 H, arom OCH₃), 1.907 (d, *J* = 7.0 Hz, 1 H, cyclopropyl CHCH), 1.464 (s, 3 H, CH₃), 1.386 (s, 3 H, CH₃), 1.233 (d, *J* = 7.0 Hz, 1 H, cyclopropyl CHCH), 1.058 (s, 3 H, CH₃), 0.772 (s, 3 H, CH₃); IR (CHCl₃) 2966, 1611, 1512, 1467, 1297, 1248, 1184, 1036, 833 cm⁻¹; MS *m/e* 324.2089 (calcd for C₂₂H₂₈O₂, *m/e* 324.2089); UV (EtOH) λ_{max} (nm) 229 (ε 23 400), 279 (ε 3380), 286 (ε 3130).

Anal. Calcd for C₂₂H₂₈O₂: C, 81.43; H, 8.70. Found: C, 81.69; H, 8.76.

Preparative Acetone-Sensitized Photolysis of (*E*)-2,5-Di(*p*-anisyl)-2,5-dimethylhexene (5a). A solution of 2.50 g (7.72 mmol) of (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene in 1000 mL of distilled acetone was irradiated with a 450-W Hanovia lamp through Pyrex for 20 h and concentrated to afford 3.1 g of a pungent, yellow oil. Chromatography on a silica gel column (148 cm × 0.27 cm), eluting with 4400 mL of 1% ether in hexane and collecting 100-mL fractions, afforded fractions 18–34 (2.23 g of cyclopropane **8**, as a colorless oil) and fractions 35–44 (320 mg (988 μmol, 12.8% recovery) of a mixture of (*E*)- and (*Z*)-2,5-di(*p*-anisyl)-2,5-dimethylhexenes (**5a** and **5b**).

The crude *trans*-1-(*p*-anisyl)-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane was recrystallized from pentane to give 2.01 g (6.20 mmol, 92.2% yield based on unrecovered **5**) of pure material as white crystals, mp 60.0–60.5 °C.

Exploratory Direct Photolysis of (*E*)-2,5-Di(*p*-anisyl)-2,5-dimethylhexene (5a). A solution of 126 mg (388 μmol) of (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene in 180 mL of *tert*-butyl alcohol was irradiated with a 450-W Hanovia lamp through Corex for 12.0 h. The solution was concentrated to afford 134 mg of a pale yellow oil. Thick-layer chromatography, eluting once with 20% ether in hexane, gave one intense band (*R_f* 0.42–0.58), 130 mg of a pale yellow oil.

Recrystallization from pentane (–20 °C) gave 38 mg of white crystals. The solid product was dissolved in toluene and subjected to separation by recycling HPLC, eluting with 0.5% ethyl acetate in pentane, to give four peaks: (1) 1.0 mg of a largely pure photoproduct, designated as **A**, a colorless oil, (*Z*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene, RRT 1.04;¹⁸

(2) 21.8 mg of white crystals, mp 92–94 °C, (*Z*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene (**5b**); (3) 13.7 mg of recovered (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene (**5a**) as a white solid, mp 76–79 °C; (4) 1.1 mg of a mixture of two photoproducts, RRT 1.31, (*E*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene, designated as **B**, and 4-(*p*-anisyl)-2,4-dimethyl-3-(*p*-methoxybenzyl)pent-1-ene, designated as **D**.

The mother liquors from the above recrystallization afforded 84 mg of a pale yellow oil, which was separated by recycling HPLC, as above: (1-a) 29.9 mg of colorless oil, containing essentially pure product **A**; (2-a) 21.3 mg of a white oil with solids, a mixture of **5b** and another photoproduct, 4,5-di(*p*-anisyl)-2,5-dimethylhex-2-ene, RRT 1.16, designated as **C**; (3-a) 10.5 mg of white, crystalline recovered **5a**, mp 77–79 °C; (4-a) 22.5 mg of a mixture of photoproducts **B** and **D**.

Photoproduct **A** (fractions 1 and 1-a) was purified by HPLC to remove minor solvent residues, giving 30.7 mg (94.8 μmol) of pure (*Z*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene (**A**) as a clear, colorless oil.

Fraction 2-a was recrystallized from pentane (–40 °C), affording 3.3 mg of white crystals of nearly pure **5b**, mp 93–94 °C. The filtrates were concentrated to give 17.2 mg (53.1 μmol) of pure 4,5-di(*p*-anisyl)-2,5-dimethylhex-2-ene (**C**) as a clear, colorless oil, uncontaminated by **5b**, which was virtually insoluble in pentane at –40 °C.

The combined samples of (*Z*)-2,5-dianisyl-2,5-dimethylhexene (**5b**) were recrystallized from pentane–ethyl acetate (–20 °C) to afford 24.6 mg (74.9 μmol) of pure material, mp 93.5–94.0 °C.

The recovered **5a** (fractions 3 and 3-a) was recrystallized from pentane (–20 °C) to afford 24.0 mg (74.1 μmol) of pure product, mp 78–79 °C.

The combined fractions 4 and 4-a were chromatographed on a silver nitrate impregnated silica gel²³ column (58 cm × 0.11 cm, packed with a 5:1 mixture of high-purity¹⁸ hexane and benzene). Elution with 400 mL of 0% ether in 5:1 hexane–benzene, 800 mL of 1% ether, and 1800 mL of 3% ether, collecting 80-mL fractions and monitoring by TLC, gave fractions 1–10 (3.1 mg of an off-white solid, nearly pure product **B**, mp 146–148 °C) and fractions 11–37 (19.1 mg (59.0 μmol) of pure product **D**, colorless oil).

The sample of (*E*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene (**B**) was recrystallized from ethyl acetate in hexane, giving 2.8 mg (8.6 mmol) of white crystals of pure material, mp 147–148 °C.

The (*E*)- and (*Z*)-2,5-di(*p*-anisyl)-2,5-dimethylhexenes (**5a** and **5b**) were recovered in a total yield of 48.8 mg (151 μmol, 38.8%). The yields of the four photoproducts, **A**, **B**, **C**, and **D**, were 39.9%, 11%, 22.3%, and 24.8%, respectively, based on unrecovered starting material, corresponding to ratios of (**A** + **B**):**C**:**D** of 1.9:1.0:1.1. The mass balance after isolation of products was 119 mg (94.3%).

The spectral data for (*Z*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene (**5b**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.101 (d, *J* = 8.9 Hz, 4 H, arom), 6.718 (d, *J* = 8.9 Hz, 4 H, arom), 5.590 (s, 2 H, vinyl), 3.777 (s, 6 H, arom OCH₃), 1.194 (s, 12 H, CH₃); IR (CHCl₃) 2966, 1612, 1513, 1469, 1302, 1253, 1185, 1038, 832 cm⁻¹; MS *m/e* 324.2096 (calcd for C₂₂H₂₈O₂, *m/e* 324.2089); UV (EtOH) λ_{max} (nm) 229 (ε 20 400), 278 (ε 3380), 285 (ε 2830).

Anal. Calcd for C₂₂H₂₈O₂: C, 81.43; H, 8.70. Found: C, 81.29; H, 8.77.

The spectral data for (*Z*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene (**A**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.289 (d, *J* = 9.2 Hz, 2 H, arom), 6.827 (d, *J* = 9.0 Hz, 4 H, arom), 6.728 (d, *J* = 8.8 Hz, 2 H, arom), 6.408 (d, *J* = 12.7 Hz, 1 H, vinyl), 5.548 (d, *J* = 12.7 Hz, 1 H, vinyl), 3.808 (s, 3 H, arom OCH₃), 3.780 (s, 3 H, arom OCH₃), 1.379 (s, 6 H, CH₃), 1.379 (s, 6 H, CH₃); IR (CHCl₃) 2976, 1606, 1510, 1465, 1296, 1247, 1220, 1186, 1143, 1034, 833 cm⁻¹; MS *m/e* 324.2086 (calcd for C₂₂H₂₈O₂, *m/e* 324.2089); UV (EtOH) λ_{max} (nm) 230.5 (ε 21 300), 278 (ε 2240), 284.5 (ε 1990).

Anal. Calcd for C₂₂H₂₈O₂: C, 81.43; H, 8.70. Found: C, 81.47; H, 8.90.

The spectral data for (*E*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene (**B**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.259 (d, *J* = 8.9 Hz, 2 H, arom), 7.253 (d, *J* = 8.9 Hz, 2 H, arom), 6.845 (d, *J* = 8.9 Hz, 2 H, arom), 6.819 (d, *J* = 8.9 Hz, 2 H, arom), 6.165 (d, *J* = 16.4 Hz, 1 H, vinyl), 6.015 (d, *J* = 16.4 Hz, 1 H, vinyl), 3.810 (s, 3 H, arom OCH₃), 3.807 (s, 3 H, arom OCH₃), 1.351 (s, 6 H, CH₃), 1.013 (s, 6 H, CH₃); IR (CHCl₃) 2977, 1609, 1511, 1466, 1249, 1220, 1176, 1035, 832 cm⁻¹; MS *m/e* 324.2086 (calcd for C₂₂H₂₈O₂, *m/e* 324.2089); UV (EtOH) λ_{max} (nm) 264.5 (ε 26 700), 273 (sh, ε 22 300), 297 (sh, ε 3450), 310 (sh, ε 2070).

Anal. Calcd for C₂₂H₂₈O₂: C, 81.48; H, 8.70. Found: C, 81.83; H, 8.70.

The spectral data for 4,5-di(*p*-anisyl)-2,5-dimethylhex-2-ene (**C**) were

(23) Silver nitrate impregnated silica gel prepared per procedure of: Goering, H. L.; Closson, W. D.; Olson, A. C. *J. Am. Chem. Soc.* **1961**, *83*, 3507–3511.

as follows: H NMR (CDCl₃, 270 MHz) δ 7.060 (d, $J = 9.2$ Hz, 2 H, arom), 6.771 (d, $J = 9.2$ Hz, 2 H, arom), 6.746 (d, $J = 8.9$ Hz, 2 H, arom), 6.677 (d, $J = 8.9$ Hz, 2 H, arom), 5.438 (d of m, $J = 10.4, 1.5, 1.2$ Hz, 1 H, vinyl), 3.798 (s, 3 H, arom OCH₃), 3.749 (s, 3 H, arom OCH₃), 3.516 (d, $J = 10.3$ Hz, 1 H, CH), 1.667 (d, $J = 1.2$ Hz, 3 H, CH₃), 1.484 (d, $J = 1.5$ Hz, 3 H, CH₃), 1.262 (s, 6 H, CH₃); IR (CHCl₃) 2963, 1615, 1514, 1253, 1225, 1186, 1039, 834 cm⁻¹; MS m/e 324.2082 (calcd for C₂₂H₂₈O₂, m/e 324.2089); UV (EtOH) (nm) λ_{\max} 229.5 (ϵ 22 100), 279 (ϵ 3700), 286 (ϵ 3190).

Anal. Calcd for C₂₂H₂₈O₂: C, 81.43; H, 8.70. Found: C, 81.19; H, 8.97.

The spectral data for 4-(*p*-anisyl)-2,4-dimethyl-3-(*p*-methoxybenzyl)pent-1-ene (D) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.342 (d, $J = 9.2$ Hz, 2 H, arom), 6.865 (d, $J = 8.9$ Hz, 4 H, arom), 6.703 (d, $J = 8.6$ Hz, 2 H, arom), 4.884 (m, $J = 1.6$ Hz, 1 H, vinyl), 4.670 (m, $J = 0.6, 1.8$ Hz, 1 H, vinyl), 3.806 (s, 3 H, arom OCH₃), 3.731 (s, 3 H, arom OCH₃), 2.57–2.43 (m, 3 H, CH₂CH), 1.472 (t, $J = 0.6$ Hz, 3 H, CH₃), 1.409 (s, 3 H, CH₃), 1.316 (s, 3 H, CH₃); IR (CHCl₃) 2966, 1611, 1513, 1467, 1250, 1182, 1036, 833 cm⁻¹; MS m/e 324.2086 (calcd for C₂₂H₂₈O₂, m/e 324.2089); UV (EtOH) λ_{\max} (nm) 229.5 (ϵ 21 700), 280 (ϵ 3180), 287 (ϵ 2680).

Anal. Calcd for C₂₂H₂₈O₂: C, 81.42; H, 8.70. Found: C, 81.03; H, 8.86.

Photolysis Apparatus for Small-Volume Irradiations. The small-volume (8.5 mL) irradiations using a Hanovia 450-W light source were carried out in a cylindrical cell (22-mm i.d. \times 21-mm length) with 3.0-mm-thick quartz windows, warmed to 30–40 °C by means of a water jacket. The cell was placed directly against the quartz cooling jacket (50-mm o.d.) of the Hanovia immersion finger at the midpoint of the lamp, the light from the lamp being passed through a 2.0-mm-thick cylindrical Corex glass filter.

Exploratory Direct Photolysis of *trans*-1-(*p*-Anisyl)-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane (8). A solution of 110 mg (339 μ mol) of *trans*-1-(*p*-anisyl)-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane in 8.5 mL of *tert*-butyl alcohol was irradiated with a 450-W Hanovia lamp through Corex for 180 min in the apparatus for small-volume irradiations described above and concentrated to give 110 mg of yellow oil. Thick-layer chromatography, eluting once with 20% ether in hexane, afforded one intense band (R_f 0.4–0.6), 105 mg of a pale yellow oil. Separation of the mixture by recycling HPLC, eluting with 0.5% ethyl acetate in pentane, gave five peaks: (1) 37.7 mg of recovered cyclopropane 8 as an oil; (2) 33.8 mg of a colorless oil, a mixture of photoproduct A and some cyclopropane 8, with a very small amount of 2,3-di(*p*-anisyl)-2,3-dimethylbutane, RRT 1.06,¹⁸ designated as product E; (3) 1.2 mg of a cloudy oil, a mixture of products A and E with a small amount of (Z)-1,4-di(*p*-anisyl)-3,3,6-trimethylhepta-1,5-diene, designated as product F; (4) 13.1 mg of pure product C (40.4 μ mol) as a colorless oil; (5) 18.4 mg of a colorless oil, a mixture of products B and D.

Fraction 1 was purified by recycling HPLC, affording 36.9 mg of pure recovered cyclopropane 8, a white solid, mp 59–61 °C.

Fraction 2 was separated by recycling HPLC, providing two partially separated peaks: (2-a) 4.3 mg of pure recovered cyclopropane 8; (2-b) 29.9 mg of a colorless oil, containing mainly product A with some cyclopropane 8, and a small amount of product E. Fraction 2-b was fractionally crystallized from pentane (0 °C), affording 1.0 mg (3.4 μ mol) of pure product E as a white, crystalline solid, mp 188–190 °C. Product E was identified by comparison with an authentic sample²⁷ of 2,3-di(*p*-anisyl)-2,3-dimethylbutane (14) (mp 189–191 °C, lit.²⁷ mp 184 °C). The mother liquor was concentrated to give a colorless oil, containing product A and cyclopropane 8, with minor impurities, but no residual E. Separation by recycling HPLC gave 3.1 mg of pure recovered cyclopropane 8 as a white solid, mp 59–61 °C, and 24.0 mg (71.1 μ mol) of pure product A as a colorless oil.

Separation of fraction 3 by recycling HPLC afforded fraction 3-a (0.5 mg of a mixture of product A and cyclopropane 8) and fraction 3-b (0.7 mg of a white oil, mainly product F, with small amounts of products A and C). Fraction 3-b was separated by recycling HPLC, giving 0.45 mg of pure product F (1.3 μ mol) as a white oil, RRT 1.15, identified as (Z)-1,4-di(*p*-anisyl)-3,3,6-trimethylhepta-1,5-diene by its spectral data.

Fraction 5 was separated by recycling HPLC, affording fraction 5-a (0.9 mg (3 μ mol) of pure product C as a colorless oil) and fraction 5-b (17.2 mg of a white oil, a mixture of products D and B). Fraction 5-b was chromatographed on a silver nitrate impregnated silica gel column²³ (58 cm \times 0.11 cm). Elution with 500 mL of 0% ether in 5:1 hexane-benzene, 500 mL of 1% ether, and 1500 mL of 5% ether, collecting 100-mL fractions and following progress by TLC, gave fractions 2–10 (1.9 mg of nearly pure product B, a white solid) and fractions 11–25 (15.1 mg of pure product D as a colorless oil). Product B was recrystallized from hexane-ethyl acetate to give 1.8 mg of pure material as white crystals, mp 146–148 °C.

Anisylcyclopropane 8 was recovered in a yield of 44.3 mg (138 μ mol, 40.7%). The respective yields of the four photoproducts, A, B, C, and D, were 36.8%, 2.8%, 21.4%, and 23.2%, based on unrecovered starting material, corresponding to ratios of 1.8:1.0:1.1 for the products (A + B):C:D. The yields of products E and F were 1.7% and 0.6%, respectively. The mass balance after isolation of products was 101 mg (92.0%).

The spectral data for (Z)-1,4-di(*p*-anisyl)-3,3,6-trimethylhepta-1,5-diene F were as follows: H NMR (CDCl₃, 270 MHz) δ 7.117 (d, $J = 8.6$ Hz, 2 H, arom), 6.854 (d, $J = 8.9$ Hz, 2 H, arom), 6.813 (d, $J = 8.6$ Hz, 2 H, arom), 6.731 (d, $J = 8.9$ Hz, 2 H, arom), 6.415 (d, $J = 12.8$ Hz, 1 H, vinyl), 5.634 (d of m, $J = 10.4$ Hz, 1.2 Hz, 1 H, vinyl), 5.526 (d, $J = 12.8$ Hz, 1 H, vinyl), 3.795 (s, 3 H, arom OCH₃), 3.780 (s, 3 H, arom OCH₃), 3.320 (d, $J = 10.1$ Hz, 1 H, CH), 1.744 (d, $J = 0.9$ Hz, 3 H, CH₃), 1.548 (d, $J = 1.2$ Hz, 3 H, CH₃), 0.843 (s, 3 H, CH₃), 0.830 (s, 3 H, CH₃); IR (CHCl₃) 2928, 2855, 1611, 1511, 1469, 1445, 1380, 1247, 1183, 1037, 834 cm⁻¹; MS, no molecular ion was observed (however, the most intense peak was found to be m/e 175.1133, corresponding to the anisyl dimethylallyl fragment (calcd for C₁₂H₁₅O, m/e 175.1123)).

(E)-2,5-Bis(*p*-hydroxyphenyl)-2,5-dimethylhexene (24).²⁴ A mixture of 940 mg (2.90 mmol) of (E)-2,5-di(*p*-anisyl)-2,5-dimethylhexene, 25 g (0.22 mol) of potassium *tert*-butoxide, and 50 mL of dry dimethyl sulfoxide was heated at 135–140 °C by oil bath for 25 h. The cooled mixture was added to ice water and extracted with ether. Concentration of the dried extracts afforded a brown tar, devoid of any recovered (E)-2,5-di(*p*-anisyl)-2,5-dimethylhexene.

The aqueous layer was acidified with hydrochloric acid and extracted with ether. Drying and concentration of the extracts gave 3.05 g of an orange-yellow solid. The product was triturated with 60 mL of boiling ether, the solution was concentrated, and the trituration-concentration process was repeated four times. The final triturate gave 2.10 g of an orange solid.

The crude product was chromatographed (silica gel, 30 cm \times 0.37 cm, packed with 10% ether in hexane) with 1600 mL of 10% ether in hexane and 1400 mL of 15% ether in hexane, collecting 100-mL fractions, giving fractions 17–30 (920 mg of (E)-2,5-bis(*p*-hydroxyphenyl)-2,5-dimethylhexene (24) as a yellow solid). Recrystallization of the product from 60 mL of chloroform and then 50 mL of toluene afforded 846 mg (2.86 mmol, 98.5%) of pure material as white fibers, mp 203.5–204.0 °C.

The spectral data for (E)-2,5-bis(*p*-hydroxyphenyl)-2,5-dimethylhexene (24) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.203 (d, $J = 8.6$ Hz, 4 H, arom), 6.760 (d, $J = 8.6$ Hz, 4 H, arom), 5.606 (s, 2 H, vinyl), 4.565 (s, 2 H, OH), 1.366 (s, 12 H, CH₃); IR (CHCl₃) 3597, 3336, 3013, 2968, 1611, 1511, 1258, 1229, 1218, 1207, 1043, 831 cm⁻¹; MS m/e 296.1776 (calcd for C₂₀H₂₄O₂, m/e 296.1776).

Anal. Calcd for C₂₀H₂₄O₂: C, 81.04; H, 8.16. Found: C, 81.07; H, 8.17.

Standard Procedure for Trideuteriomethylation of Phenols. A sealed-tube modification of the general method of Eades²⁵ was used. A 10 mm \times 75 mm test tube was drawn out to form a bulb of 4-cm length, which was then dried and flushed with nitrogen. The tube was charged with ca. 35 mg (0.73 mmol NaH) of 50% sodium hydride oil dispersion, the mineral oil was removed by washing with dry ether, and a solution of ca. 0.35 mmol of the phenol (specified in each run) in 500 μ L of tetrahydrofuran was added dropwise. The vessel was agitated for 15 min and then cooled by ice bath, and 30 μ L (0.14 g, 0.97 mmol) of trideuteriomethyl iodide was added. The tube was cooled in dry ice, evacuated, and sealed. Thorough agitation before sealing was essential to avoid explosion due to continued evolution of hydrogen gas in the following step. The sealed tube was heated at 95–100 °C for 15–24 h. After cooling, the contents were diluted with ether and water, and the aqueous layer was extracted with ether. The dried extracts were concentrated and subjected to thick-layer chromatography.

(E)-2,5-Bis(*p*-(trideuteriomethoxy)phenyl)-2,5-dimethylhexene (5a-D6). Eight reactions were run in concert, according to the general procedure above for trideuteriomethylation of phenols, each using 35 mg (0.73 mmol NaH) of 50% NaH oil dispersion, 50.0 mg (169 μ mol) of (E)-2,5-bis(*p*-hydroxyphenyl)-2,5-dimethylhexene, 500 μ L of tetrahydrofuran, and 60 μ L (140 mg, 0.97 mmol) of trideuteriomethyl iodide. The combined extracts gave 450 mg of an off-white solid, which was purified by thick-layer chromatography, eluting once with 30% ether in hexane to afford one band (R_f 0.5–0.7), 445 mg of white solid. Recrystallization from pentane (–25 °C) gave 412 mg of pure (E)-2,5-dimethyl-2,5-bis(*p*-(trideuteriomethoxy)phenyl)hexene (5a-D6) as a white solid, mp 79.0–80.0 °C. Concentration of the mother liquors gave 40 mg of material, which was repurified by thick-layer chromatography and subsequently recrystallized from pentane to give 29 mg of additional pure

(24) Chang, F. C.; Wood, N. F. *Tetrahedron Lett.* 1964, 2969–2973.

(25) Eades, E. D. M.; Ball, D. H.; Long, L., Jr. *J. Org. Chem.* 1965, 30, 3949–3951.

product, mp 78–80 °C. The overall yield of (*E*)-2,5-dimethyl-2,5-bis(*p*-(trideuteriomethoxy)phenyl)hexene was 441 mg (1.34 mmol, 98.5%).

The spectral data for (*E*)-2,5-dimethyl-2,5-bis(*p*-(trideuterio)methoxyphenyl)hexene (**5a-D6**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.262 (d, *J* = 8.9 Hz, 4 H, arom), 6.842 (d, *J* = 8.9 Hz, 4 H, arom), 5.625 (s, 2 H, vinyl), 1.377 (s, 12 H, CH₃); IR (CHCl₃) 2967, 2256, 2220, 2071, 1610, 1509, 1294, 1248, 1186, 1111, 995, 831 cm⁻¹; MS *m/e* 330.2475 (calcd for C₂₂H₂₂O₂D₆, *m/e* 330.2466).

2,2-Dimethyl-3-(*p*-(trideuteriomethoxy)cumenyl)-1-(*p*-(trideuteriomethoxy)phenyl)cyclopropane (8-D6). A solution of 460 mg (1.39 mmol) of (*E*)-2,5-dimethyl-2,5-bis(*p*-(trideuteriomethoxy)phenyl)hexene in 725 mL of acetone was irradiated with a 450-W Hanovia lamp for 31 h through a Pyrex filter and concentrated to give 700 mg of a pungent, yellow oil, which was separated by thick-layer chromatography, eluting once with 20% ether in hexane, to give one band, 390 mg of a colorless oil. Separation by HPLC, eluting with 1% ethyl acetate in pentane, afforded three peaks: (1) 325 mg of 2,2-dimethyl-3-(*p*-(trideuteriomethoxy)cumenyl)-1-(*p*-(trideuteriomethoxy)phenyl)cyclopropane (**8-D6**), RRT 1.00; (2) 25 mg of recovered **5a-D6**, RRT 1.06; (3) 15 mg of (*Z*)-2,5-dimethyl-2,5-bis(*p*-(trideuteriomethoxy)phenyl)hexene (**5b-D6**), RRT 1.12. The stereoisomers **5a-D6** and **5b-D6** were recovered in a total yield of 40 mg (0.12 mmol, 8.6%). The cyclopropane was recrystallized from 2 mL of pentane to afford the pure material (320 mg, 970 μmol, 76.4% based on unrecovered **5a-D6** and **5b-D6**) as white crystals, mp 61.0–61.5 °C.

The spectral data for 2,2-dimethyl-3-(*p*-(trideuteriomethoxy)cumenyl)-1-(*p*-(trideuteriomethoxy)phenyl)cyclopropane (**8-D6**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.341 (d, *J* = 8.9 Hz, 2 H, arom), 7.083 (d, *J* = 8.6 Hz, 2 H, arom), 6.845 (d, *J* = 8.9 Hz, 2 H, arom), 6.809 (d, *J* = 8.6 Hz, 2 H, arom), 1.907 (d, *J* = 7.0 Hz, 1 H, cyclopropyl CHCH), 1.464 (s, 3 H, CH₃), 1.386 (s, 3 H, CH₃), 1.233 (d, *J* = 7.0 Hz, 1 H, cyclopropyl CHCH), 1.058 (s, 3 H, CH₃), 0.772 (s, 3 H, CH₃); IR (CHCl₃) 2968, 2254, 2219, 2070, 1611, 1510, 1294, 1254, 1187, 1111, 994, 831 cm⁻¹; MS *m/e* 330.2466 (calcd for C₂₂H₂₂O₂D₆, *m/e* 330.2466).

2-(*p*-Anisyl)-3-(*p*-hydroxyphenyl)-2,3-dimethylbutane (15). The general procedure of McOmie and West²⁶ was adapted. A solution of boron tribromide (4.6 mL, 12 g, 48 mmol) in 100 mL of dry chloroform was added over 3.5 h to a rapidly stirred solution of 2,3-di(*p*-anisyl)-2,3-dimethylbutane²⁷ (19.6 g, 65.8 mmol) in 1000 mL of dry chloroform, and after 10 h, 1000 mL of 1.6 N hydrochloric acid was added. The phases were separated, the aqueous layer was extracted with ether, and the combined organic extracts were dried and concentrated to give 25 g of a yellow paste. The product was chromatographed (silica gel, 50 cm × 0.53 cm column, packed with 3% ether in hexane) with 6 L of 3% ether in hexane, 10 L of 10% ether, and 4 L of 50% ether, collecting 1-L fractions, giving fractions 2–7 (4.3 g of recovered 2,3-di(*p*-anisyl)-2,3-dimethylbutane, mp 185–190 °C), fractions 9–16 (8.5 g of a yellowish solid, 2-(*p*-anisyl)-3-(*p*-hydroxyphenyl)-2,3-dimethylbutane, mp 115–122 °C), and fractions 17–20 (5.6 g of a yellow solid, mp 195–205 °C, 2,3-bis(*p*-hydroxyphenyl)-2,3-dimethylbutane).

The recovered 2,3-di(*p*-anisyl)-2,3-dimethylbutane was recrystallized from toluene, affording 4.10 g of pure material, mp 188–190 °C (13.8 mmol, 21.0% recovery).

The 2-(*p*-anisyl)-3-(*p*-hydroxyphenyl)-2,3-dimethylbutane was recrystallized from 10:1 hexane–ethyl acetate, giving 7.90 g of pure material (27.8 mmol, 53.5% based on unrecovered starting material) as white crystals, mp 122.0–122.5 °C.

The 2,3-bis(*p*-hydroxyphenyl)-2,3-dimethylbutane was recrystallized from 1:1 hexane–ethyl acetate, affording white, crystalline material (5.20 g, 19.3 mmol, 37.6% based on unrecovered starting material), mp 204–205 °C.

The spectral data for 2-(*p*-anisyl)-3-(*p*-hydroxyphenyl)-2,3-dimethylbutane (**15**) were as follows: H NMR (CDCl₃, 270 MHz) δ 6.950 (d, *J* = 8.9 Hz, 2 H, arom), 6.896 (d, *J* = 8.9 Hz, 2 H, arom), 6.718 (d, *J* = 8.9 Hz, 2 H, arom), 6.639 (d, *J* = 8.9 Hz, 2 H, arom), 4.651 (s, 1 H, OH), 3.790 (s, 3 H, arom OCH₃), 1.270 (s, 6 H, CH₃), 1.266 (s, 6 H, CH₃); IR (CHCl₃) 3598, 3350, 2988, 1611, 1512, 1482, 1465, 1380, 1295, 1250, 1184, 1147, 1037, 833 cm⁻¹; MS *m/e* 284.1778 (calcd for C₁₉H₂₄O₂, *m/e* 284.1776).

Anal. Calcd for C₁₉H₂₄O₂: C, 80.24; H, 8.51. Found: C, 79.98; H, 8.60.

The spectral data for 2,3-bis(*p*-hydroxyphenyl)-2,3-dimethylbutane were as follows: H NMR (CDCl₃, 270 MHz) δ 6.891 (d, *J* = 8.9 Hz, 4 H, arom), 6.638 (d, *J* = 8.9 Hz, 4 H, arom), 4.587 (s, 2 H, OH), 1.264 (s, 12 H, CH₃); IR (CHCl₃) 3600, 3342, 2988, 1615, 1594, 1515, 1380,

1265, 1226, 1217, 1184, 1148, 834 cm⁻¹; MS *m/e* 270.1619 (calcd for C₁₈H₂₂O₂, *m/e* 270.1620).

Anal. Calcd for C₁₈H₂₂O₂: C, 79.95; H, 8.37. Found: C, 79.95; H, 8.49.

3-(*p*-Anisyl)-2,2,3-trimethylbutanoic Acid (16).²⁸ A mixture of 1000 mL of 30% aqueous potassium hydroxide, 50.0 g (316 mmol) of potassium permanganate, 500 mL of high-purity benzene, and 2.0 g (4.6 mmol) of tetrahexylammonium bromide was stirred rapidly under mild reflux as a solution of 6.60 g (23.2 mmol) of 2-(*p*-anisyl)-3-(*p*-hydroxyphenyl)-2,3-dimethylbutane in 60 mL of benzene was added over 30 min. After 18 h of stirring without heating, the mixture was quenched with 100 mL of ethanol, stirred for 1 h, and diluted with 1000 mL of 2 N hydrochloric acid, 200 mL of water, and 1000 mL of ether. The manganese dioxide dissolved during 18 h of stirring, whereupon the aqueous layer was extracted with ether, and the combined extracts afforded 9.4 g of a red, oily solid.

An ethereal solution of the product was extracted with 0.5 N aqueous sodium hydroxide. The extracts were acidified with hydrochloric acid and extracted with ether, these extracts then being dried and concentrated to afford 2.58 g of a yellowish solid. Chromatography (silica gel, 30 cm × 0.37 cm, packed with 3% ether in hexane) with 2 L of 3% ether in hexane and 8 L of 6% ether, collecting 500-mL fractions, gave in fractions 5–18, 1.6 g of nearly pure 3-(*p*-anisyl)-2,2,3-trimethylbutanoic acid (**16**), a yellowish solid, mp 160–165 °C. Recrystallization from 3:1 hexane–ethyl acetate afforded 1.32 g (5.59 mmol, 24.1%) of pure material as colorless plates, mp 165.0–166.0 °C.

The spectral data for 3-(*p*-anisyl)-2,2,3-trimethylbutanoic acid (**16**) were as follows: H NMR (CDCl₃, 270 MHz) δ 11.5–10.5 (broad, 1 H, CO₂H), 7.296 (d, *J* = 8.9 Hz, 2 H, arom), 6.826 (d, *J* = 8.9 Hz, 2 H, arom), 3.796 (s, 3 H, arom OCH₃), 1.467 (s, 6 H, CH₃), 1.095 (s, 6 H, CH₃); IR (CHCl₃) 3017, 2980, 1693, 1612, 1514, 1475, 1467, 1295, 1251, 1216, 1189, 1144, 1035, 833 cm⁻¹; MS *m/e* 236.1412 (calcd for C₁₄H₂₀O₃, *m/e* 236.1412).

Anal. Calcd for C₁₄H₂₀O₃: C, 71.16; H, 8.53. Found: C, 71.43; H, 8.38.

3-(*p*-Anisyl)-2,2,3-trimethylbutan-1-ol (17). A 152-mg sample (644 μmol) of 3-(*p*-anisyl)-2,2,3-trimethylbutanoic acid in 6.0 mL of tetrahydrofuran was added to an ice-cooled slurry of 204 mg (5.38 mmol) of lithium aluminum hydride in 10 mL of tetrahydrofuran. The mixture was stirred for 23 h and then refluxed for 1.5 h, cooled, quenched with a mixture of Celite and magnesium sulfate heptahydrate powder, and filtered through anhydrous magnesium sulfate. Concentration left 148 mg of white 3-(*p*-anisyl)-3,3,4-trimethylbutan-1-ol, mp 58–61 °C, which was recrystallized from pentane to give 139 mg (627 μmol, 97.4%) of pure material as white, fibrous crystals, mp 62.0–62.6 °C.

The spectral data for 3-(*p*-anisyl)-3,3,4-trimethylbutan-1-ol **17** were as follows: H NMR (CDCl₃, 270 MHz) δ 7.306 (d, *J* = 9.1 Hz, 2 H, arom), 6.835 (d, *J* = 9.1 Hz, 2 H, arom), 3.797 (s, 3 H, arom OCH₃), 3.388 (s, 2 H, CH₂OH), 1.354 (s, 6 H, CH₃), 0.940 (s, 1 H, OH), 0.880 (s, 6 H, CH₃); IR (CHCl₃) 3630, 3578, 2980, 1611, 1512, 1466, 1380, 1296, 1251, 1190, 1036, 833 cm⁻¹; MS *m/e* 222.1620 (calcd for C₁₄H₂₂O₂, *m/e* 222.1620).

Anal. Calcd for C₁₄H₂₂O₂: C, 75.63; H, 9.97. Found: C, 75.63; H, 9.93.

3-(*p*-Anisyl)-2,2,3-trimethylbutanal (18). An adaptation of the general method of Corey was used.²⁹ A solution of 1.05 g (4.73 mmol) of 3-(*p*-anisyl)-3,3,4-trimethylbutan-1-ol in 15 mL of dry dichloromethane was added to a slurry of 1.61 g (7.39 mmol) of pyridinium chlorochromate in 40 mL of dry dichloromethane. The dark mixture was stirred for 75 min, diluted to 250 mL with dry ether, stirred for 15 min, and filtered through a pad of Florisil and Celite. The filtrate was concentrated, diluted with ether, and filtered through Florisil to give an off-white solid (1.13 g), mp 68–72 °C, which was recrystallized from hexane, giving 1.05 g (4.73 mmol, 85%) of 3-(*p*-anisyl)-2,2,3-trimethylbutanal as white crystals, mp 71.5–72.5 °C.

The spectral data for 3-(*p*-anisyl)-2,2,3-trimethylbutanal (**18**) were as follows: H NMR (CDCl₃, 270 MHz) δ 9.543 (s, 1 H, CHO), 7.233 (d, *J* = 9.1 Hz, 2 H, arom), 6.842 (d, *J* = 9.1 Hz, 2 H, arom), 3.801 (s, 3 H, arom OCH₃), 1.391 (s, 6 H, CH₃), 0.980 (s, 6 H, CH₃); IR (CHCl₃) 2981, 1716, 1611, 1514, 1466, 1379, 1298, 1252, 1190, 1149, 1036, 833 cm⁻¹; MS *m/e* 220.1462 (calcd for C₁₄H₂₀O₂, *m/e* 220.1463).

Anal. Calcd for C₁₄H₂₀O₂: C, 76.33; H, 9.17. Found: C, 76.23; H, 9.47.

(*E*)- and (*Z*)-1,4-Di(*p*-anisyl)-3,3,4-trimethylpentene (11a and 11b). A slurry of 16.0 g (38.2 mmol) of (*p*-methoxybenzyl)triphenylphosphonium chloride in 250 mL of tetrahydrofuran at 0 °C was treated

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with 24.2 mL of 1.5 M *n*-butyllithium in hexane (36.3 mmol) and stirred for 1 h without cooling. A 1.00-g sample (4.54 mmol) of 3-(*p*-anisyl)-2,2,3-trimethylbutanal in 45 mL of tetrahydrofuran was then added, and the mixture was refluxed for 42 h. A 250-mL portion of solvent was distilled off, and then the remaining deep red solution was diluted to 500-mL volume with hexane and filtered. The filtrate was concentrated, and the residue was triturated with hexane. Concentration left an oily solid, which was triturated with pentane.

The pentane solution afforded 5.3 g of an oily solid, which was chromatographed (silica gel, 33 cm × 3.7 cm) with 1000 mL of 3% ether in hexane, collecting 50-mL fractions, to give fractions 1–9 (a clear oil, *p*-methylanisole) and fractions 10–20 (2.9 g of an oil with solids, a mixture of the (*E*)- and (*Z*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentenes and 4,4'-dimethoxystilbene).

The mixture of olefins was chromatographed on alumina (basic, grade I, 150 cm × 2.7 cm, packed with 0.5% ether in hexane) with 5 L of 0.5% ether in hexane and 8 L of 0.8% ether, collecting 500-mL fractions to give fractions 11–14 (670 mg of a mixture of styrenes and the stilbene) and fractions 15–26 (1.14 g of an oily solid, mainly (*E*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene, which was recrystallized first from toluene and then from 50% ethyl acetate in hexane to afford 498 mg of pure material, mp 147–148 °C).

The combined mother liquors and column fractions 11–14 were separated as above by HPLC, eluting with 1.5% ethyl acetate in hexane, affording 550 mg (1.70 mmol, 37.4% yield) of pure (*Z*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene (**11a**) and 50 mg of slightly impure (*E*)-styrene, which was recrystallized from toluene to afford an additional 41-mg sample of pure material, mp 146–148 °C. The overall yield of (*E*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene (**11b**) was 539 mg (1.66 mmol, 36.6%).

The spectral data for (*Z*)- and (*E*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentenes (**11a** and **11b**) were identical with those of photoproducts A and B, respectively.

Demethylation of (*Z*)-1,4-Di(*p*-anisyl)-3,3,4-trimethylpentene (11a**).** The procedure was based on the method of Chang and Wood.²⁴ A mixture of 350 mg (1.08 mmol) of (*Z*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene, 970 mg (8.66 mmol) of potassium *tert*-butoxide, and 5.5 mL of dry dimethyl sulfoxide was stirred under nitrogen at 135–140 °C for 8.5 h, cooled, diluted with water, acidified, and extracted with ether. Concentration and drying of the extracts afforded 620 mg of a brown oil, which was subjected to thick-layer chromatography, eluting thrice with 30% ether in hexane. Two bands were collected: (1) *R*_f 0.45–0.70, 162 mg of a brown oil, a mixture of impure (*Z*)-4-(*p*-anisyl)-1-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**25**), (*Z*)-1-(*p*-anisyl)-4-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**26**), and (*E*)-4-(*p*-anisyl)-1-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**25-t**); (2) *R*_f 0.05–0.45, 240 mg of a yellow-brown oil, a mixture of (*Z*)-1,4-bis(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**27**) and (*E*)-1,4-bis(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**27-t**).

Fraction 1 was separated by thick-layer chromatography, eluting five times with 15% ether in hexane, to afford one broad band (*R*_f 0.35–0.60), 142 mg of a pale yellow oil, a largely pure mixture of the monophenols. The mixture was separated by HPLC, eluting with 6% ethyl acetate in pentane to afford two peaks: (1-a) 88 mg of a pale yellow oil, RRT 1.00, a mixture of (*Z*)-4-(*p*-anisyl)-1-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene and (*Z*)-1-(*p*-anisyl)-4-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene; (1-b) 53 mg (170 μmol, 16%) of a pale yellow oil, RRT 1.28, pure (*E*)-4-(*p*-anisyl)-1-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**25-t**).

The first band (1-a) was separated by HPLC, eluting with 6% ethyl acetate in pentane, affording two peaks, 41 mg (0.13 mmol, 12%) of pure (*Z*)-4-(*p*-anisyl)-1-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene, RRT 1.00, and 17 mg (55 μmol, 5.1%) of pure (*Z*)-1-(*p*-anisyl)-4-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene, RRT 1.04, as colorless oils.

The mixture of diphenols was separated by HPLC, eluting with 15% ethyl acetate in pentane, to give two peaks, 116 mg (392 μmol, 36.3%) of pure (*Z*)-1,4-bis(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**27**), RRT 1.00, as a pale yellow oil, and 72 mg (0.24 mmol, 22%) of pure (*E*)-1,4-bis(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**27-t**), RRT 1.04, as a pale yellow glass.

The spectral data for (*Z*)-4-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**25**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.283 (d, *J* = 8.9 Hz, 2 H, arom), 6.826 (d, *J* = 8.9 Hz, 2 H, arom), 6.761 (d, *J* = 8.6 Hz, 2 H, arom), 6.650 (d, *J* = 8.6 Hz, 2 H, arom), 6.385 (d, *J* = 12.8 Hz, 1 H, vinyl), 5.547 (d, *J* = 12.8 Hz, 1 H, vinyl), 4.766 (s, 1 H, OH), 3.806 (s, 3 H, arom OCH₃), 1.373 (s, 6 H, CH₃), 0.795 (s, 6 H, CH₃); IR (CHCl₃) 3596, 3360, 2979, 1609, 1511, 1466, 1379, 1295, 1250, 1189, 1169, 1140, 1035, 834 cm⁻¹; MS *m/e* 310.1939 (calcd for C₂₁H₂₆O₂, *m/e* 310.1933).

Anal. Calcd for C₂₁H₂₆O₂: C, 81.25; H, 8.44. Found: C, 81.39; H, 8.63.

The spectral data for (*Z*)-1-(*p*-anisyl)-4-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**26**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.230 (d, *J* = 8.9 Hz, 2 H, arom), 6.825 (d, *J* = 8.9 Hz, 2 H, arom), 6.749 (d, *J* = 8.9 Hz, 2 H, arom), 6.731 (d, *J* = 8.9 Hz, 2 H, arom), 6.403 (d, *J* = 12.8 Hz, 1 H, vinyl), 5.545 (d, *J* = 12.8 Hz, 1 H, vinyl), 4.845 (s, 1 H, OH), 3.775 (s, 3 H, arom OCH₃), 1.366 (s, 6 H, CH₃), 0.791 (s, 6 H, CH₃); IR (CHCl₃) 3597, 3330, 2980, 1610, 1511, 1466, 1294, 1217, 1190, 1170, 1142, 1095, 1036, 834 cm⁻¹; MS *m/e* 310.1936 (calcd for C₂₁H₂₆O₂, *m/e* 310.1933).

Anal. Calcd for C₂₁H₂₆O₂: C, 81.35; H, 8.44. Found: C, 81.67; H, 8.32.

The spectral data for (*E*)-4-(*p*-anisyl)-1-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**25-t**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.254 (d, *J* = 8.9 Hz, 2 H, arom), 7.192 (d, *J* = 8.6 Hz, 2 H, arom), 6.820 (d, *J* = 8.9 Hz, 2 H, arom), 6.765 (d, *J* = 8.6 Hz, 2 H, arom), 6.147 (d, *J* = 16.4 Hz, 1 H, vinyl), 6.000 (d, *J* = 16.4 Hz, 1 H, vinyl), 5.329 (s, 1 H, OH), 3.806 (s, 3 H, arom OCH₃), 1.346 (s, 6 H, CH₃), 1.005 (s, 6 H, CH₃); IR (CHCl₃) 3594, 3335, 2978, 1610, 1513, 1251, 1173, 1037, 981, 833 cm⁻¹; MS *m/e* 310.1626 (calcd for C₂₁H₂₆O₂, *m/e* 310.1933).

Anal. Calcd for C₂₁H₂₆O₂: C, 81.25; H, 8.44. Found: C, 81.39; H, 8.63.

The spectral data for (*Z*)-1,4-bis(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**27**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.234 (d, *J* = 8.9 Hz, 2 H, arom), 6.768 (d, *J* = 8.6 Hz, 2 H, arom), 6.749 (d, *J* = 8.9 Hz, 2 H, arom), 6.656 (d, *J* = 8.6 Hz, 2 H, arom), 6.387 (d, *J* = 12.8 Hz, 1 H, vinyl), 5.544 (d, *J* = 12.8 Hz, 1 H, vinyl), 4.732 (s, 1 H, OH), 4.712 (s, 1 H, OH), 1.365 (s, 6 H, CH₃), 0.789 (s, 6 H, CH₃); IR (CHCl₃) 3597, 3324, 2979, 1611, 1512, 1379, 1260, 1213, 1182, 1168, 1140, 1100, 834 cm⁻¹; MS *m/e* 296.1776 (calcd for C₂₀H₂₄O₂, *m/e* 296.1776).

Anal. Calcd for C₂₀H₂₄O₂: C, 80.02; H, 8.16. Found: C, 79.64; H, 8.19.

The spectral data for (*E*)-1,4-bis(*p*-hydroxyphenyl)-3,3,4-trimethylpentene (**27-t**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.204 (d, *J* = 8.9 Hz, 4 H, arom), 6.770 (d, *J* = 8.6 Hz, 2 H, arom), 6.744 (d, *J* = 8.9 Hz, 2 H, arom), 6.143 (d, *J* = 16.3 Hz, 1 H, vinyl), 5.991 (d, *J* = 16.3 Hz, 1 H, vinyl), 4.710 (s, 1 H, OH), 4.626 (s, 1 H, OH), 1.341 (s, 6 H, CH₃), 1.006 (s, 6 H, CH₃); IR (CHCl₃) 3597, 3320, 3021, 2982, 1611, 1513, 1260, 1218, 1183, 1171, 982, 833 cm⁻¹; MS *m/e* 296.1776 (calcd for C₂₀H₂₄O₂, *m/e* 296.1776).

Anal. Calcd for C₂₀H₂₄O₂: C, 80.74; H, 8.16. Found: C, 81.04; H, 8.35.

(*Z*)-1,4-Bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (A-D6). The reaction was run according to the general procedure above for trideuteriomethylation of phenols, utilizing 70.0 mg (1.45 mmol NaH) of 50% NaH oil dispersion, 31.0 mg (100 μmol) of (*Z*)-1,4-bis(*p*-hydroxyphenyl)-3,3,4-trimethylpentene, 800 μL of tetrahydrofuran, and 150 μL (342 mg, 2.35 mmol) of trideuteriomethyl iodide. Workup afforded 32 mg of a yellow oil, and thick-layer chromatography, eluting once with 20% ether in hexane, gave 31 mg of a colorless oil, a mixture of (*Z*)- and (*E*)-1,4-bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentenes (**A-D6** and **B-D6**, respectively).

Separation by HPLC, eluting with 0.5% ethyl acetate in pentane gave two peaks: (1) 26.4 mg (80.0 μmol, 80.0%) of (*Z*)-1,4-bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (**A-D6**), RRT 1.12,¹⁸ as a colorless oil; (2) 0.8 mg of (*E*)-1,4-bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (**B-D6**), RRT 1.43, which was recrystallized from hexane–ethyl acetate to afford 0.7 mg (2 μmol, 2%) of pure material as white crystals, mp 148–149 °C.

The spectral data for (*Z*)-1,4-bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (**A-D6**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.289 (d, *J* = 9.2 Hz, 2 H, arom), 6.827 (d, *J* = 9.0 Hz, 4 H, arom), 6.728 (d, *J* = 8.8 Hz, 2 H, arom), 6.408 (d, *J* = 12.7 Hz, 1 H, vinyl), 5.548 (d, *J* = 12.7 Hz, 1 H, vinyl), 1.379 (s, 6 H, CH₃), 0.796 (s, 6 H, CH₃); IR (CHCl₃) 2978, 2256, 2223, 2072, 1608, 1509, 1292, 1254, 1223, 1190, 1142, 1111, 1090, 995, 833 cm⁻¹; MS *m/e* 330.2467 (calcd for C₂₂H₂₂O₂D₆, *m/e* 330.2466).

The spectral data for (*E*)-1,4-bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (**B-D6**) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.259 (d, *J* = 8.9 Hz, 2 H, arom), 7.253 (d, *J* = 8.9 Hz, 2 H, arom), 6.845 (d, *J* = 8.9 Hz, 2 H, arom), 6.819 (d, *J* = 8.9 Hz, 2 H, arom), 6.165 (d, *J* = 16.4 Hz, 1 H, vinyl), 6.015 (d, *J* = 16.4 Hz, 1 H, vinyl), 1.351 (s, 6 H, CH₃), 1.013 (s, 6 H, CH₃); IR (CHCl₃) 2978, 2257, 2224, 2070, 1609, 1510, 1280, 1256, 1222, 1189, 1110, 994, 831 cm⁻¹; MS *m/e* 330.2474 (calcd for C₂₂H₂₂O₂D₂, *m/e* 330.2466).

(*E*)-1,4-Bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (B-D6). The reaction was run according to the general procedure above for trideuteriomethylation of phenols, utilizing 68.0 mg (1.42 mmol NaH) of 50% NaH oil dispersion, 30.0 mg (101 μmol) of (*E*)-1,4-bis-

(*p*-hydroxyphenyl)-3,3,4-trimethylpentene, 750 μ L of tetrahydrofuran, and 130 μ L (297 mg, 2.05 mmol) of trideuteriomethyl iodide. Workup afforded 32 mg of a yellow oil, and thick-layer chromatography, eluting once with 20% ether in hexane, gave 31 mg of a yellowish, oily solid, a mixture of (*Z*)- and (*E*)-1,4-bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentenes. Recrystallization from heptane–ethyl acetate (0 °C) gave 25.0 mg of the pure *E* isomer, mp 147–148 °C. The filtrates were concentrated and the residue was separated by HPLC, eluting with 0.5% ethyl acetate in pentane, giving (1) 2.0 mg (6.1 μ mol, 6.0%) of pure (*Z*)-1,4-bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene, a colorless oil; and (2) 2.5 mg of the pure *E* isomer as a white solid, mp 147–148 °C. The total yield of (*E*)-1,4-bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene was 27.5 mg (83.3 μ mol, 82.5%).

(*Z*)-1-(*p*-(Trideuteriomethoxy)phenyl)-4-(*p*-anisyl)-3,3,4-trimethylpentene (A-D3-1). The reaction was run according to the general procedure above for trideuteriomethylation of phenols, utilizing 35 mg (0.73 mmol NaH) of 50% NaH oil dispersion, 31.0 mg (100 μ mol) of (*Z*)-4-(*p*-anisyl)-1-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene, 650 μ L of tetrahydrofuran, and 60 μ L (0.14 g, 0.94 mmol) of trideuteriomethyl iodide. Workup afforded 35.2 mg of a yellowish oil, and thick-layer chromatography, eluting once with 20% ether in hexane, gave 34.0 mg of a colorless oil, mainly (*Z*)-1-(*p*-(trideuteriomethoxy)phenyl)-4-(*p*-anisyl)-3,3,4-trimethylpentene (A-D3-1), with a small amount of (*Z*)-1-(*p*-(trideuteriomethoxy)phenyl)-4-(*p*-anisyl)-3,3,4-trimethylpentene (B-D3-1). Separation of the mixture by HPLC, eluting with 0.5% ethyl acetate in pentane, gave two peaks: (1) 26.3 mg (80.4 μ mol, 80.4%) of pure (*Z*)-1-(*p*-(trideuteriomethoxy)phenyl)-4-(*p*-anisyl)-3,3,4-trimethylpentene, RRT 1.08,¹⁸ as a colorless oil; (2) 3.6 mg (11 μ mol, 11%) of pure (*E*)-4-(*p*-anisyl)-1-(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (B-D3-1), RRT 1.37, as a white solid, mp 147–148 °C.

The spectral data for (*Z*)-1-(*p*-(trideuteriomethoxy)phenyl)-4-(*p*-anisyl)-3,3,4-trimethylpentene (A-D3-1) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.289 (d, *J* = 9.2 Hz, 2 H, arom), 6.827 (d, *J* = 9.0 Hz, 4 H, arom), 6.728 (d, *J* = 8.8 Hz, 2 H, arom), 6.408 (d, *J* = 12.7 Hz, 1 H, vinyl), 5.548 (d, *J* = 12.7 Hz, 1 H, vinyl), 3.808 (s, 3 H, arom OCH₃), 1.379 (s, 6 H, CH₃); IR (CHCl₃) 2978, 2256, 2223, 2072, 1606, 1508, 1466, 1293, 1277, 1251, 1222, 1189, 1140, 1110, 1034, 832 cm⁻¹; MS *m/e* 327.2278 (calcd for C₂₂H₂₅O₂D₃, *m/e* 327.2277).

The spectral data for (*E*)-4-(*p*-anisyl)-1-(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (B-D3-1) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.259 (d, *J* = 8.9 Hz, 2 H, arom), 7.253 (d, *J* = 8.9 Hz, 2 H, arom), 6.845 (d, *J* = 8.9 Hz, 2 H, arom), 6.819 (d, *J* = 8.9 Hz, 2 H, arom), 6.165 (d, *J* = 16.4 Hz, 1 H, vinyl), 6.015 (d, *J* = 16.4 Hz, 1 H, vinyl), 3.810 (s, 3 H, arom OCH₃), 1.351 (s, 6 H, CH₃), 1.013 (s, 3 H, CH₃); IR (CHCl₃) 2971, 2257, 2220, 2071, 1606, 1510, 1280, 1250, 1218, 1188, 1109, 1033, 831 cm⁻¹; MS *m/e* 327.2277 (calcd for C₂₂H₂₅O₂D₃, *m/e* 327.2277).

(*Z*)-1-(*p*-Anisyl)-4-(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpent-1-ene (A-D3-2). The reaction was run according to the general procedure above for trideuteriomethylation of phenols, utilizing 25.0 mg (520 μ mol NaH) of 50% NaH oil dispersion, 36.0 mg (116 μ mol) of (*Z*)-1-(*p*-anisyl)-4-(*p*-hydroxyphenyl)-3,3,4-trimethylpentene, 700 μ L of tetrahydrofuran, and 50 μ L (0.11 g, 0.79 mmol) of trideuteriomethyl iodide. Workup afforded 35 mg of a yellowish oil, and thick-layer chromatography, eluting once with 20% ether in hexane, gave 35 mg of a colorless oil, mainly (*Z*)-1-(*p*-anisyl)-4-(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (A-D3-2), with a small amount of (*E*)-4-(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (B-D3-1). Separation of the mixture by HPLC, eluting with 0.5% ethyl acetate in pentane gave two peaks: (1) 33.2 (102 μ mol, 88.0%) mg of pure (*Z*)-1-(*p*-anisyl)-4-(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene, RRT 1.08,¹⁸ a colorless oil; (2) 1.4 mg (4.3 μ mol, 3.7%) of pure (*E*)-4-(*p*-anisyl)-1-(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene, RRT 1.37, as a white solid, mp 147–149 °C.

The spectral data for (*Z*)-1-(*p*-anisyl)-4-(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (A-D3-2) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.289 (d, *J* = 9.2 Hz, 2 H, arom), 6.827 (d, *J* = 9.0 Hz, 4 H, arom), 6.728 (d, *J* = 8.8 Hz, 2 H, arom), 6.408 (d, *J* = 12.7 Hz, 1 H, vinyl), 5.548 (d, *J* = 12.7 Hz, 1 H, vinyl), 3.780 (s, 3 H, arom OCH₃), 1.379 (s, 6 H, CH₃), 1.379 (s, 6 H, CH₃); IR (CHCl₃) 2978, 2257, 2223, 2072, 1609, 1510, 1468, 1292, 1248, 1191, 1174, 1112, 1034, 995, 832 cm⁻¹; MS *m/e* 327.2278 (calcd for C₂₂H₂₅O₂D₃, *m/e* 327.2277).

Separation of a Mixture of Deuteriated and Nondeuteriated (*Z*)-1,4-Di(*p*-anisyl)-3,3,4-trimethylpentenes A-D0, A-D3, and A-D6. A mixture of 2.5 mg (7.7 μ mol) of (*Z*)-1,4-di(*p*-anisyl)-3,3,4-trimethylpentene (A-D0), 2.0 mg (6.6 μ mol) of (*Z*)-1-(*p*-(trideuteriomethoxy)phenyl)-4-(*p*-anisyl)-3,3,4-trimethylpentene (A-D3-1), and 1.5 mg (4.5 μ mol) of (*Z*)-1,4-bis(*p*-(trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (A-D6) was subjected to HPLC separation, eluting with 0.5% ethyl acetate

in pentane, affording three peaks, in order of elution: (1) 2.5 mg of pure A-D0, RRT 1.04;¹⁸ (2) 2.0 mg of pure A-D3-1, RRT 1.08; (3) 1.5 mg of pure A-D6, RRT 1.12.

1,2-Di(*p*-anisyl)-2-methylpropanone (20). A solution of (*p*-methoxyphenyl)magnesium bromide was prepared from 3.75 g (150 mmol) of magnesium turnings and 16.5 mL (24.8 g, 132 mmol) of *p*-bromoanisole in 500 mL of anhydrous ether. A solution of 20.0 g (114 mmol) of 2-(*p*-anisyl)-2-methylpropionitrile in 50 mL of ether was added to the rapidly stirred mixture, which was then stirred under reflux for 3.5 h. The tan slurry was quenched with 250 mL of water and filtered through Celite. The aqueous layer was extracted with ether, and concentration of the organic extracts gave an orange oil. The crude imine, used without purification, was dissolved in 300 mL of ethanol, 100 mL of water, and 25 mL of concentrated sulfuric acid. After 24 h, the solution was poured into 1000 mL of water and extracted with ether, and the extracts were washed with water and saturated aqueous sodium carbonate solution, dried, and concentrated to afford 37 g of a dark oil, impure 1,2-di(*p*-anisyl)-2-methylpropanone (20).

The crude ketone was chromatographed on a silica gel column (38 cm \times 0.47 cm) with 3750 mL of 5% ether in hexane, collecting 250-mL fractions, to give fractions 1–4 (anisole and *p*-bromoanisole) and fractions 5–15 (30 g of yellow, impure ketone). Distillation of the ketone under reduced pressure gave fraction 1 (4.5 g (26 mmol, 23% recovery) of pure recovered nitrile (105–110 °C, 1.00–1.05 Torr), fraction 2 (0.7 g of a white solid and a colorless oil (185–190 °C, 1.20–1.25 Torr), and fraction 3 (24 g of the ketone (190–193 °C, 1.20–1.25 Torr) as a white solid, mp 59–61 °C). Recrystallization of the ketone from ether (–20 °C) gave 22.9 g (80.6 mmol, 91.3% yield based on unrecovered nitrile) of pure material.

The spectral data for 1,2-di(*p*-anisyl)-2-methylpropanone (20) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.552 (d, *J* = 9.2 Hz, 2 H, arom), 7.213 (d, *J* = 8.9 Hz, 2 H, arom), 6.876 (d, *J* = 8.9 Hz, 2 H, arom), 6.715 (d, *J* = 9.2 Hz, 2 H, arom), 3.798 (s, 3 H, arom OCH₃), 3.769 (s, 3 H, arom OCH₃), 1.573 (s, 6 H, CH₃); IR (CHCl₃) 3012, 1667, 1601, 1513, 1465, 1253, 1186, 1165, 1148, 1043, 978, 843, 833 cm⁻¹; MS *m/e* 284.1410 (calcd for C₁₈H₂₀O₃, *m/e* 284.1412).

Anal. Calcd for C₁₈H₂₀O₃: C, 76.03; H, 7.09. Found: C, 76.11; H, 7.06.

4,5-Di(*p*-anisyl)-2,5-dimethylhex-2-en-3-ol (21). A solution of isobutenylmagnesium bromide³⁰ was prepared by addition with stirring of a solution of 12.0 mL (16.4 g, 122 mmol) of isobutenyl bromide in 175 mL of tetrahydrofuran to a mildly refluxing slurry of 3.20 g (132 mmol) of magnesium powder in 10 mL of tetrahydrofuran over 3 h. The solution was refluxed 7 h, then cooled by ice bath, and treated with a solution of 6.65 g (23.4 mmol) of 1,2-di(*p*-anisyl)-2-propanone in 25 mL of tetrahydrofuran over 20 min. After 10 h, the mixture was quenched with water, filtered through Celite, and extracted with ether, and concentration of the dried extracts gave 8.8 g of a pale yellow oil.

Column chromatography of the crude alcohol (silica gel, 105 cm \times 0.37 cm) with 5000 mL of 3% ether in hexane, collecting 500-mL fractions, gave fractions 4–10 (7.21 g of 4,5-di(*p*-anisyl)-2,5-dimethylhex-2-en-3-ol (21) as a colorless oil). The alcohol was crystallized from pentane to afford 5.99 g (17.7 mmol, 75.6% yield) of pure material as a white solid, mp 68.0–69.0 °C.

The spectral data for 4,5-di(*p*-anisyl)-2,5-dimethylhex-2-en-3-ol (21) were as follows: H NMR (CDCl₃, 270 MHz) δ 7.227 (d, *J* = 8.9 Hz, 2 H, arom), 7.131 (d, *J* = 8.9 Hz, 4 H, arom), 6.797 (d, *J* = 8.9 Hz, 2 H, arom), 6.735 (d, *J* = 8.9 Hz, 2 H, arom), 5.976 (m, *J* = 1.2 Hz, 1 H, vinyl), 3.803 (s, 6 H, arom OCH₃), 1.828 (s, 1 H, OH), 1.660 (d, *J* = 1.2 Hz, 3 H, CH₃), 1.322 (s, 3 H, CH₃), 1.270 (d, *J* = 1.2 Hz, 3 H, CH₃), 1.257 (s, 3 H, CH₃); IR (CHCl₃) 3600, 3009, 1610, 1512, 1467, 1296, 1250, 1184, 1035, 834 cm⁻¹; MS *m/e* 340.2038 (calcd for C₂₂H₂₈O₃, *m/e* 340.2038).

Anal. Calcd for C₂₂H₂₈O₃: C, 77.61; H, 8.29. Found: C, 77.74; H, 8.37.

4,5-Di(*p*-anisyl)-2,5-dimethyl-4-methoxyhex-2-ene (22).²⁵ A 7.5-g sample of 50% NaH oil dispersion (0.16 mol of NaH) was freed of oil by ether washing and stirred in 40 mL of tetrahydrofuran, and a solution of 4,5-di(*p*-anisyl)-2,5-dimethylhex-2-en-3-ol (5.00 g, 14.7 mmol) in 40 mL of tetrahydrofuran was added, followed by 9.5 mL (24 g, 0.17 mol) of iodomethane. The mixture was refluxed for 7 h, then 6.0 mL (15 g, 0.11 mmol) sample of iodomethane was added, and after 12 h, the white slurry was cooled and concentrated to 40-mL volume under reduced pressure. Dilution with pentane, filtration, and concentration of the solution gave a cloudy oil, which was dissolved in pentane, and the solution was filtered and concentrated to give 5.5 g of a colorless oil.

(30) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* 1979, 44, 2331–2345.

Table IV. Summary of Quantum Yield Results for *trans*-1-(*p*-Anisyl)-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane

run	reactant 8, μmol	light abs, μE	prod 11a		prod 11b		prod 12		prod 13	
			μmol	ϕ	μmol	ϕ	μmol	ϕ	μmol	ϕ
1	79.6	24.0	1.5	0.063	0.68	0.028	0.95	0.040	1.2	0.050
2	94.4	33.3	3.0	0.091	0.37	0.011	1.3	0.040	1.8	0.055
3	77.8	39.3	1.9	0.047	0.96	0.025	1.5	0.038	1.6	0.040
4	81.1	48.9	2.7	0.055	1.2	0.025	1.9	0.040	2.1	0.043
5	78.3	66.4	3.8	0.058	1.1	0.017	2.7	0.041	2.7	0.041
6	80.5	88.7	5.6	0.063	1.2	0.014	3.3	0.037	3.9	0.043

Column chromatography (silica gel, 70 cm \times 0.37 cm) with 2500 mL of 0% ether in hexane, 1000 mL of 1% ether, and 2500 mL of 2% ether, collecting 500-mL fractions, gave fractions 9–13 (4.62 g (13.1 mmol, 89%) of 4,5-di(*p*-anisyl)-2,5-dimethyl-4-methoxyhex-2-ene (**22**) as a clear, colorless oil.

The spectral data for 4,5-di(*p*-anisyl)-2,5-dimethyl-4-methoxyhex-2-ene (**22**) were as follows: H NMR (CDCl_3 , 270 MHz) δ 7.083 (d, J = 8.9 Hz, 2 H, arom), 6.968 (d, J = 8.9 Hz, 4 H, arom), 6.710 (d, J = 8.9 Hz, 2 H, arom), 6.695 (d, J = 8.9 Hz, 2 H, arom), 5.600 (m, J = 1.2 Hz, 1 H, vinyl), 3.788 (s, 3 H, arom OCH_3), 3.785 (s, 3 H, arom OCH_3), 2.983 (s, 3 H, OCH_3), 1.791 (d, J = 1.2 Hz, 3 H, CH_3), 1.386 (d, J = 0.9 Hz, 3 H, CH_3), 1.282 (s, 3 H, CH_3), 1.242 (s, 3 H, CH_3); IR (CHCl_3) 3008, 2936, 1612, 1512, 1468, 1444, 1384, 1363, 1300, 1252, 1221, 1185, 1072, 1038, 835 cm^{-1} ; MS m/e 354.2239 (calcd for $\text{C}_{23}\text{H}_{30}\text{O}_3$, m/e 354.2238).

Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{O}_3$: C, 77.93; H, 8.53. Found: C, 77.70; H, 8.62.

4,5-Di(*p*-anisyl)-2,5-dimethylhex-2-ene (12**).**³¹ A 450- μL (418 mg, 6.73 mmol) sample of 1:1 sodium-potassium alloy was added by syringe to a solution of 146 mg (412 mmol) of 4,5-di(*p*-anisyl)-2,5-dimethyl-4-methoxyhex-2-ene in 4.0 mL of tetrahydrofuran. The mixture was stirred rapidly for 4 h, turning deep burgundy red, and then quenched by cautious addition of 3.0 mL of a 1:1 mixture of ethanol and tetrahydrofuran. The solution was removed from the remaining metal, diluted with water, and extracted with ether. Concentration of the dried extracts gave 230 mg of a yellow oil. Column chromatography (silica gel, 100 cm \times 0.27 cm) with 14 L of 0.5% ether in hexane, collecting 500-mL fractions, gave fractions 18–28 (120 mg (370 μmol , 89.8%) of pure 4,5-di(*p*-anisyl)-2,5-dimethylhex-2-ene (**12**) as a colorless oil). The spectral data were identical with those of the authentic photoproduct C.

Oxidation of 4-(*p*-Anisyl)-2-methyl-3-(*p*-methoxycumenyl)but-1-ene (13**).**⁷ A solution of 25.0 mg (77.2 μmol) of 4-(*p*-anisyl)-2-methyl-3-(*p*-methoxycumenyl)but-1-ene (photoproduct D) in 1.00 mL of dioxane and 350 μL of water was reacted with 0.5 mg, 2 μmol of osmium tetroxide for 25 min, and then 110 mg (514 μmol) of sodium metaperiodate was added to the brown mixture. The mixture was stirred for 40 h, at which time the yellow slurry was extracted with water and ether. Concentration of the dried extracts gave a dark green oil. Thick-layer chromatography, eluting once with 10% ether in hexane and once with 16% ether, gave two mobile bands: (1) 1.6 mg (4.9 μmol , 6.8%) of recovered 4-(*p*-anisyl)-2-methyl-3-(*p*-methoxycumenyl)but-1-ene (R_f 0.56); (2) 17.0 mg of a white solid, 3-(*p*-methoxybenzyl)-4-(*p*-anisyl)-4-methylpentan-2-one (R_f 0.27).

The 3-(*p*-anisylmethyl)-4-(*p*-anisyl)-4-methylpentan-2-one was recrystallized from ethanol, affording 16.7 mg (51.3 μmol , 71.2% based on unrecovered D) of pure material as white crystals, mp 108.5–109.0 $^\circ\text{C}$. The IR spectrum showed a strong absorption at 1705 cm^{-1} , indicative of a saturated ketone function. The structure of the ketone was determined by single-crystal X-ray diffraction analysis (vide infra).^{6,22}

The spectral data for 3-(*p*-methoxybenzyl)-4-(*p*-anisyl)-4-methylpentan-2-one (**23**) were as follows: H NMR (CDCl_3 , 270 MHz) δ 7.321 (d, J = 8.9 Hz, 2 H, arom), 6.909 (d, J = 8.9 Hz, 4 H, arom), 6.874 (d, J = 8.9 Hz, 2 H, arom), 6.739 (d, J = 8.9 Hz, 2 H, arom), 3.804 (s, 3 H, arom OCH_3), 3.745 (s, 3 H, arom OCH_3), 3.102 (d of d, J = 2.7 Hz, 11.7 Hz, 1 H, CHCHH), 2.822 (d of d, J = 12.8 Hz, 11.9 Hz, 1 H, CHCHH), 2.509 (d of d, J = 2.4 Hz, 12.1 Hz, 1 H, CHCHH), 1.471 (s, 3 H, CH_3), 1.388 (s, 3 H, CH_3); IR (CHCl_3) 3011, 1704, 1612, 1513, 1250, 1180, 1029, 833, 750 cm^{-1} ; MS m/e 326.1868 (calcd for $\text{C}_{21}\text{H}_{26}\text{O}_3$, m/e 326.1882).

Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_3$: C, 77.27; H, 8.03. Found: C, 77.03; H, 8.02.

Crossover Experiment. Cophotolysis of *trans*-1-(*p*-Anisyl)-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane (**8-D0**) and 2,2-Dimethyl-3-(*p*-trideuteriomethoxy)cumenyl)-1-(*p*-trideuteriomethoxy)phenyl)-cyclopropane (**8-D6**). A solution of 55.2 mg (170 μmol) of **8-D0** and 56.4

mg (171 μmol) of **8-D6** in 8.5 mL of *tert*-butyl alcohol was irradiated for 180 min with a 450-W Hanovia medium-pressure mercury lamp through Corex in the apparatus for small-volume irradiations described above, and concentration afforded 111 mg of a pale yellow oil. Thick-layer chromatography, eluting once with 20% ether in hexane gave one band, 109 mg of a colorless oil. The mixture was separated by recycling HPLC, eluting with 0.5% ethyl acetate in pentane, and the resulting fractions were subjected to further careful separation by HPLC. The process was repeated until sufficient separation of components had been effected to allow analysis of the fractions by 270-MHz proton NMR to determine their compositions. The yields of the components, in order of elution, were as follows: **8-D0** (15.9 mg, 14.7%), **A-D0** (16.0 mg, 14.8%), **E-D0** (0.35 mg, 0.52%), **A-D3** (1.46 mg, 1.34%), **8-D6** (15.0 mg, 13.6%), **E-D3 + E-D6** (1.39 mg, 2.0%), **A-D6** (16.0 mg, 14.5%), **C-D0** (8.16 mg, 7.55%), **C-D3** (0.77 mg, 0.71%), **C-D6** (8.45 mg, 7.67%), **D-D0** (9.52 mg, 8.81%), **B-D0** (0.56 mg, 0.51%), **D-D6** (9.73 mg, 8.84%), and **B-D6** (0.55 mg, 0.50%).

The yield of "crossover" products **A-D3** was 4.4% of the total yield of product **A** (d_0 , d_3 , and d_6). Likewise, the yield of "crossover" products **C-D3** was 4.4% of the total yield of **C**.

Reactivity of Photoproducts on Direct Irradiation. Control Runs. Run A. Cophotolysis of (*Z*)-1,4-Di(*p*-anisyl)-3,3,4-trimethylpentene (A-D0**) and (*Z*)-1,4-Bis(*p*-trideuteriomethoxy)phenyl)-3,3,4-trimethylpentene (**A-D6**).** A solution of 15.4 mg (47.5 μmol) of **A-D0** and 15.6 mg (47.3 μmol) of **A-D6** in 8.5 mL of *tert*-butyl alcohol was irradiated through Corex for 180 min with a 450-W Hanovia medium-pressure mercury lamp in the apparatus for small-volume irradiations described above and then concentrated to afford 31.3 mg of an oil. Thick-layer chromatography, eluting once with 20% ether in hexane, gave a single band, 31.0 mg of a colorless oil. Analysis by proton NMR showed that the mixture contained 96.0% of recovered (*Z*)-styrenes (**A**) but also approximately 2.5% of the (*E*)-styrenes (**B**) and 1.2% of the photoproducts **C**. Separation of the (*Z*)-styrenes from the *E* isomers was effected by HPLC. The mixture of (*Z*)-styrenes was then subjected to careful separation by recycling HPLC, affording two large peaks, corresponding to **A-D0** and **A-D6**, in order of elution, with some overlap. Since the peak for potential crossover products **A-D3** should have fallen in the region of overlap of **A-D0** and **A-D6**, the overlap region was collected and concentrated and subjected to further HPLC separation, affording two peaks, **A-D0** and **A-D6**, without any evidence for a peak corresponding to the crossover products **A-D3**. Since concentrations of **A-D3** on the order of 0.5% would have been easily detectable, the yield of crossover products **A-D3** was less than 0.5%. The isolated yields of the products were **A-D0** (14.0 mg), **A-D6** (14.4 mg), and **B-D0/B-D6** (0.4 mg).

Reactivity of Photoproducts on Direct Irradiation. Control Runs. Run B. 4,5-Di(*p*-anisyl)-2,5-dimethylhex-2-ene (12**).** A solution of 16.0 mg (49.4 μmol) of 4,5-di(*p*-anisyl)-2,5-dimethylhex-2-ene (photoproduct C) in 8.5 mL of *tert*-butyl alcohol was irradiated with a 450-W Hanovia lamp for 180 min through Corex in the apparatus for small-volume irradiations described above. The solution was concentrated to afford a colorless oil (16.1 mg). The proton NMR spectrum showed pure recovered starting material, with no detectable rearrangement products.

Reactivity of Photoproducts on Direct Irradiation. Control Runs. Run C. 4-(*p*-Anisyl)-2-methyl-3-(*p*-methoxycumenyl)but-1-ene (13**).** A solution of 17.5 mg (54.0 μmol) of 4-(*p*-anisyl)-2-methyl-3-(*p*-methoxycumenyl)but-1-ene (photoproduct D) in 8.5 mL of *tert*-butyl alcohol was irradiated with a 450-W Hanovia lamp for 180 min through Corex in the apparatus for small-volume irradiations described above, and the solution was concentrated to afford 17.6 mg of a colorless oil. The proton NMR spectrum showed pure recovered starting material, with no detectable rearrangement products.

Summary of Direct Quantum Yield Results for *trans*-1-(*p*-Anisyl)-2-(*p*-methoxycumenyl)-3,3-dimethylcyclopropane (8**).** The quantum yield measurements were performed on the microbench apparatus⁸ in 40 or 50 mL of *tert*-butyl alcohol using 289-nm light. Photolyses employed an Osram HBO 200-W high-pressure mercury lamp and a Bausch and Lomb Model 33-86-79 monochromator having a 5.4-mm entrance slit and a 3.0-mm exit slit, providing a 22-nm half-height bandwidth. Light

(31) Ziegler, K.; Schnell, B. *Ann.* 1924, 437, 227.

output was measured by digital electronic actinometry,⁹ and all runs were calibrated with ferrioxalate actinometry.⁹ The photolysis solutions were purged with purified nitrogen for 1 h before and during irradiation. Workup consisted of concentration of the photolysate, addition of *o*-benzyl as an internal NMR integration standard, and analysis in CDCl₃ solution by 270-MHz proton NMR to determine the relative quantities of the photoproducts. The results are summarized in Table IV.

Single-Crystal X-ray Structure Determinations. General Procedure.⁶ Crystals suitable for analysis were prepared by slow crystallization from appropriate solvents. Preliminary examinations and collection of data were carried out on a Syntex-Nicolet P₁ diffractometer, equipped with a graphite monochromated Mo K α radiation source. The structures were solved by direct methods using the MULTAN80⁶ package, employing full-matrix least-squares refinement, and hydrogen atoms were located from difference Fourier syntheses. The final cycles of the least-squares refinement assumed the non-hydrogen atoms to vibrate anisotropically and the hydrogen atoms to vibrate isotropically. Final electron density difference maps showed no significant features. All calculations were performed with a Digital Equipment VAX 11/750.

Single-Crystal X-ray Structure of (*E*)-2,5-Di(*p*-anisyl)-2,5-dimethylhexene (5a).²² Crystals of (*E*)-2,5-di(*p*-anisyl)-2,5-dimethylhexene were prepared by slow crystallization from pentane. Unit cell parameters were obtained by least-squares refinement of 25 reflections (26.6° > 2 θ > 4.31°). Data were collected in the range 7 > *h* > -7, 10 > *k* > 0, 21 > *l* > 0, with 4 reflections monitored every 50 with no significant intensity variation, 1372 unique data, 1172 with *F* > 3 σ (*F*). Lorentz and polarization corrections were applied and the structure was solved under *P*₂/*c* symmetry. Refinement of 165 parameters converged to *R*₁(*F*) = 0.049 and *R*_w(*F*) = 0.063. The results and structural parameters are available as supplementary material.

Single-Crystal X-ray Structure of *trans*-1-(*p*-Anisyl)-2,2-dimethyl-3-(*p*-methoxycumenyl)cyclopropane (8).²² Crystals of *trans*-1-(*p*-anisyl)-2,2-dimethyl-3-(*p*-methoxycumenyl)cyclopropane were prepared

by slow crystallization from pentane. Unit cell parameters were obtained by least-squares refinement of 25 reflections (35.7° > 2 θ > 18.2°). Data were collected in the range 14 > *h* > 0, 14 > *k* > 0, 23 > *l* > 0, with 4 reflections monitored every 50 with no significant intensity variation, 2198 unique data, 1144 with *F* > 3 σ (*F*). Lorentz and polarization corrections were applied and the structure was solved under PNA2₁ symmetry. Refinement of 329 parameters converged to *R*₁(*F*) = 0.043 and *R*_w(*F*) = 0.050. The results and structural parameters are available as supplementary material.

Single-Crystal X-ray Structure of 4-(*p*-Anisyl)-3-(*p*-methoxybenzyl)-4-methylpentanone (23).²² Crystals of 4-(*p*-anisyl)-3-(*p*-methoxybenzyl)-4-methylpentanone were prepared by slow crystallization from ethanol. Unit cell parameters were obtained by least-squares refinement of 25 reflections (15.9° > 2 θ > 3.5°). Data were collected in the range 5 > *h* > 0, 15 > *k* > 0, 26 > *l* > 0, with 4 reflections monitored every 50 with no significant intensity variation, 1250 unique data, 768 with *F* > 3 σ (*F*). Lorentz and polarization corrections were applied and the structure was solved under PBCA symmetry. Refinement of 217 parameters converged to *R*₁(*F*) = 0.051 and *R*_w(*F*) = 0.033. The results and structural parameters are available as Supplementary Material.

Acknowledgment. Support of this research by the National Science Foundation and by NIH Grant GM07487 is gratefully acknowledged. NSF supported the mechanistic aspects while NIH support was used for the synthetic aspects.

Supplementary Material Available: Crystal data and collection parameters, positional parameters, interatomic distances, bond angles, anisotropic and isotropic temperature factors, and ORTEP drawings of 5a, 8, and 23 (19 pages). Ordering information is given on any current masthead page.

Stereochemistry of Substitution of Good Nucleofuges at the Stereoconvergence Region as a Tool for Investigating the Rapid Step of Nucleophilic Vinylic Substitution¹

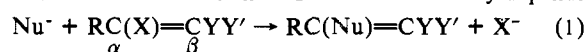
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Revised Manuscript Received September 22, 1987

Abstract: Methyl α -cyano- β -X-*p*-nitrocinnamates (5; X = Cl, Br, OMs, OTs, OTf) were prepared. The five (*E*) isomers and the (*Z*) isomers (X = Cl, Br, OMs) were separated and their structures assigned. Substitution of the eight substrates by *p*-MeC₆H₄S⁻M⁺ and *p*-MeC₆H₄O⁻M⁺ (M = Li, Na, K), of the (*E*) isomers by *p*-O₂NC₆H₄S⁻Na⁺, and of (*E*)-5-Cl by *p*-O₂NC₆H₄O⁻Na⁺ in CD₃CN always gave a mixture of the (*E*) and (*Z*) substitution products. The kinetically controlled (*E*)/(*Z*) product ratios and the equilibrium ratios derived by nucleophilic isomerization of the initially formed ratios were determined. The (*Z*) isomers gave higher extents of retention than the (*E*) isomers, and in no case was a complete stereoconvergence obtained. A relatively small dependence of the extent of the stereoconvergence on a change in the nucleofuge, the counterion, and the nucleophile characterizes the reaction. It was suggested that the reaction proceeds via the rate-determining formation of an intermediate carbanion, which then expels the nucleofuge. The order of nucleofugalities of our leaving groups and the effect of the nucleofuge on the rotational barriers were analyzed and compared with the experimental results. It is concluded that the stereochemistry of the substitution is determined in the rapid step by a rate-determining competitive intramolecular 60 and 120° rotation in the carbanion, leading to the retained and the inverted product, respectively. This is followed by a fast expulsion of the nucleofuge from the appropriate carbanionic conformers. Both hyperconjugative and steric factors affect the intramolecular rotation rates. The change in the nucleofuge does not give information on the position of the transition state along the reaction coordinate in the C-X bond cleavage step.

The stereochemistry of bimolecular nucleophilic vinylic substitution (eq 1; Nu = nucleophile, X = nucleofuge, Y, Y' = activating groups) is one of the strongest tools for investigating the mechanism of the reaction.² The stereochemistry depends



(1) Nucleophilic Attacks on Carbon-Carbon Double Bonds. 36. Part 35: Rappoport, Z.; Gazit, A. *J. Am. Chem. Soc.* 1987, 109, 6698.

mainly on the nature of the nucleofuge and the activating groups Y, Y' and in special cases also on the nucleophile. With poor

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