A Photochemical Long-Range Pinacol Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1,2]

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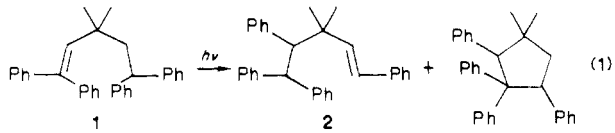
In a previous study we uncovered a rearrangement in which a phenyl group migrated 1,4 from a benzhydryl carbon to an excited diphenylvinyl chromophore. The present study aimed at generalizing this bizarre rearrangement and also in ascertaining if an aryl migration would occur from a carbinol carbon. Indeed, the irradiation of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol led smoothly to 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone. The overall mechanism involves a transannular phenyl migration in a process reminiscent of a pinacol rearrangement. At conversions above 20% and at wavelengths other than 280 nm, a secondary process was observed wherein a type II fragmentation afforded 1,1,2-triphenyl-3-methyl-2-butene and acetophenone. The initial rearrangement and primary process was shown to proceed via the excited singlet of the tetraphenyldimethylpentenol while the corresponding triplet proved unreactive. An alternate mechanism leading directly from the tetraphenyldimethylpentenol to acetophenone and the triphenylbutene was considered as possibly accounting for part of the overall fragmentation reaction. However, this was precluded by a kinetic study using our dynamic isotope dilution method. An analogous transannular migration was observed for the corresponding methyl ether, which rearranged to afford 1-methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene. Here there was no complicating type II secondary process. Another aspect studied was the facility of migration of different aryl groups. Thus it was observed that when one phenyl group of the methyl ether was replaced by *p*-cyanophenyl, only the cyanophenyl group migrated. With one phenyl group replaced by anisyl, anisyl migrated with a 2:1 preference relative to phenyl. As in the case of the tetraphenyldimethylpentenol, the singlet excited state was the reactive species. Quantum yields were determined. The tetraphenyldimethylpentenol had an efficiency of 0.0026 which was ca. 2.5 times that of our previously studied rearrangement lacking the hydroxyl group. The corresponding methyl ether had a quantum yield of 0.0041. The cyanophenyl migration efficiency was 0.0038, and the total quantum yield of the anisyl analogue was 0.0032. Also, singlet excited state reaction rates were determined by single photon counting. Finally, in the case of the tetraphenyldimethylpentenol rearrangement, deuteration studies showed that the initially formed diradical, resulting from completion of the phenyl migration, leads to product both by hydrogen transfer from the hydroxyl oxygen as well as from the adjacent carbon.

Introduction

A major goal in our organic photochemical research has been finding new reactions and then the elucidation of their mechanisms. One reaction we uncovered[3] was a 1,4-transannular phenyl migration from a benzhydryl carbon to the β-carbon of a diphenylvinyl moiety. Note eq 1. It seemed of considerable interest to explore and expand the generality of this rearrangement.



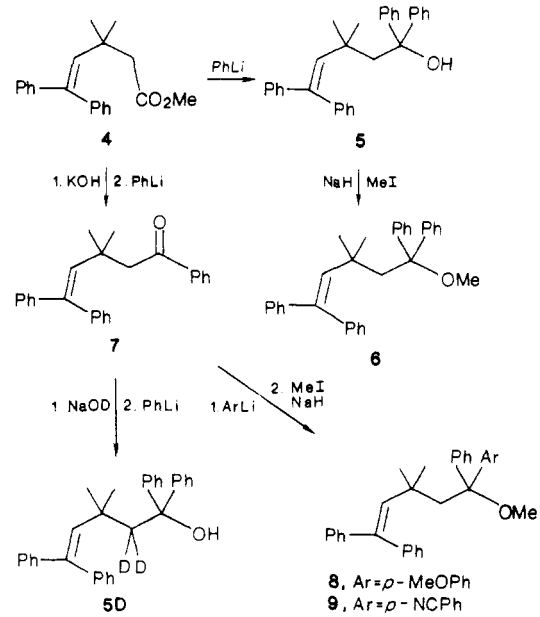
(1)

For the present study we selected 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol (**5**) as a starting point. This reactant differed from the previously investigated system in having a hydroxyl group on the carbon bearing the phenyl groups we hoped would migrate. Further, to the extent that the rearrangement was successful, tetraphenylpentenol **5** seemed likely to generate a carbonyl group at the carbinol carbon.

Results

Synthesis of Photochemical Reactants. The synthesis of the desired tetraphenylpentenol **5** is outlined in

Scheme I. Synthesis of Photochemical Reactants



Scheme I. The required reactant diphenylvinyl ester **4** was available from our previous investigations.[4] Also, the corresponding methyl ether **6** promised to provide results of interest, and its preparation is included in Scheme I. Finally, we planned on testing relative migration abilities. Hence, we proceeded with the synthesis of the methyl ethers having a single migrating aryl group bearing a para

(1) This is paper 150 of our photochemical series and paper 208 of the general series.

(2) For paper 149 note: Zimmerman, H. E.; Solomon, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6276-6289.

(3) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 5143-5152.

(4) Zimmerman, H. E.; Gruenbaum, W. T. *J. Org. Chem.* **1978**, *43*, 1997-2005.

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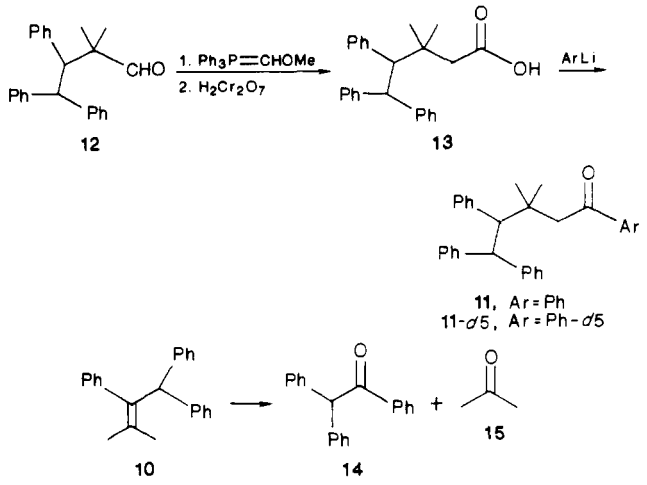
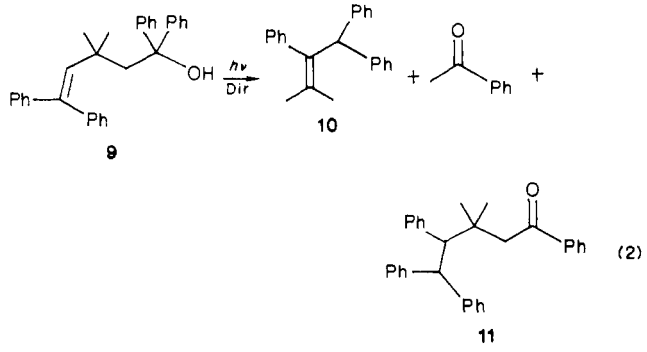
Scheme II. Structure Elucidation of Photoproducts by Degradation and Synthesis



cyano or methoxyl group. These preparations are included in Scheme I.

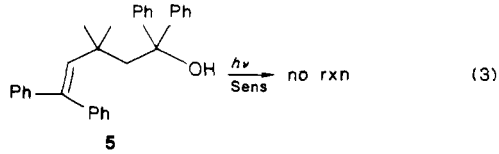
Exploratory Photolysis of the Tetraphenyldimethylpentenol (5). Direct irradiation of the tetraphenylpentenol **5** with high (>25%) conversions led to acetophenone, 1,1,2-triphenyl-3-methyl-2-butene (**10**), and 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone (**11**) as outlined in eq 2. The structures of these photoproducts



(2)

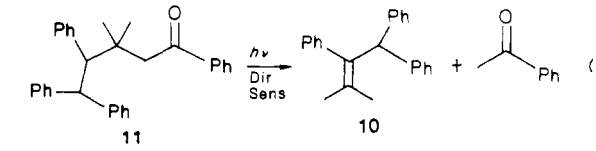
derived from synthesis and degradation as outlined in Scheme II. At lower conversions the tetraphenylpentanone **11** was formed as the main product, and it was observed (vide infra) that this compound was the primary photoproduct for irradiations carried out at 280 nm. The use of this wavelength came from the finding that the optical density of reactant **5** relative to the primary photoproduct **11** was greatest (ca. 20:1) at this wavelength. Thus at the 280-nm wavelength and with conversions up to 12%, the formation of the tetraphenylpentanone **11** was close to quantitative. It was less certain that tetraphenylpentanone **11** was the primary photoproduct for photolyses carried out at other wavelengths.

Finally, it was determined (vide infra) that sensitization with acetophenone and benzophenone was ineffective in the reaction of the tetraphenyldimethylpentenol **5**. Note eq 3.



(3)

Exploratory Photochemistry of the Tetraphenylpentanone 11. It was necessary to explore the photochemical behavior of what appeared to be the primary photoproduct, namely, 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone (**11**). Both direct and acetophenone- or xanthone-sensitized runs converted the tetraphenylpentanone **11** to 1,1,2-triphenyl-3-methyl-2-butene (**10**) and acetophenone. These were the same products observed along with the tetraphenyldimethylpentanone **11** in the original irradiation of the tetraphenyldimethylpentenol **5**. This photochemistry is shown in eq 4. Hence at this juncture there was necessary but not sufficient evidence to establish that the butene **10** and acetophenone were secondary photoproducts in the pentenol **5** irradiation. This point is considered later.



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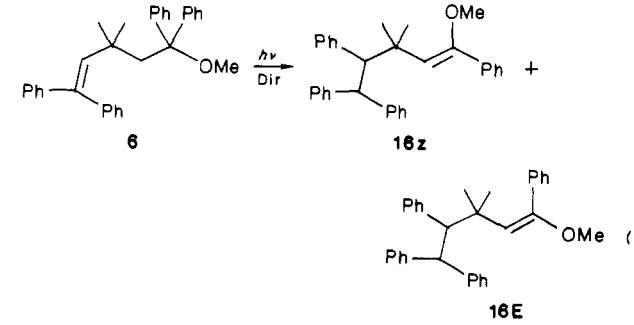
Exploratory Photochemistry of the Corresponding Methyl Ether 6. We turned next to the photochemistry of 1-methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene (**6**) with the idea that secondary photochemistry might be inhibited. Indeed, irradiation of the methoxytetraphenylpentene **6** led to a quantitative formation of the *Z* and *E* isomers of 1-methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene (**16Z** and **16E**, respectively) in a 1:1 ratio as shown in eq 5. Product structures were elucidated by



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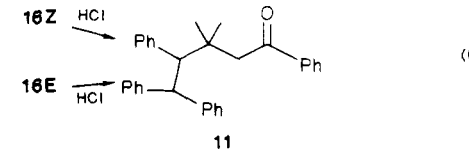
mild acid hydrolysis of the stereoisomeric enol ethers to afford ketone **11** which had been prepared as outlined in Scheme II. Note eq 6. Interestingly, the ratio of the



(6)

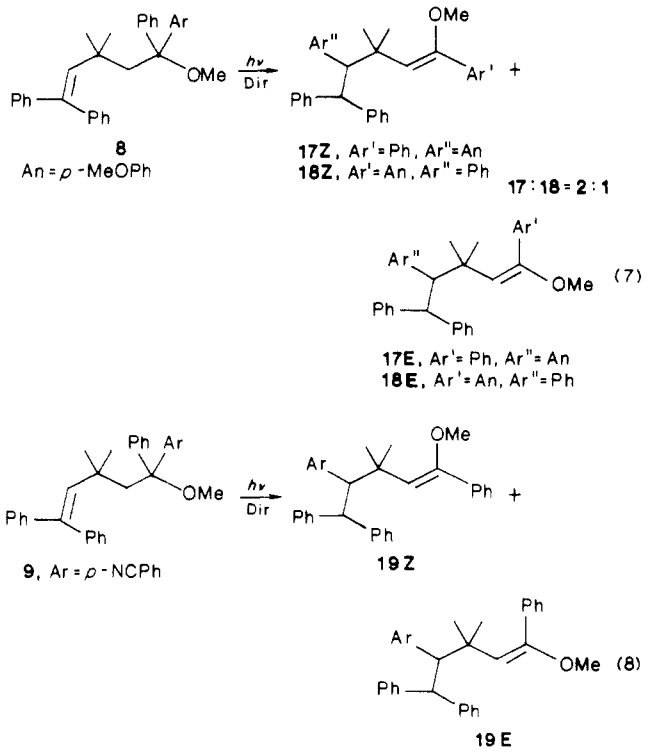
photoproduct enol ether stereoisomers appears to be kinetic since low conversion (ca. 5%) runs afforded the same ratio of stereoisomers. In this reaction the products are seen to arise from a 1,4-phenyl migration with no intrusion of secondary photochemistry. The detailed mechanism is discussed below.

Exploratory Photochemistry of *p*-Methoxy- and *p*-Cyano-Substituted Tetraarylpentenes. One of our major aims was the determination of the facility of migration of para-substituted aryl groups in this rearrangement. We began with the intramolecular competition of *p*-cyanophenyl vs. phenyl and *p*-anisyl vs. phenyl. The first test utilized the anisyl methyl ether **8** in which either the phenyl or the anisyl group might migrate to the diphenylvinyl π-bond. The second test used the cyanophenyl methyl ether **9** where the cyanophenyl group competed with a phenyl substituent. Structure elucidation of the photoproducts is outlined in Scheme III. The structure of ketone **22** was determined by X-ray crystallography. The photochemistry is as shown in eq 7 and 8.

Table I. Quantum Yield Results[a,b]

reactant	sensitizer	wavelength, nm	quantum yield
tetraphenylpentene 1[c]	none	280	0.000 80 (alkene prod)
			0.000 20 (5-ring prod)
	benzophenone	313	<0.0002
tetraphenylpentenol **5**	none	280	0.0026
	acetophenone	313	<0.0002
tetraphenylmethyl ether **6**	none	280	0.0020 (*E* isomer)
			0.0021 (*Z* isomer)
	acetophenone	313	<0.0002
p-anisyl ether **8**	none	280	0.0020 (anisyl migration) (1:1 *E*/*Z*)
			0.0011 (phenyl migration) (1:1 *E*/*Z*)
	acetophenone	313	<0.0002
p-cyano ether **9**	none	280	0.0020 (*Z* isomer)
			0.0018 (*E* isomer)
	acetophenone	313	<0.0002

[a] All runs in *t*-BuOH. [b] Error limits ±10%. [c] From ref 3.



Hence, a 1,4-aryl migration was, again, encountered. Also, it is seen that in both instances the substituted aryl group migrated in preference to the phenyl group. However, the selectivity was much greater in the case of *p*-cyanophenyl where there was migration only of the *p*-cyanophenyl group.

Quantum Yield, Multiplicity, and Excited-State Rate Determinations. The first goal in obtaining mechanistic information was the quantum yields. These were obtained by using the Wisconsin Black Box apparatus described earlier.[5] Note also the Experimental Section. A summary of these results appears in Table I. Here we have included the efficiency of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene (**1**) from our earlier study[3] for comparison purposes. The first notable observation is that none of these compounds reacts on sensitization while all do so on direct irradiation. Secondly, it is seen that introduction of the hydroxyl and methoxyl groups in the present study in reactant **5** has increased the quantum yield 2.5-fold. Additionally, the presence of *p*-methoxy and *p*-cyano groups also enhances the reaction efficiency. The sensitization results demonstrate a lack of reactivity of the triplet excited states.

Table II. Single-Photon-Counting Determination of Excited Singlet Rates

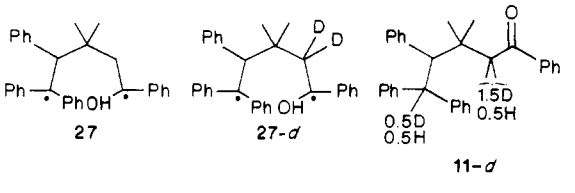
reactant	*M*[a]	temp, K	τ	$^1k_{d(tot)}$, s^{-1}	^1k_r, s^{-1}
tetraphenyl-pentene **1**	150	77	5.0 ns	2.0×10^8	
		298	34 ps	3.0×10^{10}	3.0×10^7[b]
tetraphenyl-pentenol **5**	60	77	5.4 ns	1.8×10^8	
		298	90 ps	1.1×10^{10}	2.8×10^7
tetraphenyl ether **6**	71	77	8.6 ns	1.2×10^8	
		298	121 ps	8.2×10^9	3.4×10^7
cyanophenyl ether **9**	53	77	6.5 ns	1.5×10^8	
		298	122 ps	8.0×10^9	3.0×10^7
methoxyphenyl ether **8**	40	77	6.0 ns	1.6×10^8	
		298	146 ps	(6.8×10^9)	$(1.4 \times 10^7$[c]$)$ $(7.0 \times 10^6$[d]$)$

[a] Magic multiplier. [b] Reference 3. [c] Anisyl migration. [d] Phenyl migration.

We next turned to determination of the excited singlet reaction rates. Here we used the method of single photon counting following the methodology employed in our earlier studies.[6a,b] Thus rates at room temperature were very difficultly measurable due to weak emission which limited the rate of photon counting. However, the relative fluorescence intensity at room temperature compared with 77 K has been noted to be a more reliable observable and to provide the ratio of the low-temperature to room-temperature decay rates.[6a,b] This ratio has been termed the "magic multiplier". The results are collected in Table II.

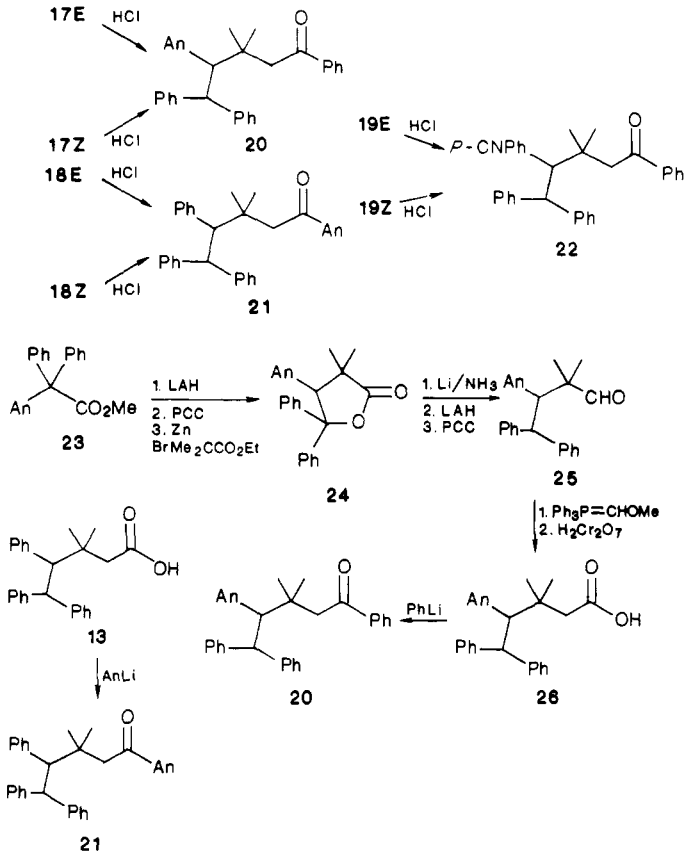
It is to be noted that the magic multiplier method depends on the temperature invariance of k_f (i.e., rate of fluorescence or the inverse of the natural lifetime). It also depends on just one chromophore absorbing and emitting.

Structural Considerations in the Rearrangement of Tetraphenylpentenol 5. In the rearrangement of the tetraphenylpentenol **5** it was clear that diradical **27** is formed by phenyl migration. What was less clear was



(5) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281–292.
(6) (a) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1973**, *95*, 5094–5095. (b) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1974**, *96*, 439–449. (c) Zimmerman, H. E.; Pratt, A. C., J. Am. Chem. Soc. **1970**, *92*, 1409–1411. (d) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6267–6271.

Scheme III. Structure Proof of the Substituted Phenyl Products



whether the hydrogen was then transferred to the benzhydryl carbon from the hydroxyl or from carbon 2. Therefore we synthesized tetraphenylpentenol **5-d** labeled at carbon 2 with deuterium. This synthesis is included in Scheme I. This compound promised to be useful in indicating if a C-2 hydrogen was being transferred in reaction of the diradical **27**.

The deuterium distribution in the product of direct irradiation of the labeled tetraphenylpentenol **5-d** was established both by NMR and mass spectral analyses. Interestingly, it was observed that the photoproduct **11** had not suffered deuterium loss. NMR analysis of the benzhydryl methine and also the C-2 methylene led to the same conclusion, namely, that the two sources of hydrogens were utilized in a 1:1 ratio.

Dynamic Isotope Dilution Studies. As noted earlier, at wavelengths other than 280 nm, acetophenone and triphenylbutene **10** were invariably encountered, even at low conversions. Even at 280 nm, except at conversions below 12% acetophenone and triphenylbutene **10** were among the products. There often is the question of whether a reactant (**A**) proceeds directly to a product (e.g., **C**), or instead is formed via an intermediate (**B**). In one of our studies, Dynamic Isotope Dilution[7] has been found to solve this problem and permit dissection of pathways **A** → **B** → **C** and **A** → **C**. The present study promised a further test of the method. Dynamic isotope dilution requires the potential intermediate **B** to be available labeled (e.g., isotopically) in some fashion. We term this **B***. The reaction is run with **B*** added to the reactant **A**, and the reaction mixture is assayed for the relative amounts of **A**, **B**, and **B*** as the reaction proceeds. A_0 is the initial amount of **A**. The function F in eq 9a is seen to be linear with the extent of conversion as measured by log (A_0/A), where A_0, A, B, B^*, B^*_0, and B_0 are amounts of the corresponding compounds and ϵ_a and ϵ_b are the extinction coefficients of **A** and **B**.

(7) Zimmerman, H. E.; Carpenter, C. W.; Weber, A. M. *J. Am. Chem. Soc.* **1985**, *107*, 1073–1075.

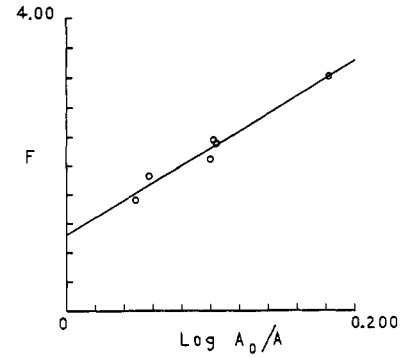


Figure 1. Plot of the function F vs. extent of conversion.

Table III. Dynamic Isotope Dilution Data[a-c]

run	A_0, mmol	A, mmol	B, mmol	B^*_0, mmol	B^*, mmol	log (A_0/A)	log F
1	0.112	0.0740	0.00840	0.0934	0.00049	0.182	3.22
2	0.129	0.101	0.00850	0.127	0.00690	0.104	2.31
3	0.132	0.115	0.00802	0.0901	0.01490	0.0573	1.85
4	0.139	0.110	0.00853	0.0831	0.00324	0.100	2.09
5	0.137	0.101	0.00106	0.109	0.00456	0.102	2.36
6	0.151	0.135	0.0119	0.129	0.0470	0.0478	1.52

results: L = 12.0; M = 0.980; R = 0.020; intercept = 1.04

[a] B_0 was zero in all runs. [b] Details are in the Experimental Section. [c] Estimated error ±10%.

Equation 9d gives the ratio of the efficiency of the direct to that of the two-step pathway.

$$F = \log \frac{B^*_0[B^*_0A - B^*A_0]}{B^*[B^*_0B - B_0B^*]} = L \log (A_0/A) + \log \frac{L-1}{M} \quad (9a)$$

$$L = \phi_{bc}\epsilon_b/(\phi_{ab} + \phi_{bc})\epsilon_a \quad (9b)$$

$$M = \phi_{ab}/(\phi_{ab} + \phi_{ac}) \quad (9c)$$

$$R = (1 - M)/M = \phi_{ac}/\phi_{ab} \quad (9d)$$

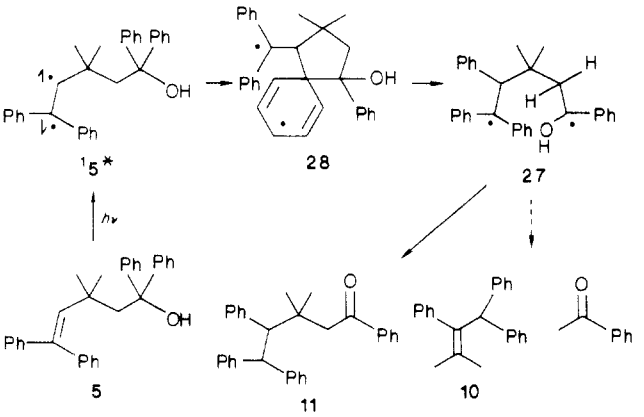
In the instance of the present photochemistry, we see that **A** corresponds to photochemical reactant tetraphenylpentenol **5** and **B** represents the triphenylpentanone **11**, while **C** corresponds to the final product(s).

A summary of the results is given in Table III, and the plot of F vs. log (A_0/A) is given in Figure 1. The plot is seen to be linear, nicely in accord with theory. The slope and intercept have values given in Table III. Since the intercept is equal to log $[(L-1)/M]$ and is known and the slope L is also known, we can solve for M. We then make use of the expression of eq 9d to obtain R, which as noted in Table III, is essentially zero. This affords the ratio of the A → C to the A → B quantum yields.

Interpretative Discussion

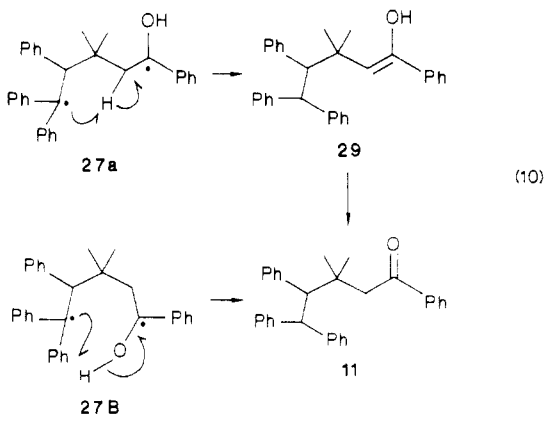
Structural Aspects of the Photochemical Transannular Pinacol Rearrangement. The 1,4-phenyl migration observed in the irradiation of the tetraphenylpentenol **5** (note eq 2) is related to the 1,4-migration encountered in our earlier study[3] and depicted in eq 1. A reasonable reaction mechanism begins with bonding of the C-1 phenyl group to the electronically excited diphenylvinyl moiety as shown in Scheme IV.[8] The chief difference

Scheme IV. Structural Mechanism of the Transannular Photochemical Pinacol Rearrangement



between this rearrangement and our earlier example is the fate of the penultimate species, namely, diradical **27** in this case. In the reaction of the non-hydroxylic tetraphenylpentene **1** of our earlier work, cyclization and disproportionation of the diradical were observed. In contrast, tetraphenylpentenol **5** undergoes no cyclization and only disproportionates to afford tetraphenylpentanone **11**.

Details of the Disproportionation Process. As noted above, one can envisage two modes of disproportionation of diradical **27** formed in the phenyl migration process. The experimental results, however, indicate an equal partition between the two different pathways shown in eq 10. A priori, one might have anticipated hydrogen transfer



(10)

from the hydroxyl group to be preferred on energetic grounds due to the greater strength of the C=O vs. the C=C bond formed. However, a seven-membered ring is required for transfer from the hydroxyl group; and, the five-ring transition state for hydrogen transfer from carbon is favored entropically. Hence, the observed 1:1 distribution of the two hydrogen transfer pathways is not unreasonable.

Selectivities in the Aryl Migrations. Migratory aptitudes have been of use in our past photochemical studies. Thus, in the case of 4,4-diarylcyclohexenones[9] cyanophenyl and anisyl groups were observed to migrate in preference

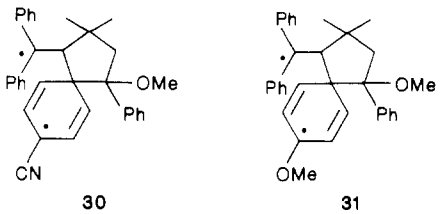
Table IV. Comparison of Excited-State Rates and Quantum Yields

compd	ϕ	$^1k_{(dtot)}$	k_r
$(Ph)_2C{=}CHC(Me)_2CH{=}C(Ph)_2$ (**32**)	0.080	1.8×10^{12}	1.4×10^{11}
$(Ph)_2C{=}CHC(Me)_2Ph$ (**33**)	0.036	5.2×10^{10}	1.9×10^{9}
tetraphenylpentenol (**5**)	0.0026	1.1×10^{10}	2.8×10^{7}

to phenyl, and this result was interpreted to signify that the excited state β-carbon was neither excessively electron-deficient nor electron-rich but, rather, odd-electron in character. The reaction in this case was one of a triplet. An example of the migration aptitudes in a singlet excited state was found in the rate enhancement by *p*-cyano and *p*-methoxyl groups in the di-π-methane rearrangement.[10]

In the present study the cyanophenyl ether **9** provided a competition between phenyl and cyanophenyl while the anisyl ether **8** gave rise to a competition between phenyl and anisyl. As noted above in Table I the cyanophenyl group migrated essentially to the exclusion of phenyl. In the anisyl case, the competition was closer with anisyl migrating with a 1.9:1 greater facility.

These results are interpretable on the basis of inspection of the half-migrated diradicals **30** and **31** where the cyano and methoxyl substituents provide extra delocalization.[11]



Consideration of the Reaction Efficiency, Multiplicity, and Reaction and Decay Rates. One interesting aspect is the low reaction efficiency of the 1,4-transannular aryl migrations as well as the low rates of excited-state reaction and decay. The quantum yields are seen (note Table I) to be of the order of 10^{-3}, much lower than the circa 4×10^{-2} efficiencies encountered in the aryl–diphenylvinyl di-π-methane rearrangement,[10] a reaction which can be viewed as an effective 1,2-aryl migration. Both the 1,4- and 1,2-aryl migrations[10] involve rearrangement to an excited diphenylvinyl chromophore. Additionally, the reaction rates are lower by a factor of ca. 10^2 than in the aryl–vinyl di-π-methane rearrangement while the decay rates are not appreciably diminished.

We attribute the low 1,4 migration efficiency and reaction rates to a slow rate of conformational equilibration and a low concentration of a conformation having the aryl group close to the electronically excited diphenylvinyl moiety.

A comparison of three somewhat related systems, all having the $Ph_2C{=}CHCMe_2Y$ moiety, is germane. The first system is the presently studied tetraphenylpentenol where Y is CH_2CPh_2OR. The second is encountered in the aryl–vinyl di-π-methane rearrangement where Y = aryl.[10] The third is divinylmethane type exemplified by 1,1,5,5-tetraphenyl-3,3-dimethyl-1,4-pentadiene (**32**).[12] Table IV lists the rates for these three compounds.

(8) (a) π–π bridging is found in a variety of photochemical reactions of which the di-π-methane rearrangement is just one. For example, in elegant studies Binkley has reported examples of phenyl–phenyl bridging in counterpart di-π-ethane[8b] and di-π-propane[8c] reactions. (b) Ross, J. A.; Schumann, W. C.; Vashi, D. B.; Binkley, R. W. *Tetrahedron Lett.* **1971**, 3283–3286. (c) Binkley, R. W.; Schumann, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 1769–1170. Binkley, R. W.; Chen, S. C.; Hehemann, D. G. *J. Org. Chem.* **1975**, *40*, 2406–2408.

(9) Zimmerman, H. E.; Rieke, R D.; Scheffer, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 2033–2047.

(10) Zimmerman, H. E.; Kreil, C. A.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1978**, *100*, 4146–4162.

(11) (a) For further evidence concluding that cyano and methoxyl provide stabilization of odd-electron centers note ref 10. (b) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *19*, 917–932.

(12) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718–1732.

We first need to consider possible modes of excited-state dissipation by reaction and decay. Three potential sources are a priori possibilities. The first, namely reaction, is a minor factor in the present instance as can be seen from the low quantum yield. The second derives from free rotor effects;[6,13] we note that free rotor energy dissipation is effective for singlets as well as triplets. The third decay mode involves $\pi-\pi$ interaction. We have found[6a] that often a parallelism in reaction and decay rates occurs and hence the quantum efficiencies remain constant for a variety of di-π-methane rearrangements.

In the presently considered series of the three reactants in Table IV, the excited-state reaction and decay rates tend to decrease with a decrease in the ease of $\pi-\pi$ bridging. Bridging can be inhibited either by distance or by unfavorable energetics if an aryl group is one of the two π-moieties. Unlike our previous study[6a] where distance and energetics were held constant, in the systems now under consideration, the reaction and decay parallelism no longer holds. Rather, the reaction rates must be inhibited more effectively than the decay rates, since the quantum efficiencies diminish in the order **32** > **33** > **5**; note Table IV.

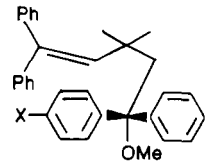
These observations are understood if one recognizes that the excited-state decay rate will reach an asymptote limited by the omnipresent free rotor mechanism[6,13] as $\pi-\pi$ bridging is inhibited.

A further interesting point is a comparison of the excited-state rates obtained for the tetraphenyl, anisyl, and *p*-cyanophenyl ethers **6**, **8**, and **9**, respectively. We have noted that both cyanophenyl and anisyl groups migrate more rapidly than the phenyl group in intramolecular competitions. With only *p*-cyanophenyl and no phenyl migration observed in the intramolecular competition, the rate of cyanophenyl migration must be at least 20-fold that of phenyl in the case of **9**. In parallel fashion from the behavior of **8**, we reason that anisyl must migrate circa 2 times as rapidly as phenyl.

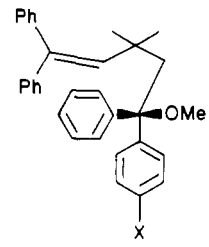
However, reference to Table II shows that in the intermolecular competition the monocyano-substituted ether **9** reacts at a rate which is only twofold that of the parent ether **6**, and, surprisingly the anisyl ether **8** reacts at a rate very close (0.8 times) to that of the parent ether **6**.

There are two conformations **8a** (or **9a**) and **8b** (or **9b**), each leading to one photoproduct. In **8a** (or **9a**) the aryl group is capable of migrating while in **8b** (or **9b**) the unsubstituted phenyl is poised to migrate. Since conformational equilibration is expected to occur at a rate below 10^8 s^{-1},[14] it is likely that the observed reaction occurs only when the molecules absorbing light are in these reactive conformations. Thus the amounts of aryl vs. phenyl migration is controlled by the ratio of concentrations of the two species (i.e., **8a** vs. **8b** or **9a** vs. **9b**) multiplied by the ratio of the probabilities that the properly placed group will migrate in each case. In the case of species **6**, the unsubstituted reactant, one of two phenyl groups is in a conformation to migrate. The relative magnitudes of the rate constants derive from a competition between totally different molecules (e.g., **6** vs. **8a**) and need not logically afford the same ratio as the intramolecular comparison.

The experimental observation is that the rates fall in the order **9** > **6** > **8**. Interestingly, singlet excitation of the anisyl reactant **8** seems likely to be partitioned and somewhat more heavily localized in the anisyl moiety



6A, X = H
8A, X = An
9A, X = *p*-CNPh



6B, X = H
8B, X = An
9B, X = *p*-CNPh

rather than the diphenylvinyl one[15] while in the cyanophenyl reactant and also the unsubstituted tetraphenyl ether **6** excitation should be heavily localized in the diphenylvinyl chromophore. Thus, the slowest singlet is the one having excitation partitioned and most concentrated in the potentially migrating group; the magic multiplier treatment thus may be only approximate. Also, only conformer **8a** should be reactive, and the conformer **8b** would be anticipated to be unreactive. The smaller portion of phenyl migration must occur from diphenylvinyl excited molecules since phenyl excitation would require an extra ca. 20 kcal mol^{-1}. It may be that in these systems, diphenylvinyl excited states rearrange with greater facility than aryl excited states. This would also account for the different intermolecular compared with intramolecular reactivities.

Finally, the free rotor effect noted above accounts for the lack of triplet reactivity and the fact that the presently studied transannular aryl migrations proceed via the singlet excited states. It has been noted that although the free rotor effect provides routes for both excited triplet and excited singlet decay, the generally slow rates of triplet reactions results in the free rotor effect being more able to quench triplet processes.[16]

The Two Alternative Mechanistic Pathways for Rearrangement–Fragmention of the Tetraphenylpentenol. The Test of Dynamic Isotope Dilution. As has been outlined in Scheme IV there are two a priori pathways leading from the tetraphenylpentenol **5** to acetophenone and the triphenylbutene **10**.

R in eq 9d gives the ratio of intervention of the two pathways, the direct route to the indirect one (i.e., A → C to A → B → C). The value 0.020 reveals that the direct route is not operating appreciably. Actually, the 2% suggested for the direct route is within experimental error of zero. A particularly important point is the complete concurrence of the dynamic isotope dilution method with the observation of only B (i.e., tetraphenylpentanone **11**) in runs extrapolated toward zero percent conversion.

Possible Concertedness in the Transannular Rearrangements. One further interesting question is whether reaction actually occurs in discrete steps and via fully developed diradicals **27** and **28** as shown in Scheme IV. In parts a and b of Figure 2, we show the partially rearranged molecule at the stage of diradical **28**. It is seen in Figure 2a that the hydroxyl hydrogen may approach the benzhydryl carbon and a pericyclic transition state is possible. More strain is incurred for concertedness in the competing reaction shown in Figure 2b where a methylene

(13) (a) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6267–6271. (b) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

(14) Piercy, J. E.; Rao, M. G. S. *J. Chem. Phys.* **1967**, *46*, 3951–3960.

(15) (a) Inspection of the absorption and singlet emission curves leads to 0–0 energies of 97 kcal mol^{-1} for *p*-methylanisole and 101 kcal mol^{-1} for 1,1-diphenylethylene. (b) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971.

(16) Zimmerman, H. E.; Penn, J. P.; Johnson, M. R. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2021–2025.

hydrogen is transferred to the benzhydryl center.

Conclusion. A specific result of this study is the generalization of the long-range aryl migration reaction first encountered in our earlier studies. More generally, the study has followed our aim of uncovering, generalizing, and understanding as many new photochemical reactions as possible.

Experimental Section[17]

1,1,5,5-Tetraphenyl-3,3-dimethyl-4-penten-1-ol. To 4.40 g (14.0 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate[4] in 75.0 mL of ether at 0 °C was added 35.8 mL (430 mmol, 1.2 M in ether) of phenyllithium. After 5.0 h at room temperature, neutral workup[17] afforded 6.53 g of a yellow oil, which was chromatographed on a 4 × 75 cm silica gel column (5% ether in hexane), and 1-L fractions were collected: fraction 2, 4.08 g (70%) of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol as a yellow oil. Recrystallization from methanol afforded 3.40 g (58%) of the alcohol as colorless plates, mp 110.0–111.5 °C. Samples for fluorescence spectroscopy were prepared by repeated recrystallization from 95% ethanol.

The spectral data were as follows: IR (neat) 3600, 3400, 3060, 3030, 2960, 2930, 2880, 1605, 1500, 1455, 1080, 1040, 1020, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.46–7.01 (m, 20 H, arom), 6.14 (s, 1 H, =CH), 2.91 (s, 1 H, OH), 2.60 (s, 2 H, CH_2), 0.77 (s, 6 H, CH_3); UV (EtOH) 260 (ϵ 21700), 270 (15900), 280 (12400), 290 (9000), 320 nm (450); MS, m/e 418.2297 (calcd for $C_{31}H_{30}O$, m/e 418.2296).

Anal. Calcd for $C_{31}H_{30}O$: C, 88.95; H, 7.46. Found: C, 88.74; H, 7.29.

1-Methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene. To a slurry of 1.15 g (48% in mineral oil, 24.0 mmol) of sodium hydride and 1.50 mL (24.0 mmol) of methyl iodide in 15.0 mL of DME was added 1.00 g (2.40 mmol) of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol in 10.0 mL of DME. After the mixture was stirred at room temperature for 48.0 h, neutral workup[17] afforded 1.25 g of a viscous yellow oil which was chromatographed on a 2 × 50 cm silica gel column (2% ether in pentane), and 500-mL fractions were collected: fraction 3, 0.930 g (88%) of 1-methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene as a colorless foam. Further silica gel chromatography gave 0.840 g (78%) of the ether as an analytically pure, colorless glass. Samples for fluorescence spectroscopy were prepared by purification by preparative HPLC (2% ether in pentane).

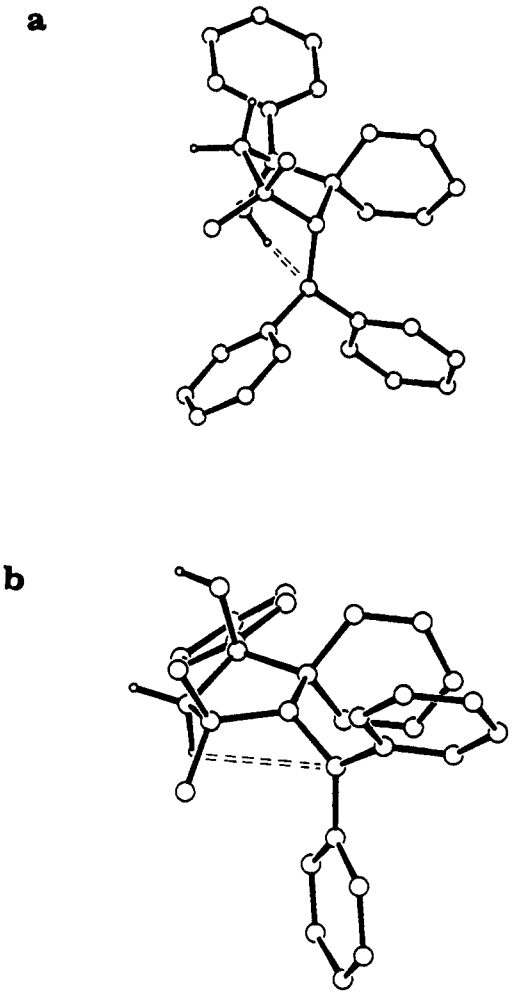


Figure 2. a. Hydroxyl hydrogen transfer. b. Methylene hydrogen transfer.

The spectral data were as follows: IR (neat) 3080, 3060, 3030, 2960, 2940, 2880, 1605, 1500, 1450, 1200, 1190, 1080, 1045, 890, 760, 720 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.38–6.98 (m, 20 H, arom), 5.98 (s, 1 H, =CH), 2.99 (s, 3 H, OCH_3), 2.52 (s, 2 H, CH_2), 0.73 (s, 6 H, CH_3); UV (EtOH) 255 (ϵ 22500), 270 (9800), 290 nm (7000); MS, m/e 432.2556 (calcd for $C_{32}H_{32}O$, m/e 432.2559).

Anal. Calcd for $C_{32}H_{32}O$; C, 88.93; H, 7.46. Found: C, 88.93, H, 7.48.

3,3-Dimethyl-5,5-diphenyl-4-pentenoic Acid. A solution of 8.30 g (28.2 mmol) of methyl 3,3-dimethyl-5,5-diphenyl-4-pentenoate[4] and 10.0 g (179 mmol) of potassium hydroxide in 100 mL of methanol was refluxed for 6.0 h. After being cooled, the mixture was diluted with water and ether extracted. The aqueous layer was then acidified to pH 2 and ether extracted. Drying and concentration in vacuo afforded 7.20 g (92%) of 3,3-dimethyl-5,5-diphenyl-4-pentenoic acid as a light yellow oil.

The spectral data were as follows: IR (neat) 3600, 3060, 3030, 2960, 2920, 2880, 1720, 1600, 1490, 1460, 1450, 1380, 1210, 1070, 1030, 1000, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 10.51 (b s, 1 H, acid), 7.58–7.22 (m, 10 H, arom), 6.13 (s, 1 H, =CH), 2.32 (s, 1 H, CH_2), 1.07 (s, 6 H, CH_3); MS, m/e 280.1465 (calcd for $C_{19}H_{20}O_2$, m/e 280.1463).

Anal. Calcd for $C_{19}H_{20}O_2$; C, 81.40; H, 7.19. Found: C, 81.69; H, 7.40.

1,5,5-Triphenyl-3,3-dimethyl-4-penten-1-one. To 27.0 mL (28.2 mmol, 1.04 M in ether) of phenyllithium in 75.0 mL of ether at 0 °C was added dropwise 3.15 g (11.3 mmol) of 3,3-dimethyl-5,5-diphenyl-4-pentenoic acid in 50.0 mL of ether. After

(17) Melting points were determined by using a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN 37921. All reactions were performed under an atmosphere of dry nitrogen unless stated otherwise. Anhydrous magnesium sulfate or sodium sulfate were used as drying agents. Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns permitting monitoring by a hand held UV lamp. Preparative thin-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel and Merck aluminum oxide 60 GF 254 neutral (Type E) alumina. High-pressure liquid chromatography (HPLC) was done by using a liquid chromatograph with an LDC 254-nm detector and LDC minipump. Analyses were performed by using a 0.25 × 25 cm polished stainless-steel column packed with 5–7 μm porous silica beads.[27] Preparative separations were performed by using a 0.95 × 50 cm column packed with 10–13 μm porous silica beads.[27] Neutral workup refers to quenching the reaction with water, thorough ether extraction, washing the organic layer with water and brine, drying, filtering, and concentration in vacuo. Acidic workup used a 5% aqueous hydrochloric acid wash after ether extraction. Basic workup employed a saturated sodium bicarbonate wash after ether extraction. Exploratory photolyses were done by using a Hanovia 450-W medium-pressure mercury lamp equipped with the appropriate 2-mm filter. All photolyses were thoroughly purged with purified nitrogen both prior to and during photolysis.

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded by using either a Brucker WP-270SY or WP-200SY, and data are reported in parts per million downfield from tetramethylsilane (δ). Infrared spectra were obtained on a Beckman Acculab 7 spectrophotometer. Mass spectra (MS) were obtained by using a Kratos MS-90 operating at 50 or 25 eV.

tert-Butyl alcohol used for photolyses was distilled from calcium hydride prior to use. Hexane employed in HPLC was washed with nitric acid and sulfuric acid (1:1), water, aqueous saturated sodium bicarbonate, and brine, dried over anhydrous calcium chloride, passed through alumina, and distilled from calcium hydride. Methylene chloride was purified by distillation from phosphorus pentoxide. Tetrahydrofuran (THF) and dimethoxyethane (DME) were purified by storage over potassium hydroxide, followed by successive distillation under a nitrogen atmosphere from calcium hydride, lithium aluminum hydride, and sodium–benzophenone ketyl.

the addition was complete, the mixture was stirred at room temperature for 16.0 h and then transferred via cannula into saturated aqueous ammonium chloride. Neutral workup[17] gave 4.56 g of a red oil which was chromatographed on a 4 × 50 cm silica gel column (5% ether in hexane), and 500-mL fractions were collected: fraction 3, 3.10 g (81%) of 1,5,5-triphenyl-3,3-dimethyl-4-penten-1-one as a clear, colorless oil.

The spectral data were as follows: IR (neat) 3040, 3020, 2980, 2920, 2860, 1680, 1500, 1450, 1350, 1220, 1060, 1000, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.80–7.10 (m, 15 H, arom), 6.23 (s, 1 H, =CH), 2.92 (s, 2 H, CH_2), 1.14 (s, 6 H, CH_3); MS, m/e 340.1831 (calcd for $C_{25}H_{24}O$, m/e 340.1827).

Anal. Calcd for $C_{25}H_{24}O$: C, 88.19; H, 7.10. Found: C, 88.21; H, 7.22.

1-(*p*-Methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-penten-1-ol. To 1.32 g (7.06 mmol) of 4-bromoanisole in 25.0 mL of ether at 0 °C was added 4.71 mL (7.05 mmol, 1.5 M in hexane) of *n*-butyllithium. After being stirred at 0 °C for 1.0 h, a solution of 1.60 g (4.70 mmol) of 1,5,5-triphenyl-3,3-dimethyl-4-penten-1-one in 20.0 mL of ether was added dropwise, warmed to room temperature, and stirred for 5.0 h. Neutral workup[17] gave 2.98 g of a light yellow oil which was chromatographed on a 2 × 50 cm silica gel column (3% ether in pentane), and 1-L fractions were collected: fraction 3, 1.96 g (93%) of 1-(*p*-methoxyphenyl)-1,1,5-triphenyl-3,3-dimethyl-4-penten-1-ol as a colorless glass.

The spectral data were as follows: IR (neat) 3500, 3060, 2960, 2940, 2900, 2840, 1600, 1510, 1500, 1300, 1250, 1190, 1040, 840, 770, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.35–6.85 (m, 19 H, arom), 6.13 (s, 1 H, =CH), 3.73 (s, 3 H, OCH_3), 2.84 (s, 1 H, OH), 2.57 (s, 2 H, CH_2), 0.80 (s, 3 H, CH_3), 0.77 (s, 3 H, CH_3); MS, m/e 448.2419 (calcd for $C_{32}H_{32}O_2$, m/e 448.2402).

Anal. Calcd for $C_{32}H_{32}O_2$: C, 85.67; H, 7.19. Found: C, 85.37; H, 7.52.

1-(*p*-Cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-penten-1-ol. To a stirred solution of 0.680 g (3.73 mmol) of 4-bromobenzonitrile in 50.0 mL of 1:1 THF/pentane at −100 °C was added 2.49 mL (3.46 mmol, 1.5 M in hexane) of *n*-butyllithium dropwise, maintaining the temperature below −85 °C.[18] After 1.5 h at this temperature, 0.790 g (2.31 mmol) of 1,5,5-triphenyl-3,3-dimethyl-4-penten-1-one in 15.0 mL of ether was added dropwise, keeping the temperature below −85 °C. This was stirred 4.0 h, then allowed to warm slowly to room temperature, and stirred for 2.0 h. Neutral workup[17] afforded 1.49 g of a red oil which was chromatographed on a 2 × 40 cm silica gel column (10% ether in hexane), and 500-mL fractions were collected: fraction 3, 0.754 g (74%) of 1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-penten-1-ol as a slightly yellow foam. Further chromatography (silica gel, 10% ether in pentane) afforded 0.680 g (66%) of analytically pure alcohol as a colorless foam.

The spectral data were as follows: IR (neat) 3600, 3080, 3030, 2970, 2880, 2240, 1610, 1500, 1460, 1360, 1275, 840 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.62–7.05 (m, 19 H, arom), 6.06 (s, 1 H, =CH), 3.06 (s, 1 H, OH), 2.60 (s, 2 H, CH_2), 0.85 (s, 3 H, CH_3), 0.78 (s, 3 H, CH_3); MS, m/e 443.2253 (calcd for $C_{32}H_{29}O$, m/e 443.2249).

Anal. Calcd for $C_{32}H_{29}O$: C, 86.65; H, 6.59. Found: C, 86.49; H, 6.70.

1-Methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene. To a slurry of 0.480 g (10.0 mmol, 48% in mineral oil) sodium hydride and 2.00 mL (52.0 mmol) of methyl iodide in 10.0 mL of DME was added 0.500 g (1.18 mmol) of 1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-penten-1-ol in 10.0 mL of DME. After the solution was stirred at room temperature for 24 h, neutral workup[17] gave 0.950 g of a light yellow oil which was chromatographed on a 2 × 40 cm silica gel column (2% ether in pentane), and 500-mL fractions were collected: fraction 3, 0.460 g (84%) of 1-methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene as a colorless foam. Further chromatography (silica gel, 2% ether in pentane) furnished 0.439 g (80%) of analytically pure ether as a glass. Samples suitable for fluorescence spectroscopy were prepared by purification by preparative HPLC (2% ether in pentane).

The spectral data were as follows: IR (neat) 3050, 3020, 2950, 2930, 2920, 1610, 1510, 1500, 1450, 1255, 1180, 1040, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.32–6.70 (m, 19 H, arom), 5.94 (s, 1 H, =CH), 3.69 (s, 3 H, arom OCH_3), 2.98 (s, 3 H, OCH_3), 0.76 (s, 6 H, CH_3); UV (EtOH) 255 (ϵ 22 000), 280 (10 600), 310 nm (2100); MS, m/e 462.2566 (calcd for $C_{34}H_{34}O_2$, m/e 462.2559).

Anal. Calcd for $C_{34}H_{34}O_2$: C, 85.67; H, 7.41. Found: C, 85.65; H, 7.51.

1-Methoxy-1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene. To a slurry of 2.68 g (56.0 mmol, 48% in mineral oil) of sodium hydride and 3.50 mL (91.0 mmol) of methyl iodide in 25.0 mL of DME was added 2.50 g (5.60 mmol) of 1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-penten-1-ol in 15.0 mL of DME. After the mixture was stirred at room temperature for 30.0 h, neutral workup[17] gave 2.95 g of a colorless oil which was chromatographed on a 2 × 60 cm silica gel column (7% ether in pentane), and 500-mL fractions were collected: fractions 4 and 5, 2.46 g (96%) of 1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-penten-1-ol as a colorless foam. Further chromatography (7% ether in pentane) afforded 2.25 g (88%) of analytically pure ether. Samples suitable for fluorescence spectroscopy were obtained by purification by preparative HPLC (5% ether in pentane).

The spectral data were as follows: IR (neat) 3040, 3010, 2960, 2840, 2220, 1610, 1515, 1495, 1445, 1370, 1230, 1190, 1110, 1086, 850, 830, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.50–6.98 (m, 19 H, arom), 5.79 (s, 1 H, =CH), 3.00 (s, 3 H, OCH_3), 2.53 (AB q, J = 15 Hz, 2 H, CH_2), 0.82 (s, 3 H, CH_3), 0.77 (s, 3 H, CH_3); UV (EtOH) 255 (ϵ 20 500), 290 nm (7000); MS, m/e 457.2457 (calcd for $C_{33}H_{31}NO$, m/e 457.2406).

Anal. Calcd for $C_{33}H_{31}NO$: C, 86.61; H, 6.82. Found: C, 86.58; H, 6.96.

(*E*)- and (*Z*)-1-Methoxy-3,3-dimethyl-4,5,5-triphenyl-1-pentene. A solution of 2.37 g (21.2 mmol) of potassium *tert*-butoxide in 45.0 mL of THF was added to a slurry of 7.26 g (21.2 mmol) (methoxymethyl)triphenylphosphonium chloride in 65.0 mL of THF at 0 °C. After being stirred for 1.0 h at 0 °C, a solution of 2.32 g (7.07 mmol) of 2,2-dimethyl-3,4,4-triphenylbutanal[3] in 40.0 mL of THF was added dropwise. This was then allowed to warm to room temperature and stirred for 7.5 h. Neutral workup[17] gave 9.98 g of a viscous brown oil, which was then chromatographed on a 2 × 100 cm column (2% ether in hexane), collecting 250-mL fractions: fractions 6 and 7, 0.90 g (37%) of (*E*)-1-methoxy-3,3-dimethyl-4,5,5-triphenyl-1-pentene; fractions 8–10, 1.34 g (53%) of (*Z*)-1-methoxy-3,3-dimethyl-4,5,5-triphenyl-1-pentene, as colorless oils.

The spectral data for the *Z* isomer were as follows: IR (neat) 3080, 3040, 3020, 2960, 2920, 1600, 1500, 1450, 1100, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.35–6.85 (m, 15 H, arom), 5.31 (d, J = 7 Hz, 1 H, =CH), 4.55 (d, J = 13 Hz, 1 H, PhCHPh), 3.94 (d, J = 13 Hz, 1 H, CHPh), 3.83 (d, J = 7 Hz, 1 H, =CH), 3.48 (s, 3 H, OCH_3), 1.06 (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3).

Anal. Calcd for $C_{26}H_{28}O$: C, 87.59; H, 7.91. Found: C, 87.44; H, 7.94.

The spectral data for the *E* isomer were as follows: IR (neat) 3080, 3040, 3020, 2960, 2920, 1620, 1600, 1500, 1250, 1080, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.42–6.85 (m, 15 H, arom), 5.95 (d, J = 13 Hz, 1 H, =CH), 4.70 (d, J = 13 Hz, 1 H, =CH), 4.46 (d, J = 13 Hz, 1 H, $CHPh_2$), 3.63 (d, J = 12 Hz, 1 H, CHPh), 3.30 (s, 3 H, OCH_3), 0.87 (s, 3 H, CH_3), 0.73 (s, 1 H, CH_3).

Anal. Calcd for $C_{26}H_{28}O$: C, 87.59; H, 7.91. Found: C, 87.59; H, 7.96.

3,3-Dimethyl-4,5,5-triphenylpentanoic Acid. To a stirred solution of a mixture of 1.05 g (2.95 mmol) of (*E*)- and (*Z*)-1-methoxy-3,3-dimethyl-4,5,5-triphenyl-1-pentene in 10.0 mL of acetone was added 2.0 mL (16.00 mmol, 8.0 N) of Jones reagent[19] and the resulting brown mixture was stirred for 2.0 h. Neutral workup[17] afforded 0.970 g (93%) of 3,3-dimethyl-4,5,5-triphenylpentanoic acid as a white solid, mp 156–159 °C. Recrystallization from ether gave 0.902 g (85%) of the acid as colorless plates, mp 162.0–163.5 °C.

The spectral data were as follows: IR ($CHCl_3$) 3500, 3080, 3060, 2980, 2960, 1710, 1600, 1500, 1460, 1240, 1080, 1040, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 10.31 (b s, 1 H, acid), 7.65–6.80 (m, 15 H, arom), 4.53 (d, J = 12 Hz, 1 H, PhCHPh), 4.17 (d, J = 12

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Hz, 1 H, CHPh), 2.00 (AB q, J = 5 Hz, 2 H, CH_2), 0.85 (s, 3 H, CH_3), 0.77 (s, 3 H, CH_3).

Anal. Calcd for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31. Found: C, 83.62; H, 7.35.

1,4,5,5-Tetraphenyl-3,3-dimethyl-1-pentanone. To 7.00 mL (11.2 mmol, 1.6 M in ether) of phenyllithium in 10.0 mL of ether at 0 °C was added dropwise a solution of 1.79 g (5.00 mmol) of 3,3-dimethyl-4,5,5-triphenylpentanoic acid in 20.0 mL of ether. The resulting mixture was stirred at room temperature for 4 h. Neutral workup[17] gave 2.10 g of a reddish brown oil which was chromatographed on a 2 × 40 cm silica gel column (5% ether in hexane), and 500-mL fractions were collected: fraction 3, 1.81 g (86%) of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone as a colorless foam. Recrystallization from pentane/ether gave 1.54 g (74%) of the ketone as colorless prisms, mp 127–128 °C.

The spectral data were as follows: IR (neat) 3080, 3050, 3020, 2940, 2920, 2860, 1685, 1595, 1585, 1490, 1450, 1360, 1210, 1070, 1030, 1000, 790, 680 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.55–6.79 (m, 20 H, arom), 4.57 (AB q, J = 9 Hz, 2 H, methines), 2.54 (AB q, J = 8 Hz, 2 H, CH_2), 1.14 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3); UV (EtOH) 255 (ϵ 9700), 270 (2700), 280 nm (725); MS, m/e 418.2298 (calcd for $C_{31}H_{30}O$, m/e 418.2297).

Anal. Calcd for $C_{31}H_{30}O$: C, 88.95; H, 7.22. Found: C, 88.78; H, 7.49.

1-(Pentadeuteriophenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentanone. To a stirred solution of 975 mg (6.06 mmol) of bromobenzene-d_5[20] and 15.0 mL of ether at 0 °C was added 4.04 mL (6.06 mmol) of n-butyllithium. After 1.0 h, 723 mg (2.02 mmol) of 3,3-dimethyl-4,5,5-triphenylpentanoic acid in 25.0 mL of ether was added dropwise to this solution. After being stirred for 10 h, the reaction was quenched by addition via cannula to a saturated ammonium chloride solution. Neutral workup[17] gave 1.20 g of a brown oil which was chromatographed on a 2 × 50 cm silica gel column (5% ether in hexane), and 500-mL fractions were collected: fraction 3, 765 mg (90%) of 1-(pentadeuteriophenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentanone as a colorless foam. Recrystallization afforded 685 mg (80%) of the pentadeuterated ketone as colorless plates, mp 118–121 °C. From the ratio of the m/e 423 (d_5) and 418 (d_0) peaks in the MS a lower limit for the amount of pentadeuterated ketone present could be set at 97%.

The spectral data were as follows: IR (neat) 3080, 3055, 3020, 2940, 2920, 2860, 2280 (wk, D str), 1685, 1595, 1585, 1490, 1450, 1360, 1210, 1070, 1030, 1000, 790, 680 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.55–6.79 (m, 15 H, arom), 4.57 (AB q, J = 9 Hz, 2 H, methines), 2.54 (AB q, J = 8 Hz, 2 H, CH_2), 1.14 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3); MS, m/e 423.2648 (calcd for $C_{31}H_{25}D_5O$, m/e 423.2617).

1,5,5-Triphenyl-2,2-dideuterio-3,3-dimethyl-4-penten-1-one. A 0.872 M sodium deuteroxide solution was prepared from 25.0 mL of deuterium oxide (>98% deuterium) and 0.502 g (21.8 mol) of sodium. This was then added to a solution of 1.60 g (4.70 mmol) of 1,5,5-triphenyl-3,3-dimethyl-4-penten-1-one in 15.0 mL of anhydrous dioxane and stirred for 3 days. Neutral workup[17] gave 1.46 g (91%) of the ketone as a yellow oil. ^1H NMR integration of the C-2 methylene peak revealed that the ketone was 92% deuterated at C-2. Further reaction of this material under the same conditions gave 1.37 g (87%) of 1,5,5-triphenyl-2,2-dideuterio-3,3-dimethyl-4-penten-1-one as a light yellow oil which was used without further purification. ^1H NMR integration (200 MHz) of the C-2 methylene vs. a C-3 methyl group revealed that C-2 was now 97% deuterated.

The spectral data were as follows: IR (neat) 3040, 3020, 2980, 2920, 2860, 1680, 1500, 1450, 1350, 1220, 1060, 1000, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.80–7.10 (m, 15 H, arom), 6.23 (s, 1 H, =CH), 1.14 (s, 6 H, CH_3); MS, m/e 342.1947 (calcd for $C_{25}H_{22}D_2O$, m/e 342.1953).

1,1,5,5-Tetraphenyl-2,2-dideuterio-3,3-dimethyl-4-penten-1-ol. To a stirred solution of 0.550 g (1.61 mmol) of 1,5,5-triphenyl-2,2-dideuterio-3,3-dimethyl-4-penten-1-one and 15.0 mL of ether at 0 °C was added 1.73 mL (1.80 mmol, 1.04 M in ether) of phenyllithium. After the mixture was stirred for 3.0 h, neutral workup[17] gave 0.723 g of a yellow oil which was chromatographed on a 2 × 40 cm column (5% ether in hexane), and 500-mL fractions were collected: fraction 3, 0.523 g (77%) of the alcohol as a colorless oil. Recrystallization from hexane gave 0.480 g (71%) of 1,1,5,5-tetraphenyl-2,2-dideuterio-3,3-dimethyl-4-penten-1-ol as colorless plates, mp 112–114 °C. ^1H NMR integration of the C-2 methylene vs. a C-3 methyl group showed that C-2 was 97% deuterated. This was confirmed by comparison of m/e 420 (d_2) and 418 (d_0) peaks in the MS.

The spectral data were as follows: IR (neat) 3600, 3400, 3060, 3030, 2960, 2930, 2880, 1605, 1500, 1455, 1080, 1040, 1020, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.46–7.01 (m, 20 H, arom), 6.14 (s, 1 H, =CH), 2.91 (s, 1 H, OH), 0.77 (s, 6 H, CH_3); MS, m/e 420.2436 (calcd for $C_{31}H_{28}D_2O$, m/e 420.2429).

2,2-Diphenyl-2-(*p*-methoxyphenyl)ethanol. To a suspension of 1.20 g (31.6 mmol) of lithium aluminum hydride and 150 mL of ether was added dropwise 2.75 g (7.90 mmol) of methyl 2,2-diphenyl-2-(*p*-methoxyphenyl) acetate[21] in 25.0 mL of ether. The resulting solution was refluxed for 2.0 h and cooled to 0 °C and 1.20 mL of water cautiously added, followed by the addition of 1.20 mL of 10% aqueous hydrochloric acid and 1.20 mL of water. The gray solid was then filtered and the filtrate concentrated in vacuo to afford 2.40 g (100%) of 2,2-diphenyl-2-(*p*-methoxyphenyl)ethanol as a viscous yellow oil. Recrystallization from hexane gave 2.29 g (95%) of the alcohol as a colorless solid, mp 101.0–101.5 °C.

The spectral data were as follows: IR ($CHCl_3$) 3575, 3080, 3040, 3005, 2982, 1615, 1515, 1260, 1070, 1045, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.38–6.79 (m, 14 H, arom), 4.60 (d, J = 7 Hz, 2 H, CH_2), 3.79 (s, 3 H, OCH_3), 1.56 (t, J = 7 Hz, 1 H, OH); MS, m/e 304.1463 (calcd for $C_{21}H_{20}O_2$, m/e 304.1463).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.73; H, 6.86.

2,2-Diphenyl-2-(*p*-methoxyphenyl)acetaldehyde. To a slurry of 8.30 g (39.0 mmol) of pyridinium chlorochromate[22] in 50.0 mL of methylene chloride was added 7.80 g (26.0 mmol) of 2,2-diphenyl-2-(*p*-methoxyphenyl) ethanol in 25.0 mL of methylene chloride. The resulting mixture was stirred for 2.0 h and filtered through Florisil. The filtrate was concentrated in vacuo to afford 7.41 g (90%) of the air-sensitive aldehyde as a light yellow oil, which crystallized slowly. Recrystallization of the solid from methanol afforded 6.90 g (87%) of 2,2-diphenyl-2-(*p*-methoxyphenyl)acetaldehyde as colorless plates, mp 72–74 °C.

The spectral data were as follows: IR (neat) 3085, 3060, 3035, 3000, 2955, 2840, 1735, 1605, 1500, 1450, 1290, 1260, 1190, 1090, 1040, 830, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 10.31 (s, 1 H, aldehyde), 7.53–6.82 (m, 14 H, arom), 3.95 (s, 3 H, OCH_3). MS m/e 302.1307 (calcd for $C_{21}H_{18}O_2$, m/e 302.1307).

2,2-Dimethyl-3-(*p*-methoxyphenyl)-4-hydroxy-4,4-diphenylbutanoic Acid Lactone. To a slurry of 1.50 g (23.0 mmol) activated zinc[23] in 50.0 mL of benzene at reflux was added a solution of 2.63 g (12.25 mmol) of ethyl 2-bromoisobutyrate, 3.70 g (12.25 mmol) of 2,2-diphenyl-2-(*p*-methoxyphenyl)acetaldehyde, and 75.0 mL of benzene. The mixture was refluxed for 36.0 h, cooled to 0 °C, and quenched by the addition of 90.0 mL of 10% aqueous sulfuric acid. Neutral workup[17] gave 3.90 g of a yellow oil consisting of starting material and the desired product which was chromatographed on a 2 × 75 cm silica gel column (10% ether in hexane), and 500-mL fractions were collected: fractions 4–6, 0.75 g (20%) of unreacted starting aldehyde; 9–11, 2.75 g (59%), 2,2-dimethyl-3-(*p*-methoxyphenyl)-4,4-diphenyl-4-hydroxy-1-butanoic acid lactone as a colorless solid, mp 125.0–131.5 °C. Recrystallization from ether gave 2.35 g (50%) of the lactone as colorless needles, mp 129.0–131.5 °C.

The spectral data were as follows: IR ($CHCl_3$) 3060, 3030, 2980, 2960, 1765, 1610, 1515, 1250, 1180, 1040, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) 7.66–6.66 (m, 14 H, arom), 4.19 (s, 1 H, CHPh), 3.74 (s, 3 H, OCH_3), 1.10 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3).

Anal. Calcd for $C_{23}H_{24}O_2$: C, 79.28; H, 6.94. Found: C, 79.66; H, 6.58.

2,2-Dimethyl-3-(*p*-methoxyphenyl)-4,4-diphenylbutanoic Acid. To 350 mL of anhydrous ammonia at −78 °C was added 0.120 g (17.1 mmol) of lithium. A solution of 2.00 g (5.24 mmol) of 2,2-dimethyl-3-(*p*-methoxyphenyl)-4-hydroxy-4,4-diphenyl-1-

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butanoic acid lactone in 25.0 mL of THF was then added to the blue solution at this temperature. The resulting red solution was warmed to liquid ammonia reflux and stirred for 2.0 h. After the reaction was quenched with 1.50 g (28.3 mmol) of ammonium chloride and evaporation of the ammonia, acidic workup[17] afforded 2.01 g (98%) of 2,2-dimethyl-3-(*p*-methoxyphenyl)-3,3-diphenylbutanoic acid as a slightly yellow solid, mp 229–235 °C. Recrystallization of the solid from methylene chloride gave 1.96 g (97%) of the acid as colorless plates, mp 235–239.5 °C.

The spectral data were as follows: IR ($CHCl_3$) 3600, 3060, 3030, 2990, 2960, 2930, 1700, 1610, 1510, 1250, 1180, 1040, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 10.31 (b s, 1 H, acid), 7.48–6.75 (m, 14 H, arom), 4.44 (d, J = 8 Hz, 1 H, PhCHPh), 4.24 (d, J = 8 Hz, 1 H, CHPh), 3.69 (s, 3 H, OCH_3), 1.24 (s, 3 H, CH_3), 0.89 (s, 3 H, CH_3).

Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48. Found: C, 78.53; H, 7.83.

2,2-Dimethyl-3-(*p*-methoxyphenyl)-4,4-diphenyl-1-butanol. To 0.500 g (13.0 mmol) of lithium aluminum hydride in 40.0 mL of THF was added 1.96 g (5.10 mmol) of 2,2-dimethyl-3-(*p*-methoxyphenyl)-4,4-diphenylbutanoic acid in 25.0 mL of THF. After the solution was refluxed for 10.0 h, neutral workup[17] gave 1.76 g (92%) of 2,2-dimethyl-3-(*p*-methoxyphenyl)-4,4-diphenyl-1-butanol as a light green oil. Recrystallization from hexane afforded 1.54 g (81%) of the alcohol as colorless prisms, mp 133–135 °C.

The spectral data were as follows: IR ($CHCl_3$) 3575, 3080, 3040, 3010, 2980, 2960, 1615, 1515, 1260, 1190, 1070, 1045, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.35–6.85 (m, 14 H, arom), 4.49 (d, J = 12 Hz, 1 H, $CHPh_2$), 3.86 (d, J = 12 Hz, 1 H, AnCH), 2.90 (d, J = 6 Hz, 2 H, CH_2), 1.05 (t, J = 6 Hz, 1 H, OH), 0.81 (s, 3 H, CH_3), 0.79 (s, 3 H, CH_3).

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.01; H, 8.51.

2,2-Dimethyl-3-(*p*-methoxyphenyl)-4,4-diphenylbutanal. To a slurry of 1.17 g (5.84 mmol) of pyridinium chlorochromate[22] in 25.0 mL of methylene chloride was added 1.36 g (3.65 mmol) of 2,2-diphenyl-3-(*p*-methoxyphenyl)-4,4-diphenyl-1-butanol in 15.0 mL of methylene chloride. After being stirred for 1.5 h, the mixture was filtered through Florisil, and the filtrate was concentrated in vacuo to afford 1.28 g (95%) of 2,2-dimethyl-3-(*p*-methoxyphenyl)-4,4-diphenylbutanal as a light yellow oil. Recrystallization from ether afforded 1.18 g (87%) of the aldehyde as a colorless solid, mp 157–159 °C, which is extremely sensitive to air oxidation.

The spectral data were as follows: IR (neat) 3070, 3030, 2965, 2935, 2840, 1720, 1610, 1500, 1470, 1400, 1370, 1035, 990, 860, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.96 (s, 1 H, aldehyde), 7.70–6.65 (m, 14 H, arom), 4.37 (d, J = 12 Hz, 1 H, $CHPh_2$), 3.96 (d, J = 12 Hz, 1 H, AnCH), 3.72 (s, 3 H, OCH_3), 1.18 (s, 3 H, CH_3), 0.68 (s, 3 H, CH_3); MS, m/e 334.1943 (calcd for $C_{23}H_{26}O_2$, m/e 334.1943).

(*E*)- and (*Z*)-1-Methoxy-3,3-dimethyl-4-(*p*-methoxyphenyl)-5,5-diphenyl-1-pentene. To a stirred suspension of 2.19 g (6.37 mmol) of (methoxymethyl)triphenylphosphonium chloride in 100 mL of THF at 0 °C was added 0.710 g (6.34 mmol) of potassium *tert*-butoxide in 10.0 mL of THF. The resulting solution was stirred for 2.0 h, and 1.18 g (3.18 mmol) of 2,2-dimethyl-3-(*p*-methoxyphenyl)-4,4-diphenyl-1-butanal in 15.0 mL of THF was added at 0 °C. This was stirred for an additional 5.0 h at room temperature. Neutral workup[17] afforded 2.60 g of a red oil which was chromatographed on a 2 × 100 cm silica gel column (2% ether in hexane), and 500-mL fractions were collected: fractions 3 and 4, 0.43 g (35%) of (*E*)-1-methoxy-3,3-dimethyl-4-(*p*-methoxyphenyl)-5,5-diphenyl-1-pentene as a colorless solid, mp 86–100 °C; fractions 6 and 7, 0.650 g (53%) of (*Z*)-1-methoxy-3,3-diphenyl-4-(*p*-methoxyphenyl)-5,5-diphenyl-1-pentene as a colorless solid, mp 95–102 °C. Recrystallization of the *E* isomer from pentane gave 0.320 g (26%) of a white solid, mp 101–103 °C. Recrystallization of the *Z* isomer from pentane afforded 0.530 g (43%) of a white solid, mp 102–104 °C.

The spectral data for the *E* isomer were as follows: IR ($CHCl_3$) 3060, 3020, 2960, 2920, 2840, 1625, 1575, 1210, 1190, 1110, 1045, 845, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.46–6.56 (m, 14 H, arom), 5.93 (d, J = 13 Hz, 1 H, =CH), 4.67 (d, J = 13 Hz, 1 H, =CH), 4.41 (d, J = 11 Hz, 1 H, $CHPh_2$), 3.66 (s, 3 H, arom OCH_3), 3.57 (d, J = 11 Hz, AnCH), 3.31 (s, 3 H, $=COCH_3$), 0.85 (s, 3 H, CH_3), 0.71 (s, 3 H, CH_3).

Anal. Calcd for $C_{27}H_{30}O_2$: C, 83.90; H, 7.82. Found: C, 83.65; H, 7.83.

The spectral data for the *Z* isomer were as follows: IR (neat) 3060, 3020, 2960, 2920, 2840, 1660, 1575, 1210, 1190, 1110, 1045, 845, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.46–6.51 (m, 14 H, arom), 5.31 (d, J = 7 Hz, 1 H, =CH), 4.52 (d, J = 11 Hz, 1 H, $CHPh_2$), 3.87 (d, J = 11 Hz, 1 H, AnCH), 3.82 (d, J = 7 Hz, 1 H, =CH), 3.68 (s, 3 H, arom OCH_3), 3.48 (s, 3 H, $=COCH_3$), 1.04 (s, 3 H, CH_3), 0.86 (s, 3 H, OCH_3).

Anal. Calcd for $C_{27}H_{30}O_2$: C, 83.90; H, 7.82. Found: C, 83.65; H, 7.83.

3,3-Dimethyl-4-(*p*-methoxyphenyl)-5,5-diphenylpentanoic Acid. To 0.400 g (1.03 mmol) of (*Z*)-1-methoxy-3,3-dimethyl-4-(*p*-methoxyphenyl)-5,5-diphenyl-1-pentene in 10.0 mL of acetone was added 0.500 mL (4.00 mmol, 8.0 N) of Jones reagent[19] and the resulting solution stirred for 2.0 h. Neutral workup[17] afforded 0.342 g of a yellow oil. Recrystallization from ether gave 0.281 g (71%) of 3,3-dimethyl-4-(*p*-methoxyphenyl)-5,5-diphenylpentanoic acid as a light yellow solid, mp 215–217 °C.

The spectral data were as follows: IR ($CHCl_3$) 3500 (b), 3080, 3050, 3020, 2980, 2950, 1716, 1600, 1500, 1460, 1250, 1090, 1035, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 10.31 (b s, 1 H, acid), 7.52–6.60 (m, 14 H, arom), 4.50 (d, J = 12 Hz, 1 H, $CHPh_2$), 3.86 (d, J = 12 Hz, 1 H, AnCH), 3.66 (s, 3 H, OCH_3), 2.92 (s, 2 H, CH_2), 0.82 (s, 3 H, CH_3), 0.79 (s, 3 H, CH_3).

Anal. Calcd for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.59; H, 6.60.

1,5,5-Triphenyl-3,3-dimethyl-4-(*p*-methoxyphenyl)-1-pentanone. To 0.880 g (5.61 mmol) of bromobenzene and 25.0 mL of ether at 0 °C was added 3.70 mL (5.61 mmol, 1.5 M in hexane) of *n*-butyllithium. This was stirred for 1.0 h, and a solution of 0.782 g (1.87 mmol) of 3,3-dimethyl-4-(*p*-methoxyphenyl)-5,5-diphenylpentanoic acid in 10.0 mL of ether was added dropwise. After being stirred at room temperature for 5.0 h, the reaction was inversely quenched with ammonium chloride. Neutral workup[17] afforded 0.805 g of a yellow oil. Column chromatography on a 2 × 50 cm silica gel column (7% ether in hexane) gave 0.640 g (77%) of 1,5,5-triphenyl-3,3-dimethyl-4-(*p*-methoxyphenyl)-1-pentanone as a colorless foam. Recrystallization from pentane yielded 0.540 g (64%) of the ketone as colorless plates, mp 144–146 °C.

The spectral data were as follows: IR (neat) 3060, 3030, 2990, 2940, 1680, 1600, 1505, 1440, 1360, 1240, 1180, 1030, 840, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.60–6.55 (m, 19 H, arom), 4.50 (AB q, J = 7 Hz, 2 H, $CHPh_2$ and AnCH), 3.63 (s, 3 H, OCH_3), 2.50 (AB q, J = 5 Hz, 2 H, CH_2), 1.00 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3); MS, m/e 448.6095 (calcd for $C_{32}H_{32}O_2$, m/e 448.6106).

Anal. Calcd for $C_{32}H_{32}O_2$: C, 85.67; H, 7.19. Found: C, 85.32; H, 7.24.

1-(*p*-Methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentanone. To a solution of 1.16 g (6.20 mmol) of 4-bromoanisole and 25.0 mL of ether at 0 °C was added 4.13 mL (6.20 mmol, 1.5 M in hexane) of *n*-butyllithium. This was stirred for 1.0 h, and a solution of 0.890 g (2.48 mmol) of 3,3-dimethyl-4,5,5-triphenylpentanoic acid and 15.0 mL of ether was added dropwise. After the addition was complete, the reaction was allowed to warm to room temperature and stirred for 10.0 h. Neutral workup[17] afforded 1.23 g of a clear oil which was chromatographed on a 2 × 40 cm silica gel column (5% ether in hexane), and 250-mL fractions were collected: fraction 2, 0.751 g (68%) of 1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentanone as a colorless foam. Recrystallization from pentane gave 0.290 g (26%) of the ketone as a colorless solid, mp 141.5–144.5 °C.

The spectral data were as follows: IR (neat) 3060, 3020, 2980, 2920, 2880, 1680, 1600, 1510, 1500, 1460, 1260, 1230, 1180, 1040, 750, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.65–6.65 (m, 19 H, arom), 4.50 (AB q, J = 8 Hz, 2 H, $CHPh_2$ and AnCH), 3.66 (s, 3 H, OCH_3), 2.51 (AB q, J = 8 Hz, 2 H, CH_2), 1.02 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3); MS, m/e 448.2410 (calcd for $C_{32}H_{32}O_2$, m/e 448.2402).

Anal. Calcd for $C_{32}H_{32}O_2$: C, 85.67; H, 7.19. Found: C, 86.03; H, 7.44.

Exploratory Direct Photolysis of 1,1,5,5-Tetraphenyl-3,3-dimethyl-4-penten-1-ol. A solution of 418 mg (1.00 mmol,

2.00×10^{-3} M) of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol in 500 mL of *tert*-butyl alcohol was photolyzed for 3.5 h using a Corex filter. Concentration in vacuo gave 425 mg (103%) of a brown oil which was chromatographed on a 20 × 20 cm preparative thin-layer alumina plate, eluting six times with 5% ether in hexane. The most rapidly moving band contained 36.1 mg (12%) of 1,1,2-triphenyl-3-methyl-2-pentene as a colorless oil. Recrystallization from methanol gave 22.2 mg (7%) of the alkene as colorless plates, mp 49.5–52.0 °C. Band 2 gave 12.1 mg of acetophenone (10%). Band 3 contained 50.3 mg (12%) of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone as a light yellow foam which was recrystallized from pentane to yield 38.2 mg (9%) of the ketone as a colorless solid, mp 128–129 °C, identical with synthetic material (vide supra). Band 4 contained 265 mg (63%) of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol, mp 110–112 °C.

The spectral data for 1,1,2-triphenyl-3-methyl-2-butene were as follows: IR (neat) 3080, 3060, 3020, 2910, 2840, 1600, 1500, 1450, 1080, 1040, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.26–7.02 (m, 15 H, arom), 6.72 (m, 2 H, arom), 5.51 (s, 1 H, $CHPh_2$), 1.83 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3); MS, *m/e* 298.1721 (calcd for $C_{23}H_{22}$, *m/e* 298.1733).

Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.25; H, 7.41.

Exploratory Direct Photolysis of 1-Methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene. A solution of 454 mg (1.05 mmol, 3.90×10^{-3} M) of 1-methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene in 270 mL of *tert*-butyl alcohol was irradiated for 4.0 h using a Corex filter. The solvent was removed in vacuo to afford 469 mg (103%) of a dark yellow oil which was chromatographed on a 20 × 20 cm preparative thin-layer silica gel plate, eluting five times with 3% ether in pentane. The fastest moving band contained 246 mg (54%) of 1-methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene. Band 2 contained 74.6 mg (16%) of (*Z*)-1-methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene as a colorless oil, which was purified further using preparative HPLC (2% ether in pentane) to afford 58.2 mg (13%) of the (*Z*)-enol ether as a colorless oil. Band 3 contained 78.6 mg (17%) of (*E*)-1-methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene as a colorless oil which was purified by preparative HPLC (2% ether in pentane) to afford 63.3 mg (14%) of the (*E*)-enol ether as a colorless oil.

The spectral data for (*Z*)-1-methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene were as follows: IR (neat) 3080, 3060, 3020, 2960, 2920, 2860, 1640, 1600, 1500, 1450, 1040, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.45–6.81 (m, 20 H, arom), 4.61 (d, J = 11 Hz, 1 H, $CHPh_2$), 4.68 (s, 1 H, =CH), 4.15 (d, J = 11 Hz, 1 H, CHPh), 3.39 (s, 3 H, OCH_3), 1.22 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3); UV (EtOH) 260 (ϵ 8900), 270 nm (7000); MS, *m/e* 432.2429 (calcd for $C_{32}H_{32}O$, *m/e* 432.2453).

Anal. Calcd for $C_{32}H_{32}O$: C, 88.85; H, 7.45. Found: C, 88.79; H, 7.29.

The spectral data for (*E*)-1-methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene were as follows: IR (neat) 3080, 3060, 3020, 2980, 2960, 2920, 2900, 1655, 1600, 1500, 1450, 1110, 1050, 1035, 980, 705 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.53–6.82 (m, 20 H, arom), 4.57 (d, J = 11 Hz, 1 H, $CHPh_2$), 4.52 (s, 1 H, =CH), 3.81 (d, J = 11 Hz, 1 H, CHPh), 3.18 (s, 3 H, OCH_3), 0.81 (s, 3 H, CH_3), 0.55 (s, 3 H, CH_3); UV (EtOH) 250 (ϵ 5000), 270 (2650), 290 nm (1100); MS, *m/e* 432.2433 (calcd for $C_{32}H_{32}O$, *m/e* 432.2453).

Anal. Calcd for $C_{32}H_{32}O$: C, 88.84; H, 7.45. Found: C, 88.85; H, 7.65.

Exploratory Direct Photolysis of 1,4,5,5-Tetraphenyl-3,3-dimethyl-1-pentanone. A solution of 100 mg (0.230 mmol, 1.53×10^{-3} M) of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone in 150 mL of *tert*-butyl alcohol was irradiated for 0.75 h using a Corex filter. Removal of the solvent in vacuo gave 85.0 mg (85%) of a yellow oil which was chromatographed on a 20 × 20 cm preparative thin-layer silica gel plate, eluting once with 2% ether in pentane. The fastest moving band gave 62.1 mg (91%) of 1,1,2-triphenyl-3-methyl-2-butene as a colorless oil which was recrystallized from methanol to afford 48.4 mg (71%) of the alkene as colorless plates, mp 47–51 °C, identical with material produced from the photolysis of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol. Band 2 contained 23.1 mg (84%) of acetophenone.

Exploratory Sensitized Photolysis of 1,4,5,5-Triphenyl-3,3-dimethyl-1-pentanone. A solution of 86.0 mg (0.206 mmol) of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone and 16.0 mL (129 mmol) of acetophenone in 150 mL of *tert*-butyl alcohol was photolyzed for 1.0 h through a Pyrex filter. After concentration in vacuo and removal of the acetophenone (45 °C (0.1 torr)) the resulting oil was passed through a 1 × 25 cm silica gel column (2% ether in pentane) to give 49.3 mg (80%) of 1,1,2-triphenyl-3-methyl-2-butene as a colorless oil. Recrystallization from methanol gave 38.6 mg (63%) of the alkene as colorless plates, mp 48–52 °C, identical with material obtained from the direct irradiation.

Exploratory Direct Photolysis of 1-Methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene. A solution of 490 mg (1.06 mmol, 3.93×10^{-3} M) 1-methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene in 270 mL of *tert*-butyl alcohol was irradiated for 6.0 h by using a Corex filter. Evaporation of the solvent in vacuo gave 465 mg (95%) of a dark brown oil which was chromatographed on a 20 × 20 cm preparative thin-layer silica gel plate, eluting four times with 5% ether in pentane. The fastest moving band contained 254 mg (55%) of 1-methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene. Band 2 contained 65.0 mg (14%) of a 2.4:1 mixture of (*Z*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-methoxyphenyl)-1-pentene and (*Z*)-1-methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentene. Separation of this mixture was accomplished by using preparative HPLC (1% ether in pentane, three recycles) to afford 38.1 mg (8%) of (*Z*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-methoxyphenyl)-1-pentene as a colorless foam and 12.6 mg (3%) of (*Z*)-1-methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentene, also as a colorless foam. Band 3 contained 109 mg (22%) of a 1.7:1 mixture of (*E*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-methoxyphenyl)-1-pentene and (*E*)-1-methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentene as a colorless oil which was separated by using preparative HPLC (3% ether in pentane) to afford 61.0 mg (12%) of (*E*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-methoxyphenyl)-1-pentene as a colorless foam and 36.0 mg (7%) of (*E*)-1-methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentene as a colorless foam.

The spectral data for (*Z*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-methoxyphenyl)-1-pentene were as follows: IR (neat) 3060, 3040, 3000, 2980, 2900, 2820, 1630, 1600, 1500, 1480, 1450, 1245, 1175, 1070, 1035, 835, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.48–6.59 (m, 19 H, arom), 4.64 (s, 1 H, =CH), 4.56 (d, J = 12 Hz, 1 H, $CHPh_2$), 4.08 (d, J = 12 Hz, 1 H, AnCH), 3.68 (s, 3 H, arom OCH_3), 3.41 (s, 3 H, $=COCH_3$), 1.17 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3); UV (EtOH) 250 (ϵ 9600), 270 (8100), 290 nm (4300); MS, *m/e* 462.2553 (calcd for $C_{33}H_{34}O_2$, *m/e* 462.2559.

Anal. Calcd for $C_{33}H_{34}O_2$: C, 85.67; H, 7.40. Found: C, 85.86; H, 7.00.

The spectral data for (*Z*)-1-methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,4,5-triphenyl-1-pentene were as follows: IR (neat) 3060, 3040, 3000, 2980, 2900, 2820, 1630, 1600, 1500, 1480, 1450, 1245, 1175, 1070, 1035, 835, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.46–6.60 (m, 19 H, arom), 4.62 (s, 1 H, =CH), 4.56 (d, J = 12 Hz, 1 H, $CHPh_2$), 4.08 (d, J = 12 Hz, 1 H, AnCH), 3.68 (s, 3 H, arom OCH_3), 3.41 (s, 3 H, $=COCH_3$), 1.17 (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3); UV (EtOH) 250 (ϵ 12000), 260 (9600), 280 nm (6900); MS, *m/e* 462.2550 (calcd for $C_{33}H_{34}O_2$, *m/e* 462.2559).

Anal. Calcd for $C_{33}H_{34}O_2$: C, 85.67; H, 7.40. Found: C, 85.67; H, 7.40.

The spectral data for (*E*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-methoxyphenyl)-1-pentene were as follows: IR (neat) 3080, 3060, 3030, 3000, 2960, 2940, 2910, 1640, 1620, 1500, 1480, 1450, 1250, 1195, 1110, 1030, 850, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.48–6.66 (m, 19 H, arom), 4.53 (d, J = 12 Hz, 1 H, $CHPh_2$), 4.51 (s, 1 H, =CH), 3.72 (d, J = 12 Hz, 1 H, AnCH), 3.67 (s, 3 H, arom OCH_3), 3.18 (s, 3 H, $=COCH_3$), 0.79 (s, 3 H, CH_3), 0.53 (s, 3 H, CH_3); UV (EtOH) 250 (ϵ 6200), 270 (5300), 290 nm (1900); MS, *m/E* 462.2547 (calcd for $C_{33}H_{34}O_2$, *m/e* 462.2559).

Anal. Calcd for $C_{33}H_{34}O_2$: C, 85.67; H, 7.40. Found: C, 85.73; H, 7.25.

The spectral data for (*E*)-1-methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,4,5-triphenyl-1-pentene were as follows: IR (neat) 3080, 3040, 2990, 2950, 2920, 2840, 1660, 1610, 1500, 1495, 1460, 1450, 1250, 1175, 1110, 1035, 835, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.51–6.85 (m, 19 H, arom), 4.52 (s, 1 H, =CH), 4.57 (d,

J = 12 Hz, 1 H, $CHPh_2$), 3.80 (d, J = 12 Hz, 1 H, AnCH), 3.81 (s, 3 H, arom OCH_3), 3.17 (s, 3 H, $=COCH_3$), 0.81 (s, 3 H, CH_3), 0.56 (s, 3 H, CH_3); UV (EtOH) 250 (ϵ 10500), 270 nm (6900); MS, m/e 462.2547 (calcd for $C_{33}H_{34}O_2$, m/e 462.2559).

Anal. Calcd for $C_{33}H_{34}O_2$: C, 85.67; H, 7.40. Found: C, 85.70; H, 7.45.

Exploratory Direct Photolysis of 1-Methoxy-1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene. A solution of 375 mg (0.821 mmol, 3.04×10^{-3} M) of 1-methoxy-1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene in 270 mL of *tert*-butyl alcohol was photolyzed through a Corex filter for 6.0 h. Concentration in vacuo gave 373 mg (99%) of a yellow oil which was chromatographed on a 20 × 20 cm preparative thin-layer silica gel plate, eluting five times with 8% ether in pentane. The fastest moving band contained 219 mg (58%) of 1-methoxy-1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene. Band 2 contained 68.0 mg (18%) of (*Z*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentene as a colorless foam which was subjected to preparative HPLC (8% ether in pentane) to afford 56.3 mg (15%) of the (*Z*)-enol ether as a colorless foam. Band 3 gave 77.2 mg (20%) of (*E*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentene as a colorless oil. Further purification by preparative HPLC afforded 58.6 mg (16%) of the (*E*)-enol ether as a colorless foam.

The spectral data for (*Z*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentene were as follows: IR (neat) 3080, 3040, 2995, 2960, 2890, 2850, 2250, 1670, 1620, 1510, 1470, 1400, 1230, 1130, 1050, 865, 790, 765, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.55–6.55 (m, 19 H, arom), 4.55 (d, J = 8 Hz, 1 H, $CHPh_2$), 4.53 (s, 1 H, =CH), 4.29 (d, J = 8 Hz, 1 H, CHAr), 3.42 (s, 3 H, OCH_3), 1.17 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3); UV (EtOH) 250 (ϵ 14900), 270 (7660), 290 nm (2100); MS, m/e 457.2419 (calcd for $C_{33}H_{31}NO$, m/e 457.2406).

Anal. Calcd for $C_{33}H_{31}NO$: C, 86.61; H, 6.83. Found: C, 86.52; H, 6.97.

The spectral data for (*E*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentene were as follows: IR (neat) 3060, 3010, 2980, 2940, 2880, 2220, 1650, 1615, 1500, 1460, 1395, 1170, 1130, 1085, 780, 715 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.44–6.78 (m, 19 H, arom), 4.55 (d, J = 8 Hz, 1 H, $CHPh_2$), 4.46 (s, 1 H, =CH), 3.90 (d, J = 8 Hz, 1 H, CHAr), 3.20 (s, 3 H, OCH_3), 0.71 (s, 3 H, CH_3), 0.57 (s, 3 H, CH_3); UV (EtOH) 250 (ϵ 15000), 270 (7900), 290 nm (2400); MS, m/e 457.2408 (calcd for $C_{33}H_{31}NO$, m/e 457.2406).

Anal. Calcd for $C_{33}H_{31}NO$: C, 86.61; H, 6.83. Found: C, 86.95; H, 6.78.

Ozonolysis of 1,1,2-Triphenyl-3-methyl-2-butene. Ozone (0.770 mmol) was passed through a solution of 50.0 mg (0.167 mmol) of 1,1,2-triphenyl-3-methyl-2-butene in 25.0 mL of 1:1 methylene chloride/methanol at −78 °C. After the mixture was stirred for 10.0 min, 1.00 mL (13.6 mmol) of dimethyl sulfide was added and the mixture stirred for 1.0 h. IR analysis showed the presence of two carbonyl peaks, one at 1715 cm^{-1} (acetone) and a second at 1675 cm^{-1} (diphenylacetophenone). Concentration in vacuo gave 32.2 mg (70%) of diphenylacetophenone as a white solid, mp 127–131 °C. Recrystallization gave 18 mg (40%) of the ketone as colorless needles, mp 135–136 °C (lit.[24] mp 136–137 °C)..

Hydrolysis of (*E*)-1-Methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene. A mixture of 45 mg (0.10 mmol) of (*E*)-1-methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene, 5.0 mL of THF, and 3.5 mL of 10% aqueous hydrochloric acid was stirred for 24 h. Basic workup[17] gave 32 mg (78%) of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone as a yellow foam. Recrystallization from pentane gave 26 mg (64%) of the ketone, mp 127–128 °C, identical with authentic material (vide supra).

Hydrolysis of (*Z*)-1-Methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene. A mixture of 39 mg (0.09 mmol) of (*Z*)-1-methoxy-1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentene, 5.0 mL of THF, and 3.5 mL of 10% aqueous hydrochloric acid was stirred for 24.0 h. Neutral workup[17] gave 29 mg (78%) of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone as a yellow foam. Recrystallization from pentane gave 23 mg (61%) of ketone, mp 127–128 °C, identical with material synthesized earlier (vide supra).

(24) Zimmerman, H. E.; Morse, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 954–966.

Hydrolysis of (*Z*)-1-Methoxy-1,5,5-triphenyl-4-(*p*-methoxyphenyl)-3,3-dimethyl-1-pentene. A solution of 13 mg (0.030 mmol) of (*Z*)-1-methoxy-1,5,5-triphenyl-4-(*p*-methoxyphenyl)-3,3-dimethyl-1-pentene, 4.0 mL of THF, and 3.5 mL of 10% aqueous hydrochloric acid was stirred for 4.0 h. Neutral workup[17] gave 10 mg (74%) of 1,5,5-triphenyl-4-(*p*-methoxyphenyl)-3,3-dimethyl-1-pentanone as a light yellow foam. Recrystallization from pentane gave 8.3 mg (58%) of the ketone as colorless plates, mp 144–146 °C, identical with authentic material.

Hydrolysis of (*E*)-1-Methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-methoxyphenyl)-1-pentene. A mixture of 15 mg (0.03 mmol) of (*E*)-1-methoxy-1,5,5-triphenyl-4-(*p*-methoxyphenyl)-3,3-dimethyl-1-pentene, 2.0 mL of THF, and 3.5 mL of 10% hydrochloric acid was stirred at room temperature for 15.0 h. Neutral workup[17] gave 11 mg (75%) of 1,5,5-triphenyl-4-(*p*-methoxyphenyl)-3,3-dimethyl-1-pentanone as a colorless solid, mp 139–141 °C. Recrystallization from 1:1 ether/pentane gave 9.6 mg (71%) of the ketone as a colorless solid, mp 143–144 °C, identical with synthetic material (vide supra).

Hydrolysis of (*E*)-1-Methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentene. A solution of 8.0 mg (0.02 mmol) of (*E*)-1-methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentene and 8.0 mL of 1:1 THF/10% aqueous hydrochloric acid was stirred for 24.0 h. Neutral workup[17] afforded 6.5 mg (85%) of 1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentanone as a colorless oil. Recrystallization from pentane gave 3.5 mg (46%) of the ketone as a colorless solid, mp 143–144 °C, identical with material synthesized earlier (vide supra).

Hydrolysis of (*Z*)-1-Methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentene. A solution of 10 mg (0.02 mmol) of (*Z*)-1-methoxy-1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentene, 2.0 mL of THF, and 3.5 mL of 10% aqueous hydrochloric acid was stirred for 4.0 h. Neutral workup[17] gave 5.6 mg (77%) of 1-(*p*-methoxyphenyl)-3,3-dimethyl-4,5,5-triphenyl-1-pentanone as a colorless solid. Recrystallization from pentane gave 3.2 mg (33%) of the ketone as a light yellow solid, mp 142–144 °C, identical with material synthesized earlier.

Hydrolysis of (*Z*)-1-Methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentene. A solution of 45 mg (0.10 mmol) of (*Z*)-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentene, 5.0 mL of ether, and 2.0 mL of concentrated hydrochloric acid was stirred for 24.0 h. Basic workup[17] afforded 35 mg (80%) of 1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentanone as a colorless solid, mp 205–210 °C. Recrystallization from ether gave 28 mg (64%) of the ketone as a colorless solid, mp 210–211 °C.

The spectral data were as follows: IR ($CHCl_3$) 3060, 3040, 3020, 2980, 2960, 2920, 2860, 2220, 1680, 1605, 1595, 1450, 1360, 1230, 850, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.70–6.85 (m, 19 H, arom), 4.80 (d, J = 12 Hz, 1 H, $CHPh_2$), 4.52 (d, J = 12 Hz, 1 H, CHPh), 2.50 (AB q, J = 8 Hz, 2 H, CH_2), 1.09 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3); MS, m/e 443.2249 (calcd for $C_{32}H_{29}NO$, m/e 443.2249).

Anal. Calcd for $C_{32}H_{29}NO$: C, 86.65; H, 6.59. Found: C, 86.31; H, 6.59.

Hydrolysis of (*E*)-1-Methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentene. A mixture of 65 mg (0.14 mmol) (*E*)-1-methoxy-1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentene, 10 mL of THF, and 5.0 mL of 10% hydrochloric acid was stirred at room temperature for 24.0 h. Neutral workup[17] afforded 55 mg (93%) of 1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentanone as a colorless solid, mp 204–209 °C. Recrystallization from ether afforded 49 mg (79%) of the ketone as colorless plates, mp 210–211 °C.

Single-Crystal X-ray Structure of 1,5,5-Triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentanone. Crystals of 1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentanone were prepared by slow crystallization from ether. Preliminary examinations and collection of diffraction data were carried out on a Syntex-Nicolet P_1 diffractometer equipped with a graphite-monochromated Mo Kα radiation source from a crystal of dimensions of 0.42 × 0.21 × 0.38 mm. The intensities of four standard reflections did not vary by more than 3% during data collection. The structure consisting of one independent molecule was solved under monoclinic $P2_1/n$ symmetry by direct methods

with the MULTAN 80 package[25] and refined by least squares. Anisotropic thermal parameters were used for all non-hydrogen atoms while isotropic thermal parameters were used for the hydrogen atoms. The final R_1 and $R_w(F)$ values converged at 0.049 and 0.055, respectively. Results and structural parameters are summarized in the supplementary material.

Photolysis of 1,1,5,5-Tetraphenyl-2,2-dideuterio-3,3-dimethyl-4-penten-1-ol. A solution of 209 mg (0.500 mmol, 2.00 × 10^{-3} M) of 1,1,5,5-tetraphenyl-2,2-dideuterio-3,3-dimethyl-4-penten-1-ol in 250 mL of *tert*-butyl alcohol was irradiated for 3.0 h through a Corex filter. The photolysate was chromatographed on a 20 × 20 cm preparative thin-layer alumina plate, eluting five times with 5% ether in pentane. The fastest moving band contained 27.2 mg (18%) of 1,1,2-triphenyl-3-methyl-2-butene as a colorless oil, which was recrystallized from methanol to afford 18.5 mg (12%) of the alkene as colorless plates, mp 42–46 °C, 49% deuterated at the 1-position as determined by 200-MHz NMR. Band 2 afforded 16.2 mg (8%) of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone as a yellow foam which was recrystallized from pentane to afford 10.4 mg (5%) of the ketone, mp 120–124 °C, with 49% deuterium in the 5-position and 26% protium at the 2-position. Band 3 contained 122 mg (58%) of 1,1,5,5-tetraphenyl-2,2-dideuterio-3,3-dimethyl-4-penten-1-ol, mp 97–104 °C, 97% deuterated at the 2-position.

Photolysis of 1,1,5,5-Tetraphenyl-3,3-dimethyl-4-penten-1-ol at 280 nm. A solution of 200 mg (0.480 mmol, 1.91 × 10^{-3} M) of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol in 250 mL of *tert*-butyl alcohol was irradiated for 2.5 h through a 2.46 × 10^{-4} M bismuth trichloride filter solution (this filter gives a transmission maximum at 282 nm (85%) and is opaque below 260 nm and above 315 nm). The photolysate was then concentrated and chromatographed on a 20 × 20 cm preparative thin-layer alumina plate, eluting with 5% ether in pentane four times. The fastest moving band contained 22.8 mg (11%) of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone as a yellow foam. Recrystallization from pentane afforded 18.4 mg (9%) of the ketone as a slightly yellow solid, mp 125–127 °C. Band 2 contained 171 mg (85%) of recovered 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol, mp 95–101 °C, as a light yellow solid.

Dynamic Isotope Dilution Experiment. Determination of the Amount of Direct Production of 1,1,2-Triphenyl-3-methylbutene.[7] In these experiments, A_0 represents the amount of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol at time zero, A is the amount of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol at the conclusion of the photolysis, B_0 is the amount of 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone-d_0 at time zero (this is zero in all cases), B is the amount of pentanone-d_0 after completion of the photolysis, B^*_0 is the amount of pentanone-d_5 at time zero, and B^* is the quantity of d_5 ketone present at the conclusion of the photolysis. All irradiations were done on a Hanovia 450-W medium-pressure mercury lamp using a 2.46 × 10^{-4} M bismuth trichloride solution as a filter (vide supra) in 110 mL of *tert*-butyl alcohol for varying amounts of time. The photolysates were concentrated in vacuo, and fluorene was added as an internal standard and the relative amounts of 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol and 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone (d_5 and d_0) were determined by using 200-MHz NMR. The photolysates were then chromatographed on 20 × 20 cm preparative thin-layer alumina plates, and the recovered 1,4,5,5-tetraphenyl-3,3-dimethyl-1-pentanone was recrystallized from pentane. The deuterium content (d_5 vs. d_0) of the ketone was determined by integration of the aromatic region vs. a methyl group by using a calibration curve made from known compositions of d_5 and d_0 ketones and by measurement of the relative intensities of the 418 and 423 peaks in the high-resolution MS. The results are summarized in Table III.

Photolysis Equipment for Quantum Yield Determinations. Quantum yields were performed on the "Wisconsin Black Box"[5] or the microoptical bench.[5] Light output was measured by a digital actinometer calibrated by ferrioxalate actinometry.[26]

Table V. Summary and Quantum Yield Results for 1,1,5,5-Tetraphenyl-3,3-dimethyl-4-penten-1-ol

run	reactant 5, mmol	light abs, mEinstein	product 11 mmol	product 11 ϕ	convn, %
1	0.306	8.80	0.0278	0.003 16	9.1
2	0.580	8.02	0.0232	0.002 89	4.0
3	0.281	4.81	0.0135	0.002 81	4.8
4	0.410	9.55	0.0267	0.002 79	6.5

Table VI. Summary of Quantum Yield Results for 1,4,5,5-Tetraphenyl-3,3-dimethyl-1-pentanone

run	reactant 11, mmol	light abs, mEinstein	additive	product 10 mmol	product 10 ϕ
1	0.0098	0.029	none	0.0011	0.38
2	0.11	0.018	none	0.00084	0.45
3	0.11	0.024	none	0.0011	0.44
4	0.10	0.032	none	0.0011	0.34
5	0.097	0.019	xanthone	0.00085	0.45

Table VII. Summary of Quantum Yield Results of 1-Methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene

run	reactant 6, mmol	light abs, mEinstein	product 16E mmol	product 16E ϕ	product 16Z mmol	product 16Z ϕ
1	0.601	12.9	0.0258	0.002 00	0.0258	0.002 00
2	0.540	13.9	0.0291	0.002 12	0.0263	0.001 92
3	0.493	15.0	0.0300	0.002 00	0.0286	0.001 91
4	0.400	16.8	0.0386	0.002 29	0.0302	0.001 78

For microbench runs, the monochromator entrance slit was set at 5.4 mm and the exit slit at 3.0 mm, to give a band pass of 22 nm at half-peak height. All microbench runs were done at 289 nm. For "Black Box"[5] runs the two filter solutions used were as follows: 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% hydrochloride acid (this combination gave a transmission maximum at 285 nm (32% transmission) and was opaque above 325 nm and below 250 nm); and filter B, (a) 0.5 M nickel sulfate in 10% sulfuric acid, (b) 0.1 M cobalt sulfate in 10% sulfuric acid, and (c) 0.1 M copper sulfate in 10% sulfuric acid (this combination gave a transmission maximum at 322 nm (40%) and was opaque below 290 nm and above 360 nm).

Summary of Direct Quantum Yield Results for 1,1,5,5-Tetraphenyl-3,3-dimethyl-4-penten-1-ol. All runs were performed on the "Black Box"[5] in 750 mL of *tert*-butyl alcohol as solvent by using filter A. All runs were analyzed by 200-MHz NMR, with fluorene as internal standard. The runs are summarized in Table IV.

Summary of Quantum Yield Results for 1,4,5,5-Tetraphenyl-3,3-dimethyl-1-pentanone. All direct runs were performed on the microbench[5] in 40 mL of *tert*-butyl alcohol at 289 nm. Runs were analyzed by 200-MHz NMR by using *p*-methoxybenzophenone as internal standard. Sensitized runs were done at 366 nm employing xanthone as the sensitizer. The results are shown in Table V.

Summary of Direct Quantum Yield Results for 1-Methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene. All runs were performed on the "Black Box"[5] by using 750 mL of *tert*-butyl alcohol as the solvent irradiating through filter A. All runs were analyzed by HPLC (4% ether in hexane), with *p*-methoxybenzophenone as the internal standard. Results are shown in Table VI.

Summary of Direct Quantum Yield Results for 1-Methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene. All runs were performed on the "Black Box"[5] in 750 mL of *tert*-butyl alcohol as solvent by using filter A. Runs were analyzed by HPLC (1.2% ether in hexane) with *p*-methoxybenzophenone as internal standard. The results are given in Table VII.

(25) (a) The MULTAN[25b] series of programs was used within a series of programs developed by C. Strouse of UCLA and modified by J. Moore and A. M. Weber, University of Wisconsin, Madison. (b) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368–376.

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(27) Zimmerman, H. E.; Tartler, D. A.; Bunce, R. A.; Ramsden, W. D.; King, R. K., unpublished results.

Table VIII. Summary of Quantum Yield Results for 1-Methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-1-pentene

run	reactant 7, mmol	light abs, mEinstein	product 17E		product 17Z		product 18E		product 18Z	
			mmol	ϕ	mmol	ϕ	mmol	ϕ	mmol	ϕ
1	0.556	19.0	0.0199	0.001 10	0.0246	0.001 29	0.0133	0.000 700	0.0110	0.000 579
2	0.504	20.4	0.0200	0.000 980	0.0245	0.001 20	0.0135	0.000 662	0.0113	0.000 554
3	0.415	23.4	0.0257	0.001 10	0.0304	0.001 28	0.0190	0.000 812	0.0129	0.000 735
4	0.376	24.3	0.0231	0.000 949	0.0341	0.001 40	0.0192	0.000 790	0.0173	0.000 712

Table IX. Summary of Quantum Yield Results for 1-Methoxy-1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-1-pentene

run	reactant 9, mmol	light abs, mEinstein	product 19E		product 19Z	
			mmol	ϕ	mmol	ϕ
1	0.836	13.2	0.0263	0.002 000	0.0237	0.001 79
2	0.803	14.6	0.0263	0.001 71	0.0263	0.001 80
3	0.740	20.5	0.0409	0.001 99	0.0389	0.001 90
4	0.672	24.3	0.0511	0.002 10	0.0438	0.001 81

Summary of Direct Quantum Yields for 1-Methoxy-1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene. Irradiation was done on the "Black Box"[5] in 750 mL of *tert*-butyl alcohol by using filter A. Analysis was done by HPLC (10% ether in hexane) by using *p*-dimethylaminobenzophenone as internal standard. The results are shown in Table VIII.

Summary of Sensitized Quantum Yields. General Procedure and Results. The "Black Box"[5] was employed for all photolyses. Acetophenone was used in all cases as the sensitizer. All photolyses were done in 750 mL of *tert*-butyl alcohol irradiating through filter B. Workup consisted of concentration of the photolysate in vacuo, removal of the acetophenone (45 °C, 0.1 torr), and NMR analysis of the photomixture. The results are summarized below.

1,1,5,5-Tetraphenyl-3,3-dimethyl-4-penten-1-ol: 96.0 mg (0.230 mmol) of pentenol, 24.0 mL (194 mmol) of acetophenone, 18 mEinstein, 88.0 mg (93%) recovered, no reaction observed, $\phi < 0.0002$.

1-Methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene: 101 mg (0.234 mmol) of ether, 24.0 mL (194 mmol) of acetophenone, 22 mEinstein, 98.0 mg (97%) recovered, no reaction, $\phi < 0.0003$.

1-Methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene: 78.3 mg (0.171 mmol) of ether, 24.0 mL (194 mmol) of acetophenone, 16 mEinstein, 72.3 mg (92%) recovered, $\phi < 0.0003$.

1-Methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene: 78.3 mg (0.171 mmol) of ether, 24.0 mL (194 mmol) of acetophenone, 16 mEinstein, 58.2 mg (84%) recovered, $\phi < 0.0003$.

Single Photon Counting. The apparatus and procedure have been described previously.[6a,b] Solvents were methylcyclohexane (Kodak Spectral Grade) and isopentane purified as described previously.[6a,b] Individual samples were prepared in a 4:1 methyl cyclohexane–isopentane solution to give an optical density in the range 0.80–1.5, thoroughly degassed by at least 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 reaction, number of runs, standard deviation in rate, and estimated error in rate): 1,1,5,5-tetraphenyl-3,3-dimethyl-4-penten-1-ol, τ = 90 ps, $k_r = 2.8 \times 10^7$ s^{-1}, 5, 0.08, 5%; 1-methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene, τ = 121 ps, $k_r = 3.0 \times 10^7$ s^{-1}, 5, 0.10, 10%. 1-Methoxy-1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene, τ = 122 ps, $k_r = 3.0 \times 10^7$ s^{-1}, 5, 0.10, 10%; 1-methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene, τ = 146 ps, $k_r = 2.1 \times 10^7$ s^{-1}, 5, 0.08, 10%.

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 250 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-dimethyl-4-penten-1-ol, M = 60 (5 runs); 1-methoxy-1,1,5,5-tetraphenyl-3,3-dimethyl-4-pentene, M = 71 (5 runs); 1-methoxy-1-(*p*-cyanophenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene, M = 53 (5 runs); 1-methoxy-1-(*p*-methoxyphenyl)-1,5,5-triphenyl-3,3-dimethyl-4-pentene, M = 41 (5 runs).

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Supplementary Material Available: ORTEP drawing of 1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentanone and tables of crystal data, interatomic distances, positional coordinates, bond angles, anisotropic thermal parameters, and isotropic thermal parameters for 1,5,5-triphenyl-3,3-dimethyl-4-(*p*-cyanophenyl)-1-pentanone (12 pages). Ordering information is given on any current masthead page.