Novel Radical Cation Reactions of Bichromophoric Systems. Transannular Aryl Migrations; Mechanistic and Exploratory Organic Photochemistry†,[1,2]

Howard E. Zimmerman* and Kurt D. Hoffacker

Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

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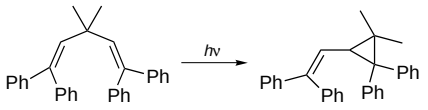
Eight aryl-substituted 1,4-pentadienes were subjected to photochemically induced electron transfer using dicyanonaphthalene and dicyanoanthracene. The radical-cations produced underwent a regioselective cyclization, wherein one electron-deficient aryl group of one diarylvinyl moiety bonds to the β-carbon of the second diarylvinyl group. A pattern of regioselectivity and reactivity was encountered. As cyclization proceeds, the odd-electron density becomes localized in the benzhydryl side chain while the positive charge becomes localized in the second portion of the molecule. Substitution in one diarylvinyl branch designed to delocalize odd-electron density but destabilize electron deficiency led to higher reactivity than the unsubstituted parent 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene. The benzhydryldihydronaphthalene photoproducts themselves proved photochemically reactive. On sensitization, the benzhydryldihydronaphthalene reacted with a transannular 1,5-migration of one aryl group of the benzhydryl moiety. Where the two benzhydryl aryl groups were different, the cyanophenyl group migrated in preference to phenyl, and both diastereomers led to the same product stereoisomer. Ab initio and semiempirical computations were in accord with the radical cation and triplet regioselectivity.

Introduction

Our past studies of bichromophoric systems includes an exhaustive study of the di-π-methane rearrangement.[3] Equation 1 gives a typical example.[4] One question arose



1 **2** (1)

whether the corresponding radical cation systems would undergo the same or a different reaction. This seemed of special interest in view of the increasing role of electron transfer in organic rearrangements.[5] More specifically, diphenylethylene itself has been the object of a considerable number of radical cation investigations.[6] The major reactivity observed has been either nucleophilic addition by solvent or bimolecular reactivity. We note that the diarylvinyl moiety has been present in a variety of reactants undergoing the di-π-methane rearrangement. However, these bichromophoric systems have not been studied under radical-cation-forming conditions. This paper describes our research in this direction.

Results

Synthesis of Reactants. Of the di-π-methane reactants of interest, several were known and were prepared by known methods; these (**18**−**21**) are shown in Scheme 1. Further reactants were obtained as depicted in Scheme 1. One interesting reaction is the formation of enone **15** from the reaction of 3,3-dimethylglutaric anhydride. An initial addition−elimination of phenyllithium to one carbonyl affords a benzoyl carboxylate that then adds two further phenyllithium molecules to afford the triphenyl ketocarbinol **14**. The sequence provides a convenient approach to such bifunctional molecules. Our previous syntheses of similar products were considerably longer.[7]

Radical Cation Reactivity of the 1,1,5,5-Tetraaryl-3,3-dimethyl-1,4-pentadienes. The absorption spectrum of the tetraphenyldiene **1** showed relatively little absorption above 300 nm. Dicyanonaphthalene (DCN) absorbed nicely in the 300−345 nm region, and the excited singlet (S_1) of DCN has a reduction potential[8] of −2.17 eV, which is sufficient to remove an electron from a diphenylvinyl group ($E_{ox} = 1.88$).[9] Effectively, the same point is made by consideration of the Weller equation[10]

$$\Delta G_{ET} = 23.06[E^{ox}(D/D^{\bullet+}) - E^{red}(A/A^{\bullet-}) - e/a\epsilon - E_{0,0}] \quad (2)$$

(i.e., **2**), which leads us to a ΔG of electron transfer of −8.0 kcal/mol. This combination seemed ideal for photochemical formation of the radical cation of tetra-

† This paper is dedicated to Frederick G. Bordwell in recognition of his unique and many brilliant contributions to physical−organic chemistry.

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(1) This is part 244 of our general series and 181 of our photochemical papers.

(2) Photochemical part 179: Zimmerman, H. E.; Kutateladze, A. G. *J. Am. Chem. Soc.* **1996**, *117*, 249−250.

(3) (a) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183−184. (b) See ref 3c,d for reviews. (c) Zimmerman, H. E. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc., New York: 1991; Vol. 11. (d) Zimmerman, H. E. In *Handbook of Photochemistry and Photobiology*; Horspool, W., Song, P. S., Eds.; CRC Press: London, 1995.

(4) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718−1727.

(5) (a) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401−449. (b) Albrecht, E.; Averdung, J.; Bischof, E. W.; Hiedbreder, A.; Kirschberg, T.; Müller, F.; Mattay, J. *J. Photochem. Photobiol. A: Chem.* **1994**, *82*, 219−232.

(6) (a) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931−5937. (b) Mizuno, K.; Ishii, M.; Otsuji, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5570−5572. (c) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1387−1389. (d) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356−7361.

(7) Zimmerman, H. E.; Nuss, J. M. *J. Org. Chem.* **1986**, *51*, 4604−4617.

(8) (a) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233. (b) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931−5937.

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(10) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259−271.

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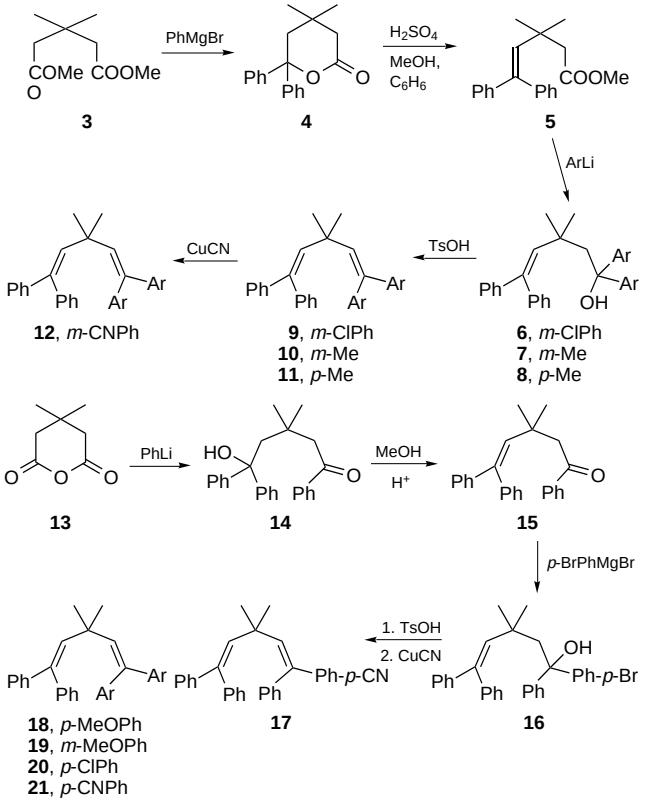
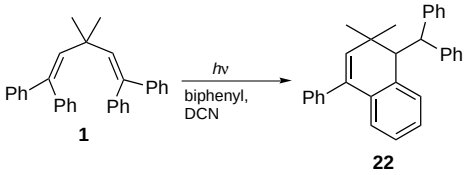
Scheme 1. Synthesis of Di-π-methane reactants



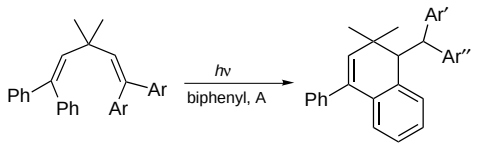
phenyldiene **1**. It was quickly ascertained that the usual di-π-methane rearrangement, depicted in eq 1, had not occurred. Rather, an isomeric product was formed. The NMR spectrum revealed two nonequivalent methyl groups, one vinyl, two methines, and 19 aromatic hydrogens. Several structures seemed possible, and an X-ray analysis led to structure **22**. Thus, the reaction can be seen to involve a cyclization in which the β-carbon of one diphenylvinyl group bonds to the ortho-carbon of a phenyl group of the second diphenylvinyl moiety. This is shown in eq 3.



(3)

With this result known, it was of interest to determine the scope of the reaction. The reaction regioselectivity was of particular interest in the reaction of unsymmetrically substituted di-π-methane systems. Cyano substitution was particularly relevant. The photolysis of 1,1-bis(*p*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**21**) with DCA in acetonitrile led to formation of a crystalline product, mp 283−284 °C. The structure of this photoproduct **23** was obtained by X-ray analysis and found to have the same basic skeleton as the product **22** of the unsubstituted diene, however, with cyano substitution in the benzhydryl moiety rather than in the dihydronaphthalene ring.

This led us to investigate the behavior of the corresponding 1,1-bis(*m*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**12**). Again, a single photoproduct, **24**, was obtained, and the structure was elucidated by X-ray crystallography. As in the *p*-cyano case (vide supra), the cyano substitution was in the benzhydryl group of the product. Also, with the bis-*p*-chloro analog **20** the reaction proceeded nicely, and *p*-chloro appeared in the benzhydryl group of photoproduct **25**. This transformation as well as the cyano examples are shown in eq 4.

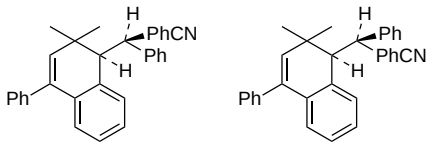


(4)

	Ar′	Ar″	A	
21	Ph-*p*-CN	Ph-*p*-CN	DCA	**23**
12	Ph-*m*-CN	Ph-*m*-CN	DCA	**24**
20	Ph-*p*-Cl	Ph-*p*-Cl	DCN	**25**
17	Ph	Ph-*p*-CN	DCA	**26a,b**

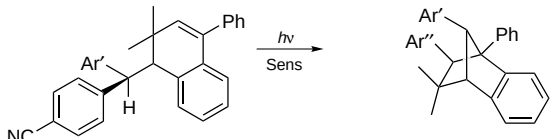
Also of interest was the radical cation photochemistry of the monocyano di-π-methane reactant **17**. Two stereoisomers were obtained, and an X-ray structure of one showed this to be the trans isomer **17t**. However, under reaction conditions these isomers interconverted at a rapid rate compared to further reaction. Two diastereomeric photoproducts were observed in a 2.4:1 ratio. The structure of the major product **26a** was established by X-ray crystallography, and the NMR spectrum of the minor isomer was almost identical except for minor peak shifts. The reaction is included in eq 4.

Interestingly, the di-*p*-tolyl analog **11** and the di-*p*-methoxy diene **18** proved unreactive.



Exploratory runs on the di-*m*-chloro **9**, di-*m*-methyl **10**, and di-*m*-methoxy **19** dienes indicated that these were reactive. However, practical problems precluded structure elucidation of the photoproduct mixtures. While for each of **9** and **10** NMR evidence indicated two regioisomers of the same basic structure as the parent **22**, the *m*-methoxy analog led to a multiplicity of products, possibly from secondary photoreactions.

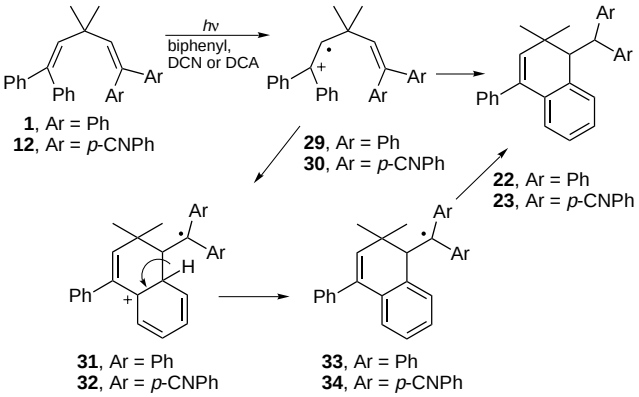
Triplet Secondary Photochemistry. One curious observation was the formation of a secondary photoproduct near the end of the photolysis of the bis(*p*-cyanophenyl) diene **21** to form bicyclic **23**. It was confirmed that this product did derive from secondary photochemistry, since the same product resulted from independent photolysis of bicyclic **23**. The structure of this photoproduct was established by X-ray crystallography as the tricyclic benzonorbornene **27** and thus clearly involved migration of a *p*-cyanophenyl group. Note eq 5. This was a reaction



(5)

not encountered with reactants having less effective electron withdrawing groups. It did not seem reasonable

Scheme 2. Radical Cation Cyclization Mechanism



that *p*-cyanophenyl migration would be preferred by electron deficiency, and it was suspected that the secondary reaction was, instead, a triplet process.

That the reaction was a triplet process was confirmed by the observation of a rapid conversion of bicyclic **23** to benzonorbornene **27** on irradiation using benzophenone as a triplet sensitizer.

As a consequence, we studied the triplet photochemistry of the monocyano bicyclic **26a,b** stereoisomers. These also had exhibited secondary photochemistry; but, in the radical cation photochemistry of the mono-*p*-cyanophenyl diene **17** the secondary photochemistry was somewhat more competitive with the initial cyclization. In order to ascertain that this monocyanophenyl rearrangement also proceeded via the triplet rather than the radical cation, bicyclic isomers **26** were subjected to sensitization by benzophenone. The reaction proceeded to afford the same product. The benzophenone-sensitized rearrangement was interesting in several respects. First, both stereoisomers of reactant **26** led to a single diastereomer of the monocyanobenzonorbornene **28**, whose structure was established by X-ray crystallography. Second, this established that there had been a preferential cyanophenyl migration, although, a priori, either a phenyl or a cyanophenyl group might have shifted. The observation of preferential cyanophenyl migration confirmed the triplet nature of the reaction. Both the reaction regioselectivity and the stereochemistry are discussed below. Equation 5, however, depicts the nature of the overall reaction.

Discussion

The Radical Cation Cyclization Mechanism. Turning first to the overall reaction mechanism, we can write the rearrangement as in Scheme 2. Here, one anticipates initial formation of the radical cation. Where the aryl groups bear electron-withdrawing substituents, the positive charge will be localized in the diphenylvinyl moiety as shown. Cyclization then leads to cation radical **31**. Ab initio computations using GAUSSIAN94[11] at the ROHF/3-21G level and with an NBO hybrid basis set[12] revealed the interesting result that the positive charge

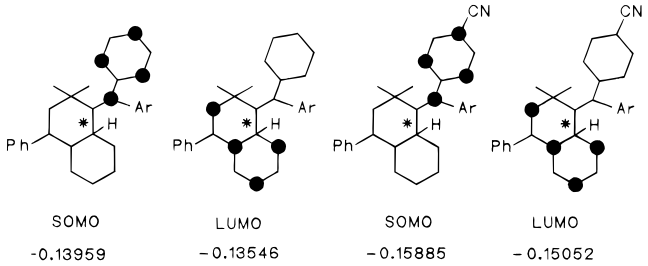


Figure 1. Close to nonbonding MO's. Note six-membered ring Ar has the same pattern of electron densities as the one drawn explicitly. MO energies in hartrees (627.5 kcal/mol per hartree).

is largely localized in the "heptatrienyl" and the odd-electron density is largely concentrated in the benzhydryl group as depicted in Scheme 2. This was true as well for the hydrocarbon system lacking the cyano groups and also the di-*p*-cyano-substituted one. Both moieties are of the odd-alternant variety, and it is of consequence that the lost electron comes from the nonbenzylic portion of the molecule (vide infra). The subsequent proton loss leads to the aromatic radical **33**. Finally, back-electron transfer and protonation affords the final photoproduct, e.g., **22**.

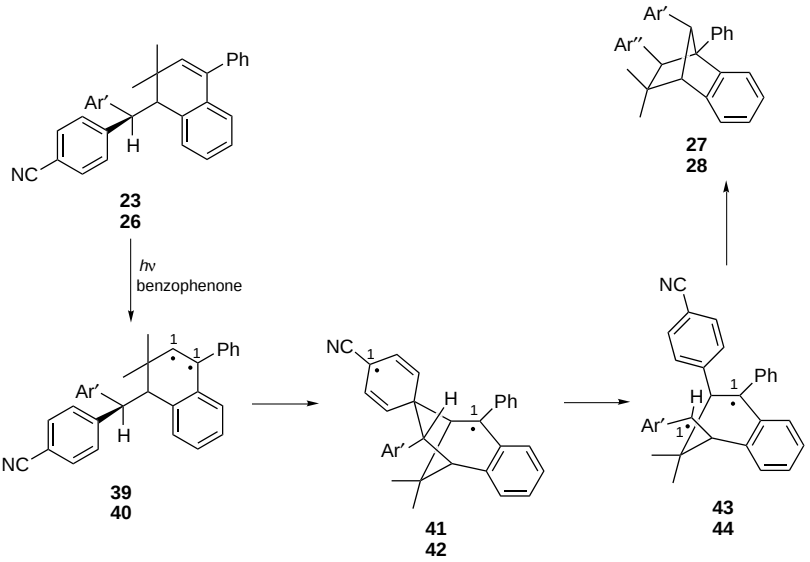
The reaction regioselectivity is in accord with this mechanism, which involves (see Scheme 2) bonding of the β-vinyl carbon of the bis(*p*-cyanophenyl)vinyl group to an ortho carbon of the diphenylvinyl moiety. However, the source of this regioselectivity is understood from the ab initio computations on radical cations **31** and **32**. With the positive charge concentrated in the heptatrienyl group, one would anticipate destablization by an electron-withdrawing group such as cyano. Additionally, the *p*-cyano substituent helps stabilize the benzhydryl radical-like portion of the molecule.

Inspection of the ab initio computations on the intermediate **31** and **32** derived from reactants **1** and **12**, respectively, showed two nearly degenerate MO's. The largest electron densities are as depicted in Figure 1. At first glance the pairs of MO's appear to be "benzylic" and "heptatrienyl" in nature. However, there is weak coupling through the newly formed σ bond, which separates the two systems and is labeled with an asterisk. The sign alternation anticipated for the nonbonding heptatrienyl system is, indeed, found in the eigenvector. However, the benzylic moieties do not show the typical plus−minus alternation. Both in the parent diene case **1** and the *p*-cyanophenyl diene **12**, the intermediates **31** and **32** have the odd-electron mainly in the benzhydryl moiety as shown in Scheme 2 and the positive charge mainly in the heptatrienyl π-system. The regioselectivity, thus, seems to arise from electron-withdrawing substituents avoiding the positive heptatrienyl system but stabilizing the odd-electron benzhydryl portion of the molecule as the reaction proceeds. In the case of the *p*-cyano substitution the cyano group thus avoids the positive portion of the molecule and stabilizes the odd-electron density. With *m*-cyano substitution the electron deficient part of the system is, again, avoided, despite little if any odd-electron delocalization in the benzhydryl group resulting.

(11) Gaussian 94, Revision C.2: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(12) NBO 4.0. Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 1994.

Scheme 3. Reaction Mechanism for the Long-Range Aryl Migration



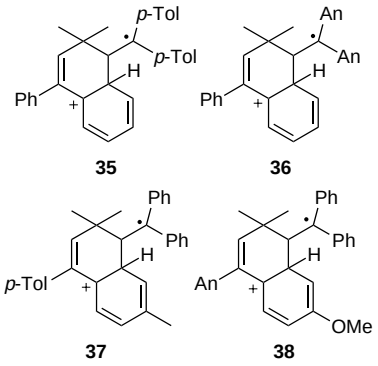


Figure 2. Four unreactive radical cation intermediate species.

If the cyclized radical-cation species, **31** or **32**, is close to the transition state for cyclization of the original radical cation, then it is understandable why the cyano substitution prefers the benzhydryl moiety in the reaction.

Another point of interest is the inhibited reactivity of the *p*-anisyl diene **18** and the di-*p*-tolyl diene **11**. In these cases there is selective stabilization of these radical cation reactants relative to the cyclized intermediates **35**−**38** (Figure 2). For one regioselectivity, **37** and **38**, the substituent, being originally located para, appears on the heptatrienyl cationic group not bearing a positive charge. For the other regioselectivity, the initial radical cation stabilization by *p*-methyl and *p*-anisyl leads to species **35** and **36** in which these groups interact only with an odd-electron moiety, odd-electron stabilization being less helpful energetically than the cationic counterpart.

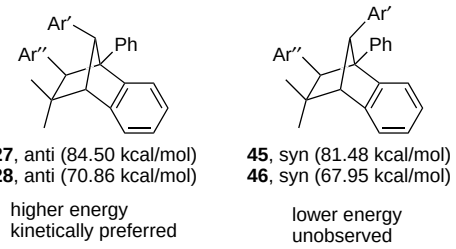
In agreement with the preceding discussion, we note that the oxidation potentials[9] for 1,1-dianisylethylene, 1,1-ditolylethylene, and diphenylethylene are 1.32, 1.66, and 1.88 eV, respectively, with the reactive tetraphenyldiene **1**, with a diphenylvinyl moiety, thus being of higher energy than the ditolyl analog by 0.2 eV or ca. 6.4 kcal/mol.

Secondary Photochemistry Due to T_1. The triplet aryl migration shown in eq 5 has precedent in some of our previous studies.[7,13] The reaction mechanism for this rearrangement is given in Scheme 3. Three aspects are particularly worthy of discussion. First, as noted above, there is a preference for cyanophenyl over phenyl migration to the terminal alkene carbon of the diarylvinyl moiety. Of the several chromophores present in reactants **23** and **26**, the triplet energy of the diphenylvinyl type moiety should be near the triplet energy of 1,1-diphenylethylene (59 kcal/mol),[14] while that of the cyanophenyl group should be near 77 kcal/mol (cf. T1 for benzonitrile).[15] With the diaryl chromophore locally excited to T_1, migration of the benzhydryl aryl group to the β-carbon of this chromophore is reasonable. We note that the free-valence of T_1 styrene is maximal at the β-carbon (0.82 vs 0.41 α),[16] accounting for migration to this site. The preference of cyanophenyl over phenyl is understood on the basis of the enhanced delocalization of the bridged triplet diradical **42** relative to the counterpart lacking a cyano group at an odd-electron center. This has analogy in the greater migratory aptitude of *p*-cyanophenyl[17] relative to phenyl as seen in the triplet rearrangement of T_1 of 4-(*p*-cyanophenyl)-4-phenylcyclohexenone.

The second aspect of interest is the lack of stereospecificity, giving rise to monocyano and dicyano triplet photoproducts **28** and **27**, respectively, independent of the reactant stereochemistry. The lack of stereospecificity signifies that T_1 species **44** has a long enough lifetime to permit free-rotation and equilibration of rotamers.

It is the third facet that is most remarkable, namely the total stereoselectivity.[18] Thus, it is the thermodynamically less stable and more sterically encumbered diastereomers in which aryl group substituted on carbon-7 of the benzonorbornenyl becomes anti to the benzo ring and proximate to the sterically bulky *gem*-dimethyl group. Note Figure 3. Both MM3 and AM1 computations were carried out on the diastereomeric photoproducts **27** (anti) vs **45** (syn) as well as **28** (anti) vs **46** (syn).

(13) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 5143−5152.
(14) Görner, H. *J. Phys. Chem.* **1982**, *86*, 2028−2035.
(15) Wagner, P. J.; May, M. L. *J. Phys. Chem.* **1991**, *95*, 10317−10321;
(16) *Dictionary of π-Electron Calculations*; Coulson, C. A., Streitwieser, A., Eds.; W. H. Freeman and Co.: San Francisco, 1965.
(17) Cf. Zimmerman, H. E.; Rieke, R. D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033−2047.
(18) "Stereoselectivity" and "stereospecificity" are used here in the context suggested originally: Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. *J. Am. Chem. Soc.* **1959**, *81*, 108−116.



27, anti (84.50 kcal/mol)
28, anti (70.86 kcal/mol)
higher energy
kinetically preferred

45, syn (81.48 kcal/mol)
46, syn (67.95 kcal/mol)
lower energy
unobserved

Figure 3. Possible diastereoisomers. "Syn" and "anti" refer to proximity to the benzo moiety. AM1 energies.

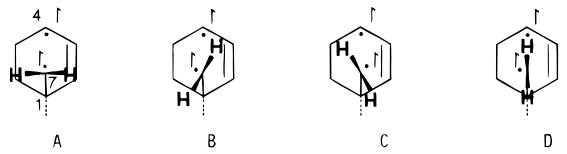


Figure 4. Conformations of the triplet diradicals **47**.

It was possible that the anti conformers of **43** (and **44**) of a precursor triplet of the general structure **47** might exhibit a much larger rate of intersystem crossing to the S_0 diradical than the syn isomer. This singlet anti diradical then would be constrained to close to the anti product. Intersystem crossing (ISC) in such diradicals is controlled mainly by spin−orbit coupling of the odd-electrons with the angular orbital momentum of the hybrids of the system. Spin−orbit coupling is a phenomenon we have studied from the theoretical viewpoint,[2,19] and this would have been interesting experimentally. The truncated diradical system in which the basic carbon skeleton, minus substituents, is depicted in several conformations in Figure 4.

However, spin−orbit coupling (SOC) computations on this basic carbon skeleton as a function of relative orientation of the two p-orbitals of the triplet diradical indicated that SOC coupling was close to symmetric relative to the rotational angle about bond 1,7 (note Figure 4); here, we take a zero degree dihedral for the conformer **D** in which the H−C−H is in the plane containing the two odd-electron centers and perpendicular to the boat-shaped ring. However, spin−orbit coupling for diradical conformers **B** and **C** in which the p-orbital at C-7 is directed 45° away from the π-bond and toward the π-bond, respectively, revealed little preference with values of 2.83 and 3.07 cm^{-1}. If anything, the slightly greater SOC for conformer **C** would predict twisting of the aryl group at C-7 toward the benzo ring in the full molecule.

Proceeding to other sources of stereoselectivity, we note that this unusual behavior seems likely to arise from one of two mechanistic possibilities. The first mechanism involves a sequence of events in which the Ar′$\dot{C}$H moiety becomes axial, initially in a chair conformation (note Figure 5), followed by eventual formation of the boat conformation required for benzonorbornene product formation. At some point in this process, intersystem crossing must occur. Simple MM3[20] and AM1 computations were implemented starting with axial conformers of the Ar′$\dot{C}$H group but with the six-membered ring

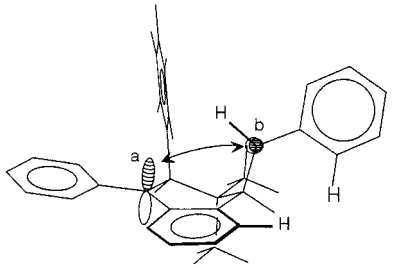
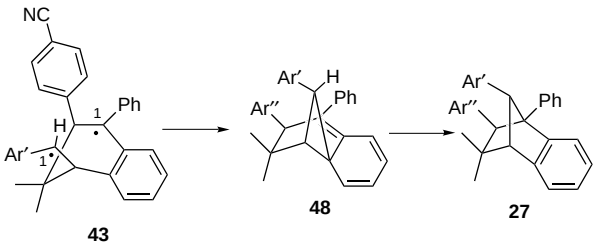


Figure 5. Anti conformer of open diradical **43** minus cyano. Overlap between top lobe of p-orbital a and back lobe of p-orbital b.

chair geometry. Independent of the starting conformation, convergence led to a rotational minimum in which the back lobe of the orbital at center b (Figure 5) overlaps more strongly with the p-orbital at center a than the front lobe at center b does. This "anti" conformer has the aryl group of the Ar′$\dot{C}$H moiety aiming away from the benzo ring, while the hydrogen at this center aims more toward the benzo moiety. The effect is steric due to repulsion between the Ar′$\dot{C}$H hydrogen and the axial phenyl group and also with repulsion between the aryl group and the benzo ortho-hydrogen. This effect is seen only relatively early in the reaction mechanism before the six-membered ring has assumed the final boat conformation.

Nevertheless, there is a second mechanistic rationale. This involves 1,3 bridging along with intersystem crossing to afford the spiro intermediate **48**. This strained species may undergo a rearomatization via a ground-state-allowed 1,3-sigmatropic rearrangement as shown in eq 6.



43 **48** **27** (6)

Conclusion. Organic photochemistry has many facets, e.g., solution photochemistry, solid state reactivity, and electron transfer reactivity. This study has focused on the last and demonstrated that, just as singlet and triplet reactivity differ, radical cation reactivity provides still another avenue for finding unique molecular behavior.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of anhydrous nitrogen unless otherwise indicated. Melting points were determined in open capillaries with a Meltemp heating block and are uncorrected. Anhydrous magnesium sulfate was used as the drying agent. Neutral workup refers to quenching the reaction with saturated ammonium chloride, extracting with ether unless otherwise specified, washing the organic layer with water and brine, drying, filtering, and concentration in vacuo. Acidic workup included a 2 M aqueous hydrochloric acid wash after ether extraction. Basic workup included a saturated aqueous sodium bicarbonate wash after ether extraction. Column chromatography was performed with silica gel (Matheson, Coleman and Bell, grade 62, 60−200 mesh) mixed with 1.0% (v/v) Silvania 2282 phosphor and slurry-packed with hexane into

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quartz columns that were monitored with a hand-held UV lamp. Plates (20 × 20 cm) for preparative thick-layer chromatography (TLC) were prepared with MN-Kieselgel G/UV 254 silica gel. Exploratory photolyses were carried out with a Hanovia 450-W medium-pressure mercury lamp equipped with a Pyrex (λ > 280 nm) 2-mm filter or with a 5-mm recirculating filter solution of 0.07 M sodium metavanadate[21] solution unless otherwise indicated. All photolysis experiments were purged with deoxygenated and dried nitrogen for 1 h before and during photolysis.[22] Acetonitrile was distilled from calcium hydride prior to use. Tetrahydrofuran (THF) was purified by successive distillation, under a nitrogen atmosphere, from calcium hydride, lithium aluminum hydride, and sodium benzophenone ketyl. Diethyl ether was freshly distilled from sodium benzophenone ketyl.

General Procedure for X-ray Crystallography Analysis. X-ray diffraction data were collected on a Nicolet (Syntax) P-1 diffractometer for single crystals of each compound. Unit cell parameters were determined by least-squares refinement of 25 reflections. Data were collected with three check reflections monitored after every 97 reflections. Data having $F > 3\sigma(F)$ were rejected. Lorentz and polarization corrections were applied, and each structure was solved under the appropriate space group symmetry by direct methods using SHELXSTL[23] or SHELX93.[24] Hydrogen atoms were calculated, and full-matrix least-squares refinement was carried out employing anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms.[28]

Methyl 3,3-Dimethyl-5,5-diphenyl-4-pentenoate (5). On the basis of the method of Zimmerman,[25] to 34.0 g (0.18 mol) of methyl 3,3-dimethylglutarate[26] in 250 mL of THF was added over 2 h a solution of phenyl Grignard prepared from 22.0 g (0.90 mol) of magnesium turnings and 97 mL (0.92 mol) of bromobenzene in 200 mL of THF. After the addition was complete, the solution was refluxed for 2.5 h, cooled to rt, quenched with saturated ammonium chloride, dried, filtered through Celite, and concentrated in vacuo to give 53 g of 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoic acid lactone (**4**) as a white solid in quantitative yield and was used without further purification.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.28 (m, 10 H), 2.60 (s, 2 H), 2.19 (s, 2 H), 1.06 (s, 6 H); IR (thin film) 2960, 1745, 1440, 1240, 1145, 1000, 990 cm^{-1}; MS *m/e* 280.1461 (calcd for $C_{19}H_{20}O_2$, 280.1463).

A solution of 53 g of crude 3,3-dimethyl-5,5-diphenyl-5-hydroxypentanoic acid lactone, 275 mL of methanol, 275 mL of benzene, and 43.5 mL (0.783 mol) of concd sulfuric acid was stirred mechanically for 4 d. Basic workup afforded 59 g of a yellow oil that was passed through a 8 × 12 cm pad of silica gel eluted with ether/hexane to give 50.00 g (94% based on starting ester) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate as a slightly yellow oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.4−7.1 (m, 10 H), 6.13 (s, 1 H), 3.63 (s, 3 H), 2.30 (s, 2 H), 1.04 (s, 6 H); IR (neat) 3055, 3020, 2955, 1950, 1735, 1595, 1445, 1325, 1165, 1200, 1230, 1030, 885, 760, 725, 705 cm^{-1}; MS *m/e* 294.1594 (calcd for $C_{20}H_{22}O_2$, 294.1620).

1,1-Bis(*m*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (9). To a solution of (*m*-chlorophenyl)magnesium bromide prepared from 3.39 g (17.8 mmol) of *m*-bromochlorobenzene in 50 mL of THF and 0.421 g (17.3 mmol) of magnesium turnings was added dropwise 2.00 g (6.80 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate in 10 mL of THF. After 2 h at reflux, neutral workup afforded a slightly yellow oil which was charged onto a 48 × 3.0 cm column. The following fractions were collected: fraction 1, 500 mL of hexane; fraction 2, 500 mL of 1% ether/hexane; fraction 3, 500 mL of 2% ether/hexane, 2.76 g (83%) of 1,1-bis(*m*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-4-penten-1-ol (**6**) as a colorless oil that was used without further purification.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.5−7.0 (m, 18 H), 6.11 (s, 1 H), 3.12 (s, 1 H), 2.53 (s, 2 H), 0.81 (s, 6 H); IR (neat) 3510, 3060, 3020, 2955, 2920, 1590, 1575, 1470, 1445, 1420, 1165, 1155, 1075 cm^{-1}; MS *m/e* 486.1517 (calcd for $C_{31}H_{28}Cl_2$, 486.1521).

To 2.76 g (5.65 mmol) of 1,1-bis(*m*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-4-penten-1-ol in 50 mL of refluxing pyridine was added 4.0 mL (43 mmol) of phosphorus oxychloride. After being refluxed for 16 h, the solution was poured into ice and acidic workup afforded a yellow oil that was charged onto a 25 × 2.5 cm column eluted with 1% ether/hexane, and the following fractions were collected: fraction 1, 750 mL, nil; fraction 2, 350 mL, 2.17 g (82%) of 1,1-bis(*m*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene as an oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50−6.75 (m, 18 H), 5.94 (s, 1 H), 5.93 (s, 1 H), 1.04 (s, 6 H); IR (neat) 3055, 3020, 2960, 2925, 2865, 1590, 1560, 1490, 1470, 1445, 1420, 1415, 1275, 1155, 1130, 1095, 1075, 1030 cm^{-1}; MS *m/e* 468.1427 (calcd for $C_{31}H_{26}Cl_2$, 468.1412); UV (CH_3CN) λ(max) = 252 (ϵ = 19 000).

1,1-Di-(*m*-tolyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (10). To a solution of *m*-tolylmagnesium bromide prepared from 3.93 g (23.0 mmol) of *m*-bromotoluene in 50 mL of THF and 0.419 g (17.3 mmol) of magnesium turnings was added dropwise 2.00 g (6.79 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate in 20 mL of THF. After the mixture was stirred for 30 min, neutral workup afforded a slightly yellow oil that was charged onto a 45 × 3.0 cm column. The following fractions were collected: fraction 1, 650 mL of hexane, 29 mg of *m*-bromotoluene; fraction 2, 500 mL of 2% ether/hexane, nil; fraction 3, 650 mL of 4% ether/hexane, 2.31 g of a yellow oil. Fraction 3 and 5 mg (3 μmol) of *p*-toluenesulfonic acid monohydrate were dissolved in 60 mL of benzene and refluxed with azeotropic removal of water for 10 h. Basic workup afforded 2.2 g of an oil that was charged onto a 49 × 3 cm column, and the following fractions were collected: fraction 1, 1150 mL of hexane; fraction 2, 1100 mL of 5% ether in hexanes, 1.75 g (60%) of 1,1-di-*m*-tolyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene as an oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.3−6.75 (m, 18 H), 5.95 (s, 1 H), 5.94 (s, 1 H), 2.27 (s, 3 H), 2.19 (s, 3 H), 1.02 (s, 6 H); IR (neat) 3055, 3020, 2960, 2920, 1600, 1490, 1445, 1375, 1360, 1130, 1075, 1035, 910, 885, 765, 700 cm^{-1}; MS *m/e* 428.2503 (calcd for $C_{33}H_{32}$, 428.2504); UV λ(max) = 252 (ϵ = 21 000). Anal. Calcd for $C_{33}H_{32}$: C, 92.47; H, 7.53. Found: C, 91.93; H, 7.66.

1,1-Di-*p*-tolyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (11). To a solution of *p*-tolyllithium prepared from 4.07 g (23.8 mmol) of *p*-bromotoluene in 100 mL of diethyl ether and 9.6 mL (20 mmol) of 2.1 M butyllithium in hexanes was added dropwise 1.60 g (5.42 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate in 50 mL of diethyl ether. After the mixture was stirred for 3 h, neutral workup afforded 2.66 g of an oil identified as 1,1-di-*p*-tolyl-3,3-dimethyl-5,5-diphenyl-4-penten-1-ol, which was used without further purification.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.5−7.0 (m, 18 H), 6.09 (s, 1 H), 2.75 (s, 1 H), 2.57 (s, 2 H), 2.25 (s, 6 H), 0.80 (s, 6 H); MS *m/e* 446.2604 (calcd for $C_{33}H_{34}O$, 446.2610).

To the crude 1,1-di-*p*-tolyl-3,3-dimethyl-5,5-diphenyl-4-penten-1-ol obtained above were added 50 mL of dry benzene and 0.01 g (50 μmol) of *p*-toluenesulfonic acid monohydrate, and the mixture was refluxed for 3 h with azeotropic removal of water using a Dean−Stark trap. Basic workup afforded 2.32 g of a yellow oil that was charged onto a 32 × 2.5 cm column and eluted with hexane to give a colorless oil that was recrystallized from benzene to give 1.40 g (60%) of 1,1-di-*p*-

(21) Sodium metavanadate solution was prepared by dissolving the appropriate amount of sodium metavanadate in 5% sodium hydroxide. A 1 cm thick solution of 0.07 M sodium metavanadate cuts off more than 99.9% of the light intensity with wavelengths shorter than 324 nm.

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tolyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene as a white solid, mp 67−70 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.3−6.9 (m, 18 H), 5.93 (s, 1 H), 5.91 (s, 1 H), 2.28 (s, 3 H), 2.27 (s, 3 H), 1.02 (s, 6 H); IR (neat) 3050, 3020, 2990, 2920, 1510, 1495, 1445, 1180, 1230, 1110, 1075, 1030, 820, 700 cm^{-1}; MS *m/e* 428.2509 (calcd for $C_{33}H_{32}$, 428.2504); UV λ(max) = 252 (ϵ = 26 000).

1,1-Bis(*m*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (12). To 2.16 g (4.60 mmol) of 3,3-dimethyl-1,1-bis(*m*-chlorophenyl)-5,5-diphenyl-1,4-pentadiene (**9**) in 25 mL of *N*-methylpyrrolidinone was added 1.48 g (16.5 mmol) of cuprous cyanide, and the mixture was refluxed for 24 h. The cooled solution was poured into 20 mL of ethylenediamine and allowed to sit for 30 min. It was then extracted into chloroform and washed with 10% ammonium hydroxide until the aqueous layer was no longer blue, water, and brine, dried, filtered, and concentrated in vacuo to give 4.83 g of red oil. The oil was charged onto a 37 × 3 cm column with the top 5 cm composed of 1:1 silica gel/Norite and eluted with 2% ether in hexanes, which yielded 256 mg (12%) of 1,1-bis(*m*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene as a colorless oil.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.6−7.0 (m, 18 H), 6.02 (s, 1 H), 5.90 (s, 1 H), 1.06 (s, 6 H); IR (neat) 3060, 3025, 2925, 2865, 2230, 1595, 1575, 1170, 800, 760, 700 cm^{-1}; MS *m/e* 450.2100 (calcd for $C_{33}H_{26}N_2$, 450.2096); UV λ(max) = 222 (ϵ = 65 000). Anal. Calcd for $C_{33}H_{26}N_2$: C, 87.97; H, 5.82. Found: C, 86.34; H, 6.15.

3,3-Dimethyl-1,5,5-triphenyl-4-penten-1-one (15). To a 0 °C solution of phenylmagnesium bromide prepared from 13.0 mL (0.123 mol) of bromobenzene and 1.70 g (0.246 mol) of lithium pieces in 150 mL of diethyl ether was added, via cannula, a solution of 5.01 g (35.2 mmol) of 3,3-dimethylglutaric anhydride in 250 mL of diethyl ether, and the solution was stirred at rt for 7 h. It was quenched by transferring the solution via cannula to beneath the surface of 200 mL of a vigorously shaken saturated ammonium chloride solution. Neutral workup afforded a yellow oil that was refluxed for 20 h with 5.5 mg (3 μmol) of *p*-toluenesulfonic acid monohydrate in 150 mL of benzene with azeotropic removal of water using a Dean−Stark trap. Basic workup afforded an oil that was charged onto a 18 × 3.5 cm column with the top 3 cm being composed of 50/50 Norite/silica gel and eluted with 2% ether in hexanes, which yielded 7.19 g (60%) of 3,3-dimethyl-1,5,5-triphenyl-4-penten-1-one as a colorless oil.[7]

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80−7.10 (m, 15 H), 6.23 (s, 1 H), 2.92 (s, 2 H), 1.14 (s, 6 H); IR ($CHCl_3$) 3055, 3025, 2960, 2930, 2870, 1690, 1675, 1595, 1490, 1465, 1455, 1355, 1240, 1220, 1180, 1075, 1030, 1010; MS *m/e* 340.1834 (calcd for $C_{25}H_{24}O$, 340.1827).

3,3-Dimethyl-1-(*p*-bromophenyl)-1,5,5-triphenyl-4-penten-1-ol (16). To 7.8 mL (17.9 mmol) of 2.3 M butyllithium in hexane and 50 mL of diethyl ether at 0 °C was added 4.21 g (17.8 mmol) of *p*-dibromobenzene in 50 mL of ether via a cannula. After 30 min, 5.13 g (15.1 mmol) of 3,3-dimethyl-1,5,5-triphenyl-4-penten-1-one in 40 mL of diethyl ether was added dropwise via cannula. After the mixture was stirred 2 h, neutral workup afforded a yellow oil that was charged onto a 17 × 3.5 cm column, and the following fractions were collected: fraction 1, 500 mL of 2% ether/hexane; fraction 2, 600 mL of 4% ether/hexane, 6.90 g of an oil. The oil was crystallized from pentane and recrystallized from benzene/hexane to give 5.44 g (93%) of 3,3-dimethyl-1-(*p*-bromophenyl)-1,5,5-triphenyl-4-penten-1-ol as a white solid, mp 102−105 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.5−7.0 (m, 19 H), 6.12 (s, 1 H), 2.96 (s, 1 H), 2.57 (s, 2 H), 0.81 (s, 3 H), 0.79 (s, 3 H); IR (thin film) 3520, 3055, 2960, 1485, 1070, 1010, 910, 820, 760, 700 cm^{-1}; MS *m/e* 496.1410 (calcd for $C_{31}H_{29}OBr$, 496.1401). Anal. Calcd for $C_{31}H_{29}OBr$: C, 74.85; H, 5.88. Found: C, 75.30; H, 6.11.

(*E*)-3,3-Dimethyl-1-(*p*-cyanophenyl)-1,5,5-triphenyl-1,4-pentadiene (17). To 5.62 g (11.7 mmol) of 3,3-dimethyl-1-(*p*-bromophenyl)-1,5,5-triphenyl-4-penten-1-ol were added 100 mL of dry benzene and 0.1 g (0.5 mmol) of *p*-toluenesulfonic acid monohydrate and the mixture refluxed for 24 h with azeotropic removal of water using a Dean−Stark trap. Basic workup afforded an oil that was charged onto a 19 × 3.5 cm column and eluted with ether/hexane to give 5.13 g of a mixture of (*E*)- and (*Z*)-3,3-dimethyl-1-(*p*-bromophenyl)-1,5,5-triphenyl-1,4-pentadienes as a tacky solid that was used without further purification.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.7−7.4 (m, 38 H), 5.96 (s, 1 H), 5.95 (s, 1 H), 5.93 (s, 1 H), 5.91 (s, 1 H), 1.03 (s, 6 H), 1.02 (s, 6 H); IR (neat) 2960, 1735, 1595, 1490, 1445, 1070, 1015, 825, 760 cm^{-1}; MS *m/e* 480.1282 (calcd for $C_{31}H_{27}Br$, 480.1274).

To 5.1 g (11 mmol) of (*E*)- and (*Z*)-3,3-dimethyl-1-(*p*-bromophenyl)-1,5,5-triphenyl-1,4-pentadienes in 70 mL of *N*-methylpyrolidinone was added 1.698 g (19.0 mmol) of cuprous cyanide, and the mixture was refluxed for 20 h. The cooled solution was poured into 10 mL of ethylenediamine and allowed to sit for 1 h. It was then extracted into chloroform and washed with 10% ammonium hydroxide until the aqueous layer was no longer blue, water, and brine, dried, filtered, and concentrated in vacuo to give 4.83 g of a red oil. The oil was chromatographed on a 19 × 3.5 cm column, and the following fractions were collected: fraction 1, 400 mL of hexane and 500 mL of 5% ether/hexane, 2.03 g of an oily mixture; fraction 2, 250 mL of 8% ether/hexane, 2.75 g of an oil. Crystallization of fractions 1 and 2 with pentane gave 1.23 g (27%) of (*E*)-3,3-dimethyl-1-(*p*-cyanophenyl)-1,5,5-triphenyl-1,4-pentadiene, mp 136 °C. The structure of diene **17** was established by X-ray crystallography.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50−6.90 (m, 19 H), 6.00 (s, 1 H), 5.96 (s, 1 H), 1.05 (s, 6 H); IR (thin film) 2915, 2225, 1600, 1495, 1445, 1155, 1120, 1070, 1030, 835, 760, 700 cm^{-1}; MS *m/e* 425.2150 (calcd for $C_{32}H_{27}N$, 425.2143). Anal. Calcd for $C_{32}H_{27}N$: C, 90.31; H, 6.39. Found: C, 90.16; H, 6.60.

DCN-Sensitized Irradiation of 3,3-Dimethyl-1,1,5,5-tetraphenyl-1,4-pentadiene (1). A solution of 0.189 g (0.472 mmol) of 3,3-dimethyl-1,1,5,5-tetraphenyl-1,4-pentadiene[4] and 0.124 g (0.693 mmol) of 1,4-dicyanonaphthalene in 50 mL of acetonitrile was irradiated through a Pyrex filter with a 100 W Hanovia lamp for a total of 9.5 h. The solvent was removed in vacuo, and the crude photolysate was charged onto a 32 × 2.5 cm column and eluted with hexanes. The following fractions were collected: fraction 1, 1650 mL, nil; fraction 2, 500 mL, 85 mg of a yellow oil that contained starting material and a product. The oil from fraction 2 was recrystallized from hexanes to give 20 mg (11%) of 1-benzhydryl-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**22**) as colorless crystals (mp 172.5−173 °C). The structure of dihydronaphthalene **22** was established by X-ray crystallography.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.50−6.70 (m, 19 H), 6.56 (d, J = 1 Hz, 1 H), 4.55 (d, J = 8.6 Hz, 1 H), 3.43 (dd, J = 8.6, 1 Hz, 1 H), 1.03 (s, 3 H), 0.97 (s, 3 H); MS *m/e* 400.2184 (calcd for $C_{31}H_{28}$, 400.2191). Anal. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05. Found: C, 93.38; H, 7.27.

Short DCA-Sensitized Irradiation of 1,1-Bis(*p*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (21). A solution of 0.104 g (0.232 mmol) of 1,1-bis(*p*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene,[27] 0.015 g (65 μmol) of 9,10-dicyanoanthracene, and 42 mg (0.27 mmol) of biphenyl in 200 mL of acetonitrile was irradiated through a solution filter for a total of 45 min. The solvent was removed in vacuo, the crude photolysate was charged onto a 39 × 3 cm column, and the following fractions were collected: fraction 1, 475 mL of 5% ether in hexane, 37 mg of biphenyl; fraction 2, 1 L of 20% ether in hexane, 98 mg of an oil. Fraction 2 was crystallized from chloroform in hexane to give 90 mg (86%) of 1-[bis(*p*-cyanophenyl)methyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**23**) as colorless crystals, mp 283−284 °C. The

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(28) The author has deposited atomic coordinates for **17**, **22**−**25**, **26a**, **27**, and **28** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

structure of dihydronaphthalene **23** was established by X-ray crystallography.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.80−6.70 (m, 16 H), 6.52 (d, J = 7 Hz, 1 H), 5.71 (d, J = 1.2 Hz, 1 H), 4.68 (d, J = 8.7 Hz, 1 H), 3.41 (dd, J = 8.8, 1 Hz, 1 H), 1.05 (s, 3 H), 0.93 (s, 3 H); IR (thin film) 2980, 2950, 2220, 1605, 1500, 1445, 1415, 1350, 840, 820, 770, 755, 700 cm^{-1}; MS *m/e* 450.2098 (calcd for $C_{33}H_{26}N_2$, 450.2096); UV λ(max) = 236 (ϵ = 25 000). Anal. Calcd for $C_{33}H_{26}N_2$: C, 87.97; H, 5.82. Found: C, 88.12; H, 5.82.

Extended DCA-Sensitized Irradiation of 1,1-Bis(*p*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (21). A solution of 162 mg (0.358 mmol) of 1,1-bis(*p*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene,[27] 20 mg (0.089 mmol) of 9,10-dicyanoanthracene, and 61 mg (0.396 mmol) of biphenyl in 200 mL of acetonitrile was irradiated through a solution filter for a total of 2.5 h. The solvent was removed in vacuo, the crude photolysate was charged onto a 33 × 3 cm column, and the following fractions were collected: fraction 1, 500 mL of 1% ether in hexane, 60 mg of biphenyl; fraction 2, 950 mL of 1% ether in hexane, nil; fraction 3, 400 mL of 50% ether in hexane, 140 mg of an oil. Fraction 3 was placed on a silica gel TLC plate and eluted twice with 10% ether in hexane, once with 15% ether in hexane, and once with 50% ether in hexane. The fastest moving band (band 1) contained an oil that was crystallized from chloroform in hexane to give 55 mg (34%) of 2,3-benzo-6-*anti*-7-*anti*-bis(*p*-cyanophenyl)-5,5-dimethyl-1-phenylbicyclo[2.2.1]heptene (**27**) as colorless crystals (mp 259−260 °C). The slower band (band 2) contained an oil that was crystallized from chloroform in hexane to give 75 mg (46%) of 1-[bis(*p*-cyanophenyl)methyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**23**) as colorless crystals, mp 283−284 °C. The structure of heptene **27** was established by X-ray crystallography.

The spectral data for 2,3-benzo-6-*anti*-7-*anti*-bis(*p*-cyanophenyl)-5,5-dimethyl-1-phenylbicyclo[2.2.1]heptene (**27**) were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) d 7.8−6.7 (m, 16 H), 6.25 (d, J = 7.2 Hz, 1 H), 4.33 (s, 1 H), 3.87 (s, 1 H), 3.16 (s, 1 H), 0.85 (s, 3 H), 0.46 (s, 3 H); IR (thin film) 3055, 3040, 3005, 2965, 2225, 1605, 1505, 1465, 1460, 1180, 1120, 1035, 910, 835 cm^{-1}; MS *m/e* 450.2058 (calcd for $C_{31}H_{26}N_2$, 450.2096). Anal. Calcd for $C_{31}H_{26}N_2$: C, 87.97; H, 5.82. Found: C, 86.07; H, 5.92.

DCA-Sensitized Irradiation of 1,1-Bis(*m*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (12). A solution of 0.125 g (0.278 mmol) of 1,1-bis(*m*-cyanophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, 3.4 mg (15 μmol) of 9,10-dicyanoanthracene, and 32 mg (0.21 mmol) of biphenyl in 200 mL of acetonitrile was irradiated through a filter solution for 70 min. Solvent was removed in vacuo to give a yellow oil that was charged onto a 31 × 3 cm column. The following fractions were collected: fraction 1, 250 mL of 10% ether in hexanes and 250 mL of 16% ether in hexanes, 20 mg of biphenyl; fraction 2, 500 mL of 16% ether in hexanes, 35 mg of starting material; fraction 3, 150 mL of 16% ether in hexanes, 29 mg of a yellow oil. The oil was recrystallized from chloroform in hexanes to give 24 mg (19%) of 1-[bis(*m*-cyanophenyl)methyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**24**) as colorless crystals, mp 246 °C. The structure of dihydronaphthalene **24** was established by X-ray crystallography.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.8−6.7 (m, 16 H), 6.52 (d, J = 7.5 Hz, 1 H), 5.73 (d, J = 1.1 Hz, 1 H), 4.65 (d, J = 8.5 Hz, 1 H), 3.36 (dd, J = 8.4, 1 Hz, 1 H), 1.06 (s, 3 H), 0.94 (s, 3H); IR (neat) 2230, 1485, 1440, 1350, 1075, 805, 765, 725, 700 cm^{-1}; MS *m/e* 450.2091 (calcd for $C_{33}H_{26}N_2$, 450.2096).

DCN-Sensitized Irradiation of 1,1-Bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (20). A solution of 366 mg (0.777 mmol) of 1,1-bis(*p*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene,[27] 144 mg (0.550 mmol) of 1,4-dicyanonaphthalene, and 0.098 g (0.64 mmol) of biphenyl in 200 mL of acetonitrile was irradiated through Pyrex for a total of 90 min. The solvent was removed in vacuo, the crude photolysate was charged onto a 32 × 2.5 cm column, and the following fractions were collected: fraction 1, 400 mL of hexane and 900 mL of 1% ether in hexane, 90 mg of biphenyl; fraction 2, 300 mL of 1% ether in hexane, 316 mg of a yellow oil. The oil from fraction 3 was placed on a silica gel TLC plate and eluted twice with 4% ether in hexanes. The fastest moving band (band 1) contained 63 mg of starting material. The slower band (band 2) contained an oil that was crystallized from pentane to give 241 mg (66%) of 1-[bis(*p*-chlorophenyl)-methyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**25**) as colorless crystals, mp 142−143 °C. The structure of dihydronaphthalene **25** was established by X-ray crystallography.

The spectral data were the following: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.5−6.5 (m, 17 H), 5.68 (d, J = 1.3 Hz, 1 H), 4.50 (d, J = 8.0 Hz, 1 H), 3.33 (dd, J = 8.0, 1.3 Hz, 1 H), 1.03 (s, 3 H), 0.97 (s, 3 H); IR (thin film) 3020, 2960, 1490, 1090, 1015, 830, 760, 700 cm^{-1}; MS *m/e* 468.1415 (calcd for $C_{31}H_{26}Cl_2$, 468.1429). Anal. Calcd for $C_{31}H_{26}Cl_2$: C, 79.31; H, 5.58. Found: C, 79.33; H, 5.81.

DCA-Sensitized Irradiation of 3,3-Dimethyl-1-(*p*-cyanophenyl)-1,5,5-triphenyl-1,4-pentadiene (17). A solution of 250 mg (0.587 mmol) of 3,3-dimethyl-1-(*p*-cyanophenyl)-1,5,5-triphenyl-1,4-pentadiene, 8.5 mg (37 μmol) of 9,10-dicyanoanthracene, and 72 mg (0.47 mmol) of biphenyl in 180 mL of acetonitrile was irradiated through a solution filter for a total of 9 h. The solvent was removed in vacuo, the crude photolysate was charged onto a 42 × 3 cm column, and the following fractions were collected: fraction 1, 1000 mL of hexane and 800 mL of 2% ether in hexane, 37 mg of biphenyl; fraction 2, 200 mL of 2% ether in hexane, 27 mg of a yellow oil; fraction 3, 500 mL of 2% ether in hexane, 55 mg of an oil; fraction 4, 1650 mL of 2% ether in hexane, 127 mg of DCA and other unidentified materials. Fraction 2 was crystallized from chloroform in hexane to give 25 mg (10%) of 2,3-benzo-6-*anti*-(*p*-cyanophenyl)-1,7-*anti*-diphenyl-5,5-dimethylbicyclo[2.2.1]heptene (**28**) as colorless crystals (mp 232−234.5 °C). Fraction 3 was dissolved in pentane and allowed to crystallize. The first crop gave 16 mg (6%) of (*RS*/*SR*)-1-(*p*-cyanophenyl)phenylmethyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**26b**) as a white solid (mp 190−192 °C), and a second crop gave 35 mg (14%) of (*RR*/*SS*)-1-[(*p*-cyanophenyl)-phenylmethyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**26a**) as colorless crystals (mp 132−133 °C). The structures of heptene **28** and dihydronaphthalene **26a** were established by X-ray crystallography.

The spectral data for 2,3-benzo-6-*anti*-(*p*-cyanophenyl)-1,7-*anti*-diphenyl-5,5-dimethylbicyclo[2.2.1]heptene (**28**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.8−6.8 (m, 17 H), 6.24 (d, J = 7.2 Hz, 1 H), 4.36 (s, 1 H), 3.87 (s, 1 H), 3.13 (s, 1 H), 0.83 (s, 3 H), 0.50 (s, 3 H); IR (neat) 2225, 1735, 1455, 1270, 1155, 1035, 800 cm^{-1}; MS *m/e* 425.2164 (calcd for $C_{32}H_{27}N$, 425.2143). Anal. Calcd for $C_{32}H_{27}N$: C, 90.31; H, 6.39. Found: C, 90.44; H, 6.48.

The spectral data for (*RS*/*SR*)-1-(*p*-cyanophenyl)phenylmethyl)-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**26b**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.8−6.65 (m, 17 H), 6.53 (d, J = 7.2 Hz, 1 H), 5.68 (d, J = 1.3 Hz, 1 H), 4.60 (d, J = 8.9 Hz, 1 H), 3.39 (dd, J = 8.7, 1 Hz, 1 H), 1.05 (s, 3 H), 0.93 (s, 3 H); IR (neat) 3020, 2960, 2225, 1605, 1495, 1445, 1215, 835, 755, 700 cm^{-1}; MS *m/e* 425.2136 (calcd for $C_{33}H_{32}$, 425.2143). Anal. Calcd for $C_{32}H_{27}N$: C, 90.31; H, 6.39. Found: C, 90.00; H, 6.62.

The spectral data for (*RR*/*SS*)-1-[(*p*-cyanophenyl)phenylmethyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (**26a**) were the following: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65−6.80 (m, 17 H), 6.55 (d, J = 6.9 Hz, 1 H), 5.73 (d, J = 1 Hz, 1 H), 4.63 (d, J = 8.6 Hz, 1 H), 3.45 (dd, J = 8.6, 1 Hz, 1 H), 1.10 (s, 3 H), 0.97 (s, 3 H); IR (neat) 3020, 2955, 2225, 1600, 1495, 1445, 1215, 835, 765, 700 cm^{-1}; MS *m/e* 425.2141 (calcd for $C_{33}H_{32}$, 425.2143). Anal. Calcd for $C_{32}H_{27}N$: C, 90.31; H, 6.39. Found: 89.83; H, 6.44.

DCN-Sensitized Irradiation of 3,3-Dimethyl-1-(*p*-cyanophenyl)-1,5,5-triphenyl-1,4-pentadiene (17). A solution of 0.430 g (1.01 mmol) of 3,3-dimethyl-1-(*p*-cyanophenyl)-1,5,5-triphenyl-1,4-pentadiene, 182 mg (1.02 mmol) of 1,4-dicyanonaphthalene, and 0.127 g (0.82 mmol) of biphenyl in 200 mL of acetonitrile was irradiated through Pyrex for a

total of 5.6 h. The solvent was removed in vacuo, the crude photolysate was charged onto a 41 × 3 cm column, and the following fractions were collected: fraction 1, 500 mL of hexane and 200 mL of 2% ether in hexane, 101 mg of biphenyl; fraction 2, 500 mL of 2% ether in hexane, 159 mg (37%) of starting material; fraction 3, 300 mL of 2% ether in hexane, 200 mg (47%) of a 1:1 mixture of dihydronaphthalenes **26a** and **26b** by ^{1}H NMR.

DCN-Sensitized Irradiation of 1,1-Bis(*m*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (9). A solution of 0.571 g (1.22 mmol) of 1,1-bis(*m*-chlorophenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, 0.228 g (1.28 mmol) of 1,4-dicyanonaphthalene, and 186 mg (0.59 mmol) of biphenyl in 200 mL of acetonitrile was irradiated through a Pyrex filter for 2.5 h. Solvent was removed to give a yellow oil that was charged onto a 47 × 2.5 cm column. The following fractions were collected: fraction 1, 900 mL of hexanes, nil; fraction 2, 500 mL of hexanes and 150 mL of 2% ether in hexanes, 92 mg of biphenyl; fraction 3, 600 mL of 2% ether in hexanes, 439 mg of a yellow oil. ^{1}H NMR showed that fraction 3 contained starting material and two products.

DCN-Sensitized Irradiation of 1,1-Di-*m*-tolyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (10). A solution of 305 mg (0.71 mmol) of 1,1-di-*m*-tolyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene, 131 mg (0.74 mmol) of 1,4-dicyanonaphthalene, and 91 mg (0.59 mmol) of biphenyl in 220 mL of acetonitrile was irradiated through a Pyrex filter for 1 h. Solvent was removed to give a yellow oil that was charged onto a 40 × 3 cm column. The following fractions were collected: fraction 1, 750 mL of hexane and 500 mL of 1% ether in hexane, 75 mg of biphenyl; fraction 2, 300 mL of 1% ether in hexane, 196 mg of an oil. ^{1}H NMR showed that fraction 3 contained starting material and two products.

DCN-Sensitized Irradiation of 1,1-Bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (18). A solution of 0.504 g (1.10 mmol) of 1,1-bis(*p*-methoxyphenyl)-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene[24] and 0.391 g (2.19 mmol) of 1,4-dicyanonaphthalene in 200 mL of acetonitrile was irradiated through a Pyrex filter for a total of 19 h. ^{1}H NMR showed no products. The crude photolysate was charged onto a 59 × 2 cm column, and elution with 5.5 L of 0.5% ether in hexanes yielded 382 mg (76%) of starting material.

Benzophenone-Sensitized Irradiation of 1-[Bis(*p*-cyanophenyl)methyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (23). A solution of 4.3 mg (9.5 μmol) of 1-[bis(*p*-cyanophenyl)methyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene and 4.2 mg (23 μmol) of benzophenone in 2 mL of acetonitrile in an NMR tube was irradiated through a filter solution for 2.3 h. After concentration in vacuo the ^{1}H NMR showed a complete conversion to 2,3-benzo-6-*anti*-7-*anti*-bis-(*p*-cyanophenyl)-5,5-dimethyl-1-phenylbicyclo[2.2.1]heptene (**27**) as the only observable product.

Table 1. Results of Optimized ROHF/3-21G Calculation Intermediate 31

	E(ROHF)	*E*(MCSCF)	SOC(RMS)
A	−267.461 21	−267.510 15	2.03
B	−267.451 08	−267.494 30	2.83
C	−267.448 32	−267.494 26	3.07
D	−267.436 41	−267.477 23	0.17

Benzophenone-Sensitized Irradiation of (*RR*/*SS*)-1-[(*p*-Cyanophenyl)phenylmethyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (26a). A solution of 2.7 mg (6.0 μmol) of (*RR*/*SS*)-1-[(*p*-cyanophenyl)phenylmethyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene and 2.5 mg (14 μmol) of benzophenone in 2 mL of acetonitrile in an NMR tube was irradiated through a filter solution for 4 h. After concentration in vacuo the ^{1}H NMR showed complete conversion to 2,3-benzo-6-*anti*-(*p*-cyanophenyl)-1,7-*anti*-diphenyl-5,5-dimethylbicyclo-[2.2.1]heptene (**28**) as the only observable product.

Benzophenone-Sensitized Irradiation of (*RS*/*SR*)-1-[(*p*-Cyanophenyl)phenylmethyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene (26b). A solution of 2.1 mg (4.9 μmol) of (*RS*/*SR*)-1-[(*p*-cyanophenyl)phenylmethyl]-1,2-dihydro-2,2-dimethyl-4-phenylnaphthalene and 2.1 mg (12 μmol) of benzophenone in 2 mL of acetonitrile in an NMR tube was irradiated through a filter solution for 2 h. After concentration in vacuo the ^{1}H NMR showed a 40% conversion to 2,3-benzo-6-*anti*-(*p*-cyanophenyl)-1,7-*anti*-diphenyl-5,5-dimethylbicyclo-[2.2.1]heptene (**28**) as the only observable product.

Computations. Structures for intermediates **31** and **32** were obtained with full geometry optimization with the Gaussian94 package of programs[11] using ROHF/3-21G (Table 1). Atomic charges and eigenvectors were obtained using Weinhold's NBO analysis.[12] 1-Electron spin−orbit coupling constants for diradical **47** were obtained by first geometry optimizing the diradical while holding the diradical centers approximately 2 Å apart using Gamess with ROHF/sto-3g. Single point calculations were then performed on structures obtained from the optimized structure by rotating the *exo*-methylene group. Eigenvectors from ROHF/sto-3g calculations were used as starting points for mcscf calculations. Spin−orbit coupling for each conformation was then calculated using the energies and spin−orbit coupling for four conformations of diradical **47** (cf. Table 1).

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