and transformed with 32K (zero filling) and with a 4–6-Hz line broadening. The samples ($CDCl_3$ as solvent) were carefully degassed with nitrogen, and the level of the liquid in the tube was kept at the minimum (0.4 mL) compatible with a reasonable resolution. The temperature was maintained constant (within ±0.1 °C) throughout the whole experiment.

Acknowledgment. One of the authors (L.L.) gratefully thanks Dr. J. K. M. Sanders, Cambridge, U.K., for reading the manuscript prior to publication and for helpful comments on the NOE experiments. Financial support from the Ministry of Scientific Research (MURST) and from the National Research Council, Rome, is also acknowledged.

Registry No. **1a**, 130523-07-8; **1b**, 130523-10-3; **1c**, 130523-14-7; **1d**, 130523-18-1; **2a**, 21614-05-1; **2b**, 130523-11-4; **2c**, 130523-15-8; **2d**, 130523-19-2; **3a**, 130523-08-9; **3b**, 130523-12-5; **3c**, 130523-16-9; **3d**, 130523-20-5; **4a**, 130523-09-0; **4b**, 130523-13-6; **4c**, 130523-17-0; **4d**, 130523-21-6; **5**, 130523-24-9; **6**, 130523-22-7; *N*-isopropyl(2-isopropyl-1-naphthyl)amine, 130523-23-8; 2-methyl-1-nitronaphthalene, 881-03-8; 2-ethyl-1-nitronaphthalene, 130523-25-0; 2-isopropyl-1-nitronaphthalene, 98515-20-9; 2-methyl-1-naphthylamine, 36357-84-3; 2-ethyl-1-naphthylamine, 36357-84-3; *N*-ethyl(2-methyl-1-naphthyl)amine, 60632-35-1; *N*-isopropyl(2-methyl-1-naphthyl)amine, 130523-26-1; *N*-ethyl(2-ethyl-1-naphthyl)amine, 130551-55-2; *N*-isopropyl(2-ethyl-1-naphthyl)-amine, 130523-27-2; *N*-ethyl(2-isopropyl-1-naphthyl)amine, 130523-28-3; *N*-ethyl(2-*tert*-butyl-1-naphthyl)amine, 110014-57-8; *N*-isopropyl(2-*tert*-butyl-1-naphthyl)amine, 130523-29-4; *tert*-butyl alcohol, 75-65-0; 2-*tert*-butyl-1-naphthylamine, 110014-56-7; 1-naphthylamine, 134-32-7; 8-methyl-1-naphthylamine, 130523-30-7; *N*-ethyl(8-methyl-1-naphthyl)amine, 130523-31-8; 1-methyl-8-nitronaphthalene, 90745-27-0; 1-methylnaphthalene, 90-12-0; 1-methyl-4-nitronaphthalene, 880-93-3; 2-isopropyl-1-naphthylamine, 106213-85-8.

Rearrangement of 1,3-Diradicals. Arylcyclopropane Photochemistry†,[1,2]

Howard E. Zimmerman* and Jenifer A. Heydinger

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

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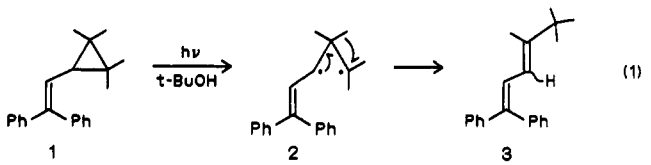
The photochemistry of a series of aryl-substituted cyclopropanes was investigated as part of our continuing investigations of these systems. The literature held a puzzling discrepancy in which several similar reactants exhibited differing photochemistry. A series of 3-aryl-1,1,2,2-tetramethylcyclopropanes was found to rearrange photochemically to give primarily two types of products, the anticipated 4-aryl-2,3,3-trimethyl-1-butenes and, additionally, 1-aryl-2,3,3-trimethyl-1-butenes. The latter arise from regioselective methyl migration of intermediate singlet 1,3-diradicals. Also, the usual Griffin carbene fragmentation was encountered as a minor pathway. Biphenylyl-, *p*-cyanophenyl-, and *p*-anisyl-substituted cyclopropanes were studied. Also, the photochemistry of 3-phenyl-1,1,2,2-tetramethylcyclopropane was reinvestigated and found to conform to the general pattern of reactivity. Throughout, it was the singlet excited states responsible for the observed reactivity, and the triplet counterparts were found to be unreactive. In addition, the photochemistry of 3-biphenylyl-2,2-dimethyl-1,1-diphenylcyclopropane was studied. Again, the triplet was unreactive. The singlet gave rise to 4-biphenylyl-2-methyl-3,3-diphenyl-1-butene exclusively. The differing behavior of the various arylcyclopropanes is discussed from a mechanistic viewpoint. In the case of the 3-aryl-1,1,2,2-tetramethylcyclopropanes, the regioselectivity of the 1,3-diradical intermediate favors migration toward the less delocalized odd-electron center. This selectivity is understood on a quantum mechanical basis. Finally, quantum yields are reported.

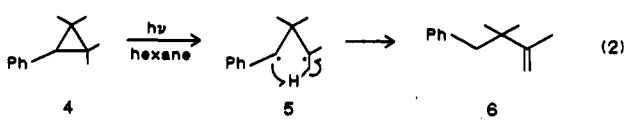
Introduction

The photochemistry of π-substituted cyclopropanes is extensive.[3] Our own research has focussed on unusual rearrangements,[4] and one aspect of interest has been the behavior of 1,3-diradicals.[4a,b,e] Particularly fascinating have been rearrangements in which substituents on C-2 of the 1,3-diradical migrate to one of the odd-electron centers. One example is shown in eq 1, involving a rearrangement



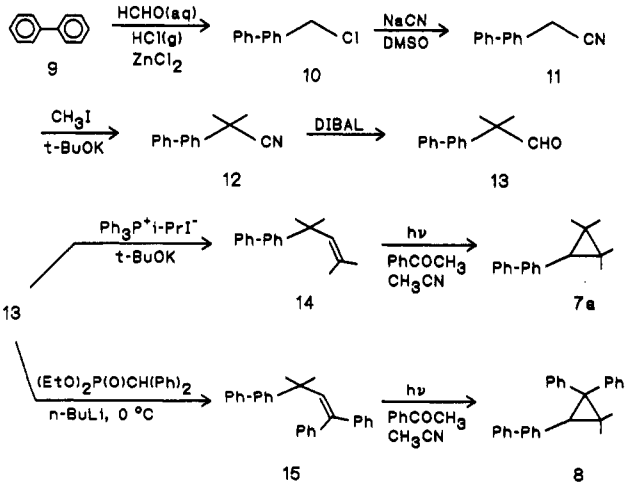
(1)

of a singlet 1,3-diradical.[5] In contrast, the most common behavior of such 1,3-diradicals has been intramolecular hydrogen transfer as depicted in eq 2.[3]



(2)

Scheme I. Syntheses of Biphenylyl-Containing Cyclopropanes 7a and 8



In view of the wide variation in behavior in cyclopropane photochemistry, we decided to investigate in detail 3-

† Dedicated to the 60th birthdays of Horst Prinzbach and Kurt Schaffner.

(1) This is paper 161 of our photochemical series and 222 of the general papers.

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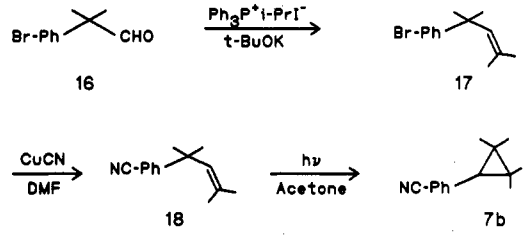
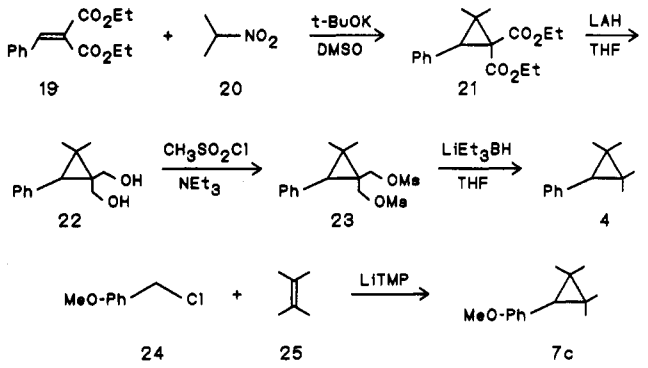
Scheme II. Synthesis of (p-Cyanophenyl)cyclopropane 7b



Scheme III. Synthesis of Phenylcyclopropane 4 and Anisylcyclopropane 7c



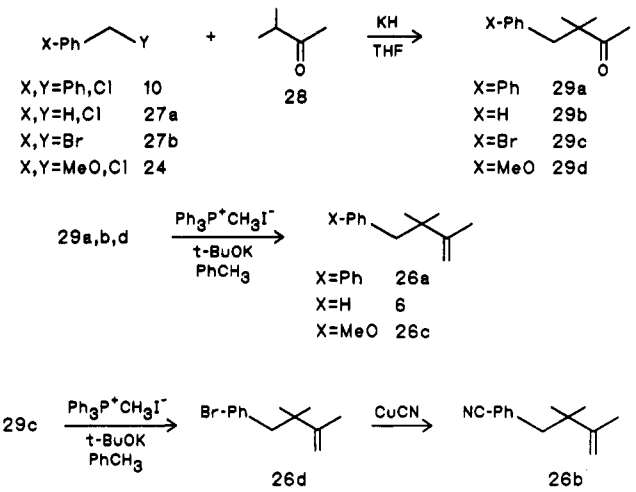
aryl-1,1,2,2-tetramethylcyclopropanes and also a 3-aryl-2,2-dimethyl-1,1-diphenylcyclopropane. Both the dependence of reaction course on structure and the regioselectivity were of interest.

Results

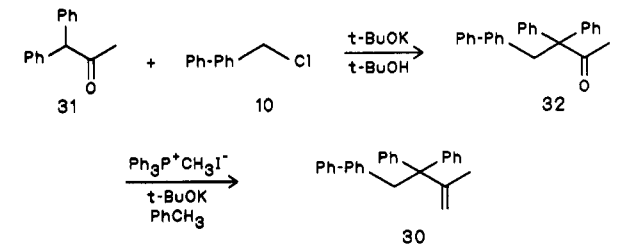
Synthesis of Photochemical Reactants. Our research began with the synthesis of a series of 3-aryl-1,1,2,2-tetramethylcyclopropanes (**7a–c**) and also 3-biphenylyl-2,2-dimethyl-1,1-diphenylcyclopropane (**8**). Scheme I summarizes the syntheses of the biphenylyl-containing cyclopropanes. The preparation of the counterpart (*p*-cyanophenyl)cyclopropane **7b** is outlined in Scheme II. The syntheses of cyclopropanes **7a**, **7b**, and **8** utilized the di-π-methane rearrangement[6] with sensitization; the yields were in the range of 70–90% and provided examples of the utility of the reaction.

Although 1,1,2,2-tetramethyl-3-phenylcyclopropane (**4**) was a known compound,[7] this reactant was required in quantity and an alternative synthesis was devised. This is given in Scheme III. The critical step employed the Michael addition of the conjugate base of 2-nitropropane

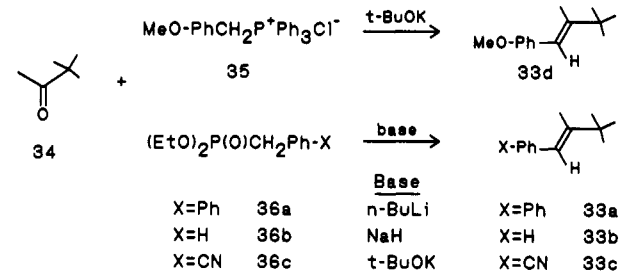
Scheme IV. Synthesis of Potential Photoproducts



Scheme V. Synthesis of 4-Biphenylyl-2-methyl-3,3-diphenyl-1-butene (30)



Scheme VI. Synthesis of 1-Aryl-2,3,3-trimethyl-1-butenes



with diethyl benzalmalonate followed by three-ring closure. This was patterned after the findings of Ono,[8] who reported cyclopropane formation using 2-nitropropane and Michael acceptor systems. A further point of interest is the use of lithium triethylborohydride[9] for reduction of the dimesylate **23**. Better yields resulted compared with the more standard lithium aluminum hydride reduction.

Finally, the synthesis of 3-*p*-anisyl-1,1,2,2-tetramethylcyclopropane (**7c**) is included in Scheme III. Although the yields in this carbenoid approach were low (ca. 14%), the brevity of the method made it convenient.

Synthesis of Potential Photoproducts. It was clear from the literature studies of cyclopropanes,[3] including the pioneering studies of Griffin,[10] that a number of 4-aryl-2,3,3-trimethyl-1-butenes (**6**, **26a–c**) were likely photoproducts from photolysis of the tetramethylcyclopropanes **4** and **7a–c**. These compounds were synthesized for com-

(2) (a) For paper 221 of our general series, see: Zimmerman, H. E.; Wang, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 1280–1281. (b) For paper 220 of our general series and 160 of the photochemical papers, note: Zimmerman, H. E.; Lamers, P. H. *J. Org. Chem.* **1989**, *54*, 5788–5804.

(3) For a general review, see: Hixson, S. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1970; Vol. 4, Chapter 3.

(4) (a) Zimmerman, H. E.; Oaks, F. L.; Campos, P. *J. Am. Chem. Soc.* **1989**, *111*, 1007–1018. (b) Zimmerman, H. E.; Kamath, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 900–911. (c) Zimmerman, H. E.; Carpenter, C. W. *J. Org. Chem.* **1988**, *53*, 3298–3305. (d) Zimmerman, H. E.; Samuel, C. J. *J. Am. Chem. Soc.* **1975**, *97*, 4025–4036. (e) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 8749–8761.

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

(6) (a) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183–184. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933. (c) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718–1727. (d) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. (e) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., ed.; Academic: New York, 1980; Vol. 3, pp 131–166.

(7) (a) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042–4053. (b) Kristinsson, H.; Griffin, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 1579–1580. (c) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282–7292.

(8) (a) Ono, N.; Yanai, T.; Hamamoto, I.; Kamimura, A.; Kaji, A. *J. Org. Chem.* **1985**, *50*, 2806–2807. (b) Annen, K.; Hofmeister, H.; Laurent, H.; Seeger, A.; Weichert, R. *Chem. Ber.* **1978**, *111*, 3094–3104. (c) Bergmann, E. D.; Ginsberg, D.; Pappo, R. In *Organic Reactions*; Adams, R., Ed.; Wiley: New York, 1959; Vol. 10, pp 179–563.

(9) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669–1671.

(10) Kristinsson, H.; Griffin, G. W. *Tetrahedron Lett.* **1966**, 3259–3265.

parison purposes, and this is outlined in Scheme IV.

Similarly, it appeared that 4-biphenylyl-2-methyl-3,3-diphenyl-1-butene (**30**) was a likely photoproduct from irradiation of dimethyldiphenylcyclopropane 8. This preparation is depicted in Scheme V.

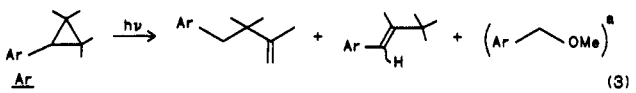
With the methyl migration rearrangement depicted in eq 1 in mind, we decided to synthesize a series of 1-aryl-2,3,3-trimethyl-1-butenes (**33a–d**). Our preliminary results confirmed that these were, indeed, needed. The syntheses are outlined in Scheme VI.

Finally, our initial findings suggested the need for authentic samples of 4-(methoxymethyl)biphenyl (**37a**) as well as benzyl methyl ether[11a] (**37b**) and the *p*-cyano- and *p*-methoxybenzyl methyl ethers[11b] (**37c** and **37d**). These were prepared by literature methods.[11]

Exploratory Photolyses of Aryl-Substituted Cyclopropanes. With many of the potential photoproducts in hand, we proceeded to investigate the irradiation of the tetramethylcyclopropanes **4** and **7a–c**.

Direct irradiation of 3-biphenylyl-1,1,2,2-tetramethylcyclopropane (**7a**) in a variety of solvents (i.e., methanol, acetonitrile, benzene, pentane) led to two main photoproducts in approximately 2:1 ratios. The major product proved to be identical with 4-biphenylyl-2,3,3-trimethyl-1-butene (**26a**). Clearly, this arises from the anticipated Griffin 1,4-hydrogen transfer reaction[10] (note eq 3 below).

Interestingly, the second photoproduct was found to be 1-biphenylyl-2,3,3-trimethyl-1-butene (**33a**). This is seen to result from fission of cyclopropyl bond-1,3 along with a 1,2-methyl migration. This reaction has precedent in our earlier finding[5] of a methyl migration in the photochemistry of the (diphenylvinyl)tetramethylcyclopropane 1 cited above in eq 1. Equation 3 summarizes the overall photochemistry of the biphenylylcyclopropane **7a**.



(3)

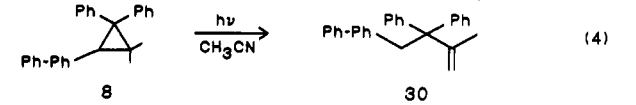
Ar				
Ph-Ph	7a	26a	33a	(37a)
Ph	4	6	33b	(37b)
NC-Ph	7b	26b	33c	(37c)
MeOPh	7c	26c	33d	(37d)

a) Observed only on photolysis in methanol

A final point is that in methanol, 4-(methoxymethyl)-biphenyl (**37a**) was formed in minor quantity. The mechanism for formation of this photoproduct, which resulted from three-ring fragmentation, is considered below.

The tetramethylcyclopropanes **4**, **7b**, and **7c** exhibited similar behavior, giving rise to the corresponding 4-aryl-2,3,3-trimethyl-1-butenes **6**, **26b**, and **26c** and 1-aryl-2,3,3-trimethyl-1-butenes **33b**, **33c**, and **33d** in approximate ratios of 2:1. This chemistry is included in eq 3.

We turned next to the direct photolysis of 3-biphenylyl-2,2-dimethyl-1,1-diphenylcyclopropane (**8**). Differing from the photochemistry of the tetramethyl cyclopropanes (vide supra), only one photoproduct resulted, and this proved to be identical with the authentic 4-biphenylyl-2-methyl-3,3-diphenyl-1-butene (**30**) that had previously been synthesized. This transformation is illustrated in eq 4.



(4)

8 30

(11) (a) Brown, C. A.; Barton, D.; Sivaram, S. *Synthesis* **1974**, 434–436. (b) Torii, S.; Inokuchi, T.; Takagishi, S.; Horike, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2173–2188.

Table I. Relative Quantum Yields of Fluorescence

compound[a]	λ_{max}	ϕ_f[b]
biphenylylcyclopropane **7a**	331	0.024
phenylcyclopropane **4**	334	0.029
(cyanophenyl)cyclopropane **7b**	348	0.0098
(methoxyphenyl)cyclopropane **7c**	326	0.081
dimethyldiphenylcyclopropane **8**	333	0.16

[a] Solution in methanol. Excitation at 265 nm. [b] Quantum yields of fluorescence were determined relative to biphenyl (ϕ_f 0.18).[15a] Error of ±5%.

Table II. Quantum Yield Results

reactant[a]	solvent	quantum[b] yield, ϕ	product
biphenylylcyclopropane **7a**	MeOH	0.019	(*E*)-olefin **33a**
		0.013	(*Z*)-olefin **33a**
		0.064	butene **26a**
		0.0011	methyl ether **37a**
phenylcyclopropane **4**	MeOH	0.0032	(*E*)-olefin **33b**
		0.011	(*Z*)-olefin **33b**
		0.029	butene **6**
		0.0049	methyl ether **37b**
(cyanophenyl)cyclopropane **7b**	MeOH	0.013	(*E*)-olefin **33c**
		0.0048	(*Z*)-olefin **33c**
		0.036	butene **26b**
		0.0013	methyl ether **37c**
(cyanophenyl)cyclopropane **7b**	pentane	0.014	(*E*)-olefin **33c**
		0.033	(*Z*)-olefin **33c**
		0.070	butene **26b**
anisylcyclopropane **7c**	MeOH	0.0062	(*E*)-olefin **33d**
		0.015	(*Z*)-olefin **33d**
		0.099	butene **26c**
		0.0070	methyl ether **37d**
dimethyldiphenylcyclopropane **8**	CH_3CN	0.036	butene **30**

[a] Irradiation at 248 nm. [b] Error of ±10%.

Sensitized irradiations of the tetramethyl- and dimethyldiphenylcyclopropanes were carried out by using acetophenone (E_T = 74 kcal/mol)[12] with the biphenylyl-substituted cyclopropanes (E_T = 69 kcal/mol)[13] and acetone (E_T = 80 kcal/mol)[14] with the remaining compounds. All of these cyclopropanes were found to be unreactive as triplets.

Finally, photolyses of the diphenylvinylcyclopropane 1 were performed in acetonitrile and pentane to compare behavior with the original study,[5] which utilized *tert*-butyl alcohol. The reaction proved solvent independent with formation only of diphenyl diene **3**.

Fluorescence Emission. One relevant type of information is the quantum efficiencies of fluorescence of the compounds of interest. These are given in Table I. For these measurements, biphenyl was used as a secondary standard.

Quantum Yield Determinations. Runs made in the 2–12% conversion range exhibited linearity when efficiencies were plotted against extent of conversion. The dependence on extent of conversion was low enough to permit accurate extrapolation to zero reaction. This dependence arises because the photoproducts have chromophores similar to those of the reactants. Table II lists the extrapolated, zero-percent conversion quantum yields.

(12) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenberg, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466–5468.

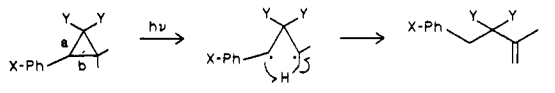
(13) (a) The 0–0 triplet energy of biphenylyl-containing compounds[13b] and biphenyl itself[13c] have been reported as 69 kcal/mol. (b) Zimmerman, H. E. King, R. K.; Xu, J.-H.; Caufield, C. E. *J. Am. Chem. Soc.* **1985**, *107*, 7724–7732. (c) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820–2825.

(14) Borkman, R. G.; Kerns, D. R. *J. Chem. Phys.* **1966**, *44*, 945–949.

(15) (a) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic: New York, 1971; pp 176–177. (b) Heinzelmann, W.; Labhart, H. *Chem. Phys. Lett.* **1969**, *4*, 20–24.

Interpretative Discussion

Griffin Reaction Pathway: Griffin Hydrogen-Transfer Process. The formation of the major product in all of the cyclopropane photolyses studied can be interpreted as arising from three-ring bond fission to afford a singlet[3] diradical followed by intramolecular hydrogen transfer as outlined in eq 5. This is a rearrangement first

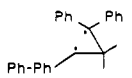


(5)

X=Ph,Y=CH_3	7a	38a	26a
X=H,Y=CH_3	4	5	6
X=CN,Y=CH_3	7b	38b	26b
X=MeO,Y=CH_3	7c	38c	26c
X,Y=Ph	8	38d	30

described by Griffin.[10] The reaction has been studied in subsequent work by Mazzochi,[16] Hixson,[17] and others.[17b-19]

One interesting aspect is the formation of photoproduct **30** from the less stabilized of two alternative diradicals derived from the dimethyldiphenylcyclopropane **8**. Thus, fission of bond a would afford a diradical (**39**) with an

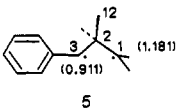


39

odd-electron subject to benzhydryl delocalization; the counterpart scission of bond b results in the less effective[20a] *gem*-dimethyl stabilization. Not only are isopropyl radicals less stable than their benzhydryl counterparts but also photochemical precedent has revealed[5] that loss of a dimethyl-stabilized odd-electron center is favored over loss of a diphenyl-stabilized one. However, in ring opening of biphenylylcyclopropane **8** the preferred formation of the less delocalized of the two alternative diradicals has precedent in our previous studies.[4a] This phenomenon is discussed below.

Related to this discussion of three-ring bond opening are the fluorescence efficiencies listed in Table I. We note that the quantum yield of fluorescence for the biphenyl-substituted dimethyldiphenylcyclopropane **8** (i.e., 0.16) is only slightly lower than that known (i.e., 0.18)[15a] for biphenyl. This suggests that any ring opening of S_1 of **8** must be slow and inefficient compared with fluorescence emission. The same conclusion cannot be drawn for the tetramethylcyclopropanes **4**, **7a**, **7b**, and **7c** with their different chromophores. Moreover, we note that the total of fluorescence and reaction quantum yields are much less than unity, signifying that the major fate of S_1 species is radiationless decay as in biphenyl itself, which has a reasonably high intersystem crossing efficiency (ϕ 0.51).[15b]

There is another point. That the fluorescence efficiency of the dimethyldiphenylcyclopropane **8** is so close to that of biphenyl itself (note Table I) rules out one explanation for lack of scission of the benzhydryl-substituted three-ring bond, namely, that this bond opens reversibly and nonadiabatically with the resulting diradical being incapable of reaction. Two alternatives remain. If ring opening were



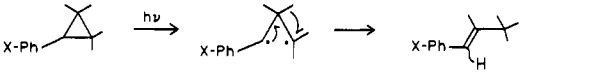
5

Figure 1. 1,3-Diradical **5** and electron densities at C-1 and C-3.

adiabatic, the fluorescence efficiency would not be diminished. Alternatively steric effects might preclude phenyl delocalization of the incipient benzhydryl diradical.

Finally, we note that fragmentation of the diradicals of type **38** and **39** can result in carbene formation by fission of the second of the original cyclopropyl bonds. This is alternative to direct carbene formation from the initial singlet excited state. One might attempt to use fission of diradical **39**, affording carbene, to rationalize the absence of other photoproducts derived from this species (i.e., **39**). However, the quantum efficiencies for carbene formation are too low to indicate a diversion of diradical **39** in this fashion.

1,2-Migration of Centrally Substituted Groups in 1,3-Diradicals: Overall Reaction Course. The formation of the 1-aryl-2,3,3-trimethyl-1-butene photoproducts (i.e., **33a–d**) involves a 1,2-migration of an alkyl group as depicted in eq 6. The proposed mechanism involves



(6)

X=Ph	7a	38a	33a
X=H	4	5	33b
X=CN	7b	38b	33c
X=MeO	7c	38c	33d

a 1,3-diradical and migration of the central alkyl group. Such rearrangements in acyclic, untethered systems are rare. In contrast, hydrogen migration reactions have been frequently encountered.[21] The first photochemical example of an alkyl migration, reported in 1970,[5] is given in eq 1. Further observations of alkyl migrations in photochemically generated 1,3-diradicals have been reported.[22]

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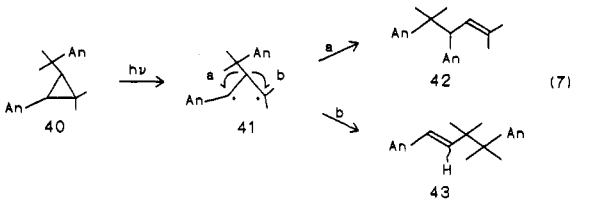
One recent case[4b] is particularly germane to the present study, in addition to that in eq 1. This involved a 1,2 *p*-methoxycumenyl migration as outlined in eq 7.[24]



(7)

Multiplicity of the 1,2-Migration Reaction. All of the reactions encountered in the present study occurred on direct irradiation. In addition, the observation of the lack of triplet reactivity in sensitization runs where energy transfer is exothermic (vide supra) reveals that the triplet excited states are unreactive. Since triplet cyclopropanes readily ring open to afford 1,3-diradicals,[3] we can conclude that it is lack of rearrangement of the triplet diradicals rather than the absence of their formation. Earlier, we noted[4b] that triplet 1,3-diradicals exhibit a proclivity to ring-close while the singlets tend to rearrange.

Reaction Mechanism and Regioselectivity. The rearrangement of the present study and those depicted in eqs 1 and 7 all show a common regioselectivity wherein the migrating group moves to the less delocalized odd-electron diradical center. In an attempt to understand the reaction mechanism, including the regioselectivity, molecular orbital computations were employed.

The first thought was that migration might be preferred to the more positive center of the 1,3-diradical (i.e., C-1). MNDO-CI calculations[25a,b] with geometry optimization were employed. However, as shown in Figure 1, the more electron-deficient diradical center was the benzylic carbon, C-3.

A second and more successful approach was the computation of the S_0 and S_1 reaction hypersurfaces, starting with diradical 5 and proceeding to the two alternative reaction product structures. Again, MNDO with configuration interaction and geometry optimization was employed. Bond length 1–12 was systematically decreased to enforce methyl migration toward C-1. At each point, this one bond length was fixed and the remaining bond lengths and angles were optimized. Similarly, for migration toward C-3, bond length 3–12 was diminished in 0.2-Å increments. The S_0 and S_1 hypersurfaces obtained correspond to optimized geometries of S_1 at each point.[26] These surfaces are given in Figure 2.

The reaction pathway obtained is optimized for reaction on the S_1 surface, while the S_0 surface corresponds to this same geometric trajectory.[26a] It is seen that the lower energy transition state on the S_1 surface leads to S_1 of the observed photoproduct, while the S_0 surface leads to the unobserved product.[26b,c]

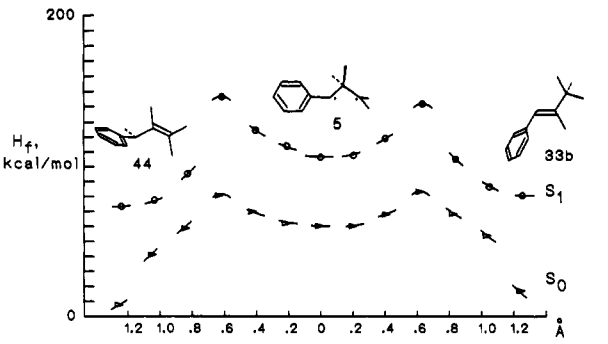


Figure 2. Reaction hypersurface for methyl migration showing displacement of C-12 from starting diradical geometry toward C-1 and C-3.

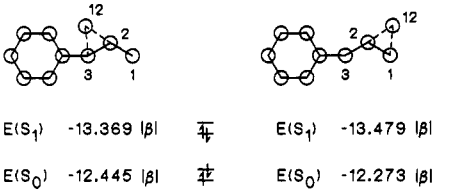


Figure 3. One-electron energies for the two half-reaction species. One-electron energy units are the absolute value of β, the resonance integral. The energies should be compared only within the same electronic state since two-electron terms have been omitted.

S_1 diradical 5 obtained by singlet three-ring opening seems likely to have sufficient vibrational energy to surmount one of the two S_1 energy barriers and arrive at a product geometry as shown in Figure 2. Each product S_1 appears as an energy minimum and radiationless decay to S_0 ground state is anticipated.[26d]

It is always intellectually unsatisfying to use calculations predicting an effect without assessing the inherent sources of the result. A simple understanding of the regioselectivity results from consideration of the basis orbitals most involved in the rearrangement. However, it was necessary to use ab initio calculations[25c,d] to determine which configurations best represent the ground state (i.e., S_0) and the first excited singlet (S_1). Interestingly, the ground state of the half-migrated species is primarily represented by the configuration having promotion of a single electron, while S_1 is best represented by the configuration with two electrons in the highest bonding MO. Note Figure 3.

We then utilized a truncated set of orbitals in the half-migrated species, with numbering corresponding to the atoms in Figure 2. The migrating group is represented by orbital 12 and migration is from orbital 2 toward either orbital 1 or 3. Orbital 3 is seen to be in the benzylic position. This truncated set corresponds to those orbitals involved in bond formation or dissipation.

Simple one-electron (i.e., Hückel) computations using the proper electronic configurations gave the energies included in Figure 3. The predicted regioselectivity for S_0 and S_1 is in agreement with the more involved MNDO-CI computations.

Methyl Migration versus the Griffin Hydrogen-Transfer Reaction. One interesting facet is the complete absence of the Griffin hydrogen-transfer reaction in diphenylvinylcyclopropane 1. This contrasts with the aryl-substituted examples presently studied where the Griffin reaction slightly predominated. It seems likely that the hydrogen-transfer process requires appreciable electron density at the diradical site doing the hydrogen abstraction.

(24) In that study[4b] a minor competing pathway involved dissociation–recombination. However, the ca. 12% intervention of this pathway was too minor to alter the conclusion of direction of regioselectivity.

(25) (a) QCPE Program No. 455, Quantum Chemistry Program Exchange, Indiana University; Stewart, J. J. P.; Seiler, F. J. *QCPE Bull.* **1985**, *5*, 133–144. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4912. (c) Schmidt, M. W.; Boatz, J. A.; Baldridge, K. K.; Koseki, S.; Gordon, M. S.; Elbert, S. T.; Lam, B. *QCPE Bull.* **1987**, *7*, 115. (d) Original Program QG01 by Dupuis, M.; Spangler, D.; Wendoloski, J. J. University of California: Berkeley; 1980.

(26) (a) Optimization of S_1 rather than S_0 geometries was selected, since it was clear that the reaction originates from S_1. This means that, while the S_0 energies correspond to the same geometries as S_1 for each point along the reaction coordinate, they do not represent minimized S_0 points. (b) This conclusion is not completely rigorous, since the S_0 surface is not independently minimized. (c) The MNDO S_1 barriers for the 1,3-diradical rearrangement are 28.7 and 24.6 kcal/mol while those for S_0 are 20.6 and 22.8. These should be construed qualitatively. (d) Since vertical excitation does not afford the zeroth vibrational level of such cyclopropanes, it is likely the excess vibrational energy is available initially for ring opening and for the subsequent methyl migration.

In diradical 2 derived from the diphenylvinylcyclopropane 1, there is extra electron delocalization resulting from the additional double bond. This is a large effect compared with para substitution by phenyl, cyano, or methoxy in the arylcyclopropane examples.[20b,c]

Conclusion. The present study is part of our continuing efforts to obtain generalizations in the chemistry of excited states. In the specific case of cyclopropane photochemistry, the two main processes of the singlet excited states are the Griffin hydrogen-transfer reaction and the 1,2-migration of the 1,3-diradicals derived from ring opening.

Experimental Section[27]

4-(Chloromethyl)biphenyl (10). Hydrogen chloride gas was vigorously bubbled through a stirred boiling solution of 105.5 g (0.684 mol) of biphenyl, 102.5 g (0.752 mol) of zinc chloride, 300 mL of 37% aqueous formaldehyde (3.4 mol), and 300 mL of concentrated aqueous hydrochloric acid for 22 h. After cooling, the mixture was extracted with ether. The extracts were washed with saturated aqueous sodium carbonate and dried over sodium carbonate. Concentration in vacuo gave 110 g of a gummy white solid. A portion of this solid (18.2 g) was chromatographed on a 4 × 45 cm silica gel column eluted with hexane: fraction 1 (0.9 L), 6.90 g of a mixture of biphenyl and 4-(chloromethyl)biphenyl; fractions 2–5 (2 L), 6.11 g of 4-(chloromethyl)biphenyl; fractions 6–7 (2 L), 2.18 g of 4,4′-bis(chloromethyl)biphenyl. The material from fractions 2–5 was recrystallized from hexane to yield 4.56 g of white crystalline 4-(chloromethyl)biphenyl, mp 68–69 °C (lit.[29] mp 68 °C). The remainder of the material was chromatographed and recrystallized in similar fashion to give a total of 27.6 g (20%) of the desired product.

2-Biphenylylacetonitrile (11). A solution of 1.02 g (20.7 mmol) of sodium cyanide in 5 mL of DMSO was heated to 90 °C. A solution of 3.31 g (17.2 mmol) of 4-(chloromethyl)biphenyl in 8 mL of DMSO was added during 15 min while the temperature was maintained between 90 and 130 °C. The reaction was cooled to ambient temperature and stirred for 4 h. Neutral workup[27] gave 3.00 g of a solid, which was recrystallized from ethanol to afford 2.81 g (85%) of 2-biphenylylacetonitrile as white crystals, mp 88–89 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$) δ 7.63–7.36 (m, 9 H, Ar), 3.80 (s, 2 H, CH_2); IR ($CHCl_3$) 3078, 3059, 3028, 3009, 2994, 2249, 1490, 1415, 1221, 1137, 1120, 1105, 1009 cm^{-1}; MS *m/e* 193.0893 (calcd for $C_{14}H_{11}N$, *m/e* 193.0892).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74. Found: C, 87.22; H, 5.75.

2-Biphenylyl-2-methylpropionitrile (12). A solution of 2.39 g (12.4 mmol) of 2-biphenylylacetonitrile and 1.70 mL (27.3 mmol) of methyl iodide in 16 mL of THF was added to a stirred suspension of 3.09 g (27.5 mmol) of potassium *tert*-butoxide in 34 mL of THF at −78 °C during 20 min. After 1 h, the mixture was warmed to ambient temperature and stirred an additional 4 h. Neutral workup[27] gave 2.64 g of a yellow solid, which was recrystallized from ethanol to give 2.58 g (94%) of 2-biphenylyl-2-methylpropionitrile as a cream-colored solid, mp 74–77 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$) δ 7.64–7.30 (m, 9 H, Ar), 1.77 (s, 6 H, CH_3); IR ($CHCl_3$) 3020, 3010, 2994, 2220, 1487, 1106, 1010, 839 cm^{-1}; MS *m/e* 221.1210 (calcd for $C_{16}H_{15}N$, *m/e* 221.1206).

Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83. Found: C, 86.64; H, 7.00.

2-Biphenylyl-2-methylpropanal (13). To a solution of 2.57 g (11.6 mmol) of 2-biphenylyl-2-methylpropionitrile in 70 mL of toluene at −78 °C was slowly added 14.0 mL (14.0 mmol) of 1 M diisobutylaluminum hydride in hexane. After being stirred at −78 °C for 2 h, the mixture was warmed to ambient temperature, stirred an additional 2 h, and then quenched at 0 °C by cautious addition of 10% aqueous hydrochloric acid. Basic workup[27] gave a pink solid, which was chromatographed on a 3.5 × 7.5 cm neutral alumina column eluted with 250 mL of 10% ether in hexane, giving 2.10 g of a white solid. Recrystallization from 10% ether in hexane afforded 1.96 g (75%) of 2-biphenylyl-2-methylpropanal, mp 63–66 °C.

The spectral data were the following: ^{1}H NMR (acetone-d_6) δ 9.55 (s, 1 H, CHO), 7.70–7.31 (m, 9 H, Ar), 1.48 (s, 6 H, CH_3); IR ($CHCl_3$) 3055, 3027, 3015, 3008, 2974, 2932, 2812, 2713, 1720, 1486, 1214, 1007, 843 cm^{-1}; MS *m/e* 224.1201 (calcd for $C_{16}H_{16}O$, *m/e* 224.1202).

4-Biphenylyl-2,4-dimethyl-2-pentene (14). To a solution of 7.17 g (16.6 mmol) of isopropyltriphenylphosphonium iodide in 34 mL of toluene was added 1.87 g (16.6 mmol) of potassium *tert*-butoxide. After 1 h, a solution of 0.744 g (3.32 mmol) of 2-biphenylyl-2-methylpropanal in 8.7 mL of toluene was added in one portion, and the mixture was heated at reflux for 45 min. Neutral workup[27] followed by chromatography on a 3 × 40 cm silica column eluted with 1.5 L of hexane gave 0.700 g of a white solid. Recrystallization from methanol afforded 0.593 g (71%) of 4-biphenylyl-2,4-dimethyl-2-pentene as white crystals, mp 48–49 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$) δ 7.70–7.30 (m, 9 H, Ar), 5.53 (m, 1 H, vinyl), 1.71 (d, *J* = 1.2 Hz, 3 H, CH_3), 1.43 (s, 6 H, CH_3), 1.21 (d, *J* = 1.0 Hz, 3 H, CH_3); IR ($CHCl_3$) 3039, 3009, 2967, 2932, 2867, 1487, 1447, 1102, 1072, 1006, 839 cm^{-1}; UV (MeOH) λ_{max} 259 nm (ε 28 900); MS *m/e* 250.1720 (calcd for $C_{19}H_{22}$, *m/e* 250.1721).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.16; H, 8.83.

3-Biphenylyl-1,1,2,2-tetramethylcyclopropane (7a): Sensitized Photolysis of 4-Biphenylyl-2,4-dimethyl-2-pentene. A solution of 0.502 g (2.01 mmol) of 4-biphenylyl-2,4-dimethyl-2-pentene and 12.0 mL (103 mmol) of acetophenone in 250 mL of acetonitrile was irradiated through a metavanadate filter solution (λ > 320 nm) for 3 h.[27] Solvent and sensitizer were removed in vacuo to give a yellow oil, which was chromatographed on a 3 × 30 cm silica column; elution with 300 mL of hexane gave 0.474 g of a white solid. Recrystallization from methanol afforded 0.362 g (72%) of 3-biphenylyl-1,1,2,2-tetramethylcyclopropane as white plates, mp 64–65 °C.

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.56–7.13 (m, 9 H, Ar), 1.54 (s, 1 H, cyclopropyl), 1.20 (s, 6 H, CH_3), 0.98 (s, 6 H, CH_3); IR ($CHCl_3$) 3023, 2983, 2942, 2912, 2874, 1600, 1459, 1218, 1213, 856 cm^{-1}; MS *m/e* 250.1722 (calcd for $C_{19}H_{22}$, *m/e* 250.1721); UV (MeOH) λ_{max} 258 nm (ε 20 300).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.29; H, 8.89.

(27) Melting points were determined on a calibrated hot-stage apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. All reactions are performed under an atmosphere of dry nitrogen. Anhydrous magnesium sulfate was used as the drying agent. Column chromatography was performed on silica gel (Matheson, Coleman, and Bell, grade 62, 60–200 mesh) or basic alumina (Fisher Scientific, 80–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns permitting monitoring by a hand-held UV lamp. Preparative thick-layer chromatography was carried out with MN-Kieselgel G/UV 254 silica gel. High-pressure liquid chromatography (HPLC) was performed on a liquid chromatograph employing an LDC 254-nm detector and an LDC 6000-psi minipump, using a 0.95 × 50 cm polished stainless steel column packed with 5–15-μm porous silica beads.[28] Neutral workup refers to quenching the reaction with water, extracting with ether unless otherwise specified, washing the organic layer with water and brine, drying, filtering, and concentrating in vacuo. Acidic workup included a 10% aqueous hydrochloric acid wash after ether extraction. Basic workup included a saturated aqueous sodium bicarbonate wash after ether extraction. Exploratory photolyses were carried out with a Hanovia 450-W medium-pressure mercury lamp equipped with the appropriate 2-mm filter or with a recirculating filter solution (0.015 M sodium metavanadate in 5% aqueous sodium hydroxide, λ > 320 nm). All photolysis solutions were thoroughly purged with purified nitrogen[29] both prior to and during photolysis. Acetonitrile, pentane, methanol, and toluene were distilled from calcium hydride. Acetone was dried over potassium carbonate and distilled. Dichloromethane was purified by distillation from phosphorus pentoxide. Dimethyl formamide (DMF) was distilled from barium oxide. Dimethyl sulfoxide (DMSO) was distilled from sodium hydroxide. 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.

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Exploratory Direct Photolysis of 3-Biphenylyl-1,1,2,2-tetramethylcyclopropane (7a) in Methanol. A solution of 76.0 mg (0.304 mmol) of 3-biphenylyl-1,1,2,2-tetramethylcyclopropane in 150 mL of methanol was irradiated through a Vycor filter (λ > 270 nm) for 1.3 h. Concentration in vacuo gave 76.1 mg of a yellow oil, which was chromatographed on a 20 × 20 cm preparative thick-layer silica gel plate and eluted six times with 1% ether in pentane. The fastest moving band (band 1, R_f 0.9) contained 25.9 mg of a mixture of (*E*)- and (*Z*)-1-biphenylyl-2,3,3-trimethyl-1-butene. Band 2 (R_f 0.8) contained 45.6 mg (60.0%) of 4-biphenylyl-2,3,3-trimethyl-1-butene (**26a**) as a colorless oil. Band 3 (R_f 0.3) contained 2.4 mg (4.0%) of 4-(methoxymethyl)biphenyl (**37a**) as a colorless oil. The mixture from bands 1 and 2 was subjected to HPLC using a 0.95 × 50 cm silica gel column.[27] Elution with pentane gave fraction 1 (R_f 9 min), 17.7 mg (23.3%) of an oil, which was crystallized from methanol to give 10.3 mg of (*Z*)-1-biphenylyl-2,3,3-trimethyl-1-butene (**(*Z*)-33a**), mp 64–67 °C, and fraction 2 (R_f 11 min), 2.8 mg (3.4%) of (*E*)-1-biphenylyl-2,3,3-trimethyl-1-butene (**(*E*)-33a**), mp 59–60 °C.

The spectral data for (*Z*)-1-biphenylyl-2,3,3-trimethyl-1-butene (**(*Z*)-33a**) were the following: ^{1}H NMR (benzene-d_6) δ 7.51–7.12 (m, 9 H, Ar), 6.47 (m, 1 H, vinyl), 1.80 (d, J = 1.3 Hz, 3 H, CH_3), 1.04 (s, 9 H, CH_3); an NOE[31] difference measurement with irradiation of the δ 1.80 methyl group led to an ca. 8% increase in the δ 6.47 vinyl signal; IR ($CHCl_3$) 3001, 2960, 2900, 2863, 1486, 1457, 1447, 1361, 1009, 871, 819 cm^{-1}; MS m/e 250.1725 (calcd for $C_{19}H_{22}$, m/e 250.1721); UV (MeOH) λ_{max} 260 nm (ϵ 18 400).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 90.93; H, 8.95.

The spectral data for (*E*)-1-biphenylyl-2,3,3-trimethyl-1-butene (**(*E*)-33a**) were the following: ^{1}H NMR (benzene-d_6) δ 7.55–7.16 (m, 9 H, Ar), 6.51 (m, 1 H, vinyl), 1.82 (d, J = 1.1 Hz, 3 H, CH_3), 1.11 (s, 9 H, CH_3); an NOE[31] difference measurement with irradiation of the δ 1.11 methyl groups led to an ca. 10% increase in the δ 6.51 vinyl signal; IR ($CHCl_3$) 3020, 2961, 2925, 2870, 2852, 1486, 1263, 1223, 1214, 1210, 1006 cm^{-1}; MS m/e 250.1721 (calcd for $C_{19}H_{22}$, m/e 250.1721); UV (MeOH) λ_{max} 266 nm (ϵ 17 200).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.39; H, 8.88.

The spectral data for 4-biphenylyl-2,3,3-trimethyl-1-butene (**26a**) were the following: ^{1}H NMR (benzene-d_6) δ 7.54–7.44 (m, 7 H, Ar), 7.26–7.06 (m, 2 H, Ar), 4.83 (m, 1 H, vinyl), 4.71 (m, 1 H, vinyl), 2.58 (s, 2 H, CH_2), 1.75 (s, 3 H, CH_3), 1.00 (s, 6 H, CH_3); IR ($CHCl_3$) 3023, 3015, 2981, 2938, 1635, 1600, 1487, 1451, 1378, 898 cm^{-1}; MS m/e 250.1715 (calcd for $C_{19}H_{22}$, m/e 250.1721); UV (MeOH) λ_{max} 255 nm (ϵ 20 200).

Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.04; H, 8.93.

The spectral data for 4-(methoxymethyl)biphenyl (**37a**) were the following: ^{1}H NMR (benzene-d_6) δ 7.49–7.16 (m, 9 H, Ar), 4.27 (s, 2 H, CH_2), 3.14 (s, 3 H, OCH_3); IR ($CHCl_3$) 3031, 3012, 2929, 2895, 2858, 2826, 1487, 1381, 1096, 1009, 849, 825 cm^{-1}; MS m/e 198.1045 (calcd for $C_{14}H_{14}O$, m/e 198.1045); UV (MeOH) λ_{max} 248 nm (ϵ 7430).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.43; H, 7.27.

Diethyl (Biphenylylmethyl)phosphonate (36a).[32] A mixture of 1.74 mL (10.2 mmol) of triethyl phosphite and 2.04 g (10.0 mmol) of 4-(chloromethyl)biphenyl were heated to 140–150 °C for 24 h. After cooling, excess triethylphosphite was removed in vacuo. The resulting solid was chromatographed on a 2.5 × 40 cm silica column: fraction 1 (500 mL of 50% ether in hexane), 0.113 g of starting material; fraction 2 (200 mL of ether), nil; fraction 3 (2500 mL of ether), 2.75 g (90%) of diethyl (biphenylylmethyl)phosphonate as a white solid, mp 43–46 °C.

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.47–7.11 (m, 9 H, Ar), 3.87 (m, 4 H, OCH_2), 3.00 (d, J = 21.7 Hz, 2 H, $ArCH_2P$), 0.98 (t, J = 7.1 Hz, 6 H, CH_3); IR ($CHCl_3$) 3079, 2994, 2908, 1488, 1244, 1217, 1097, 1055, 1030, 969, 854 cm^{-1}; MS m/e 304.1221 (calcd for $C_{17}H_{21}O_3P$, m/e 304.1229).

(*E*)-1-Biphenylyl-2,3,3-trimethyl-1-butene ((*E*)-33a**).** To a 0 °C solution of 0.914 g (3.00 mmol) of diethyl (biphenylylmethyl)phosphonate in 18 mL of DME was added 1.88 mL (3.01 mmol) of 1.6 M *n*-butyllithium in hexane. After 30 min, a solution of 0.25 mL (2.0 mmol) of pinacolone in 4 mL of DME was added, and the resulting solution was stirred for 30 min. The reaction was then refluxed for 20 h. Neutral workup[27] resulted in 0.695 g of a yellow oil, which was chromatographed on a 3 × 40 cm silica column; elution with 900 mL of hexane gave 31.5 mg of a white solid, which was recrystallized from methanol to give 22.8 mg (5%) of (*E*)-1-biphenylyl-2,3,3-trimethyl-1-butene, mp 59–60 °C. The spectral data were identical with those found for the material produced from the direct irradiation of 3-biphenylyl-1,1,2,2-tetramethylcyclopropane (**7a**).

4-Biphenylyl-3,3-dimethyl-2-butanone (29a). To a suspension of 0.171 g (4.27 mmol) of potassium hydride in 7.5 mL of THF was added 0.30 mL (2.80 mmol) of 3-methyl-2-butanone. After 30 min, a solution of 0.573 g (2.83 mmol) of 4-(chloromethyl)biphenyl in 3 mL of THF was added, and the mixture stirred for 24 h. Neutral workup[27] gave 0.749 g of a yellow oil, which was chromatographed on a 3 × 40 cm silica column eluted with 850 mL of 2% ether in hexane, providing 0.709 g of a white solid. This was recrystallized from hexane to yield 0.638 g (90%) of 4-biphenylyl-3,3-dimethyl-2-butanone as a white solid, mp 60–61 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$) δ 7.60–7.15 (m, 9 H, Ar), 2.85 (s, 2 H, CH_2), 2.15 (s, 3 H, CH_3), 1.16 (s, 6 H, CH_3); IR ($CHCl_3$) 3016, 3008, 2971, 2949, 2904, 1700, 1487, 1469, 1369, 1350, 1121, 1106 cm^{-1}; MS m/e 252.1521 (calcd for $C_{18}H_{20}O$, m/e 252.1515).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.77; H, 8.23.

4-Biphenylyl-2,3,3-dimethyl-1-butene (26a). To a solution of 0.924 g (2.29 mmol) of methyltriphenylphosphonium iodide in 15 mL of toluene was added 0.260 g (2.31 mmol) of potassium *tert*-butoxide. After stirring for 1 h, a solution of 0.102 g (0.457 mmol) of 4-biphenylyl-3,3-dimethyl-2-butanone in 5 mL of toluene was added in one portion and the mixture was heated at reflux for 2.5 h. Neutral workup[27] gave 0.208 g of material that was chromatographed on a 3 × 55 cm silica column; elution with 2.7 L of pentane gave 0.0911 g (80%) of a colorless oil, which solidified upon standing, mp 28–30 °C. The spectral data were identical with those found for the material produced from the direct irradiation of 3-biphenylyl-1,1,2,2-tetramethylcyclopropane (**7a**).

4-(Methoxymethyl)biphenyl (37a). A solution of 0.227 g (1.23 mmol) of 4-biphenylylmethanol and 0.10 mL (1.57 mmol) of methyl iodide in 10 mL of THF was added to a suspension of 38.5 mg (1.60 mmol) of sodium hydride in 10 mL of THF at 0 °C. After 1 h, the reaction was warmed to ambient temperature and stirred an additional 18 h. Neutral workup[27] gave 0.265 g of a yellow oil, which was chromatographed on a 20 × 20 cm preparative thick-layer silica gel plate, eluting three times with 4% ether in pentane. The fastest moving band (R_f 0.6) provided 0.233 g (95%) of 4-(methoxymethyl)biphenyl as a colorless oil. The spectral data were identical with those found for the material produced from the direct irradiation of 3-biphenylyl-1,1,2,2-tetramethylcyclopropane (**7a**).

3-Biphenylyl-3-methyl-1,1-diphenyl-1-butene (15). To a 0 °C solution of 0.687 g (2.26 mmol) of diethyl (diphenylmethyl)phosphonate[33] in 10 mL of DME was added 1.40 mL (2.10 mmol) of 1.5 M *n*-butyllithium in hexane. After 1 h, a solution of 0.165 g (0.733 mmol) of 2-biphenylyl-2-methylpropanal in 2 mL of DME was added at 0 °C. The reaction mixture was stirred for 40 min before neutral workup.[27] The resulting yellow oil was chromatographed on a 3 × 40 cm silica column eluted with hexane to yield 0.237 g (86%) of 3-biphenylyl-3-methyl-1,1-diphenyl-1-butene as a colorless oil, which solidified upon standing, mp 48–51 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$) δ 7.60–7.12 (m, 17 H, Ar), 6.95–6.90 (m, 2 H, Ar), 6.44 (s, 1 H, vinyl), 1.38 (s, 6 H, CH_3); IR ($CHCl_3$) 3061, 3024, 3012, 2969, 2924, 1600, 1490, 1447, 1220, 880 cm^{-1}; MS m/e 374.2062 (calcd for $C_{29}H_{26}$, m/e 374.2036); UV (MeOH) λ_{max} 260 nm (ϵ 29 000).

(31) Sanders, J. K. M.; Mersh, J. D. *Prog. NMR Specrosc.* **1982**, *15*, 353–400.

(32) Sahm, W.; Schinzel, E.; Roesch, G.; Ger. Pat. 2,105,305; *Chem. Abstr.* **1973**, *78*, 31420b.

(33) Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *34*, 1775–1803.

Anal. Calcd for $C_{29}H_{26}$: C, 93.00; H, 7.00. Found: C, 93.02; H, 7.09.

3-Biphenylyl-2,2-dimethyl-1,1-diphenylcyclopropane (8): Sensitized Photolysis of 3-Biphenylyl-3-methyl-1,1-diphenyl-1-butene. A solution of 26.4 mg (0.0705 mmol) of 3-biphenylyl-3-methyl-1,1-diphenyl-1-butene and 15 mL (129 mmol) of acetophenone in 150 mL of acetonitrile was irradiated through a filter solution[27] for 3 h. Solvent and sensitizer were removed in vacuo and the crude photolysate was chromatographed on a 20 × 20 cm preparative thick-layer silica gel plate and eluted twice with 2% benzene in pentane. The fastest moving band (band 1, R_f 0.55) contained 13.9 mg (53%) of starting material and band 2 (R_f 0.45) contained 9.8 mg of a slightly yellow solid, which was recrystallized from methanol to yield 7.6 mg (29%) of 3-biphenylyl-2,2-dimethyl-1,1-diphenylcyclopropane, mp 134–135 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$) δ 7.60–7.11 (m, 17 H, Ar), 6.96–6.92 (m, 2 H, Ar), 2.66 (s, 1 H, cyclopropyl), 1.38 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3); IR ($CHCl_3$) 3059, 3030, 3010, 2947, 2921, 2868, 1667, 1600, 1491, 1445, 1115, 841 cm^{-1}; MS *m/e* 374.2028 (calcd for $C_{29}H_{26}$, *m/e* 374.2036); UV (MeOH) λ_{max} 265 nm (ε 33 500).

Anal. Calcd for $C_{29}H_{26}$: C, 93.00; H, 7.00. Found: C, 92.61; H, 7.00.

Exploratory Direct Photolysis of 3-Biphenylyl-2,2-dimethyl-1,1-diphenylcyclopropane (8) in Acetonitrile. A solution of 17.8 mg (0.0475 mmol) of 3-biphenylyl-2,2-dimethyl-1,1-diphenylcyclopropane in 150 mL of acetonitrile was irradiated through a Vycor filter for 6.5 min. Solvent was removed in vacuo to give 16.1 mg of a yellow oil, which was chromatographed on a preparative thick-layer silica gel plate and eluted once with 2% benzene in pentane. The fastest moving band (R_f 0.3) contained 15.3 mg (86%) of a colorless oil, shown by NMR to be essentially pure 4-biphenylyl-2-methyl-3,3-diphenyl-1-butene. Crystallization from methanol gave 9.3 mg (52%) of 4-biphenylyl-2-methyl-3,3-diphenyl-1-butene (**30**), mp 91–93 °C.

The spectral data for butene (**30**) were the following: ^{1}H NMR ($CDCl_3$) δ 7.52–7.23 (m, 17 H, Ar), 6.66–6.62 (m, 2 H, Ar), 5.33 (s, 1 H, vinyl), 5.15 (s, 1 H, vinyl), 3.61 (s, 2 H, CH_2), 1.56 (s, 3 H, CH_3); IR ($CHCl_3$) 3095, 3060, 3034, 3014, 2956, 2911, 1600, 1510, 1448, 1218 cm^{-1}; MS *m/e* 374.2036 (calcd for $C_{29}H_{26}$, *m/e* 374.2036); UV (MeOH) λ_{max} 258 nm (ε 27 700).

Anal. Calcd for $C_{29}H_{26}$: C, 93.00; H, 7.00. Found: C, 92.99; H, 7.28.

4-Biphenylyl-3,3-diphenyl-2-butanone (32). A modification of the method of Schultz was used.[34] To 8.0 mL of *tert*-butyl alcohol was added 0.221 g (1.97 mmol) of potassium *tert*-butoxide; 0.231 g (1.10 mmol) of 1,1-diphenylacetone was added and the mixture heated at reflux for 0.5 h. Then a solution of 0.290 g (1.43 mmol) of 4-(chloromethyl)biphenyl in 2 mL of ether was added dropwise and the mixture was refluxed for 2 h, cooled to ambient temperature, and allowed to stir overnight before neutral workup.[27] The crude material was chromatographed on a 3 × 40 cm silica column eluted with 500 mL hexane, 1 L of 0.5% ether in hexane, and 1 L of 0.5% ether in hexane to give 0.298 g of a solid, which was recrystallized from hexane to afford 0.241 g (58%) of 4-biphenylyl-3,3-diphenyl-2-butanone as a white solid, mp 79–81 °C.

The spectral data were the following: ^{1}H NMR ($CDCl_3$) δ 7.52–7.19 (m, 17 H, Ar), 6.69–6.65 (m, 2 H, Ar), 3.68 (s, 2 H, CH_2), 2.05 (s, 3 H, CH_3); IR ($CHCl_3$) 3074, 3021, 3010, 1704, 1600, 1496, 1486, 1450, 1444, 1366, 1185 cm^{-1}; MS *m/e* 376.1820 (calcd for $C_{28}H_{24}O$, *m/e* 376.1828).

Anal. Calcd for $C_{28}H_{24}O$: c, 89.33; H, 6.43. Found: C, 88.99; H, 6.56.

4-Biphenylyl-2-methyl-3,3-diphenyl-1-butene (30). To a solution of 0.642 g (1.59 mmol) of methyltriphenylphosphonium iodide in 8 mL of toluene was added 0.202 g (1.80 mmol) of potassium *tert*-butoxide. After 1 h, a solution of 0.119 g (0.316 mmol) of 4-biphenylyl-3,3-diphenyl-2-butanone in 2 mL of toluene was added in one portion and the mixture was refluxed for 2 h. Neutral workup[27] gave an oil, which was chromatographed on a preparative thick-layer silica gel plate eluted three times with 1% benzene in pentane. The fastest moving band (R_f 0.7) contained 36.9 mg of a solid, which was recrystallized from methanol to yield 18.3 mg (15%) of 4-biphenylyl-2-methyl-3,3-diphenyl-1-butene, mp 91–93 °C. The spectral data were identical with those found for the material produced from the direct irradiation of 3-biphenylyl-2,2-dimethyl-1,1-diphenylcyclopropane (8).

1,1-Dicarbethoxy-2,2-dimethyl-3-phenylcyclopropane (21). A modification of the method of Ono[8a] was used. To a solution of 2.22 g (19.8 mmol) of potassium *tert*-butoxide in 400 mL of freshly distilled DMSO was added 1.78 mL (19.8 mmol) of 2-nitropropane. After 15 min, 1.64 g (6.60 mmol) of diethyl benzalmalonate was added and the mixture stirred for 60 h. Neutral workup[27] gave a yellow oil, which was chromatographed on a 2 × 25 cm neutral alumina column eluted with 150 mL of 20% ether in hexane, providing 1.53 g of a colorless oil. Distillation gave 1.49 g (78%) of 1,1-dicarbethoxy-2,2-dimethyl-3-phenylcyclopropane as an oil, bp 94–98 °C (0.10 mm).

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.31–7.04 (m, 5 H, Ar), 4.18–3.86 (m, 4 H, OCH_2), 3.24 (s, 1 H, cyclopropyl), 1.50 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 0.99 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 0.87 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3); IR ($CHCl_3$) 3029, 2984, 2962, 1723, 1447, 1368, 1314, 1248, 1222, 1216, 1195, 1106 cm^{-1}; MS *m/e* 290.1519 (calcd for $C_{17}H_{22}O_4$, *m/e* 290.1519.

Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.53; H, 7.73.

1,1-Bis(hydroxymethyl)-2,2-dimethyl-3-phenylcyclopropane (22). A solution of 2.16 g (7.45 mmol) of 1,1-dicarbethoxy-2,2-dimethyl-3-phenylcyclopropane in 10 mL of THF was added to a suspension of 0.850 g (22.4 mmol) of lithium aluminum hydride in 125 mL of THF at 0 °C. After 1 h, the mixture was allowed to warm to ambient temperature, stirred overnight, and then quenched with magnesium sulfate heptahydrate and filtered. Neutral workup[27] gave 1.48 g (96%) of 1,1-bis(hydroxymethyl)-2,2-dimethyl-3-phenylcyclopropane as a white solid. An analytically pure sample could be prepared by recrystallization from ether in hexane, mp 73–75 °C.

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.19–7.07 (m, 5 H, Ar), 3.96 (d, J_{ab} = 11.3 Hz, 1 H, OCH_2), 3.82 (d, J_{ab} = 11.2 Hz, 1 H, OCH_2), 3.58 (dd, J_{ab} = 11.3, *J* = 1.1 Hz, 1 H, OCH_2), 3.44 (dd, J_{ab} = 11.2 Hz, *J* = 1.1 Hz, 1 H, OCH_2), 2.60 (br s, 2 H, OH), 1.70 (s, 1 H, cyclopropyl), 1.24 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3); IR ($CDCl_3$) 3623, 3615, 2986, 2953, 2927, 2879, 1445, 1378, 1029, 1014, 925, 913 cm^{-1}; MS *m/e* 175.1125 (calcd for $C_{12}H_{15}O$ (parent − CH_3O), 175.1124).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.90; H, 8.75.

1,1-Bis[[(methylsulfonyl)oxy]methyl]-2,2-dimethyl-3-phenylcyclopropane (23). To a 0 °C solution of 1.08 g (5.22 mmol) of 1,1-bis(hydroxymethyl)-2,2-dimethyl-3-phenylcyclopropane in 80 mL of dichloromethane was added 2.20 mL (15.8 mmol) of triethylamine. After 15 min, 0.82 mL (10.6 mmol) of methanesulfonyl chloride was added. The reaction was warmed to ambient temperature and stirred for 16 h. After the reaction mixture was washed with saturated aqueous sodium bicarbonate and dried, solvent was removed in vacuo to give 1.83 g (97%) of 1,1-bis[[(methylsulfonyl)oxy]methyl]-2,2-dimethyl-3-phenylcyclopropane as a cream-colored solid, mp 67–69 °C (decomp).

The spectral data were the following: ^{1}H NMR ($CDCl_3$) δ 7.35–7.13 (m, 5 H, Ar), 4.49 (m, 3 H, OCH_2), 3.97 (d, *J* = 10.6 Hz, 1 H, OCH_2), 3.11 (s, 3 H, SO_2CH_3), 2.99 (s, 3 H, SO_2CH_3), 2.33 (s, 1 H, cyclopropyl), 1.42 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3); IR ($CHCl_3$) 3030, 2961, 1361, 1215, 1175, 972, 935, 850, 816 cm^{-1}.

1,1,2,2-Tetramethyl-3-phenylcyclopropane (4). A solution of 1.83 g (5.06 mmol) of 1,1-bis[[(methylsulfonyl)oxy]methyl]-2,2-dimethyl-3-phenylcyclopropane in 170 mL of THF was added during 1.5 h to 50.0 mL (50.0 mmol) of 1.0 M lithium triethylborohydride in THF at 0 °C. After addition was complete, the reaction was refluxed for 18 h, cooled, and quenched with water; 63 mL of 3 N aqueous sodium hydroxide and 63 mL of 30% hydrogen peroxide were added. Neutral workup[27] using pentane gave a yellow oil, which was chromatographed on a 2 × 30 cm silica column eluted with 250 mL of pentane, giving 0.905 g of a pale yellow oil. This was chromatographed on a 2.5 × 75 cm silica column eluted with pentane: fraction 1 (250 mL), nil; fraction 2–3 (225 mL), 0.622 g of the cyclopropane; fraction 4 (100 mL), impure cyclopropane. The material from fraction 4 was chromatographed on two preparative thick-layer silica gel plates and

(34) Schultz, E. M.; Bicking, J. B.; Mickey, S.; Crossley, F. S. *J. Am. Chem. Soc.* **1953**, *75*, 1072–1074.

each was eluted three times with pentane. The fastest moving bands from the two plates contained an additional 0.115 g of the cyclopropane for a total of 0.737 g (84%) of 1,1,2,2-tetramethyl-3-phenylcyclopropane as a colorless liquid, bp 32–36 °C (0.20 mm) (lit.[35] 61 °C, 3.5 mm).

Exploratory Direct Photolysis of 1,1,2,2-Tetramethyl-3-phenylcyclopropane (4) in Methanol. A solution of 63.8 mg (0.366 mmol) of 1,1,2,2-tetramethyl-3-phenylcyclopropane in 150 mL of methanol was irradiated through a Vycor filter for 12 min. Concentration in vacuo gave 74.0 mg of a yellow oil, which was chromatographed on a 20 × 20 cm preparative thick-layer silica gel plate and eluted four times with pentane: band 1 (R_f 0.85), 17.3 mg (27.1%) of (*Z*)-2,3,3-trimethyl-1-phenyl-1-butene ((*Z*)-**33b**); band 2 (R_f 0.80), 1.5 mg (2.4%) of (*E*)-2,3,3-trimethyl-1-phenyl-1-butene ((*E*)-**33b**); band 3 (R_f 0.70), 20.9 mg (32.8%) of 2,3,3-trimethyl-4-phenyl-1-butene (**6**); band 4 (R_f 0.60), 2.8 mg of unidentifiable materials. The base-line material was eluted once with 4% ether in pentane: band 5 (R_f 0.20), 5.5 mg of unidentifiable materials; band 6 (R_f 0.15), 4.6 mg (10.3%) of (methoxymethyl)benzene[11a] (**37b**).

The spectral data for (*Z*)-2,3,3-trimethyl-1-phenyl-1-butene ((*Z*)-**33b**) were the following: ^{1}H NMR (benzene-d_6) δ 7.25–6.98 (m, 5 H, Ar), 6.43 (m, 1 H, vinyl), 1.76 (d, *J* = 1.2 Hz, 3 H, CH_3), 0.99 (s, 9 H, CH_3); an NOE[31] difference measurement with irradiation of the δ 1.76 methyl group led to an ca. 6% increase in the δ 6.43 vinyl signal; IR ($CHCl_3$) 3060, 3010, 2965, 2930, 2868, 1488, 1480, 1461, 1441, 1378, 1362, 1199 cm^{-1}; MS *m/e* 174.1408 (calcd for $C_{13}H_{18}$, *m/e* 174.1409); UV (MeOH) λ_{max} 228 nm (ε 5380).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.50; H, 10.77.

The spectral data for (*E*)-2,3,3-trimethyl-1-phenyl-1-butene ((*E*)-**33b**) were the following: ^{1}H NMR (benzene-d_6) δ 7.22–7.02 (m, 5 H, Ar), 6.46 (m, 1 H, vinyl), 1.75 (d, *J* = 1.2 Hz, 3 H, CH_3), 1.08 (s, 9 H, CH_3); an NOE[31] difference measurement with irradiation of the δ 1.08 methyl groups led to an ca. 7% increase in the δ 6.46 vinyl signal; IR ($CHCl_3$) 3011, 2966, 2909, 2870, 1491, 1476, 1467, 1444, 1393, 1368, 1361, 1120 cm^{-1}; MS *m/e* 174.1400 (calcd for $C_{13}H_{18}$, *m/e* 174.1409); UV (MeOH) λ_{max} 244 nm (ε 5800).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.20; H, 10.37.

The spectral data for 2,3,3-trimethyl-4-phenyl-1-butene (**6**) were the following: ^{1}H NMR (benzene-d_6) δ 7.21–7.01 (m, 5 H, Ar), 4.79 (m, 1 H, vinyl), 4.66 (m, 1 H, vinyl), 2.54 (s, 2 H, CH_2), 1.71 (s, 3 H, CH_3), 0.96 (s, 6 H, CH_3); IR ($CHCl_3$) 3025, 3010, 2069, 2939, 2876, 1635, 1494, 1450, 1374, 897 cm^{-1}; MS *m/e* 174.1408 (calcd for $C_{13}H_{18}$, *m/e* 174.1409); UV (MeOH) λ_{max} 262 nm (ε 207).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.43; H, 10.48.

Exploratory Direct Photolysis of 1,1,2,2-Tetramethyl-3-phenylcyclopropane (4) in Methanol: Low Conversion. A solution of 38.7 mg (0.222 mmol) of 1,1,2,2-tetramethyl-3-phenylcyclopropane (**4**) in 150 mL of methanol was irradiated through a Vycor filter for 4 min. Concentration in vacuo gave an oil, which was shown by NMR analysis to be a 1:2.5:0.5:12 mixture of (*E*)- and (*Z*)-2,3,3-trimethyl-1-phenyl-1-butene (**33b**):2,3,3-trimethyl-4-phenyl-1-butene (**6**):(methoxymethyl)-benzene (**37b**):starting material, respectively (26% conversion).

(*E*)-2,3,3-Trimethyl-1-phenyl-1-butene ((*E*)-33b). To a 0 °C solution of 3.02 g (13.3 mmol) of diethyl (phenylmethyl)-phosphonate[36] in 25 mL of DME was added 1.52 g (13.6 mmol) of potassium *tert*-butoxide. After 15 min, 1.11 mL (8.88 mmol) of pinacolone was added; the resulting mixture was stirred at 0 °C for 2 h and then at ambient temperature for 16 h. Neutral workup[27] gave 2.05 g of a yellow liquid, which was chromatographed on a 3 × 45 cm silica column eluted with 500 mL of hexane, giving 0.917 g of an oil. Distillation afforded 0.896 g (58%) of (*E*)-2,3,3-trimethyl-1-phenyl-1-butene as a colorless liquid, bp 40–42 °C (0.13 mm). The spectral data were identical with those found for the material produced from the direct irradiation of 1,1,2,2-tetramethyl-3-phenylcyclopropane (**4**).

3,3-Dimethyl-4-phenyl-2-butanone (29b). To a suspension of 1.16 g (29.0 mmol) of potassium hydride in 50 mL of THF was slowly added 2.10 mL (19.6 mmol) of 3-methyl-2-butanone. After 1 h, 2.80 mL (24.3 mmol) of benzyl chloride was added and the mixture was stirred for 16 h. Neutral workup[27] gave 4.35 g of a slightly yellow liquid, which was distilled to give 3.31 g (96%) of 3,3-dimethyl-4-phenyl-2-butanone as a colorless liquid, bp 57–63 °C (0.35 mm).

The spectral data were the following: ^{1}H NMR ($CDCl_3$) δ 7.33–7.08 (m, 5 H, Ar), 2.81 (s, 2 H, CH_2), 2.12 (s, 3 H, CH_3), 1.12 (s, 6 H, CH_3); IR ($CHCl_3$) 3023, 3011, 2968, 2932, 1700, 1492, 1464, 1453, 1366, 1355, 1217, 1108 cm^{-1}; MS *m/e* 176.1206 (calcd for $C_{12}H_{16}O$, *m/e* 176.1202).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.43; H, 9.20.

2,3,3-Trimethyl-4-phenyl-1-butene (6). To a solution of 20.8 g (51.4 mmol) of methyltriphenylphosphonium iodide in 125 mL of toluene was added 5.77 g (51.4 mmol) of potassium *tert*-butoxide. After 1 h, a solution of 2.96 g (16.8 mmol) of 3,3-dimethyl-4-phenyl-2-butanone in 15 mL of toluene was added and the mixture was heated at reflux for 12 h before neutral workup.[27] The solid obtained was chromatographed on a 3 × 25 cm silica column eluted with 1.1 L of hexane to give 2.59 g of a yellow liquid. Distillation afforded 1.79 g (61%) of 2,3,3-trimethyl-4-phenyl-1-butene as a colorless liquid, bp 53–55 °C (0.75 mm). The spectral data were identical with those found for the material produced from the direct irradiation of 1,1,2,2-tetramethyl-3-phenylcyclopropane (**4**).

3-*p*-Anisyl-1,1,2,2-tetramethylcyclopropane (7c). A modification of the method of Olofson[37] was used. Lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was formed immediately prior to use by the slow addition of 13.9 mL (22.2 mmol) of 1.6 M *n*-butyllithium in hexane to 3.75 mL (22.2 mmol) of 2,2,6,6-tetramethylpiperidine in 28 mL of ether. The LiTMP solution was added to a solution of 3.00 mL (22.1 mmol) of 4-methoxybenzyl chloride[38] in 9.4 mL of 2,3-dimethyl-2-butene; rate of addition and reaction temperature were adjusted to cause reflux. After addition was complete, the mixture was refluxed for 12 h. Acidic workup[27] gave a yellow oil, which was chromatographed on a 2 × 55 cm alumina column: fraction 1 (400 mL of hexane), nil; fraction 2 (1 L hexane), 0.537 g of cyclopropane **7c**; fraction 3 (1 L of 5% ether in hexane), 0.209 g of impure cyclopropane **7c**, which was chromatographed on a 2 × 46 cm alumina column eluted with 1.5 L of hexane to give 0.147 g of cyclopropane **7c**. The combined cyclopropane fractions were distilled to give 0.616 g (14%) of 3-*p*-anisyl-1,1,2,2-tetramethylcyclopropane as a colorless liquid, bp 74–78 °C (0.70 mm).

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.10–7.06 (m, 2 H, Ar), 6.86–6.80 (m, 2 H, Ar), 3.35 (s, 3 H, OCH_3), 1.50 (s, 1 H, cyclopropyl), 1.19 (s, 6 H, CH_3), 0.97 (s, 6 H, CH_3); IR ($CHCl_3$) 2999, 2986, 2938, 2870, 1512, 1463, 1291, 1244, 1173, 1038, 847 cm^{-1}; MS *m/e* 204.1522 (calcd for $C_{14}H_{20}O$, *m/e* 204.1515); UV (MeOH) λ_{max} 278 nm (ε 1530), 284 (1300).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.28; H, 10.22.

Exploratory Direct Photolysis of 3-*p*-Anisyl-1,1,2,2-tetramethylcyclopropane (7c) in Methanol. A solution of 74.3 mg (0.364 mmol) of 3-*p*-anisyl-1,1,2,2-tetramethylcyclopropane in 150 mL of methanol was irradiated through a Vycor filter for 21 min. Concentration in vacuo provided 82.0 mg of an oil, which was chromatographed on a preparative thick-layer silica gel plate eluted six times with 2% benzene in pentane. Bands 1 and 2 (R_f 0.50, 0.45) contained 13.2 mg of a mixture of (*E*)- and (*Z*)-1-*p*-anisyl-2,3,3-trimethyl-1-butene. Band 3 (R_f 0.40) contained 41.9 mg (56.4%) of 4-*p*-anisyl-2,3,3-trimethyl-1-butene (**26c**) as an oil. Band 4, immediately above base line, contained impure 1-methoxy-4-(methoxymethyl)benzene[11b] (**37d**), which was chromatographed on a 20 × 20 cm preparative thick-layer silica gel plate eluted twice with 5% ether in pentane. Band 1 contained 6.2 mg (11.2%) of the methyl ether **37d** as an oil. The mixture of (*E*)- and (*Z*)-1-*p*-anisyl-2,3,3-trimethyl-1-butene was subjected to HPLC.[27] Elution with 1% ether in pentane provided fraction

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1 (R_f 12 min), 9.0 mg (12.1%) of (*Z*)-1-*p*-anisyl-2,3,3-trimethyl-1-butene ((*Z*)-**33d**), and fraction 2 (R_f 14 min), 3.7 mg (5.0%) of (*E*)-*p*-anisyl-2,3,3-trimethyl-1-butene ((*E*)-**33d**).

The spectral data for (*Z*)-*p*-anisyl-2,3,3-trimethyl-1-butene ((*Z*)-**33d**) were the following: ^{1}H NMR (benzene-d_6) δ 7.10–7.06 (m, 2 H, Ar), 6.77–6.45 (m, 2 H, Ar), 6.45 (m, 1 H, vinyl), 3.32 (s, 3 H, OCH_3), 1.79 (d, J = 1.3 Hz, 3 H, CH_3), 1.03 (s, 9 H, CH_3); an NOE[31] difference measurement with irradiation of the δ 1.79 methyl group led to an ca. 10% increase of the δ 6.45 vinyl signal; IR ($CHCl_3$) 3020, 2966, 2911, 1605, 1507, 1467, 1285, 1243, 1214, 1179, 1173, 1035 cm^{-1}; MS m/e 204.1507 (calcd for m/e 204.1515); UV (MeOH) λ_{max} 234 nm (ϵ 8080), sh 278 (1710).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.32; H, 9.88.

The spectral data for (*E*)-*p*-anisyl-2,3,3-trimethyl-1-butene ((*E*)-**33d**) were the following: ^{1}H NMR (benzene-d_6) δ 7.20–7.16 (m, 2 H, Ar), 6.85–6.81 (m, 2 H, Ar), 6.47 (m, 1 H, vinyl), 3.34 (s, 3 H, OCH_3), 1.81 (d, J = 1.1 Hz, 3 H, CH_3), 1.12 (s, 9 H, CH_3); an NOE[31] difference measurement with irradiation of the δ 1.12 methyl groups led to an ca. 18% increase in the δ 6.47 vinyl signal; IR ($CHCl_3$) 3009, 2963, 2935, 2919, 2871, 1607, 1510, 1467, 1249, 1218, 1177, 1038 cm^{-1}; MS m/e 204.1517 (calcd for $C_{14}H_{20}O$, m/e 204.1515); UV (MeOH) λ_{max} 250 nm (ϵ 13 300).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.19; H, 10.04.

The spectral data for 4-*p*-anisyl-2,3,3-trimethyl-1-butene (**26c**) were the following: ^{1}H NMR (benzene-d_6) δ 6.99–6.92 (m, 2 H, Ar), 6.83–6.75 (m, 2 H, Ar), 4.82 (m, 1 H, vinyl), 4.70 (m, 1 H, vinyl), 3.33 (s, 3 H, OCH_3), 2.54 (s, 2 H, CH_2), 1.74 (d, J = 0.7 Hz, 3 H, CH_3), 0.99 (s, 6 H, CH_3); IR ($CHCl_3$) 3009, 2965, 2935, 1610, 1512, 1465, 1248, 1219, 1178, 1037, 897 cm^{-1}; MS m/e 204.1517 (calcd for $C_{14}H_{20}O$, m/e 204.1515); UV (MeOH) λ_{max} 276 nm (ϵ 1630), 2.84 (1300).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.29; H, 9.69. Found: C, 82.30; H, 9.87.

(*E*)-1-*p*-Anisyl-2,3,3-trimethyl-1-butene ((*E*)-33d). To a solution of 12.1 g (28.8 mmol) of *p*-anisyltriphenylphosphonium chloride in 150 mL of toluene was added 3.24 g (28.9 mmol) of potassium *tert*-butoxide. After 1 h, 1.20 mL (9.60 mmol) of pinacolone was added and the mixture was refluxed for 8 h. Neutral workup[27] gave a yellow oil, which was chromatographed on a 2.5 × 50 cm silica column eluted with 650 mL of 2% ether in hexane. The material obtained was distilled to yield 0.461 g (24%) of (*E*)-1-*p*-anisyl-2,3,3-trimethyl-1-butene as a colorless liquid, bp 70–72 °C (0.80 mm). The spectral data were identical with those found for the material produced from the direct irradiation of 3-*p*-anisyl-1,1,2,2-tetramethylcyclopropane (**7c**).

4-*p*-Anisyl-3,3-dimethyl-2-butanone (20d). To a solution of 1.00 g (24.9 mmol) of potassium hydride in 50 mL of THF was slowly added 2.40 mL (22.4 mmol) of 3-methyl-2-butanone. After 1 h, 2.34 mL (17.3 mmol) of 4-methoxybenzyl chloride[38] was slowly added and the mixture was stirred for 20 h. Neutral workup[27] provided 3.80 g of a yellow liquid, which was distilled to give 2.91 g (82%) of 4-*p*-anisyl-3,3-dimethyl-2-butanone, bp 78–83 °C (0.30 mm).

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 6.96–6.71 (m, 4 H, Ar), 3.30 (s, 3 H, OCH_3), 2.61 (s, 2 H, CH_2), 1.74 (s, 3 H, CH_3), 0.91 (s, 6 H, CH_3); IR ($CHCl_3$) 3011, 2969, 2935, 1700, 1611, 1512, 1466, 1355, 1248, 1179, 1120, 1037 cm^{-1}; MS m/e 206.1291 (calcd for $C_{13}H_{18}O_2$, m/e 206.1307).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.49; H, 8.79.

4-*p*-Anisyl-2,3,3-trimethyl-1-butene (26c). To a solution of 20.3 g (50.2 mmol) of methyltriphenylphosphonium iodide in 130 mL of toluene was added 5.68 g (50.7 mmol) of potassium *tert*-butoxide. After 1 h, a solution of 2.06 g (9.99 mmol) of 4-*p*-anisyl-3,3-dimethyl-2-butanone in 8 mL of toluene was added in one portion. The mixture was then refluxed for 20 h. Neutral workup[27] followed by chromatography on a 3 × 40 cm silica column eluted with 950 mL of hexane gave 2.00 g of a slightly yellow oil, which was distilled to give 1.79 g (88%) of 4-*p*-anisyl-2,3,3-trimethyl-1-butene as a colorless liquid, bp 62–68 °C (0.18 mm). The spectral data were identical with those found for the material produced from the direct irradiation of 3-*p*-anisyl-1,1,2,2-tetramethylcyclopropane (**7c**).

2,4-Dimethyl-4-(4′-bromophenyl)-2-pentene (17). To a solution of 16.5 g (38.2 mmol) of isopropyltriphenylphosphonium iodide in 160 mL of toluene was added 4.29 g (38.2 mmol) of potassium *tert*-butoxide. After stirring for 1 h, 2.89 g (12.7 mmol) of 2-methyl-2-(4′-bromophenyl)propanal[39] was added in one portion and the mixture was refluxed for 1 h. Neutral workup[27] gave a yellow liquid; distillation afforded 2.72 g (84%) of 2,4-dimethyl-4-(4′-bromophenyl)-2-pentene as a colorless liquid, bp 65–70 °C (0.25 mm).

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.33–7.26 (m, 2 H, Ar), 7.04–6.94 (m, 2 H, Ar), 5.40 (m, 1 H, vinyl), 1.57 (d, J = 1.3 Hz, 3 H, CH_3), 1.22 (s, 6 H, CH_3), 1.06 (d, J = 1.1 Hz, 3 H, CH_3); IR ($CHCl_3$) 3011, 2966, 2931, 2915, 1489, 1447, 1393, 1098, 1073, 1008, 826 cm^{-1}; MS m/e 252.0514 (calcd for $C_{13}H_{17}Br$, m/e 252.0514).

Anal. Calcd for $C_{13}H_{17}Br$: C, 61.67; H, 6.77. Found: C, 61.65; H, 6.89.

4-(4′-Cyanophenyl)-2,4-dimethyl-2-pentene (18). A modification of the methods of Schecter[40a] and Newman[40b] was used. A mixture of 1.92 g (7.57 mmol) of 2,4-dimethyl-4-(4′-bromophenyl)-2-pentene and 0.802 g (8.96 mmol) of copper(I) cyanide were refluxed in 3.0 mL of DMF for 6 h. After cooling, the mixture was poured into 25 mL of 5% aqueous sodium cyanide and ether extracted. The extracts were washed with 5% aqueous sodium cyanide, water, and brine and dried. Removal of solvent in vacuo provided 1.51 g of a brown oil, which was chromatographed on a 3 × 33 cm silica column; elution with 1.1 L of 1% ether in hexane gave 1.32 g of a slightly yellow liquid. Distillation gave 1.31 g (87%) of 2,4-dimethyl-4-(4′-cyanophenyl)-2-pentene as a colorless liquid, bp 82–84 °C (0.45 mm).

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.10–7.06 (m, 2 H, Ar), 6.96–6.92 (m, 2 H, Ar), 5.31 (m, 1 H, vinyl), 1.54 (d, J = 1.3 Hz, 3 H, CH_3), 1.12 (s, 6 H, CH_3), 0.92 (d, J = 1.1 Hz, 3 H, CH_3); IR ($CHCl_3$) 3022, 2968, 2932, 2915, 2871, 2229, 1606, 1501, 1466, 1447, 1096, 839 cm^{-1}; MS m/e 199.1357 (calcd for $C_{14}H_{17}N$, m/e 199.1362); UV (MeOH) λ_{max} 238 nm (ϵ 9320).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60. Found: C, 84.22; H, 8.58.

3-(4′-Cyanophenyl)-1,1,2,2-tetramethylcyclopropane (7b): Sensitized Photolysis of 4-(4′-Cyanophenyl)-2,4-dimethyl-2-pentene. A solution of 1.06 g (5.33 mmol) of 4-(4′-cyanophenyl)-2,4-dimethyl-2-pentene in 150 mL of acetone was irradiated through a Pyrex filter for 7 h. Solvent was removed in vacuo to give 1.08 g of a white solid, which was chromatographed on a 3 × 45 cm silica column. Elution with 1.1 L of 1% ether in hexane gave 1.03 g of material, which was distilled to give 0.988 g (93%) of 3-(4′-cyanophenyl)-1,1,2,2-tetramethylcyclopropane, bp 83–88 °C (0.40 mm), which solidified upon standing, mp 53–57 °C.

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.09–7.05 (m, 2 H, Ar), 6.73–6.69 (m, 2 H, Ar), 1.18 (s, 1 H, cyclopropyl), 1.04 (s, 6 H, CH_3), 0.71 (s, 6 H, CH_3); IR ($CHCl_3$) 3023, 2988, 2942, 2924, 2890, 2872, 2229, 1608, 1505, 1461, 1380, 856 cm^{-1}; MS m/e 199.1356 (calcd for $C_{14}H_{17}N$, m/e 199.1362); UV (MeOH) λ_{max} 248 nm (ϵ 8640).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60. Found: C, 84.39; H, 8.52.

Exploratory Direct Photolysis of 3-(4′-Cyanophenyl)-1,1,2,2-tetramethylcyclopropane (7b) in Methanol. A solution of 90.2 mg (0.453 mmol) of 3-(4′-cyanophenyl)-1,1,2,2-tetramethylcyclopropane in 150 mL of methanol was irradiated through a Vycor filter for 55 min. Solvent was removed in vacuo, giving 94.5 mg of a yellow oil, which was chromatographed on a preparative thick-layer silica gel plate eluted six times with 2% ether in pentane. Bands 1 and 2 (R_f 0.85, 0.80) contained 23.2 mg of a mixture of (*E*)- and (*Z*)-1-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene. Band 3 (R_f 0.75) contained 4-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene (**26b**), which was recrystallized from pentane to give 54.5 mg (60.4%), mp 46–46.5 °C. The remainder of the plate was eluted once with 20% ether in pentane. The band

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immediately above base line (R_f 0.3) contained 4.6 mg (6.9%) of 4-(methoxymethyl)benzonitrile[11b] (**37c**) as an oil. The mixture of (*E*)- and (*Z*)-1-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene was subjected to HPLC.[27] Elution with 2% ether in pentane provided fraction 1 (R_f 13 min), 15.2 mg (16.9%) of (*Z*)-1-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene ((*Z*)-**33c**) as an oil, which solidified upon standing, mp 47–49 °C, and fraction 2, 4.8 mg (5.3%) of (*E*)-1-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene ((*E*)-**33c**) as an oil.

The spectral data for (*Z*)-1-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene ((*Z*)-**33c**) were the following: ^{1}H NMR (benzene-d_6) δ 6.96–6.92 (m, 2 H, Ar), 6.73–6.70 (m, 2 H, Ar), 6.02 (m, 1 H, vinyl), 1.65 (d, J = 1.3 Hz, 3 H, CH_3), 0.82 (s, 9 H, CH_3); an NOE[31] difference measurement with irradiation of the δ 1.65 methyl group led to an ca. 6% increase of the δ 6.02 vinyl signal; IR ($CHCl_3$) 3019, 2967, 2916, 2909, 2871, 2230, 1603, 1363, 1219, 1213, 872 cm^{-1}; MS m/e 199.1361 (calcd for $C_{14}H_{17}N$, m/e 199.1362); UV (MeOH) λ_{max} 236 nm (ε 10 800), sh 256 nm (ε 8150).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60. Found: C, 84.41; H, 8.63.

The spectral data for (*E*)-1-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene ((*E*)-**33c**) were the following: ^{1}H NMR (benzene-d_6) δ 7.05–7.01 (m, 2 H, Ar), 6.76–6.72 (m, 2 H, Ar), 6.12 (m, 1 H, vinyl), 1.51 (d, J = 1.2 Hz, 3 H, CH_3), 0.99 (s, 9 H, CH_3); an NOE[31] difference measurement with irradiation of the δ 0.99 methyl groups led to an ca. 8% increase in the δ 6.12 vinyl signal; IR ($CHCl_3$) 3024, 2967, 2910, 2871, 2229, 1636, 1605, 1502, 1479, 1467, 1363, 874 cm^{-1}; MS m/e 199.1357 (calcd for $C_{14}H_{17}N$, m/e 199.1362); UV (MeOH) λ_{max} 257 nm (ε 8160), 294 (6020).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60. Found: C, 84.44; H, 8.52.

The spectral data for 4-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene (**26b**) were the following: ^{1}H NMR (benzene-d_6) δ 7.05–7.00 (m, 2 H, Ar), 6.62–6.58 (m, 2 H, Ar), 4.71 (m, 1 H, vinyl), 4.50 (m, 1 H, vinyl), 2.26 (s, 2 H, CH_2), 1.59 (d, J = 0.8 Hz, 3 H, CH_3), 0.78 (s, 6 H, CH_3); IR ($CHCl_3$) 3022, 2970, 2935, 2230, 1609, 1454, 1378, 900, 857, 843 cm^{-1}; MS m/e 199.1359 (calcd for $C_{14}H_{17}N$, m/e 199.1362); UV (MeOH) λ_{max} 238 nm (ε 8210), 280 (893), 268 (1230).

Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60. Found: C, 84.22; H, 8.61.

Exploratory Direct Photolysis of 3-(4′-Cyanophenyl)-1,1,2,2-tetramethylcyclopropane (7b) in Pentane. A solution of 20.0 mg of 3-(4′-cyanophenyl)-1,1,2,2-tetramethylcyclopropane (0.100 mmol) in 150 mL of pentane was irradiated through a Vycor filter for 4 min. Solvent was removed in vacuo to give 25.3 mg of an oil, which was shown to be a 1.0:1.5:0.65 mixture of (*E*)- and (*Z*)-1-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene (**33c**), 4-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene (**26b**), and starting material, respectively, by NMR analysis (80% conversion).

(*E*)-1-(4′-Cyanophenyl)-2,3,3-trimethyl-1-butene ((*E*)-33c). To a suspension of 0.295 g (12.30 mmol) of sodium hydride in 30 mL of DME was added a solution of 3.02 g (11.9 mmol) of diethyl [(4-cyanophenyl)methyl]phosphonate[41] in 12 mL of DME. After 0.5 h, 1.15 mL (9.20 mmol) of pinacolone was added and the reaction was stirred for 16 h. Neutral workup[27] provided 1.50 g of a brown oil, which was chromatographed on a 3 × 40 cm silica column eluted with 1.4 L of 1% ether in hexane to give 0.748 g of an oil. Distillation gave 0.743 g (41%) of (*E*)-1-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene as an oil, bp 86–91 °C (0.35 mm), which solidified upon standing, mp 25–26 °C. The spectral data were identical with those found for the material produced from the direct irradiation of 3-(4′-cyanophenyl)-1,1,2,2-tetramethylcyclopropane (**7b**).

4-(4′-Bromophenyl)-3,3-dimethyl-2-butanone (29c). To a suspension of 0.980 g (24.4 mmol) of potassium hydride in 50 mL of THF was slowly added 2.40 mL (22.4 mmol) of 3-methyl-2-butanone. After 0.5 h, a solution of 4.32 g (17.3 mmol) of 4-bromobenzyl bromide in 10 mL of THF was added slowly and the mixture was allowed to stir for 16 h. Neutral workup[27] gave 4.31 g of a yellow oil, which was distilled to give 3.18 g (72%) of 4-(4′-bromophenyl)-3,3-dimethyl-2-butanone, bp 100–110 °C (1.0 mm).

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.25–7.17 (m, 2 H, Ar), 6.70–6.61 (m, 2 H, Ar), 2.44 (s, 2 H, CH_2), 1.68 (s, 3 H, CH_3), 0.78 (s, 6 H, CH_3); IR ($CHCl_3$) 3013, 2970, 2930, 1702, 1489, 1469, 1405, 1366, 1356, 1073, 1013, 831 cm^{-1}; MS m/e 254.0306 (calcd for $C_{12}H_{15}BrO$, m/e 254.0307).

Anal. Calcd for $C_{12}H_{15}BrO$: C, 56.49; H, 5.92. Found: C, 56.86; H, 5.91.

4-(4′-Bromophenyl)-2,3,3-trimethyl-1-butene (26d). To a solution of 18.8 g (46.4 mmol) of methyltriphenylphosphonium iodide in 125 mL of toluene was added 5.21 g (46.4 mmol) of potassium *tert*-butoxide. After 1 h, a solution of 2.37 g (9.28 mmol) of 4-(4′-bromophenyl)-3,3-dimethyl-2-butanone in 10 mL of toluene was added in one portion and the mixture was refluxed for 22 h. Neutral workup[27] followed by chromatography of the crude product on a 3 × 33 cm silica column eluted with 600 mL of hexane gave 1.89 g of a liquid; distillation afforded 1.81 g (77%) of 4-(4′-bromophenyl)-2,3,3-trimethyl-1-butene as a colorless liquid, bp 70–72 °C (0.30 mm).

The spectral data were the following: ^{1}H NMR (benzene-d_6) δ 7.28–7.21 (m, Ar, 2 H), 6.66–6.59 (m, 2 H, Ar), 4.75 (m, 1 H, vinyl), 4.58 (m, 1 H, vinyl), 2.31 (s, 2 H, CH_2), 1.64 (d, J = 1.2 Hz, 3 H, CH_3), 0.85 (s, 6 H, CH_3): IR ($CHCl_3$) 2969, 2935, 2874, 1636, 1488, 1464, 1454, 1377, 1073, 1013, 899, 835 cm^{-1}; MS m/e 252.0519 (calcd for $C_{13}H_{17}Br$, m/e 252.0514).

Anal. Calcd for $C_{13}H_{17}Br$: C, 61.67; H, 6.77. Found: C, 61.94; H, 6.76.

4-(4′-Cyanophenyl)-2,3,3-trimethyl-1-butene (26b). A modification of the methods of Shechter[40a] and Newman[40b] was used. A mixture of 1.73 g (6.82 mmol) of 4-(4′-bromophenyl)-2,3,3-trimethyl-1-butene and 1.35 g (15.1 mmol) of copper(I) cyanide in 30 mL of *N*-methyl-2-pyrrolidone was heated to reflux for 32 h. After cooling slightly, the warm mixture was poured into 50 mL of 5% aqueous sodium cyanide and extracted with ether. Extracts were washed with 5% aqueous sodium cyanide, water, and brine and dried. Removal of solvent in vacuo gave 1.312 g of a brown oil, which was chromatographed on a 3 × 43 cm silica column: fraction 1 (300 mL hexane), nil; fraction 2 (350 mL of hexane), uncharacterized materials; fraction 3 (425 mL of 3% ether in hexane), nil; fraction 4 (500 mL of 3% ether in hexane), 0.953 g of a mixture of the desired product and starting material, which solidified upon standing. Recrystallization from hexane gave 0.597 g (44%) of 4-(4′-cyanophenyl)-2,3,3-trimethyl-1-butene as a colorless solid, mp 46–46.5 °C. The spectral data were identical with those found for the material produced from the direct irradiation of 3-(4′-cyanophenyl)-1,1,2,2-tetramethylcyclopropane (**7b**).

Photolysis Equipment for Quantum Yield Determinations. Quantum yields were performed by using the "Wisconsin Black Box".[42] Light output was measured with a digital actimometer[43] calibrated by ferrioxalate actimometry.[44] The following filter solution combination was used: (a) 2.00 M nickel sulfate in 5% sulfuric acid, (b) 0.8 M cobalt sulfate in 5% sulfuric acid, and (c) 0.0090 M 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate[45] in water; this combination gave a transmission maximum at 248 nm (85% transmission) and was opaque above 272 nm and below 232 nm. All runs were performed in 260 mL of solvent and were analyzed by NMR with triphenylmethane as the internal standard.

Fluorescence Measurements. Fluorescence measurements were determined at 295 K in methanol on an SIM Aminco SLM 8000 spectrometer equipped with a Hanovia 901C-1 150-W Xenon arc lamp. Concentrations of 10^{-4} M were used to minimize scatter. Excitation wavelengths of 265 nm were used and emission was scanned between 290 and 380 nm. Quantum yields of fluorescence relative to biphenyl[23] were determined and the results have been presented in Table I.

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Quantum Mechanics Calculations. Quantum mechanics calculations were performed with the MOPAC package[25a] employing the MNDO[25b] approximation, using configuration interaction of four. The distance between the odd-electron center of interest and the migrating methyl was varied; geometries were otherwise fully optimized. The energies for successive points in Figure 2 are for S_0 76.7, 44.0, 58.8, 80.8, 69.8, 61.9, 60.3, 60.2, 68.0, 82.9, 68.3, 53.8, 17.0, and for S_1 101.7, 104.7, 117.4, 153.6, 138.3, 130.2, 124.9, 125.2, 134.1, 149.5, 124.0, 110.9, and 106.3 kcal/mol.

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Conformationally Restricted Leukotriene Antagonists. Synthesis of Chiral 4-Hydroxy-4-alkylcyclohexanecarboxylic Acids as Leukotriene D_4 Analogues

Robert J. Cregge*

Merrell Dow Research Institute, 9550 Zionsville Road, Indianapolis, Indiana 46268

Nelsen L. Lentz and Jeffrey S. Sabol

Merrell Dow Research Institute, 2110 East Galbraith Road, Cincinnati, Ohio 45215

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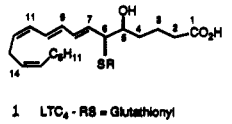
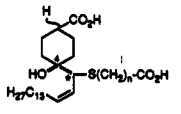
Eight conformationally restricted LTD_4 analogues, **2a–d** (n = 1, 2), were prepared in nine steps from methyl 4-hydroxybenzoate (**3**). The key step in this approach is the Sharpless asymmetric epoxidation of allylic alcohol **8** in which all four possible epoxy alcohol diastereomers **9a–d** were prepared. A single-crystal X-ray analysis of **9b** and application of the Sharpless model for predicting epoxidation stereoselectivity led to the assignment of relative stereochemistry and absolute configuration of **9a–d**. These high optical purity epoxy alcohols were then converted to chiral LTD_4 analogues **2a–d** (n = 1, 2) in three steps.

Introduction

The peptidoleukotrienes, leukotrienes C_4, D_4, and E_4 (**1**), comprise a family of closely related arachidonic acid metabolites which possess most of the biological activity attributed to slow-reacting substance of anaphylaxis (SRS-A). Released upon antigenic stimulation of sensitized human and animal lung tissue, they cause potent bronchoconstriction, increased microvascular permeability and altered mucous production and transport.[1] It is widely



1 LTC_4 - RS = Glutathionyl
LTD_4 - RS = Cysteinylglycinyl
LTE_4 - RS = Cysteinyl

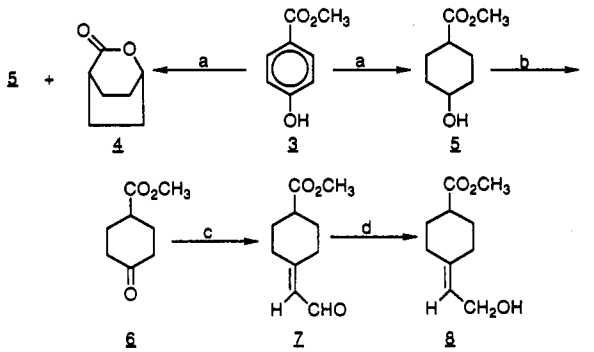


2a-d (n=1,2)

believed that a leukotriene antagonist would provide a new and effective therapy for allergic asthma and other immediate hypersensitivity diseases.

In vitro biological evaluation of synthetic leukotriene analogues has provided some insight into the portions of the molecule critical to receptor affinity. Several conclusions may be made concerning the molecular features characterizing a good leukotriene agonist and hence what factors constitute the critical recognition elements for the leukotriene receptor. The most important functional moieties of the leukotrienes are the peptidyl carboxyl group,[2a] the C-5 hydroxyl group,[2b] and the C-7 olefin.[2c]

Scheme I[a]



[a] Conditions: (a) H_2, 5% Rh/alumina, MeOH, 55 psi, 18 h; (b) PCC, CH_2Cl_2, room temperature; (c) $CH_3CH{=}NC(CH_3)_3$, LDA, -78 °C, $(EtO)_2POCl$, then H_3O^+; (d) $NaBH_4$, MeOH, 0 °C.

The 5(S),6(R) absolute configuration is extremely important,[2d] suggesting that a particular orientation of this region is necessary for binding. Also, the maintenance of lipophilicity in the hydrophobic region (C-13 to C-20) is needed.[2e]

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