raphy[28] (5-g column, elution with 20% ethyl acetate in hexane) provided 1,2,4,6-tetra-*O*-acetyl-α-D-mannopyranose (**26**) as a colorless syrup: yield, 154 mg (86%); ^{1}H NMR ($CDCl_3$, $(CH_3)_4Si$) δ 2.07 (s, 3), 2.12 (s, 3), 2.13 (s, 3), 2.18 (s, 3), 2.53 (br d, 1, exchangeable with D_2O), 3.97 (m, 1), 4.09 (m, 2), 4.28 (dd, 1, J = 12.3, 4.9 Hz), 5.08 (m, 2), 6.10 (d, 1, J = 1.4 Hz).

1,2,4,6-Tetra-*O*-acetyl-3-*O*-carbamoyl-α-D-mannopyranose (28). Method A. A solution of tetraacetate **26** (154 mg, 0.44 mmol) in 20 mL of pyridine containing 2 mg of (*N*,*N*-dimethylamino)pyridine was treated with 175 mg (0.87 mmol) of *p*-nitrophenyl chloroformate. The reaction mixture was stirred at 25 °C for 20 h and then diluted with 150 mL of benzene and washed successively with portions of 0.5 M H_2SO_4, saturated aqueous $NaHCO_3$, and water. The dried (Na_2SO_4) solution was concentrated to afford the 3-*O*-*p*-nitrophenyl carbonate derivative **27** as a pale yellow syrup: ^{1}H NMR ($CDCl_3$, $(CH_3)_4Si$) δ 2.06 (s, 6), 2.13 (s, 3), 2.16 (s, 3), 4.00–4.48 (m, 3), 5.13–5.64 (m, 3), 6.17 (d, 1, J = 1.5 Hz), 7.45 and 8.30 (m, 4).

The syrup was dissolved in 12 mL of dichloromethane and treated with 4 mL of tetrahydrofuran that had been saturated with ammonia. The combined solution was maintained at 25 °C for 14 h, then concentrated, and purified by flash chromatography[28] (10-g silica gel column; elution was with 1:1 hexane–ethyl acetate). 1,2,4,6-Tetra-*O*-acetyl-3-*O*-carbamoyl-α-D-mannopyranose (**28**) was obtained as a colorless syrup: ^{1}H NMR ($CDCl_3$, $(CH_3)_4Si$) δ 2.06 (s, 3), 2.08 (s, 3), 2.16 (s, 3), 2.17 (s, 3), 4.03 (m, 1), 4.08 (dd, 1, J = 12.2, 2.3 Hz), 4.28 (dd, 1, J = 12.2, 4.7 Hz), 4.79 (br s, 2, exchangeable with D_2O), 5.23–5.36 (m, 3), 6.08 (d, 1, J = 1.3 Hz).

(28) Still, W. C.; Kahn, J.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Anal. Calcd for $C_{15}H_{21}NO_{11}$: C, 46.02; H, 5.41. Found: C, 46.03; H, 5.57.

Method B. Ortho ester **22** (28 mg, 0.075 mmol) was dissolved in 1 mL of glacial acetic acid and stirred at 25 °C for 14 h. The solution was concentrated (codistillation with portions of toluene) and the residue was treated with 1.5 mL of 2:1 pyridine–acetic anhydride at 25 °C for 2 h. The reaction mixture was treated with ice, and the solution was concentrated to provide mannose derivative **28** as a colorless syrup, yield 22 mg (88%). This material was identical (silica gel TLC, ^{1}H NMR) with the material obtained by method A.

2,4,6-Tri-*O*-acetyl-3-*O*-carbamoyl-α-D-mannopyranosyl Chloride (23). 1,2,4,6-Tetra-*O*-acetyl-3-*O*-carbamoyl-α-D-mannopyranose (**28**) (210 mg, 0.54 mmol) in 5 mL of dry dimethoxyethane was treated with anhydrous hydrogen chloride at −10 °C for 20 min. The reaction flask was stoppered tightly, and the reaction mixture was maintained at 25 °C for an additional 24 h. The solution was concentrated, and the residue was purified by flash chromatography[28] on silica gel (10-g column, elution with 1:1 hexane–ethyl acetate). Mannopyranosyl chloride **23** was obtained as a colorless syrup, yield 125 mg (63%). Crystallization of the syrup from ether–hexane provided **23** as colorless needles, mp 131–133 °C (no mp depression on admixture with a sample of **23** derived from **22**).

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Di-π-methane Rearrangements of Highly Sterically Congested Molecules: Inhibition of Free-Rotor Energy Dissipation. Mechanistic and Exploratory Organic Photochemistry[1,2]

Howard E. Zimmerman* and David N. Schissel

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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Four highly sterically congested di-π-methane reactants were synthesized and their photochemistry was studied. These were 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene (**1**), 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene (**2**), 1,1-dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene (**3**), and 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene (**4**). Diene **4** was unreactive, and evidence was obtained for rapid singlet energy dissipation. Dienes **1**, **2**, and **3** exhibited normal singlet reactivity despite the severe steric congestion. Interestingly, a remarkable enhancement in triplet reactivity was encountered for the diisopropyl diene **1** and the dimesityl diene **3**. In contrast to the prototype 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**28**) whose efficiency was known to be 0.0047, the triplet quantum efficiency for diene **1** was 0.018 and that for diene **3** was 0.043. Molecular mechanics was employed to correlate steric effects with the observed photochemistry.

An interesting facet of the di-π-methane rearrangement[3] of acyclic 1,4-dienes is the observation[3b,4b] that the triplet excited states are generally unreactive. This lack of reactivity has been ascribed to a "free-rotor effect"[4] in which a double bond twists with intersystem crossing to ground state and dissipation of excitation energy. However, there are exceptions to the generalization, so that some acyclic di-π-methane systems do exhibit triplet reactivity. Among these exceptions are molecules with substitution by phenyl and other delocalizing groups on the central carbon.[5] It seemed that this enhancement of reactivity might arise from delocalization effects by substituents on the central carbon or, instead, from steric congestion inhibiting free rotation. We wished to investigate acyclic di-π-methane systems incorporating bulky groups to determine if triplet

(1) This is paper 147 of our photochemical series.

(2) For paper 146, note: Zimmerman, H. E.; Lynch, D. C., *J. Am. Chem. Soc.* **1985**, *107*, 7745–7756.

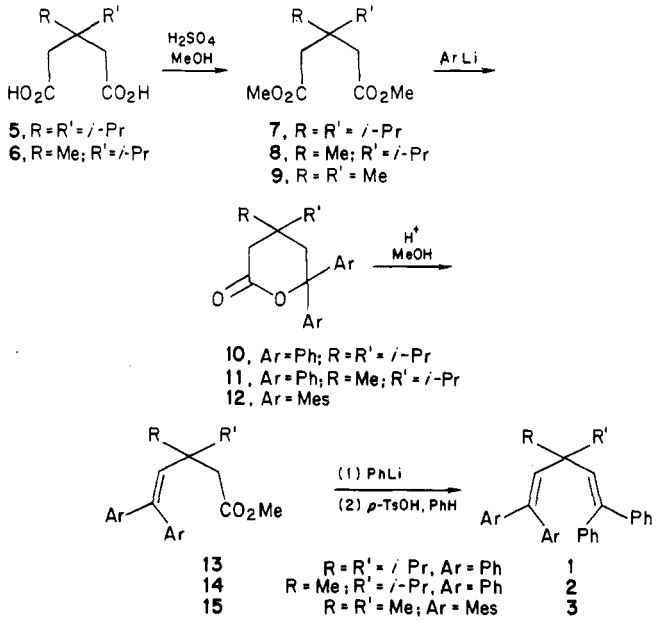
(3) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933. (b) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718–1727. (c) For general reviews, see: Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551 as well as ref 3d. (d) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; Vol. 3, P. DeMayo, Ed.; Academic Press: New York, 1980.

(4) (a) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 1411–1413. (b) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6267–6271. (c) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718–3725.

(5) (a) Zimmerman, H. E.; Boettcher, R. J.; Braig, W. *J. Am. Chem. Soc.* **1973**, *95*, 2155–2163. (b) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383. (c) Zimmerman, H. E.; Factor, R. E. *Tetrahedron Suppl.* **1981**, *37*, 125–141.

0022-3263/86/1951-0196$01.50/0

Scheme I. Syntheses of the Dienes 1, 2, and 3



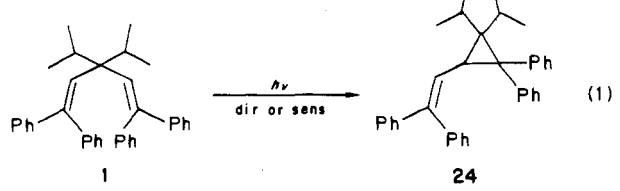
efficiency would be enhanced. Four di-π-methane systems were selected for study. These were 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene (**1**), 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene (**2**), 1,1-dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene (**3**), and 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene (**4**).

Results

Syntheses of Reactant Dienes. The syntheses of the diisopropyl diene **1**, monoisopropyl diene **2**, and dimesityl diene **3** are outlined in Scheme I. The synthesis of diisopropyl diene **1** posed the most difficulty but was accessible beginning with the known 3,3-diisopropylglutaric acid (**5**).[6]

The preparation of tetramethyl diene **4** is presented in Scheme II. This approach was necessitated by the failure of lactone **17** to afford unsaturated ester **23** under the conditions employed for the other lactones—**10**, **11**, and **12**—as shown in Scheme I.

Exploratory Photolysis of 1,1,5,5-Tetraphenyl-3,3-diisopropyl-1,4-pentadiene. Preparative irradiation of diisopropyl diene **1** led to a single photoproduct, mp 189–190 °C. Here both direct irradiation and sensitization with acetophenone or benzophenone proved practical. The NMR spectrum revealed a characteristic AB quartet suggestive of the CHCH= moiety of many di-π-methane products.[3b] X-ray structure determination confirmed this assumption and led to the assignment of photoproduct **24**. The corresponding ORTEP drawing is given in Figure 1 of the supplementary material section. Hence, the photoreaction may be depicted as in eq 1.

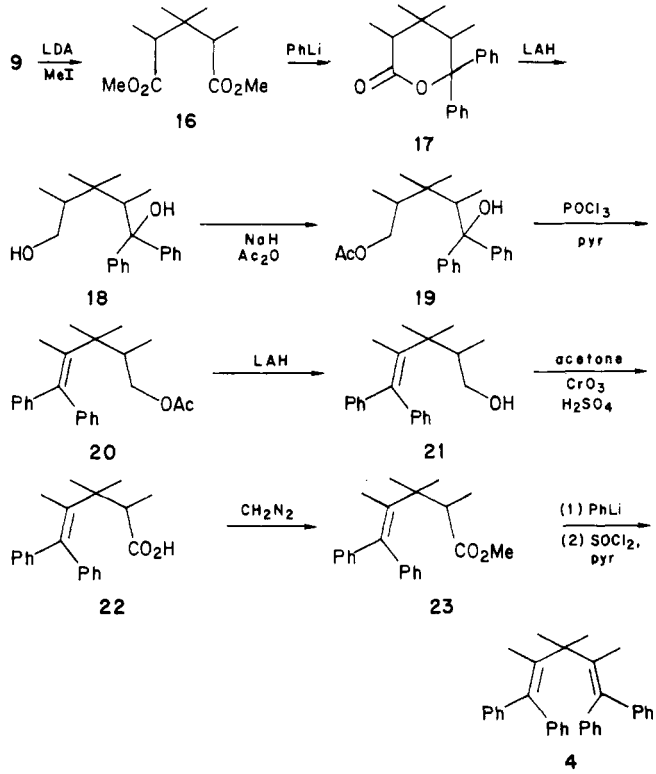


(1)

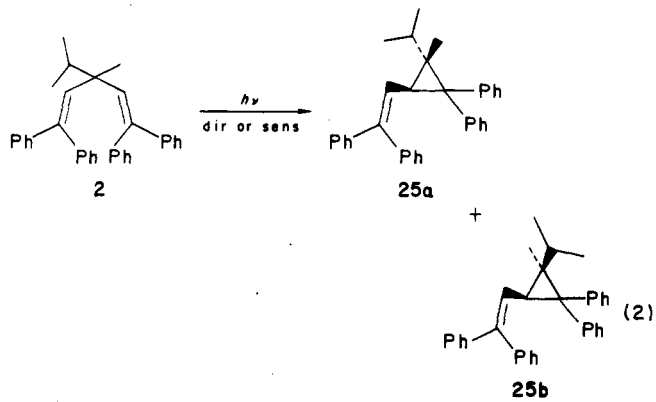
Similar irradiation of the monoisopropyl diene **2** led to photoproducts **25a** and **25b** in a 2:1 ratio. These isomers,

(6) Bruice, T. C.; Bradbury, W. C. *J. Am. Chem. Soc.* **1965**, *87*, 4838–4845.

Scheme II. Synthesis of Tetramethyl Diene 4



again, appeared from their NMR spectra to be vinylcyclopropanes. The structure of the major photoproduct was confirmed by X-ray. That of the minor isomer was indicated by its photochemical interconversion with the major stereoisomer and also was confirmed by X-ray. The ORTEP drawings are given in Figures 2a and 2b of the supplementary material section. The photolysis of monoisopropyl diene **2** thus may be depicted as in eq 2.



(2)

Again, as noted in eq 2, both direct and sensitized photolyses led to di-π-methane product. While the major photoproduct was readily isolated by column chromatography, the minor isomer was obtained with difficulty and only by selective destruction of the major photoproduct by ozonolysis.

Thus far we had explored the photochemical reactivity of di-π-methane systems with bulky groups at carbon-3. We turned to 1,1-dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene (**3**) which promised to provide an assessment of the effect of steric hindrance due to large vinyl substituents. Direct and sensitized irradiation of dimesityl diene **3** led to a single photoproduct **26**. The NMR spectrum, again, revealed a typical vinyl—methine AB quartet; and thus the product seemed likely to be one of the two possible regioisomeric vinylcyclopropanes, that is,

Table I. Quantum Yield Results[a,b]

reactant	sensitizer	wavelength, nm	quantum yield
diisopropyl diene 1	none	289	0.063
	acetophenone[c,d]	337	0.018
isopropyl diene 2	none	289	0.12 (trans), 0.038 (cis)
	acetophenone	337	0.0052 (trans), 0.0014 (cis)
dimesityl diene 3	none	289	0.16
	acetophenone[d]	337	0.043
dimethyl diene 4	none	289	<0.0001
	acetophenone	337	<0.0001

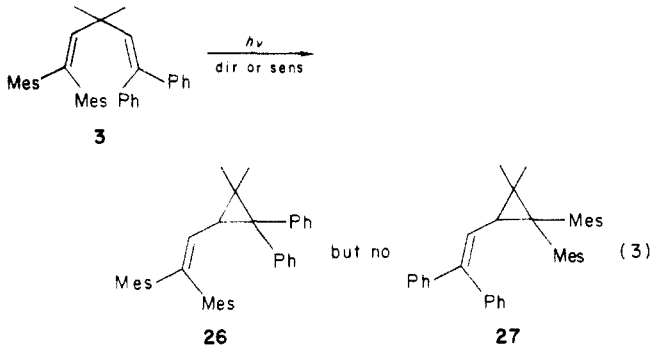
[a] All runs in *t*-BuOH. [b] Error limits ±10%. [c] Identical results obtained with benzophenone. [d] Identical results obtained in benzene.

Table II. Single Photon Counting Results

reactant	M[a]	temp, K	τ	$^1k_{d(tot)}$, s^{-1}	^1k_r, s^{-1}
diisopropyl diene 1	19	300	14 ps	7.1×10^{10}	4.5×10^9
		77	0.27 ns	3.8×10^9	
isopropyl diene 2	51	300	5.7 ps	1.8×10^{11}	2.1×10^{10}[b]
					6.7×10^9[c]
		77	0.29 ns	3.4×10^9	
dimesityl diene 3	24	300	230 ps	4.3×10^9	7.0×10^8
		77	5.5 ns	1.8×10^8	

[a] Magic multiplier. [b] Major photoproduct. [c] Minor photoproduct.

26 or 27, anticipated from such a di-π-methane rearrangement. An exciting question concerned which isomer it was and why such marked regioselectivity resulted. The first question was answered by an X-ray structure determination; the structure was that of **26**. The corresponding ORTEP drawing is shown in Figure 3 of the supplementary material section. The photochemistry of dimesityl diene **3** is outlined in eq 3.



Clearly the preferred regioselectivity is formation of the isomer having the bulky mesityl groups on the residual double bond.

We next turned to the tetramethyl diene **4**. This diene proved to be photochemically stable to both direct and sensitized photolysis conditions.

Quantum Yield Measurements. The results of direct and sensitized quantum yield determinations are summarized in Table I. Acetophenone (E_T 74.1 kcal/mol[7a]) was employed in all cases for sensitization, and benzophenone (E_T 69.2 kcal/mol[7b]) was also used in the case of the diisopropyl diene **1**. The diene concentrations were maintained in the range of 1×10^{-3} to 5×10^{-3} M with the idea of having the energy acceptor concentration low enough to avoid singlet energy transfer but high enough for complete triplet transfer.[8] Indeed, the quantum yields were independent of the diene concentrations over a ca. two- to three-fold ratio. Also, the 98 kcal/mol singlet energy[9] for styryl and diphenylvinyl moieties is considerably above the 79 kcal/mol value for acetophenone[10] and 74 kcal/mol value for benzophenone,[10] and any singlet transfer should be precluded by this very high endothermicity. In one case, that of the diisopropyl diene **1**, the efficiency was shown to be independent of which of two different energy sensitizers were used, hence indicating complete triplet energy transfer.

Single Photon Counting Measurement of Singlet Lifetimes and Reaction Rates. We employed the general method described by us previously[11] with an on-line PDP-11/55[5c,12] minicomputer for control and data reduction. Singlet decay rates were measured for dienes **1**, **2**, and **3**. However diene **4** was nonfluorescent at room temperature and only very weakly fluorescent at 77 K, thus precluding rate measurement. Single exponential decay was encountered in all cases measured (note Experimental Section). Since the room temperature rates were too rapid for direct measurement, the method of magic multipliers[11] was employed. This uses the ratio of low-temperature to room-temperature fluorescence intensities to afford the ratio of room-temperature to low-temperature excited-state decay rates. The results are summarized in Table II.

Interpretative Discussion

Steric Effects on Triplet Reactivity. A most remarkable observation was the enhanced reactivity of the triplet excited states of the most sterically congested dienes investigated. Thus inspection of Table I reveals that diisopropyl diene **1** and dimesityl diene **3** are ca. 4 and 9 times as efficient, respectively, as the prototypical tetraphenyldimethyl diene **28** (eq 4) whose triplet quantum yield had been observed to be 0.0047.[3b] A priori, three effects of steric congestion on reaction efficiency might be anticipated. First, there might be steric hindrance to the geometric change required for reaction; this would di-

(7) (a) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenberry, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466–5468. (b) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537–4541.

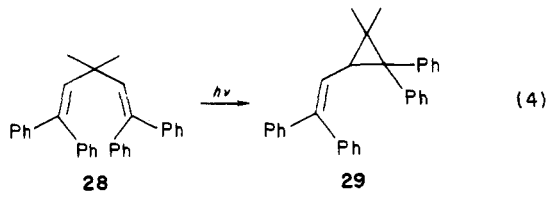
(8) Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 906–912.

(9) (a) E_S for styrene was calculated for the 0–0 transition (294 nm = 98 kcal/mol) as obtained from the absorption and fluorescence spectra.[9c] (b) E_S was obtained similarly for diphenylethylene for the 0–0 transition (296 nm = 97 kcal/mol) by using the absorption and fluorescence spectra given in ref 9c, p 175. (c) Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed.; Academic Press: New York, 1971; p 174.

(10) Kanda, Y.; Kaseda, H.; Matumura, T. *Spectrochim. Acta* **1964**, *20*, 1387–1392.

(11) (a) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1973**, *95*, 5094–5095; (b) **1974**, *96*, 439–449.

(12) (a) Zimmerman, H. E.; Blood, J., unpublished results. (b) Blood, J. Ph.D. Thesis, University of Wisconsin, 1981.



28 29 (4)

minish, rather than increase, efficiency. Second, selective inhibition of free-rotor[4] triplet radiationless decay is possible. A third possibility is a Thorpe–Ingold type effect,[13] wherein central isopropyl substitution enhanced the π–π bridging step of the di-π-methane rearrangement mechanism.[3]

For consideration of such steric effects, molecular mechanics[14] seemed ideal. Relevant to the first of the three factors considered (vide supra), MMPI[14c] revealed no correlation between the observed increased reactivity and the strain energy resulting from the initial vinyl–vinyl bonding of the di-π-methane mechanism.

We thus turned to the second factor potentially controlling reactivity. Here molecular mechanics was used to assess the energy of π-bond twisting involved in excited-state free-rotor energy dissipation. For simplicity, MMPI was employed here with ground-state bonding being assumed despite our being interested in vinyl twisting in the triplet. Thus, an artificial energy increase is introduced by MMPI due to twisting about the assumed ground-state diarylvinyl double bond; in triplets double-bond twisting is electronically energetically favorable. Nevertheless, the artificial π-bonding effect is common to all molecules and thus cancels, hence leaving a measure of steric effects on twisting.

Table III lists the energies of twisting for the comparison of tetraphenyldimethyl diene **28** and for the diisopropyl diene **1**. Additionally, the energy differences for one angle of twist for the monoisopropyl diene **2** and for the dimesityl diene **3** are included.

It is seen from the molecular mechanics results that twisting about the π-bond of the diisopropyl diene **1** is inhibited relative to the prototype tetraphenyldimethyl diene **28**; an extra 11 kcal/mol barrier results for 90° twisting and 5 kcal/mol for 60° twisting.

The case of the monoisopropyl diene **2** seems intermediate, with an inhibition to twisting only slightly greater than the parent tetraphenyl diene **28**.

Experimentally, the dimesityl diene **3** provided the second dramatic example of free-rotor inhibition. Here a ca. ninefold enhancement of reaction efficiency compared with tetraphenyl diene **28** was observed. As noted in Table III, MMPI predicts a small increased energetic resistance to free rotation relative to the prototype diene **28**. The MMPI prediction is of an effect intermediate between the tetraphenyldimethyl diene **28** prototype and the diisopropyl diene **1**, while the dimesityl diene **3** reacts most efficiently. Hence, the correlation of twisting energy with quantum efficiency is only qualitative.

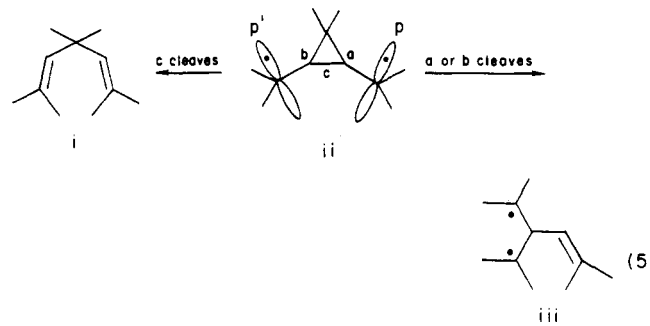
Table III. Twisting Energies of Dienes

compound[a]	twist angle, deg	rel steric energy,[b] kcal/mol
tetraphenyl dimethyl diene **28**	0	0
	30	1.0
	60	6.5
	90	19.3
diisopropyl diene **1**	0	0
	30	2.0
	60	11.7
	90	30.5
isopropyl diene **2**	60	8.9
dimesityl diene **3**	60	9.1

[a] Extended ("*W*") conformation. [b] Energies are relative to the untwisted dienes.

A complete contrast in the consequences of steric effects on reactivity was observed for the tetramethyl diene **4** which did not react at all. Realization that di-π-methane bridging requires six substituents on a three-membered ring suggests that bridging is precluded by extreme steric effects. Indeed, application of molecular mechanics confirms this supposition. MMPI afforded a 13 kcal/mol greater steric energy of bridging (i.e., steric energy of the dicarbinyl diradical minus that of the reactant) for the tetramethyl diene **4** compared with that of the tetraphenyldimethyl diene **28**.

The third factor considered as influencing the di-π-methane reactivity was a Thorpe–Ingold type effect. Reference to eq 5 shows two types of behavior of the cyclopropyldicarbinyl diradicals postulated[3] as intermediate species in the di-π-methane rearrangement.



i ii iii (5)

It can be seen that forward reaction requires overlap of one of the two carbinyl p orbitals of diradical ii with the three-ring bond being severed (i.e., a or b), while reversion to reactant requires overlap of both carbinyl p orbitals with the central bond c. Hence it was of considerable interest to note that MMPI, when applied to the various cyclopropyldicarbinyl diradicals—prototype diradical **28D**, diisopropyl diradical **1D**, monoisopropyl diradical **2D**, dimesityl diradical **3D**, and tetramethyl diradical **4D**—led, with one exception, to a qualitative correlation between reactivity and the dihedral angle between the carbinyl p orbitals (p and p′) and the three-ring bonds. We expect increased reactivity where one or both of the angles p–a and p′–b approach 0° and the angles p–c and p′–c approach 90°. The opposite holds true for reversion to reactant. Thus (note Table IV), both the diisopropyl diradical **1D** and the monoisopropyl diradical **2D** are better aligned to react than the prototype diradical **28D** and do show greater reactivity. The tetramethyl diradical **4D**, on the other hand, is best suited for reversion to reactant and is seen to be completely unreactive. The exception is the dimesityl diradical **3D** where increased reactivity is predicted, but at the diphenyl center, leading to the wrong regioisomeric product (refer to eq 3). We note that the

(13) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080–1106. (b) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 305–329.

(14) (a) A variation of Tribble[14b] was written to permit more ready construction of three-dimensional molecules. This added a variety of graphic features but used the basic MMPI[14c] and MM2[14e] programs in Tribble. (b) Pensak, D. *Ind. Res. Dev.* **1983**, *25*, 74–78. (c) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893–3907. (d) The MM2[14e] program was used as an alternative to MMPI because it provided calculated twist angles for the mesityl groups in tetramesitylethylene in better agreement with the values reported in an X-ray crystallographic study[15] than those values from MMPI. (e) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134.

(15) Hoekstra, A.; Vos, A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1716–1718.

Table IV. Dihedral Angles between Carbinyl p Orbitals and Cyclopropyldicarbinyl Diradical Three-Ring Bonds in Minimum Energy Conformations

diradical	angle p–a, deg	angle p′–b, deg	angle p–c, deg	angle p′–c, deg	quantum efficiency
28*D*	29	34	41	37	0.0047
1*D*	18	31	60	45	0.018
2*D*	16[a]	30[b]	55[a]	47[b]	0.0066
3*D*	40[c]	18[d]	30[c]	46[d]	0.043
4*D*	44	44	29	29	<0.0001

[a] Trans to isopropyl. [b] Cis to isopropyl. [c] Dimesityl center. [d] Diphenyl center.

Table V. Comparison of Low-Temperature Lifetimes[a]

compound	M[b]	τ, ns	$^1k_{d(tot)}$, s^{-1}
diisopropyl diene **1**	19	0.27	3.8×10^9
monoisopropyl diene **2**	51	0.29	3.4×10^9
tetraphenyl diene **28**	225	0.12	8.1×10^9
dimesityl diene **3**	24	5.5	1.8×10^8
diphenyltetramethyl diene **30**	222	3.1	3.2×10^8

[a] All results at 77K. [b] Magic Multiplier.

Thorpe–Ingold effect considered here differs from the usual one in affecting orbital overlap rather than probability of encounter of terminal atoms in a chain.

Except for the dimesityl example, both free-rotor inhibition and the Thorpe–Ingold effect operate in the same direction, and it does appear that the observed behavior of the dienes under study can be understood as deriving from both effects.

Steric Effects on Singlet Reactivity. The effects of steric congestion on singlet reactivity, in terms of reaction efficiencies (i.e., the ϕ's), were smaller than those on triplet reactivity. The diisopropyl diene **1** reacted with an efficiency of 80% of the parent tetraphenyldimethyl diene **28** while the monoisopropyl diene **2** and the dimesityl diene **3** were twice as efficient. The tetramethyl diene **4** was totally unreactive, hence, paralleling the triplet behavior. The much smaller steric effects in singlet reactivity seem most likely to derive from the same sources which make triplet excited states more susceptible to free-rotor radiationless decay than their singlet counterparts. Thus singlet rearrangement rates are generally larger compared with triplet rates, and free-rotor decay is less competitive.[3c,d]

Turning to the singlet rate constants, we recognize that these provide better measures of reactivity than quantum yields alone as has been noted before.[16,11a] A comparison of the present rates with those measured for the parent, noncongested tetraphenyl diene **28** is instructive. It is seen that steric hindrance does impede the rearrangement of the diisopropyl diene **1** ($k_r = 4.5 \times 10^9$ s^{-1}) relative to the model tetraphenyl diene **28** ($k_r = 1.4 \times 10^{11}$ s^{-1}).[11a] At 77 K, we see by reference to Table V, that the singlets of diisopropyl diene **1** and monoisopropyl diene **2** are only ca. twofold longer lived than those of prototype diene **28**. As is discussed below, the noncongested diphenyltetramethyl diene **30** (note eq 6) affords a more suitable model for the electronics of the dimesityl diene **3**; this derives from the inhibited conjugation between mesityl and vinyl groups present in diene **3**. Reference to Table V, again, reveals that the 77 K lifetimes for the dimesityl diene **3** and its reference compound **30** are very close. In the case of the tetramethyl diene **4** the very weak fluorescence can be attributed to an enhanced rate of twisting about the styryl double bonds, leading to excited singlet decay, as a "free-rotor effect".

Hence, we may conclude that noncongested molecules in a glassy matrix decay at rates similar to congested ones and, therefore, that decay at 77 K is controlled by (e.g., electronic) factors other than molecular motion.

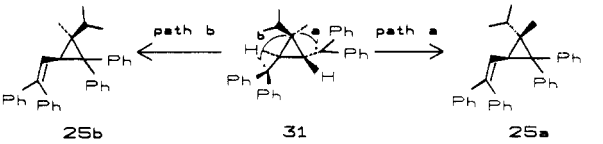


Figure 4. Stereoselectivity of bicycling of the cyclopropyldicarbinyl diradical **31** to afford cyclopropane products.

Also, in complete contrast to noncongested molecules, the dependence of the lifetimes on temperature for the congested dienes is small. In previous studies[11] we defined M (the "magic multiplier") as the ratio of low-temperature to room-temperature lifetimes and have provided reasoning why these vary linearly with excited singlet lifetimes. In these earlier studies,[11] for an appreciable number of di-π-methane systems, all noncongested, M was observed to remain in the range of ca. 200–250. The congested molecules of the present study all have values of the magic multiplier of ca. 20–50. It does seem general that rigid molecules tend to exhibit smaller temperature dependences of their fluorescence than those of flexible molecules. Here steric congestion confers molecular rigidity.

Stereoselectivity of Three-Ring Formation. An interesting observation concerns the singlet and triplet photochemistry of monoisopropyl diene **2**. A ca. 3:1 preference for formation of the trans stereoisomer of 1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane (**25a**) was observed. This has precedent in the singlet photochemistry of the 3-methyl-3-ethyl di-π-methane system where a ca. 5:4 preference for the cyclopropane with ethyl trans to the residual π-moiety was observed.[17] Presently, the same stereoselectivity is observed both for singlet and triplet reactions. One view of the stereochemistry envisages initial formation of the *trans*-cyclopropyldicarbinyl diradical **31**. The final step of the di-π-methane rearrangement involves three-ring formation with inversion of configuration at the "methane" carbon; this is quantum mechanically equivalent[18] to a bicycle process wherein the methane carbon moves along the four carbon chain, finally bonding to carbons 1 and 2. In the present instance there are two such pathways, one leading to cis product and one to trans. This is shown in Figure 4. It is seen that pathway a leading to the trans isomer **25a** is preferred as a consequence of the smaller van der Waals interactions encountered as a result of the diphenylvinyl and isopropyl groups being transoid.

Stereoelectronic Effects on Regioselectivity. An intriguing facet of the di-π-methane rearrangement of dimesityl diene **3** is the complete regioselectivity leading to the product with the mesityl groups on the residual double bond. For hydrocarbon systems lacking either electron donating or withdrawing groups, the generalization has been put forth that the less delocalized center in the

(16) Zimmerman, H. E.; Baum, A. A. *J. Am. Chem. Soc.* **1971**, *93*, 3646–3653.

(17) Zimmerman, H. E.; Robbins, J. D.; McKelvey, R. D.; Samuel, C. J.; Sousa, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 4630–4643.

(18) Zimmerman, H. E. *Chimia* **1982**, *36*, 423–428.

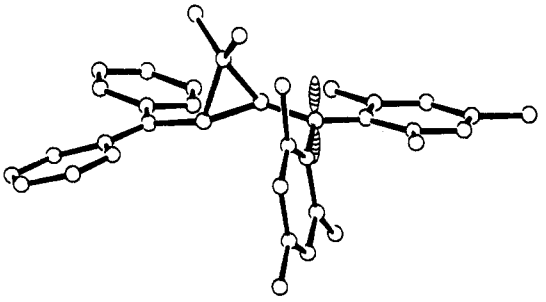
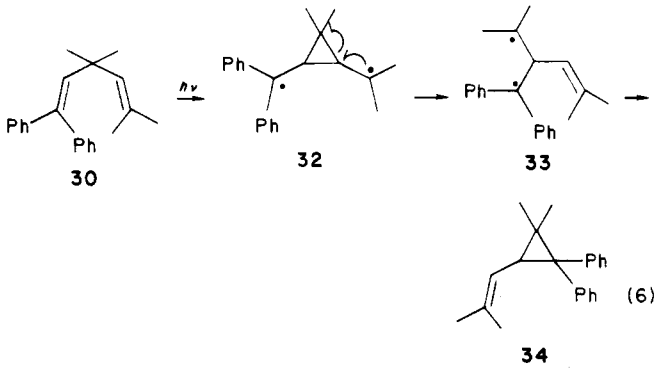


Figure 5. ORTEP drawing of dimesityldiphenyl diradical **35**.

cyclopropyldicarbinyl diradical species is the one dissipated in three-ring opening.[19] The basic premise is that such selectivity maximizes electron delocalization as the three ring opens by virtue of maintaining the more delocalized diradical moiety. For example, in the cyclopropyldicarbinyl diradical **32** derived from diene **30**[19] (note eq 6), the isopropylidene moiety is regenerated as a consequence of this principle of maintaining maximum delocalization.



(6)

In the present instance, molecular mechanics[14d] indicated that in diradical **35** the mesityl groups tend to twist perpendicular to one another (mesityls are twisted 76° and 6.5° out of the plane of the p orbital; phenyls are twisted 16° and 7.5°). The MM2 structure in Figure 5 shows that there is greater delocalization to be lost at the benzhydryl diradical center than at the dimesitylmethyl alternative.

Conclusion

The present study is seen to show that steric congestion leads to an inhibition of vibrationally occasioned radiationless decay with a net enhancement of triplet reactivity and a somewhat lesser effect on singlet reactivity.

Experimental Section[20]

Dimethyl 3,3-Diisopropylglutarate. A solution of 12.0 g (0.055 mol) of 3,3-diisopropylglutaric acid[6] in 50 mL of methanol containing 0.50 mL of concentrated sulfuric acid was refluxed for 12 h. The solution was concentrated followed by basic workup.[20d] Distillation gave 12.0 g (90%) of dimethyl 3,3-diisopropylglutarate as a colorless liquid, bp 95–110 °C (3 mm): 100-MHz NMR ($CDCl_3$) δ 3.66 (s, 6 H, OCH_3), 2.54 (s, 4 H, CH_2), 2.11 (septet, 2 H, J = 7 Hz, CH), 0.93 (d, 12 H, J = 7 Hz, CH_3); IR (neat film) 2945, 2875, 1730, 1458, 1433, 1282, 1251, 1140, 1105, 755 cm^{-1}; MS, m/e 244.1674 (calcd for $C_{13}H_{24}O_4$ 244.1675).

Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 63.87; H, 9.84.

3,3-Diisopropyl-5,5-diphenyl-5-hydroxypentanoic Acid Lactone. To a stirred solution of 8.18 g (0.033 mol) of dimethyl 3,3-diisopropylglutarate in 50 mL of anhydrous ether was added dropwise over 0.5 h 140 mL (0.168 mol) of ethereal 1.2 M phenyllithium followed by stirring for 1 h. The mixture was poured into 100 mL of 0 °C saturated ammonium chloride solution. Neutral workup[20d] afforded 8.6 g of a brown oil. The oil was chromatographed on a 3 × 30 cm silica gel/hexane slurry packed column. Elution with 5% ether/hexane gave, after 250 mL containing biphenyl, 7.1 g (64%) of lactone as a yellow solid, mp 75–86 °C. Recrystallization of the latter from methanol gave 6.70 g (60%) of 3,3-diisopropyl-5,5-diphenyl-5-hydroxypentanoic acid lactone, mp 90–92 °C: The spectral data were as follows: 100-MHz NMR ($CDCl_3$) δ 7.63–7.17 (m, 10 H, Ar), 2.60 (s, 2 H, CH_2), 2.15 (s, 2 H, CH_2), 1.73 (septet, 2 H, J = 7 Hz, CH), 0.83 (d, 12 H, J = 7 Hz, CH_3); IR ($CHCl_3$) 3020, 2945, 1735, 1593, 1487, 1443, 1260, 1220, 1058, 910 cm^{-1}; MS, m/e 336.2090 (calcd for $C_{23}H_{28}O_2$ 336.2089).

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.20; H, 8.30. Found: C, 81.99; H, 8.10.

Methyl 3,3-Diisopropyl-5,5-diphenyl-4-pentenoate. Gaseous hydrogen chloride was passed into a solution of 6.07 g (0.018 mol) of 3,3-diisopropyl-5,5-diphenyl-5-hydroxypentanoic acid lactone in 100 mL of methanol for 2 h at a rate to maintain gentle refluxing. After concentration, the residual brown oil was chromatographed on a 4 × 100 cm silica gel/hexane slurry packed column. Hexane was used as the eluting solvent, and 50-mL fractions were collected: fractions 11–16, 1.7 g of an uncharacterized white solid; 17–50, 2.50 g (40%) of the ester, mp 69–74 °C. Recrystallization from methanol afforded 2.41 g (38%) of methyl 3,3-diisopropyl-5,5-diphenyl-4-pentenoate, mp 73–75 °C: 100-MHz NMR ($CDCl_3$) δ 7.05–6.93 (m, 10 H, Ar), 5.68 (s, 1 H, vinyl), 3.38 (s, 3 H, OCH_3), 2.23 (septet, 2 H, J = 7 Hz, CH), 1.97 (s, 2 H, CH_2), 1.03 (d, 6 H, J = 7 Hz, CH_3), 0.91 (d, 6 H, J = 7 Hz, CH_3); IR ($CHCl_3$) 3020, 2950, 2870, 1720, 1592, 1350, 1160, 1140, 1040, 1000, 900, 870 cm^{-1}; MS, m/e 350.2247 (calcd for $C_{24}H_{30}O_2$ 350.2246).

Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.35; H, 8.63. Found: C, 82.14; H, 8.71.

1,1,5,5-Tetraphenyl-3,3-diisopropyl-1,4-pentadiene. To a stirred solution of 2.50 g (7.14 mmol) of methyl 3,3-diisopropyl-5,5-diphenyl-4-pentenoate in 100 mL of anhydrous ether was added dropwise over 15 min 17.8 mL (21.4 mmol) of ethereal 1.2 M phenyllithium followed by stirring at room temperature for 3 h. The mixture was poured into 100 mL of saturated ammonium chloride solution. Neutral workup[20d] gave a yellow solid, mp 91–95 °C, identified by NMR as 1,1,5,5-tetraphenyl-3,3-diisopropyl-4-penten-1-ol: 100 MHz ($CDCl_3$) δ 7.20–6.60 (m, 20 H, Ar), 6.02 (s, 1 H, vinyl), 2.56 (br s, 3 H, CH_2 and OH), 1.94 (septet, 2 H, J = 7 Hz, CH), 0.82 (d, 12 H, CH_3). Without further purification this was dissolved in 50 mL of benzene containing 100 mg of *p*-toluenesulfonic acid. The mixture was refluxed for 12 h and poured into 100 mL of saturated sodium bicarbonate solution. Neutral workup[20d] gave a yellow solid, mp 110–117 °C. The solid was eluted through a 3 × 40 cm silica gel/hexane slurry packed column with 1 L of hexane to give, after recrystallization from hexane, 2.50 g (77%) of 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene, mp 123–124 °C: 100-MHz NMR ($CDCl_3$) δ 7.28–6.80 (m, 20 H, Ar), 5.90 (s, 2 H, vinyl), 1.97 (septet, 2 H, J = 7 Hz, CH), 0.85 (d, 12 H, J = 7 Hz, CH_3); IR ($CHCl_3$) 3040, 3000, 2960, 1598, 1490, 1440, 1380, 1340, 1245, 1000, 930, 900 cm^{-1}; UV (95% ethanol) λ_{max} 246 nm (ε 22 000), 289 (1600), 337 (<1); MS, m/e 456.2830 (calcd for $C_{35}H_{36}$ 456.2817).

Anal. Calcd for $C_{35}H_{36}$: C, 92.00; H, 8.00. Found: C, 92.01; H, 7.89.

5,5-Dimesityl-3,3-dimethyl-5-hydroxypentanoic Acid Lactone. Ethereal mesityllithium was prepared from 1.91 g (0.271

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

(20) (a) Melting points were determined with a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, 37921. (b) All reactions were run under dry nitrogen unless otherwise stated. Anhydrous sodium sulfate or magnesium sulfate was used as the drying agent. Column chromatography was performed on silica gel (MCB, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into quartz columns with external UV monitoring. HPLC was performed with 254-nm detection at 2000 psi using a 12 in. × 1/8 in. column packed with 7–10 μm porous silica beads.[27] (c) *tert*-Butyl alcohol was distilled from calcium hydride before use. Photograde benzene was prepared by washing with saturated aqueous potassium permanganate and concentrated sulfuric acid, water, sulfuric acid until no discoloration, saturated aqueous sodium bicarbonate, and brine, followed by drying, refluxing over calcium hydride for 10 h, and distillation under nitrogen. (d) Neutral workup refers to dilution with ether, washing with water and brine, drying, filtering, and concentrating in vacuo. Acidic workup added an initial 5% HCl wash after dilution. Basic workup added an initial saturated $NaHCO_3$ wash after dilution.

mol) of lithium metal and 20.0 mL (0.131 mol) of bromomesitylene in 75 mL of anhydrous ether by refluxing for 24 h. To this solution was added dropwise over 15 min 5.0 mL (0.022 mol) of dimethyl 3,3-dimethylglutarate[21] in 25 mL of ether. The solution was refluxed for 9 h, cooled, and filtered through glass wool into 150 mL of saturated ammonium chloride solution. Neutral workup[20d] afforded a solution of solid lactone in mesitylene and bromomesitylene. The solid was collected by filtration and recrystallized from hexane to give 4.95 g (52%) of 5,5-dimesityl-3,3-dimethyl-5-hydroxypentanoic acid lactone, mp 126–128 °C: 270-MHz NMR ($CDCl_3$) δ 6.76 (s, 4 H, Ar), 2.86 (s, 2 H, CH_2), 2.27 (s, 12 H, *o*-Ar CH_3), 2.23 (s, 2 H, CH_2), 2.21 (s, 6 H, *p*-Ar CH_3); 1.25 (s, 6 H, CH_3); IR ($CHCl_3$) 2930, 2860, 1725, 1605, 1468, 1290, cm^{-1}; MS, *m/e* 364.2526 (calcd for $C_{25}H_{32}O_2$ 364.2402).

Anal. Calcd for $C_{25}H_{32}O_2$: C, 82.37; H, 8.85. Found: C, 82.51; H, 8.96.

Methyl 5,5-Dimesityl-3,3-dimethyl-4-pentenoate. A solution of 10.3 g (0.028 mol) of 5,5-dimesityl-3,3-dimethyl-5-hydroxypentanoic acid lactone in 400 mL of methanol containing 100 mg of *p*-toluenesulfonic acid was refluxed for 12 h. Concentration left 10.1 g (95%) of white solid, mp 124–128 °C. Recrystallization from methanol afforded 9.20 g (87%) of methyl 5,5-dimesityl-3,3-dimethyl-4-pentenoate, mp 129–130 °C: 270-MHz NMR ($CDCl_3$) δ 6.75 (s, 2 H, Ar), 6.71 (s, 2 H, Ar), 5.53 (s, 1 H, vinyl), 3,53 (s, 3 H, OCH_3), 2.34 (s, 2 H, CH_2), 2.24 (s, 18 H, Ar CH_3), 1.09 (s, 6 H, CH_3); IR ($CHCl_3$) 2970, 2850, 1735, 1610, 1035, 1015, 860 cm^{-1}; MS, *m/e* 378.2560 (calcd for $C_{26}H_{34}O_2$ 378.2559).

Anal. Calcd for $C_{26}H_{34}O_2$: C, 82.49; H, 9.05. Found: C, 82.18; H, 9.09.

1,1-Dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene. To a solution of 0.51 g (1.32 mmol) of methyl 5,5-dimesityl-3,3-dimethyl-4-pentenoate in 25 mL of anhydrous benzene was added dropwise over 5 min 6.6 mL (3.96 mmol) of ethereal 0.66 M phenyllithium. An additional 25 mL of benzene was added, and the mixture was refluxed for 12 h. The cooled mixture was poured into saturated ammonium chloride solution followed by neutral workup[20d] to afford 1.30 g of a light brown oil identified by NMR as 5,5-dimesityl-1,1-diphenyl-3,3-dimethyl-4-pentenol: 100-MHz ($CDCl_3$) δ 7.60–6.90 (m, 10 H, phenyl), 6.76 (s, 4 H, mesityl), 5.42 (s, 1 H, vinyl), 2.52 (br s, 3 H, CH_2 and OH), 2.22 (s, 12 H, *o*-Ar CH_3), 2.16 (s, 6 H, *p*-Ar CH_3), 0.86 (s, 6 H, CH_3). Without further purification the oil was dissolved in 25 mL of benzene containing 0.10 g of *p*-toluenesulfonic acid and refluxed for 15 h. The mixture was poured into water followed by neutral workup[20d] to leave 1.34 g of brown oil which was chromatographed on a 4 × 40 cm silica gel/hexane slurry packed column. Elution with 1.2 L of hexane gave 530 mg (83%) of white solid, mp 93–96 °C. Recrystallization from methanol gave 490 mg (77%) of 1,1-dimesityl-5,5-diphenyl-3,3-dimethyl-1.4-pentadiene, mp 94–96 °C: 270-MHz NMR ($CDCl_3$) δ 7.40–7.05 (m, 8 H, phenyl), 6.80 (s, 4 H, mesityl), 6.70–6.60 (m, 2 H, phenyl), 6.13 (s, 1 H, vinyl), 5.45 (s, 1 H, vinyl), 2.28 (s, 12 H, *o*-Ar CH_3), 2.20 (s, 6 H, *p*-Ar CH_3), 1.02 (s, 6 H, CH_3); IR ($CHCl_3$) 2990, 2955, 1605, 1487, 1472, 1456, 1439, 1371, 847 cm^{-1}; UV (95% ethanol) λ_{max} 242 nm (ϵ 28 550), 256 sh (18 200), 289 (2300), 337 (<1); MS, *m/e* 484.3131 (calcd for $C_{37}H_{40}$ 484.3130).

Anal. Calcd for $C_{37}H_{40}$: C, 91.68; H, 8.32. Found: C, 91.50; H, 8.29.

Dimethyl 2,3,3,4-Tetramethylglutarate. To a solution of lithium diisopropyl amide prepared at −78 °C from 46.0 mL (0.068 mol) of 1.5 M *n*-butyllithium in hexane and 10.9 mL (0.078 mol) of diisopropylamine in 60 mL of THF was added dropwise over 5 min 5.0 g (0.026 mol) of dimethyl 3,3-dimethylglutarate[21] in 10 mL of THF. The mixture came to 0 °C over 3 h and then was recooled to −78 °C, followed by fast addition of 4.30 mL (0.078 mol) of methyl iodide. The mixture was stirred at room temperature for 20 h and was quenched by pouring into 100 mL of 10% HCl. Acidic workup[20d] left 5.8 g of brown liquid which was quickly eluted through a 3 × 40 cm silica gel/hexane slurry packed column with 5% ether in hexane to give 5.34 g of yellow liquid. Distillation gave 4.81 g (86%) of dimethyl 2,3,3,4-tetramethylglutarate as a colorless liquid, bp 60–65 °C (0.5 mm). The spectral data for the mixture of diastereomers were as follows: 200-MHz NMR ($CDCl_3$) δ 3.65 (s, 6 H, OCH_3), 2.57 (q, 1 H, *J* = 7.0 Hz, CH), 2.54 (q, 1 H, *J* = 7.0 Hz, CH), 1.08 (d, 3 H, *J* = 7.0 Hz, CH_3), 0.99 (s, 6 H, CH_3), 0.96 (d, 3 H, *J* = 7.0 Hz, CH_3); IR (neat) 2950, 2870, 1735, 1440, 1375, 1350, 1030, 980 cm^{-1}; MS, *m/e* 216.1361 (calcd for $C_{11}H_{20}O_4$ 216.1361.

Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.14; H, 9.36.

2,3,3,4-Tetramethyl-5,5-diphenyl-5-hydroxypentanoic Acid Lactone. To a solution of 4.00 g (0.018 mmol) of dimethyl 2,3,3,4-tetramethylglutarate in 100 mL of ether was added dropwise over 0.5 h 81.0 mL (0.065 mol) of ethereal 0.8 M phenyllithium. The mixture was refluxed for 20 h, cooled, and poured into 150 mL of 0 °C saturated ammonium chloride solution. Neutral workup[20d] afforded 5.38 g of light brown oil. Trituration from hexane and filtration gave 3.7 g (67%) of solid lactone, mp 98–102 °C. Recrystallization from hexane afforded 3.02 g (54%) of 2,3,3,4-tetramethyl-5,5-diphenyl-5-hydroxypentanoic acid lactone, mp 101–102 °C: 270-MHz NMR ($CDCl_3$) δ 7.54–7.10 (m, 10 H, Ar), 3.02 (q, 1 H, *J* = 7.4 Hz, CH), 2.25 (q, 1 H, *J* = 6.8 Hz, CH), 1.10 (s, 3 H, CH_3), 1.04 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.87 (s, 3 H, CH_3), 0.69 (d, *J* = 7.4 Hz, CH_3); IR ($CHCl_3$) 2985, 1738, 1450, 1350, 1215, 1120 cm^{-1}; MS *m/e* 308.1777 (calcd for $C_{21}H_{24}O_2$ 308.1776).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 82.08; H, 7.96.

1,1-Diphenyl-2,3,3,4-tetramethylpentane-1,5-diol. A mixture of 4.00 g (0.013 mol) of 2,3,3,4-tetramethyl-5,5-diphenyl-5-hydroxypentanoic acid lactone and 3.70 g (0.097 mol) of lithium aluminum hydride in 80 mL of THF was stirred at room temperature for 12 h and then refluxed for 1 h. The cooled mixture was quenched by slow addition of 3.0 g of $NaSO_4 \cdot 10H_2O$ followed by pouring into 200 mL of water. Neutral workup[20d] afforded 3.32 g (82%) of 1,1-diphenyl-2,3,3,4-tetramethylpentane-1,5-diol as a noncrystalline glassy foam: 270-MHz NMR ($CDCl_3$) δ 7.67–7.42 (m, 4 H, Ar), 7.38–7.04 (m, 6 H, Ar), 3.89 (dd, 1 H, *J* = 13.5, 5.0 Hz, C*H*H), 3.25 (dd, 1 H, *J* = 13.5, 7.0 Hz, CH*H*), 3.09 (q, 1 H, *J* = 6.8 Hz, CH), 2.52 (s, 1 H, OH), 1.87 (s, 1 H, OH), 1.58 (m, 1 H, CH), 0.98 (s, 3 H, CH_3), 0.91 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.86 (d, 3 H, *J* = 6.8 Hz, CH_3), 0.46 (s, 3 H, CH_3); IR ($CHCl_3$) 3590, 3400, 2980, 2875, 1595, 1480, 1445, 1155, 1018, 910 cm^{-1}; MS, *m/e* 312.2086 (calcd for $C_{21}H_{28}O_2$ 312.2089).

Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.72; H, 9.03. Found: C, 80.96; H, 8.89.

1,1-Diphenyl-2,3,3,4-tetramethyl-5-acetoxy-1-pentanol. To a 0 °C solution of 10.1 g (0.210 mol) of a 50% dispersion of sodium hydride in mineral oil (DME washed) in 200 mL of DME was added 6.53 g (0.021 mol) of 1,1-diphenyl-2,3,3,4-tetramethylpentane-1,5-diol in 50 mL of DME. The mixture was stirred at 0 °C for 10 min, and then 10.3 mL (0.11 mol) of acetic anhydride was added dropwise over 2 min. The solution was stirred at room temperature for 20 h and then carefully poured onto 300 g of ice. Neutral workup[20d] afforded 6.95 g (96%) of an oily orange solid, mp 135–137 °C. Recrystallization from pentane gave 6.34 g (85%) of 1,1-diphenyl-2,3,3,4-tetramethyl-5-acetoxy-1-pentanol, mp 132–133 °C: 270-MHz NMR ($CDCl_3$) δ 7.63–7.50 (m, 4 H, Ar), 7.38–7.10 (m, 6 H, Ar), 4.39 (dd, 1 H, *J* = 10.75, 3.13 Hz, (C*H*H), 3.71 (dd, 1 H, *J* = 10.75, 8.72 Hz, CH*H*), 3.13 (q, 1 H, *J* = 6.88 Hz, CH), 2.27 (s, 1 H, OH), 2.08 (s, 3 H, $C(O)CH_3$), 1.76 (m, 1 H, CH), 0.97 (s, 3 H, CH_3), 0.94 (d, 3 H, *J* = 6.88 Hz, CH_3), 0.83 (d, 3 H, *J* = 6.86 Hz, CH_3), 0.46 (s, 3 H, CH_3); IR ($CHCl_3$) 3600, 2980, 1725, 1600, 1440, 1240, 1030 cm^{-1}; MS, *m/e* 354.2190 (calcd for $C_{23}H_{30}O_3$ 354.2195).

Anal. Calcd for $C_{23}H_{30}O_3$: C, 77.93; H, 8.53. Found: C, 77.94; H, 8.47.

2,3,3,4-Tetramethyl-5,5-diphenyl-1-acetoxy-4-pentene. To a mechanically stirred solution of 9.79 g (0.028 mol) of 1,1-diphenyl-2,3,3,4-tetramethyl-5-acetoxy-1-pentanol in 300 mL of pyridine at 0 °C was added dropwise 40.0 mL (0.43 mol) of phosphorus oxychloride followed by refluxing for 20 h, cooling to −78 °C, and quenching by the addition of 100 mL of water. Acidic workup[20d] gave 8.06 g (86%) of 2,3,3,4-tetramethyl-5,5-diphenyl-1-acetoxy-4-pentene as a light brown oil: 270-MHz NMR ($CDCl_3$) δ 7.38–7.05 (m, 10 H, Ar), 4.29 (dd, 1 H, *J* = 10.55, 3.64 Hz, C*H*H), 3.80 (dd, 1 H, *J* = 10.55, 9.34 Hz, CH*H*), 2.10 (m, 1 H, CH), 2.07 (s, 3 H, $C(O)CH_3$), 1.65 (s, 3 H, $C{=}CCH_3$), 0.95 (d, 3 H, *J* = 6.80 Hz, CH_3), 0.92 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3); IR (neat) 3020, 2980, 1734, 1592, 1485, 1440, 1385, 1360, 1240,

(21) Babler, J. H.; Haack, R. A. *Synth. Commun.* **1983**, *13*, 905–911.

1045, 770, 745 cm^{-1}; MS, *m/e* 336.2083 (calcd for $C_{23}H_{28}O_2$ 336.2089).

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.23; H, 8.31.

2,3,3,4-Tetramethyl-5,5-diphenyl-4-pentenol. A solution of 2.43 g (7.23 mmol) of 2,3,3,4-tetramethyl-5,5-diphenyl-1-acetoxy-4-pentene and 0.82 g (21.7 mmol) of lithium aluminum hydride in 80 mL of THF was stirred at room temperature for 20 h and then refluxed for 1 h. The cooled mixture was quenched by addition of 3.0 g of a 3:1 $Na_2SO_4 \cdot 10H_2O$:Celite mixture. Neutral workup[20d] afforded 2.27 g of colorless oil. The oil was chromatographed on a 4 × 40 cm silica gel/hexane slurry packed column, eluting with 20% ether in hexane. The results were as follows: 500 mL, nil; 200 mL, 200 mg of unidentified material; 300 mL, nil; 1 L, 1.77 g (83%) of 2,3,3,4-tetramethyl-5,5-diphenyl-4-pentenol as a colorless oil. The spectral data were as follows: 200 MHz NMR ($CDCl_3$) δ 7.30–7.06 (m, 10 H, Ar), 3.87 (dd, 1 H, *J* = 10.6, 3.6 Hz, CH*H*), 2.34 (dd, 1 H, *J* = 10.6, 9.3 Hz, C*H*H), 1.98 (m, 1 H, CH), 1.67 (s, 3 H, C=CCH_3), 1.24 (br s, 1 H, OH), 0.95 (d, 3 H, *J* = 7.6 Hz, CH_3), 0.90 (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3); IR (neat) 3560, 3320, 2950, 1590, 1490, 1445, 1380, 1070, 1025, 1005, 780, 750, 700 cm^{-1}; MS, *m/e* 294.1986 (calcd for $C_{21}H_{26}O$ 294.1984).

Anal. Calcd for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.41; H, 8.86.

2,3,3,4-Tetramethyl-5,5-diphenyl-4-pentenoic Acid. To 3.98 g (0.013 mol) of 5,5-diphenyl-2,3,3,4-tetramethyl-4-pentenol in 100 mL of acetone at 0 °C was quickly added 17.0 mL of Jones reagent solution (267 g of CrO_3 in 400 mL of H_2O and 230 mL of concentrated H_2SO_4 diluted to 1 L with water). After being stirred for 0.5 h at room temperature, excess reagent was destroyed by addition of 1.0 g of sodium bisulfite followed by pouring into 150 mL of water. Neutral workup[20d] left 3.86 g (96%) of white solid, mp 120–127 °C. Recrystallization from pentane gave 3.48 g (83%) of 2,3,3,4-tetramethyl-5,5-diphenyl-4-pentenoic acid, mp 130–131 °C: 200-MHz NMR ($CDCl_3$) δ 7.29–7.00 (m, 10 H, Ar), 2.88 (q, 1 H, *J* = 7.02 Hz, CH), 1.66 (s, 3 H, C=CCH_3), 1.14 (d, 3 H, *J* = 7.02 Hz, CH_3), 1.13 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3); IR ($CHCl_3$) 3400–2400, 1705, 1490, 1460, 1445, 1415, 1240 cm^{-1}; MS, *m/e* 308.1777 (calcd for $C_{21}H_{24}O_2$ 308.1776).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78, H, 7.84. Found: C, 82.03; H, 7.73.

Methyl 2,3,3,4-Tetramethyl-5,5-diphenyl-4-pentenoate. Ethereal diazomethane was prepared from 5.35 g (21.4 mmol) of DuPont EXR-101 as described by Moore and Reed[22] and distilled into a solution of 3.48 g (0.012 mol) of 2,3,3,4-tetramethyl-5,5-diphenyl-4-pentenoic acid in 100 mL of ether. The solution remained for 2 h at room temperature, and then the excess diazomethane was removed with a stream of nitrogen. The solution was concentrated to leave 3.62 g (98%) of methyl 2,3,3,4-tetramethyl-5,5-diphenyl-4-pentenoate as a colorless oil: 270-MHz NMR ($CDCl_3$) δ 7.37–7.07 (m, 10 H, Ar), 3.68 (s, 3 H, OCH_3), 2.86 (q, 1 H, *J* = 7.3 Hz, CH), 1.62 (s 3 H, C=CCH_3), 1,12 (d, 3 H, *J* = 7.3 Hz, CH_3), 1.09 (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3); IR (neat) 3020, 2970, 1730, 1595, 1490, 1445, 1395, 1375, 1350, 1250, 1200, 1150, 1120, 1085, 1080, 1035, 770, 755, 700 cm^{-1}.

Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.94; H, 8.13. Found: C, 81.81; H, 8.03.

1,1,5,5-Tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene. To a solution of 3.69 g (0.012 mol) of methyl 2,3,3,4-tetramethyl-5,5-diphenyl-4-pentenoate in 140 mL of ether was added dropwise over 0.5 h 50 mL (0.033 mol) of ethereal 0.66 M phenyllithium. The mixture was refluxed for 3 h, cooled, and poured into 200 mL of saturated ammonium chloride solution. Neutral workup[20d] afforded 6.09 g of a colorless oil identified by NMR as 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-4-pentenol: 270-MHz NMR ($CDCl_3$) δ 7.51–6.80 (m, 20 H, Ar), 3.38 (q, 1 H, *J* = 7.2 Hz, CH), 2.26 (s, 1 H, OH), 1.70 (s, 3 H, C=CCH_3), 1.18 (s, 3 H, CH_3), 1.10 (d, 3 H, *J* = 7.2 Hz, CH_3), 0.58 (s, 3 H, CH_3). Without further purification the oil was dissolved in 150 mL of pyridine containing 6.0 mL (0.082 mol) of thionyl chloride and stirred at room temperature for 3 h. The mixture was poured onto 200 g of ice and subjected to neutral workup,[20d] affording 6.08 g of brown oil. The oil was chromatographed on a 4 × 100 cm silica gel/hexane slurry packed column. Elution with 2.5 L of hexane gave 2.75 g (54%) of white solid, mp 95–102 °C. Recrystallization from methanol gave 2.60 g (51%) of 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene, mp 99–102 °C: 200-MHz NMR ($CDCl_3$) δ 7.30–6.98 (m, 20 H, Ar), 1.68 (s, 6 H, C=CCH_3), 1.01 (s, 6 H, CH_3); IR ($CHCl_3$) 3035, 2985, 2960, 1595, 1490, 1445, 1380, 1110, 1070, 1030, 1010 cm^{-1}; UV (95% ethanol) λ_{max} 268 nm sh (ε 4400), 228 sh (21 000), 289 (220), 337 (<1); MS, *m/e* 428.2503 (calcd for $C_{33}H_{32}$ 428.2504).

Anal. Calcd for $C_{33}H_{32}$: C, 92.47; H, 7.52. Found: C, 92.24; H, 7.59.

Dimethyl 3-Isopropyl-3-methylglutarate. A mixture of 49.2 g (0.262 mol) of 3-isopropyl-3-methylglutaric acid[6] and 1.0 mL of concentrated sulfuric acid in 300 mL of methanol was refluxed for 20 h. The cooled mixture was poured into water and subjected to neutral workup[20d] followed by distillation of the residue to give 43.5 g (77%) of dimethyl 3-isopropyl-3-methylglutarate as a clear, colorless liquid, bp 85–90 °C (1.5 mm): 200-MHz NMR ($CDCl_3$) δ 3.61 (s, 6 H, OCH_3), 2.46 (s, 4 H, CH_2), 1.82 (septet, 1 H, *J* = 6.8 Hz, CH), 0.99 (s, 3 H, CH_3), 0.83 (d, 6 H, *J* = 6.8 Hz, CH_3); IR (neat) 2985, 2940, 1740, 1460, 1440, 1385, 1355, 1335, 1230, 1170, 1050, 1010 cm^{-1}.

Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found: C, 61.21; H, 9.21.

5,5-Diphenyl-3-isopropyl-3-methyl-5-hydroxypentanoic Acid Lactone. To a 0 °C solution of 15.0 g (0.080 mol) of dimethyl 3-isopropyl-3-methylglutarate in 150 mL of anhydrous ether was added dropwise over 0.5 h 265 mL (0.175 mol) of ethereal 0.66 M phenyllithium. The mixture was refluxed for 3 h, cooled, and poured into 500 mL of saturated ammonium chloride solution. Neutral workup[20d] left 16.8 g of light brown oil which was chromatographed on a 5 × 40 cm silica gel/hexane slurry packed column. Elution with hexane (3 L) gave 14.3 g (58%) of 5,5-diphenyl-3-isopropyl-3-methyl-5-hydroxypentanoic acid lactone as a colorless oil after removal of biphenyl in the first 500 mL: 270-MHz NMR ($CDCl_3$) δ 7.80–7.05 (m, 10 H, Ar), 2.64 (d, of AB q, 1 H, *J* = 15.0 Hz, C*H*H), 2.52 (d of AB q, 1 H, *J* = 15.0 Hz, CH*H*), 2.22 (d of AB q, 1 H, *J* = 15.6 Hz, C*H*H), 2.14 (d of AB q, 1 H, *J* = 15.6 Hz, CH*H*), 1.58 (septet, 1 H, *J* = 6.7 Hz, CH), 0.94 (s, 3 H, CH_3), 0.93 (d, 3 H, *J* = 6.7 Hz, CH_3), 0.85 (d, 3 H, *J* = 6.7 Hz, CH_3); IR (neat) 3025, 2950, 2860, 1755, 1600, 1270, 1235, 1120, 1055, 1000 cm^{-1}; MS, *m/e* 308.1776 (calcd for $C_{21}H_{24}O_2$ 308.1776).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.72; H, 7.87.

Methyl 5,5-Diphenyl-3-isopropyl-3-methyl-4-pentenoate. A solution of 13.5 g (0.044 mol) of 5,5-diphenyl-3-isopropyl-3-methyl-5-hydroxypentanoic acid lactone and 1.0 mL of concentrated hydrochloric acid in 300 mL of methanol was refluxed for 12 h. The cooled mixture was poured into 300 mL of water followed by neutral workup[20d] giving 12.5 g of a light brown oil. The oil was chromatographed on a 5 × 40 cm silica gel/hexane slurry packed column. Elution with 2% ether/hexane gave 11.8 g (83%) of methyl 5,5-diphenyl-3-isopropyl-3-methyl-4-pentenoate as a colorless oil: 270-MHz NMR ($CDCl_3$) δ 7.41–6.90 (m, 10 H, Ar), 6.07 (s, 1 H, vinyl), 3.66 (s, 3 H, OCH_3), 2.43 (d of AB q, 1 H, *J* = 15.0 Hz, C*H*H), 2.34 (d of AB q, 1 H, *J* = 15.0 Hz, CH*H*), 1.82 (septet, 1 H, *J* = 6.7 hz, CH), 0.95 (d, 3 H, *J* = 6.7 Hz, CH_3), 0.90 (d, 3 H, *J* = 6.7 Hz, CH_3), 0.78 (s, 3 H, CH_3); IR (neat) 2980, 1738, 1600, 1495, 1465, 1445, 1165 cm^{-1}; MS, *m/e* 322.1931 (calcd for $C_{22}H_{26}O_2$ 322.1933).

Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.79; H, 8.26.

1,1,5,5-Tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene. To a 0 °C solution of 5.00 g (0.015 mol) of methyl 5,5-diphenyl-3-isopropyl-3-methyl-4-pentenoate in 100 mL of anhydrous ether at 0 °C was added dropwise over 10 min 51.7 mL (0.034 mol) of ethereal 0.66 M phenyllithium followed by reflux for 2 h. The mixture was poured into 300 mL of saturated ammonium chloride solution. Neutral workup[20d] afforded 7.4 g of a brown oil identified by NMR as 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-4-penten-1-ol: 270-MHz ($CDCl_3$) δ 7.48–7.41 (m, 4 H, Ar), 7.30–6.97 (m, 16 H, Ar), 6.05 (s, 1 H, vinyl), 3.28 (s, 1 H, OH), 2.70 (d of AB q, 1 H, *J* = 13.3 Hz, C*H*H), 2.61 (d of AB q, 1 H, *J* = 13.3 Hz, CH*H*),

(22) Moore, J. A.; Reed, D. E. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 351.

1.68 (septet, 1 H, J = 7.1 Hz, CH), 0.90 (d, 3 H, J = 7.1 Hz, CH_3), 0.87 (d, 3 H, J = 7.1 Hz, CH_3), 0.34 (s, 3 H, CH_3). Without further purification the oil was dissolved in 300 mL of benzene containing 100 mg of *p*-toluenesulfonic acid and was refluxed for 20 h. The mixture was poured into 300 mL of water followed by neutral workup[20d] to give 6.8 g of a brown oil which was chromatographed on a 3 × 100 cm silica gel/hexane slurry packed column. Elution was with hexane. The fractions were as follows: 1.8 L, nil; 1 L, 4.94 g (77%) of the diene, mp 98–107 °C, which was recrystallized from methanol to give 4.31 g of 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene, mp 103–104 °C. The spectral data were as follows: 200-MHz NMR ($CDCl_3$) δ 7.30–6.92 (m, 20 H, Ar), 5.93 (s, 2 H, vinyl), 1.86 (septet, 1 H, J = 6.7 Hz, CH), 0.94 (d, 6 H, J = 6.7 Hz, CH_3), 0.65 (s, 3 H, CH_3); IR ($CHCl_3$) 3020, 2970, 1590, 1485, 1440, 1070 cm^{-1}; MS, m/e 428.2505 (calcd for $C_{33}H_{32}$ 428.2503); UV (95% EtOH) λ_{max} 250 nm (ϵ 23 900), 289 (2300), 337 (<1).

Anal. Calcd for $C_{33}H_{32}$: C, 92.30; H, 7.52. Found: C, 92.30; H, 7.54.

General Conditions for Exploratory Photolyses. Solutions were purged with purified[23] nitrogen for 1.0 h prior to and during the photolyses. Irradiations were carried out with a Hanovia 450-W medium-pressure lamp through either 2.0 mm Corex (λ >270 nm) or 2.0 mm Pyrex (λ >300 nm) filters.

Exploratory Direct Photolysis of 1,1,5,5-Tetraphenyl-3,3-diisopropyl-1,4-pentadiene. A solution of 260 mg (0.570 mmol) of 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene in 250 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 1.0 h through Corex. Concentration left 298 mg of a yellow solid that was chromatographed on a 1 × 40 cm silica gel/hexane slurry packed column. Elution was with hexane, and 15-mL fractions were collected: fractions 3–4, 184 mg (71%) of 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene, mp 122–124 °C; 5, 37.4 mg of a mixture of starting diene and cyclopropane product; 6–8, 35.5 mg (14%) of cyclopropane. Recrystallization from methanol gave 29.9 mg (12%) of 1,1-diphenyl-2,2-diisopropyl-3-(2,2-diphenylvinyl)cyclopropane, mp 189–190 °C: 270-MHz NMR ($CDCl_3$) δ 7.60–7.45 (m, 6 H, Ar), 7.45–6.92 (m, 14 H, Ar), 5.82 (d, 1 H, J = 11.10 Hz, vinyl), 2.25 (d, 1 H, J = 11.10 Hz, cyclopropyl CH), 1.94 (septet, 1 H, J = 6.88 Hz, CH), 1.45 (d, 3 H, J = 6.88 Hz, CH_3), 1.17 (d, 3 H, J = 6.88 Hz, CH_3), 1.05–0.85 (m, 7 H, CH_3 and CH); IR ($CHCl_3$) 3040, 2960, 1595, 1390, 1365, 1180, 1145, 1070, 1030 cm^{-1}; UV (95% EtOH) λ_{max} 246 nm (ϵ 22 000); MS, m/e 456.2818 (calcd for $C_{35}H_{36}$ 456.2817).

Anal. Calcd for $C_{35}H_{36}$: C, 92.00; H, 8.00. Found: C, 92.12; H, 8.07.

Exploratory Acetophenone-Sensitized Photolysis of 1,1,5,5-Tetraphenyl-3,3-diisopropyl-1,4-pentadiene. A solution of 203 mg (0.445 mmol) of 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene and 1.04 g (8.80 mmol) of acetophenone in 200 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 1.0 h through Pyrex. The solution was concentrated, and residual acetophenone was removed by bulb-to-bulb distillation (40 °C, 0.010 mm). The residue was chromatographed on a 1 × 100 cm silica gel/hexane slurry packed column. Elution was with hexane, with 20-mL fractions being collected: fractions 1–5, 119 mg (57%) of 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene, mp 123–124 °C; 6–7, 13.5 mg of overlap; 8–11, 106 mg of cyclopropane that was recrystallized from methanol to give 87 mg (42%) of 1,1-diphenyl-2,2-diisopropyl-3-(2,2-diphenylvinyl)cyclopropane, mp 188–190 °C, identical in spectral properties to material isolated in the direct photolysis.

Exploratory Benzophenone-Sensitized Photolysis of 1,1,5,5-Tetraphenyl-3,3-diisopropyl-1,4-pentadiene. A solution of 200 mg (0.438 mmol) of 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene and 1.56 g (8.57 mmol) of benzophenone in 250 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 1.0 h through Pyrex. The solution was concentrated to leave an oil that was chromatographed on a 1 × 40 cm silica gel/hexane slurry packed column. Elution was with 500 mL of hexane. Two bands were observed: band one, 214 mg of a mixture of 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene and 1,1-diphenyl-2,2-diisopropyl-3-(2,2-diphenylvinyl)cyclopropane; band two, 1.52 g of recovered benzophenone. The mixture from band one was further chromatographed on a 1 × 50 cm silica gel/hexane slurry packed column, eluting with hexane to give 20-mL fractions: fractions 3–5, 41 mg (21%) of recovered diene, mp 122–124 °C; 7–10, 146 mg (73%) of 1,1-diphenyl-2,2-diisopropyl-3-(2,2-diphenylvinyl)cyclopropane. The cyclopropane was recrystallized from methanol to give 113 mg (57%) of material, mp 189–190 °C, with spectral properties identical with those of the material isolated in the direct photolysis.

Exploratory Direct Photolysis of 1,1-Dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene. A solution of 158 mg (0.326 mmol) of 1,1-dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene in 150 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 15 min through Corex. The solution was concentrated in vacuo to leave 184 mg of yellow foam that was chromatographed on a 3 × 40 cm silica gel/hexane slurry packed column. Elution was as follows. 2.5 L of Hexane, nil; 2.5% methylene chloride/hexane in 30-mL fractions: 1–11, 95 mg (60%) of recovered diene starting material, mp 94–96 °C; 4–6, 9.8 mg of overlap; 7–20, 47 mg (30%) of cyclopropane that was recrystallized from methanol to give 35 mg (22%) of 1,1-diphenyl-2,2-dimethyl-3-(2,2-dimesitylvinyl)cyclopropane, mp 184–186 °C.

The spectral data for the cyclopropane were as follows: 200-MHz NMR ($CDCl_3$) δ 7.45–6.85 (m, 10 H, Ar), 6.80 (s, 2 H, Ar), 6.75 (s, 2 H, Ar), 5.30 (d, 1 H, J = 10.0 Hz, vinyl), 2.29–2.15 (5 s, 18 H, Ar CH_3), 2.06 (d, 1 H, J = 10.0 Hz, cyclopropyl CH), 1.30 (s, 3 H, CH_3), 1.00 (s, 3 H, CH_3); IR ($CHCl_3$) 2990, 2940, 2860, 1604, 1486, 1472, 1441, 1372, 1110, 1095, 850 cm^{-1}; MS m/e 484.3131 (calcd for $C_{37}H_{40}$ 484.3130); UV (95% EtOH) λ_{max} 264 nm sh (ϵ 18 700), 260 (19 500), 242 sh (20 500).

Anal. Calcd for $C_{37}H_{40}$: C, 91.68; H, 8.32. Found: C, 91.59; H, 8.41.

Exploratory Acetophenone-Sensitized Photolysis of 1,1-Dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene. A solution of 150 mg (0.310 mmol) of 1,1-dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene and 0.860 g (7.17 mmol) of acetophenone in 150 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 1.0 h through Pyrex. The solution was concentrated, and residual acetophenone was removed by bulb-to-bulb distillation (40 °C, 0.010 mm). The residue was chromatographed on a 1 × 40 cm silica gel/hexane slurry packed column, eluting with hexane (100 mL) and then 10% methylene chloride in hexane. Fractions of 40 mL were taken: 1–2, 51 mg (34%) of recovered diene starting material, mp 94–95 °C; 3, 20 mg of a mixture consisting mainly of starting diene; 4–12, 65 mg (43%) of 1,1-diphenyl-2,2-dimethyl-3-(2,2-dimesitylvinyl)cyclopropane, mp 184–185 °C, with spectral properties identical with those of material isolated in the direct photolysis.

Exploratory Direct Photolysis of 1,1,5,5-Tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene. A solution of 160 mg (0.374 mmol) of 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene in 250 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 6.0 h through Corex. The solution was concentrated to leave 151 mg of yellow solid which was chromatographed on a 1 × 40 cm silica gel/hexane slurry packed column. Elution with 200 mL of 10% ether in hexane gave 137 mg (86%) of recovered 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene, identical in physical and spectroscopic properties with synthetic material. No photoproducts were detectable.

Exploratory Sensitized Photolysis of 1,1,5,5-Tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene. A solution of 168 mg (0.392 mmol) of 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene and 0.92 g (7.67 mmol) of acetophenone in 170 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 6.0 h through Pyrex. The solution was concentrated and acetophenone was removed by bulb-to-bulb distillation (30 °C, 0.05 mm). The residue was chromatographed on a 1 × 40 cm silica gel/hexane slurry packed column, eluting with hexane. The first 300 mL gave 145 mg (86%) of 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene, identical in physical and spectroscopic properties with synthetic material. No photoproducts were detectable.

Control Run. Photoreduction of Benzophenone by Benzhydrol. A solution of 3.00 g (16.0 mmol) of benzophenone and 1.00 g (5.43 mmol) of benzhydrol in 250 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 2.5 h

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through Pryex to give 2.87 g of benzopinacol, mp 187–190 °C.

Energy Transfer Test. Quenching of Benzophenone Triplets by 1,1,5,5-Tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene. A solution of 3.00 g (16.0 mmol) of benzophenone, 1.00 g (5.43 mmol) of benzhydrol, and 200 mg (0.47 mmol) of 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene in 250 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 2.5 h through Pyrex. The solution was concentrated to leave 4.64 g of oil. The oil was chromatographed on a 3.0 × 100 cm silica gel/hexane slurry packed column. Fractions of 50 mL were collected: 11–20, hexane, 196 mg (98%) of unreacted 1,1,5,5-tetraphenyl-2,3,3,4-tetramethyl-1,4-pentadiene; 21–33, 2% ether/hexane, 2.78 g of benzophenone; 34–38, 3% ether/hexane, 206 mg of a mixture of benzophenone and benzopinacol; 39–45, 3% ether/hexane, 345 mg of benzopinacol, mp 188–190 °C; 46–55, 10% ether/hexane, 831 mg of benzhydrol, mp 62–66 °C.

Exploratory Sensitized Photolysis of 1,1,5,5-Tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene. A solution of 166 mg (0.388 mmol) of 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene and 0.93 g (7.75 mmol) of acetophenone in 170 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 3.0 h through Pyrex. The solution was concentrated, and the acetophenone was removed by bulb-to-bulb distillation (40 °C, 0.1 mm) to leave 196 mg of oil. Analysis by 200-MHz NMR indicated an approximately 30% conversion to a 4:1 mixture of *trans*- and *cis*-vinylcyclopropanes. The residue was chromatographed on a 4.0 × 100 cm silica gel/hexane slurry packed column, eluting with 1% methylene chloride in hexane and taking 40-mL fractions: 67–100, 97 mg (58%) of the diene starting material, mp 103–104 °C; 131–150, 22 mg (13%) of material identified as *trans*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)-cyclopropane that was recrystallized from methanol, mp 157–158 °C; 151–170, 30 mg (18%) of a 6:1 mixture of *trans*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane and *cis*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane; 171–185, 12 mg (7%) of a 2:1 mixture of trans and cis vinylcyclopropanes.

The spectral data for the *trans*-cyclopropane were as follows: 270-MHz NMR ($CDCl_3$) δ 7.52–6.94 (m, 20 H, Ar), 5.69 (d of AB q, 1 H, J = 10.6 Hz, vinyl), 2.16 (d of AB q, 1 H, J = 10.6 Hz, cyclopropyl CH), 1.09 (s, 3 H, CH_3), 0.90 (d, J = 2.8 Hz, 3 H, CH_3), 0.77 (septet, 1 H, J = 2.5 Hz, CH), 0.76 (d, 3 H, J = 1.8 Hz, CH_3); IR ($CHCl_3$) 3030, 3000, 2975, 1600, 1495, 1450, 1080, 1035 cm^{-1}; MS, m/e 428.2505 (calcd for $C_{33}H_{32}$ 428.2503); UV (95% EtOH) λ_{max} 267 nm (ε 17 100), 220 sh (22 400).

Anal. Calcd for $C_{33}H_{32}$: C, 92.47; H, 7.52. Found: C, 92.38; H, 7.46.

Exploratory Direct Photolysis of 1,1,5,5-Tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene. A solution of 171 mg (0.399 mmol) of 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene in 170 mL of anhydrous *tert*-butyl alcohol was irradiated (450-W Hanovia) for 15 min through Corex. The solution was concentrated to leave 201 mg of a yellow oil. The 200-MHz NMR spectrum of the oil showed an approximately 30% conversion to a 2:1 mixture of *trans*- and *cis*-vinylcyclopropanes. The oil was chromatographed on a 3.0 × 100 cm silica gel/hexane slurry packed column, eluting with 1% methylene chloride in hexane and taking 40-mL fractions: 51–73, 83 mg (49%) of the diene starting material, mp 102–104 °C; 97–116, 17 mg (10%) of *trans*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)-cyclopropane identical in spectral and physical properties with that from the sensitized photolysis; 117–136, 38 mg (22%) of a 2:1 mixture of *trans*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane and *cis*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane.

Ozonolysis of a Mixture of *cis*- and *trans*-1,1-Diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane. Isolation of *cis*-1,1-Diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane. A 2:1 mixture of 73 mg (0.170 mmol) of *cis*- and *trans*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane was dissolved in 50 mL of methanol containing 10 mL of methylene chloride and filtered. The solution was cooled to 0 °C, and ozone (0.55 mmol) was bubbled through. The solution was stirred for 20 min and then was purged with nitrogen for 5 min to remove excess ozone. Treatment with 0.50 g (13.1 mmol) of sodium borohydride and stirring at 0 °C for 10 min followed by heating on a steam bath for 10 min preceded concentration and neutral workup[20d] to leave 66 mg of white solid. The IR spectrum of the solid displaced a weak hydroxyl absorption. The solid was chromatographed on a 3 × 40 cm silica gel/hexane slurry packed column. Elution was a follows: 5% methylene chloride/hexane, 500 mL, nil; 500 mL 43 mg (59%) of *cis*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane; 5% ether/hexane, 1 L, nil; 20% ether/hexane, 750 mL, 17 mg of an uncharacterized oil, the spectra of which indicated decomposition of material originally placed on the column had taken place. The vinylcyclopropane was recrystallized from methanol to give 29 mg (40%) of *cis*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane, mp 154–155 °C.

The spectral data for the *cis*-cyclopropane were as follows: 270-MHz NMR ($CDCl_3$) δ 7.50–6.90 (m, 20 H, Ar), 5.75 (d of AB q, 1 H, J = 11.0 Hz, vinyl), 2.11 (d of AB q, 1 H, J = 11.0 Hz, cyclopropyl CH), 1.84 (septet, 1 H, J = 6.4 Hz, CH), 1.30 (d, 3 H, J = 6.4 Hz, CH_3), 1.06 (d, 3 H, J = 6.4 Hz, CH_3), 0.79 (s, 3 H, CH_3); IR ($CHCl_3$) 3020, 3000, 1600, 1485, 1450, 1080, 1040 cm^{-1}; MS, m/e 428.2506 (calcd for $C_{33}H_{32}$ 428.2504); UV (95% EtOH) λ_{max} 270 nm (ε 18 000), 222 sh (23 100).

Anal. Calcd for $C_{33}H_{32}$: C, 92.30; H, 7.52. Found: C, 92.41; H, 7.61.

Sensitized Interconversion of *cis*- and *trans*-1,1-Diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropanes. Mixtures of *cis*- and *trans*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane in 150 mL of anhydrous *tert*-butyl alcohol containing 1.0 mL of acetophenone were each irradiated for 1.0 h (450-W Hanovia) through Pyrex. The solutions were concentrated, and the acetopheonone was removed by bulb-to-bulb distillation (40 °C, 0.1 mm). Analysis was by 200-MHz NMR. The data are reported as follows: amount of material photolyzed, initial ratio of *trans*- to *cis*-cyclopropane, final ratio of *trans*- to *cis*-cyclopropane. Run 1; 65 mg, 5.4:1, 4.8:1. Run 2; 63 mg, 1:0, 4.2:1. Run 3; 71 mg 1:1, 4.3:1.

Photolysis Equipment for Quantum Yield Determinations. Quantum yields for all compounds except 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene were performed on the microoptical bench[24] in 46.0 mL of solvent. Quantum yields for 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene were performed on the "black box"[24] in 750 mL of solvent. Light output was measured by a digital actinometer[25] calibrated by ferrioxalate actinometry.[26] For microbench runs, the monochrometer inlet slit was set a 5.4 mm and the exit slit at 3.0 mm to give a band-pass of 22 nm at half-peak height. For "black box" runs the two filter solutions[24] used were the following: filter A (a) 2.0 M nickel sulfate in 5% sulfuric acid, (b) 0.8 M cobalt sulfate in 5% sulfuric acid, and (c) 2.46×10^{-3} M bismuth trichloride in 40% hydrochloric acid (this combination gave a transmission maximum at 285 nm (32% transmission) and was opaque above 325 nm and below 250 nm); filter B (a) 0.5 M nickel sulfate in 5% sulfuric acid, (b) 2.0 M cobalt sulfate in 5% sulfuric acid, and (c) 1.0 M cupric sulfate in 5% sulfuric acid (this combination gave a transmission maximum at 337 nm (24% transmission) and was opaque above 375 nm and below 310 nm). All runs were purged with purified nitrogen[23] for 1.0 h before and during photolysis. All runs, except those for 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene, were analyzed by HPLC, eluting with 10% methylene chloride in anhydrous hexane. Naphthalene was used as an internal standard. For 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene all runs were analyzed by 200-MHz NMR with 4-methoxybenzophenone used as an internal standard. In sensitized runs, acetophenone was removed by bulb-to-bulb distillation (40 °C, 0.010 mm) and benzophenone was removed by chromatography on silica gel (hexane elution) prior to analysis. In sensitized runs 99% of the available light was absorbed by the sensitizer. The results are summarized in Tables VI–VIII.

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Table VI. Summary of Quantum Yield Data for 1,1,5,5-Tetraphenyl-3,3-diisopropyl-1,4-pentadiene (1)[a-d]

run	diene, mmol	additive, mmol	light input, mE	% convn	photoproduct × 10^2, mmol	quantum yield
1	0.099		0.0998	4.1	0.405	0.040
2	0.099		0.0354	1.8	0.175	0.050
3	0.112		0.0230	1.2	0.132	0.057
4	0.111		0.0390	1.9	0.207	0.052
5	0.097		0.0430	2.3	0.225	0.052
6	0.095	B	0.0845	1.5	0.142	0.017
7	0.130	B	0.148	1.9	0.245	0.017
8	0.047	B	0.0620	2.2	0.104	0.017
9	0.096	B	0.0739	1.4	0.132	0.018
10	0.049	A	0.0469	1.8	0.085	0.018
11	0.100	A	0.177	3.2	0.322	0.018
12	0.099	A	0.116	2.1	0.207	0.018
13	0.0667	A	0.0732	1.3	0.0873	0.012
14	0.0328	A	0.0530	1.6	0.052	0.010
15	0.0708	A	0.156	2.1	0.149	0.0094

[a] Direct runs at 289 nm, sensitized runs at 337 nm. [b] All runs in *tert*-butyl alcohol except runs 13–15 in benzene. [c] A = 4.30×10^{-2} M acetophenone, B = 0.28 M benzophenone. [d] At 337 nm, OD of acetophenone = 4.32, OD of benzophenone = 177, OD of diene 1 <0.004.

Table VII. Summary of Quantum Yield Data for 1,1,5,5-Tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene (2)[a-d]

run	diene, mmol	additive, mmol	light input, mE	% convn	photoproduct × 10^2, mmol	quantum yield
1	1.75		0.92	4.0	8.28 (trans), 2.85 (cis)	0.090 (trans), 0.031 (cis)
2	1.75		1.82	9.0	10.8 (trans), 4.98 (cis)	0.059 (trans), 0.027 (cis)
3	1.75		3.65	12.1	12.2 (trans), 8.90 (cis)	0.034 (trans), 0.024 (cis)
4	1.75		5.35	13.9	12.8 (trans), 11.5 (cis)	0.024 (trans), 0.021 (cis)
5	1.75		7.27	15.4	12.9 (trans), 10.2 (cis)	0.018 (trans), 0.014 (cis)
6	1.12	A	11.10	5.7	5.20 (trans), 1.24 (cis)	0.0047 (trans), 0.0011 (cis)
7	1.12	A	8.21	4.7	4.20 (trans), 1.05 (cis)	0.0051 (trans), 0.0013 (cis)
8	0.58	A	3.26	3.4	1.60 (trans), 0.39 (cis)	0.0049 (trans), 0.0012 (cis)

[a] All runs in *tert*-butyl alcohol. [b] Direct runs at 285 nm, sensitized runs at 337 nm. [c] A = 1.40×10^{-2} M acetophenone. [d] At 337 nm, OD of acetophenone = 1.05, OD of diene **2** <0.002.

Table VIII. Summary of Quantum Yield Data for 1,1-Dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene (3)[a-d]

run	diene, mmol	additive, mmol	light input, mE	% convn	photoproduct × 10^2, mmol	quantum yield
1	0.0679		0.0272	5.0	0.347	0.12
2	0.0656		0.0270	4.9	0.319	0.12
3	0.0674		0.0225	4.1	0.278	0.13
4	0.0667		0.0132	2.8	0.190	0.14
5	0.0677		0.0362	6.3	0.441	0.12
6	0.0887	A	0.0992	2.4	0.211	0.021
7	0.0690	A	0.140	3.0	0.211	0.015
8	0.0306	A	0.0340	2.4	0.073	0.022
9	0.0653	A	0.0690	2.3	0.153	0.022
10	0.0722	A	0.201	6.0	0.429	0.021
11	0.117	A	0.238	5.0	0.588	0.024
12	0.0653	A	0.058	2.9	0.188	0.032

[a] Direct runs at 289 nm, sensitized runs at 337 nm. [b] All runs in *tert*-butyl alcohol except runs 6–9 in benzene. [c] A = 1.30×10^{-2} M acetophenone. [d] At 337 nm OD of acetophenone = 1.31, OD of diene **3** <0.004.

Single Photon Counting. The apparatus and procedure have been described previously.[11b,12] Solvents were methylcyclohexane (Kodak Spectro Grade) and isopentane purified as described previously.[11b] Individual samples were prepared in a 4:1 methylcyclohexane–isopentane solution to give an optical density in the range 0.80–1.5, thoroughly degassed by four freeze–thaw cycles immediately before counting and counted at 77 K until a minimum of 1500 counts in the maximum channel (512 channels total) were obtained. Data were collected at less than 5% of the 30–40-KHz lamp flash rate to ensure exclusion of double photon counting. In separate runs excitation was varied over the range 265–275 nm, and emission was monitored over the range 300–315 nm with an RCA 8850 photomultiplier. The decay rate was independent of excitation and emission wavelengths employed. A single exponential decay function was found in all cases. The data are reported as follows (compound, average lifetime, average rate of decay, number of runs, standard deviation in rate, and estimated error in rate): 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene, 0.27 ns, 3.8×10^9 s^{-1}, 4, 0.60, 16%; 1,1-dimesityl-5,5-diphenyl-3,3-dimethyl-1,4-pentadiene, 5.5 ns, 1.8×10^8 s^{-1}, 4, 0.14, 8%; 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene, 0.29 ns, 3.4×10^9 s^{-1}, 3, 0.62, 18%.

Magic Multipliers. For each compound the fluorescence spectrum was recorded in 4:1 methylcyclohexane–isopentane solution at 77 and 295 K under otherwise identical conditions using an Aminco-Kiers spectrofluorometer with a Hanovia 901C-1 150-W xenon lamp. Concentrations were adjusted to give an optical density in the range 0.8–1.5, thus minimizing scatter. An excitation wavelength of 270 nm was used for each compound. The magic multipliers were obtained from a single sample by integrating the emission intensities obtained at the two temperatures. Values obtained were as follows: 1,1,5,5-tetraphenyl-3,3-diisopropyl-1,4-pentadiene, M = 19 (4 runs); 1,1-dimesityl-5,5-diphenyl-3,3-dimethyl-1.4-pentadiene, M = 23 (3 runs); 1,1,5,5-tetraphenyl-3-isopropyl-3-methyl-1,4-pentadiene, M = 51 (3 runs).

Single-Crystal X-ray Structure Determinations. General Information.[28] Crystals suitable for analysis were prepared by slow crystallization from methanol. Preliminary examinations were carried out on a Syntex-Nicolet P_1 or, in the case of *cis*-1,1-diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclo-

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

propane, a Syntex-Nicolet P3f diffractometer equipped with a graphite monochromated Mo K_α radiation source. The structures were solved by direct methods using the MULTAN80[29] package and refined by full matrix least-squares refinement. The final cycles of the least-squares refinement[30] 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 done on a Digital Equipment VAX 11/750.

1,1-Diphenyl-2,2-diisopropyl-3-(2,2-diphenylvinyl)cyclopropane.[28] Crystals were orthorhombic, space group P(BCA), with a = 10.782 (2) Å, b = 16.599 (2) Å, c = 29.947 (4) Å, and d_{calcd} = 1.132 g cm^{-3} for Z = 8. The size of the crystal used for data collection was 0.9 × 0.8 × 0.35 m. A total of 6728 independent reflections were measured for 3.5° < 2θ < 56.8°, of which 4095 were considered to be observed [$F_o > 3\sigma(F_o)$]. The final discrepancy indices are R = 0.042 and R_w = 0.057.

1,1-Diphenyl-2,2-dimethyl-3-(2,2-dimesitylvinyl)cyclopropane.[28] Crystals were monoclinic, space group $P2_1/C$, with a = 10.627 (3) Å, b = 25.527 (6) Å, c = 11.662 (2) Å, β = 114.69(2)°, and d_{calcd} = 1.124 g cm^{-1} for Z = 4. The size of the crystal used for data collection was 0.15 × 0.20 × 0.25 mm. A total of 3931 independent reflections were measured for 3.5° < 2θ < 45.77°, of which 2002 were considered to be observed [$I > 3\sigma(I)$]. The final discrepancy indices are R = 0.051 and R_w = 0.056.

***trans*-1,1-Diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane.**[28] Crystals were triclinic, space group $P\bar{1}$, with a = 10.801 (3) Å, b = 13.141 (2) Å, c = 10.774 (2) Å, α = 114.01(2)°, β = 105.16(2)°, γ = 66.98(2)°, and d_{calcd} = 1.115 g cm^{-3} for Z = 2. The size of the crystal used for data collection was 0.28 × 0.35 × 0.40 mm. A total of 5254 independent reflections were measured for 3.5° < 2θ < 52.87°, of which 2860 were considered to be observed [$F_o > 3\sigma(F_o)$]. The final discrepancy indices are R = 0.052 and R_w = 0.058.

***cis*-1,1-Diphenyl-2-isopropyl-2-methyl-3-(2,2-diphenylvinyl)cyclopropane.**[28] Crystals were triclinic, space group $P\bar{1}$, with a = 10.062 (13) Å, b = 10.787 (10) Å, c = 13.221 (25) Å, α = 104.50 (11)°, β = 104.58 (12)°, γ = 105.13 (9)°, and d_{calcd} = 1.115 g cm^{-3} for Z = 2. The size of the crystal used for data collection was 0.15 × 0.23 × 0.50 mm. A total of 3425 independent reflections were measured for 3.5° < 2θ < 45.0°, of which 2224 were considered to be observed [$F_o > 3\sigma(F_o)$]. The final discrepancy indices are R = 0.074 and R_w = 0.083.

Molecular Mechanics Calculations. Calculations were carried out using the MMPI and MM2 programs of Allinger.[14c,e] All calculations were done on a Digital Equipment VAX 11/750. Geometries were input using the MENU[14a] program in Tribble.[14b] The extended (*W*) conformation of the dienes was found to be of lowest energy. The twist angle around one of the diphenylvinyl double bonds in each diene was then fixed at different values. The steric energy was minimized with this fixed twist angle, and all other variables were free. The twisting results from MMPI are listed in Table IV. The initial geometries of the cyclopropyldicarbinyl diradicals were generated by bonding C-2 and C-4 in the minimum energy conformations of the dienes and placing the residual diarylmethyl radical centers in a transoid relationship using the DISPLAY[14a] program in Tribble.[14b] The results for the diradicals are listed in Table V.

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Registry No. 1, 99342-80-0; 2, 99342-99-1; 3, 99342-82-2; 4, 99342-94-6; 5, 4160-97-8; 6, 4160-99-0; 7, 99342-76-4; 8, 99342-95-7; 9, 19184-67-9; 10, 99342-77-5; 11, 99342-96-8; 12, 99342-81-1; 13, 99342-78-6; 14, 99342-97-9; 15, 99342-82-2; 16 (isomer 1), 99342-84-4; 16 (isomer 2), 99342-85-5; 17, 99342-86-6; 18, 99342-87-7; 19, 99342-88-8; 20, 99342-89-9; 21, 99342-90-2; 22, 99342-91-3; 23, 99342-92-4; 24, 99343-00-7; 25a, 99343-02-9; 25b, 99343-03-0; 26, 99343-01-8; $Ph_2C{=}CHC(i\text{-}Pr)_2CH_2C(OH)Ph_2$, 99342-79-7; $Ph_2C{=}C(CH_3)C(CH_3)_2CH(CH_3)C(OH)Ph_2$, 99342-93-5; $Ph_2C{=}CHC(CH_3)(i\text{-}Pr)CH_2C(OH)Ph_2$, 99342-98-0; 5,5-dimesityl-1,1-diphenyl-3,3-dimethyl-4-pentenol, 99342-83-3.

Supplementary Material Available: Tables consisting of crystal data, intensity collections parameters, fractional coordinates, interatomic distances, and figures (25 pages). Ordering information is given on any current masthead page.

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Exocyclic Cleavage in the Alkaline Hydrolysis of Methyl Ethylene Phosphate: Pseudorotation of a Pentavalent Intermediate or Reaction via a Hexavalent Intermediate?

Ronald Kluger* and Gregory R. J. Thatcher

Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

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The observation of increasing exocyclic cleavage of methyl ethylene phosphate in alkaline solution was the first evidence for hydrolysis of a phosphate ester by reaction with 2 equiv of hydroxide. Kinetically equivalent mechanisms provide a role for a second hydroxide after the first hydroxide adds to form a pentavalent intermediate. These are (1) proton abstraction, pseudorotation, and exocyclic cleavage and (2) addition to form a hexavalent phosphorus intermediate followed by exocyclic cleavage. The mechanisms can be distinguished by patterns of isotope incorporation from solvent into the product of exocyclic cleavage. The hydrolysis of methyl ethylene phosphate was carried out in D_2O containing $D_2{}^{18}O$, and the pattern of isotopically shifted phosphorus NMR peaks of ethylene phosphate (and its hydrolysis product hydroxyethyl phosphate) rules out the involvement of hexavalent phosphorus intermediates. The formation of ethylene phosphate via anionic pentavalent intermediates contradicts predictions of a stereoelectronic theory that places great energetic advantage in cleaving the endocyclic ester bond.

Our understanding of the mechanisms of hydrolysis of phosphate esters depends largely upon the work of Westheimer in which rules describing the behavior of pentavalent phosphorus intermediates were developed.[1,2]

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