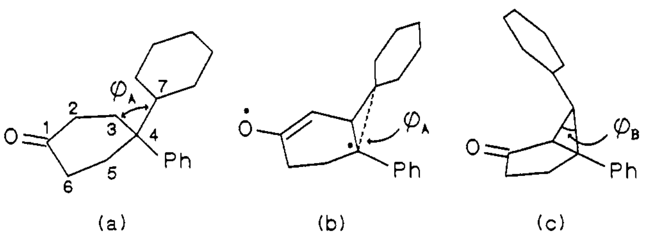

Figure 7. Reaction coordinate definitions for the diphenyl enone system: (a) starting enone; (b) intermediate 1,3-diradical; (c) bicyclic photoproduct.

Table IX. CI State Energies of Twisted Cyclohexenone

	state energies (heat of formation), kcal/mol		
dihedral angle[a]	singlet, S_0	triplet, (π–π^*)	triplet, (n–π^*)
0	−42.6055	3.5293	27.9023
30	−38.3438	−0.5605	34.7012
60	−23.8184	−1.4160	46.1230
90	7.6035	9.8496	65.9316
120	62.6563	48.7656	106.5957

[a] C-1–C-2–C-3–C-4 angle in degrees.

7b). The reaction surface was completed by starting with the optimized product structure (Figure 7c) and then opening the C-2–C-3–C-4 angle (ϕ_B) in 10° increments from 60° to 110°. In order to minimize computation time, the geometries were obtained via ground state optimization using the reaction coordinates mentioned above. The bond lengths, angles, and dihedral angles within the nonmigrating phenyl were fixed to values found in benzene, although the ipso carbon–C-4 bond was optimized and this phenyl ring was allowed to rotate. Single SCF calculations including four-electron configuration interaction were performed on each of these optimized structures to first obtain the energy of the ground state, S_0, and then that of the lowest triplet state, T_1. By inspection of the triplet SCF molecular orbitals and their configuration interaction mixing, this triplet state was found to be an n–π^* state. The state energies are summarized in Table VIII.

In addition, the effect of α–β double bond twisting of the unsubstituted cyclohex-2-enone was also investigated. The C-1–C-2–C-3–C-4 dihedral angle (cyclohexenone numbering) was varied while fully optimizing for both the ground state and lowest triplet state geometries. The state energies for the ground state, S_0, and two lowest triplet states were obtained from these geometries with a six-electron configuration interaction calculation. These are listed in Table IX. Unlike the diphenyl enone case above, the lowest triplet was found to be a π–π^* state. These results are similar to those obtained in a previous calculation.[47]

Acknowledgment. Support of this research by the National Science Foundation and NIH Grant GM07487 is gratefully acknowledged. The synthetic portions were supported by the National Institutes of Health while the mechanistic aspects were supported by NSF.

Registry No. **4**, 4528-64-7; **5**, 118017-43-9; **6**, 118017-44-0; **7**, 118017-45-1; **8**, 118017-46-2; **9**, 42420-87-1; **10**, 42420-91-7; **12a**, 118017-47-3; **12b**, 118100-96-2; **13a**, 118017-48-4; **13b**, 118100-97-3; **14a**, 118017-49-5; **14b**, 118100-98-4; **15a**, 118017-50-8; **15b**, 118100-99-5; **16a**, 118017-51-9; **16b**, 118101-00-1; *endo*-**19** (R = Me), 118070-28-3; *exo′*-**19** (R = Me), 118070-27-2; *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one cyclohexylimine, 118017-42-8; 4-(2-naphthyl)-1-bromobutane, 2657-45-6; 2-(bromomethyl)naphthalene, 939-26-4; *trans*-2,6-diphenylbicyclo[3.1.0]hexan-2-one, 21414-81-3; 4-(chloromethyl)biphenyl, 1667-11-4; 4-(bromomethyl)biphenyl, 2567-29-5; 1-bromopropane, 106-94-5; cyclohexadiene, 29797-09-9.

Supplementary Material Available: Kinetic analysis of bichromophoric naphthylalkyl enones and tables of quantum yield data for **6**, **7**, **8**, and **10** and positional parameters, interatomic distances, bond angles, and anisotropic and isotropic temperature factors for **14b** (10 pages). Ordering information is given on any current masthead page.

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(47) Devaquet, A. *J. Am. Chem. Soc.* **1972**, *94*, 5160–5167.

An Assortment of Highly Unusual Rearrangements in the Photochemistry of Vinylcyclopropanes. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received June 3, 1988*

Abstract: The singlet and triplet photochemistry of 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane and 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane was investigated. In the (diphenylvinyl)cyclopropane case, direct irradiation led via the singlet excited state to three isomers along with Griffin fragmentation products. Interestingly, the three isomers arose from fission to afford the less stable of two alternative allylic diradicals. Two of the isomers arose from unique rearrangements of the allylic diradical wherein the allylic moiety closes 1,3 and C-2 of this group either bonds to a second odd-electron center or abstracts a hydrogen. The third isomer resulted from ring opening and hydrogen transfer. In the case of the (dicyanovinyl)cyclopropane direct irradiation gave rise to a reverse di-π-methane rearrangement involving bicycling of a divalent carbon species along a π-system. Additionally, the hydrogen transfer process observed for the (diphenylvinyl)cyclopropane was again encountered. As in the case of the (diphenylvinyl)cyclopropane, there was a preference for products derived from the less stable of two alternative diradicals. The partition between the reverse di-π-methane rearrangement and the hydrogen transfer process proved solvent dependent with the latter being favored in polar solvents. The triplet of the (dicyanovinyl)cyclopropane again opened to the less stable of two diradicals and this underwent an unprecedented regioselective phenyl migration. Quantum yields were obtained for the reactions of interest.

In the mid-1960's we described several examples[3] of the di-π-methane rearrangement.[4,5] In one of these early studies[3c] secondary photochemistry of the vinylcyclopropane product was encountered. In more recent studies of vinylcyclopropanes having

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(1) This is Paper 155 of our photochemical series and Paper 215 of the general series.

(2) For Paper 154 see Zimmerman, H. E.; Weber, A. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

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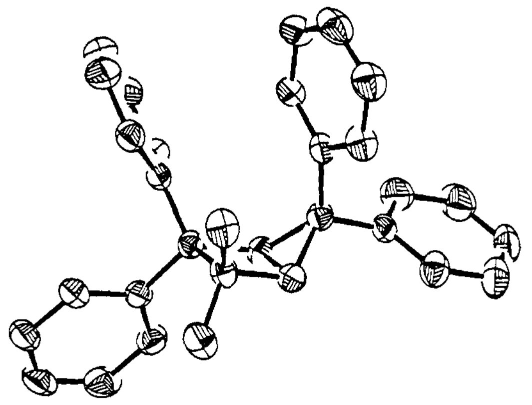


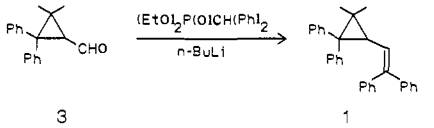
Figure 1. Ortep drawing of housane **6**.

dicyanovinyl[6] and dicarbomethoxyvinyl[7] groups, "bicycling rearrangements" were encountered. Hence it was of considerable interest to investigate further the photochemical behavior of vinylcyclopropanes with and without substitution by electron-withdrawing groups on the vinyl terminus.

For this study we selected two vinylcyclopropanes, 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**1**) and 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (**2**).

Results Section

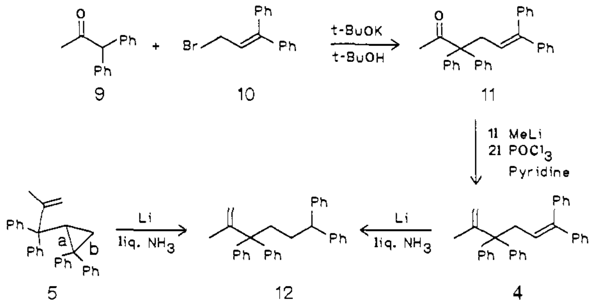
Synthesis of (Diphenylvinyl)cyclopropane I and Its Exploratory Photochemistry. Equation 1 gives the synthesis of this reactant from the known[8] aldehyde **3**.



(1)

Photolysis of (diphenylvinyl)cyclopropane **1** led to three $C_{31}H_{28}$ products, **4**, **5**, and **6**, isomeric with reactant, along with diphenylisobutylene (**7**) and 3-phenylindene (**8**).

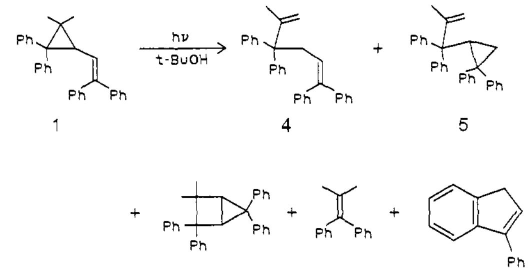
The structures of the three isomeric photoproducts were suggested by their NMR spectra. Two of these assignments (i.e. **4** and **5**) were confirmed by synthesis and degradation as depicted in eq 2. One interesting aspect is the regioselective three-membered ring opening of photoproduct **5** to afford the independently synthesized **12**. A priori, one might conceive of either of two three-membered ring bond fissions (*a* or *b*).[9]



(2)

The structure of photoproduct **6** was determined by X-ray analysis and the Ortep drawing is given in Figure 1.

With this photoproduct structural information in hand, one can depict the photochemical transformation as in eq 3. The product

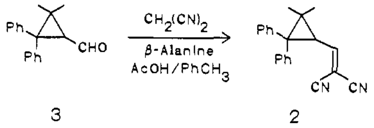


(3)

ratio for **4**:**5**:**6**:**7**:**8** was 13:17:8:13:1.

In contrast to the extensive photochemistry of (diphenylvinyl)cyclopropane **1** on direct irradiation, no reaction occurred on sensitized photolysis with thioxanthone or acetophenone.

Synthesis of (Dicyanovinyl)cyclopropane 2 and Its Exploratory Direct Photochemistry. The desired (dicyanovinyl)cyclopropane **2** was conveniently obtained from the Knoevenagel condensation of aldehyde **3**[8] with malononitrile as depicted in eq 4.



(4)

Irradiation of (dicyanovinyl)cyclopropane **2** in either *tert*-butyl alcohol or benzene led to three photoproducts (**13**, **14**, and **15**), all isomers of the reactant, as shown in eq 5a. The product ratio was 2.2:1:1.

The photochemistry in acetonitrile or methanol proceeded quite differently to afford a single isomeric photoproduct, **13**. This is depicted in eq 5b. Another point of interest is that the formation of **14** and **15** was not reversible.

The structures of these photoproducts were established by independent synthesis as outlined in Scheme I. Three items require comment. First, that the elimination reaction of the hydroxy acetate **18** occurred without rearrangement was confirmed by the product NMR spectrum which revealed (inter alia) an isopropylidene and not a styryl moiety (note the Experimental Section for details). Second, dicyanopentadiene **14** was prepared for comparison purposes.[11] Third, the sequence in Scheme I,

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(3) (a) One early example was that of the barrelene to semibullvalene rearrangement: Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183–184. (b) The mechanism was proposed by: 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) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4191–4193.

(4) (a) For further work on the di-π-methane rearrangement and its mechanism, note ref 4b–k. (b) Zimmerman, H. E.; Gannett, T. P.; Keck, G. E. *J. Org. Chem.* **1979**, *44*, 1982–1989. (c) Zimmerman, H. E.; Robbins, J. D.; McKelvey, R. D.; Samuel, C. J.; Sousa, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 4630–4643. (d) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6267–6272. (e) Zimmerman, H. E.; Baeckstrom, P.; Johnson, T.; Kurtz, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 1459–1465. (f) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6259–6267. (g) Zimmerman, H. E.; Welter, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 4131–4145. (h) Zimmerman, H. E.; Cotter, B. R. *J. Am. Chem. Soc.* **1974**, *96*, 7445–7453. (i) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718–3725. (j) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 8749–8761. (k) Zimmerman, H. E.; Pincock, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2957–2963.

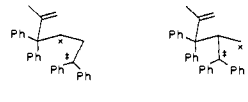
(5) (a) For reviews note ref 5b–d. (b) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. (c) Zimmerman, H. E.; Döpp, D. *Houben-Weyl, Methods of Organic Chemistry*; G. Thieme Verlag, 1975; pp 413–448. (d) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

(6) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383.

(7) Zimmerman, H. E.; Factor, R. E. *Tetrahedron* **1981**, *37*, Supplement I, 125–141.

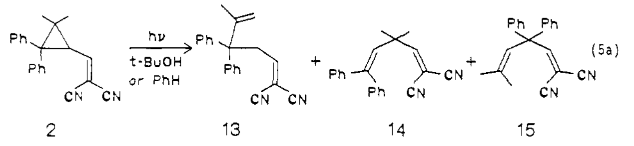
(8) Zimmerman, H. E.; Klun, R. T. *Tetrahedron* **1978**, *43*, 1775–1803.

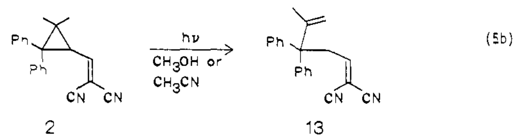
(9) The preference for *a* signifies either a preferential fission of the more substituted bond for relief of strain or a preference for formation of the more substituted odd-electron center in a radical anion phenyl substituted three-ring fission, i.e. A rather than B. This is in accordance with the view expressed by Staley[10] for the regioselectivity of metal-induced, reductive arylcyclopropane ring opening.



Diradical A Diradical B

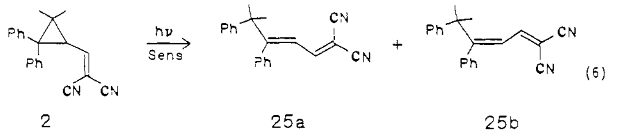
(10) Staley, S. In *Selective Organic Transformations*; Thyagrajan, B. S., Ed.; John Wiley: New York, 1972; pp 309–348.



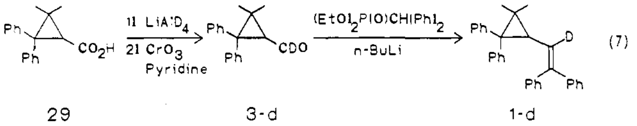


converting diphenyl diol **21** to the doubly unsaturated product **15**, required selective protection of one hydroxyl group, reaction, deprotection, and subsequent reaction of the second.

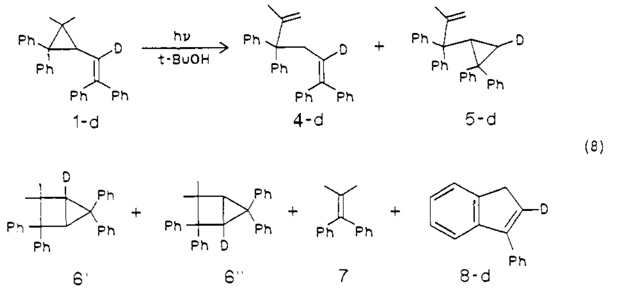
Exploratory Sensitized Photochemistry of (Dicyanovinyl)cyclopropane 2. Sensitization was effected both by acetophenone and thioxanthone, and the unusual photochemistry outlined in eq 6 was observed. It may be seen that the observed photoproducts **25a** and **25b** arise from a rearrangement in which a phenyl group has migrated. The structures of photoproducts were established by synthesis as outlined in Scheme II.



Use of Deuterium Labeling To Differentiate Among Mechanisms. As is discussed below, there are mechanistic alternatives in the photochemistry of (diphenylvinyl)cyclopropane **1** that differ in the skeletal distribution of reactant carbon atoms. A convenient approach for differentiation utilized cyclopropane **1** in which the vinyl hydrogen has been replaced by deuterium as outlined in eq 7.

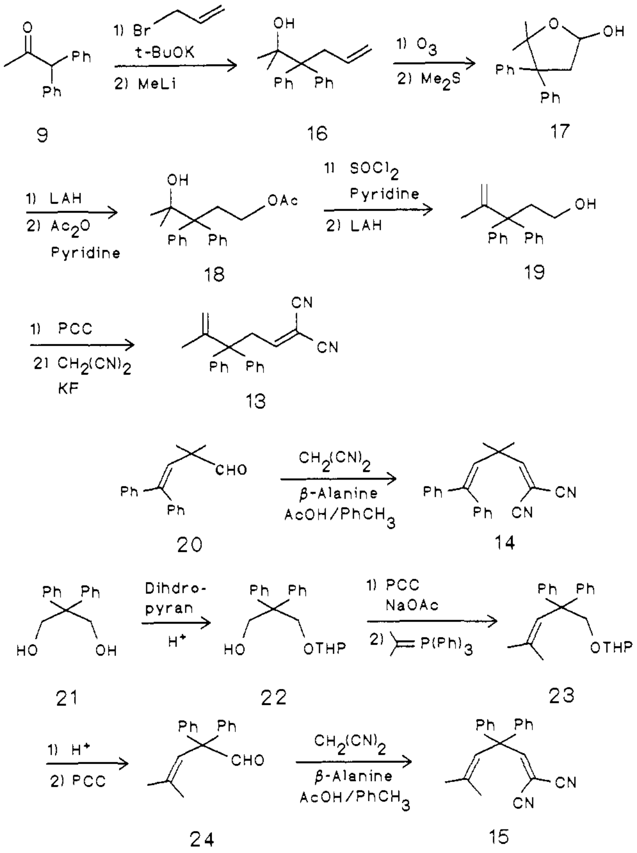


On photolysis of **1**-*d* the usual photoproducts, however labeled, were obtained. The deuterium distribution in the photoproducts is depicted below in eq 8.[12] In differentiating between structures **6′** and **6″**, NOE difference spectra were taken and are described in the Experimental Section. The ratio of regioisomer **6′** to **6″** was 5.6:1.

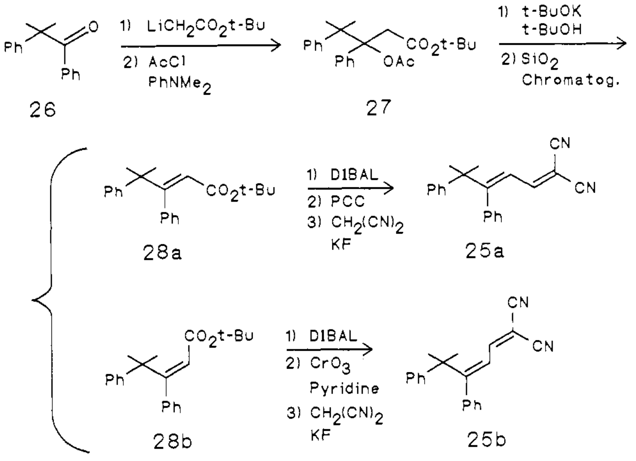


Quantum Yield Determinations. Quantum yields for the direct and sensitized irradiations were carried out with use of the black box and microbench apparatus described by us earlier.[14] Our electronic actinometer[15] was used in conjunction with frequent calibration using the standard ferrioxalate actinometer.[16] These measurements are summarized in Table I. Each determination was made at four different conversions and extrapolated to zero reaction although in most cases there was little dependence on this variable.

Scheme I. Synthesis of Products of Direct Photolysis of Dicyanocyclopropane **2**



Scheme II. Synthesis of the Triplet Photoproducts



Discussion

Mechanisms for (Diphenylvinyl)cyclopropane 1 Direct Irradiation. Structural Aspects. Two of the five photoproducts, diphenylisobutylene (**7**) and 3-phenylindene (**8**), are not unexpected. These may be envisioned as arising from a Griffin fragmentation[17] as in eq 9. 3-Phenylindene (**8**) is a known product of carbene

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(11) (a) Dicyanopentadiene **14** has been reported in a preliminary communication by Pratt;[11b] however, a comparison sample as well as physical properties was needed. (b) Alexander, D. W.; Pratt, A. C.; Rowley, D. H.; Tipping, A. E. *J. Chem. Soc., Chem. Commun.* **1978**, 101–102.

(12) Structure **8**-*d* is written with deuterium at C-2. Runs to shorter conversion indicate that this is the primary product. However, in more extended runs, deuterium is also found at C-1 (note Experimental Section), presumably due to secondary photochemistry and the known[13] skeletal rearrangement of indenes.

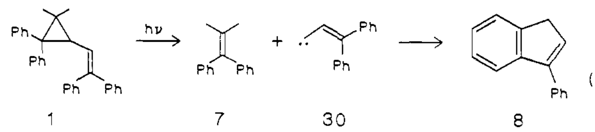
(13) Morrison, H.; Giacherio, D.; Palensky, F. J. *J. Org. Chem.* **1982**, *47*, 1051–1058.

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

(15) Zimmerman, H. E.; Cutler, T. P.; Fitzgerald, V. R.; Weight, T. J. *Mol. Photochem.* **1977**, *8*, 379–385.

(16) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518–536.

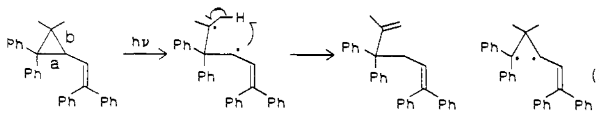
(17) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, 537–547.



1 7 30 8 (9)

30.[18] Due to its instability to silica gel chromatography, 3,3-diphenylcyclopropene (**31**), which is also a known[18] product of this carbene, was not observed.

The formation of photoproduct **4** has extensive precedent.[19] Thus, we may formulate the reaction as involving fission of bond *b* in the singlet excited state of (diphenylvinyl)cyclopropane **1**; note eq 10. The reaction involves intramolecular hydrogen transfer in the 1,3-diradical (i.e. **32**). Despite the precedent, there are two noteworthy facets.

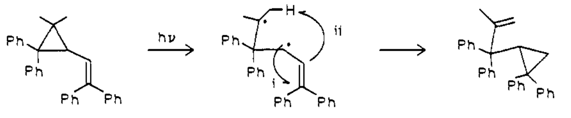


1 32 4 33 (10)

First, we see that diradical **32** is formed by fission of bond *b* rather than *a*. Here we are considering only diradicals resulting from scission of a bond conjugated with the excited diphenylvinyl chromophore. Thus the reaction proceeds via the less stable of two alternative diradicals, **32** and **33**. This preference for diradical **32** is found throughout the remaining photochemistry and is considered again below.

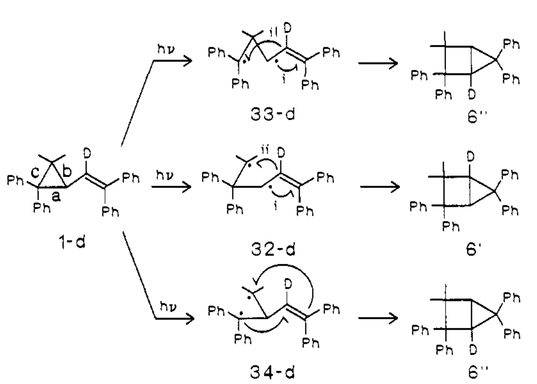
A second point concerns the hydrogen-transfer reaction of eq 10. Although the reaction begins with the excited singlet S_1, internal conversion to S_0 can occur along the reaction coordinate. The reaction proceeds via diradical **32** which, in first-order considerations, has a nonbonding degeneracy. Such a degeneracy predicts facile internal conversion from S_1 to S_0 in the ring opening plus rearrangement process.[20]

The formation of photoproducts **5** and **6** are especially novel. In order to discuss these reactions, it is helpful to consider the reaction using the deuterium-labeled reactant as in eq 8. The simplest version of the mechanisms for these reactions assumes 1,3-diradical **32** being formed first and subsequently reacting as shown in eq 11 and 12. Both reactions have the unique feature



1 32 5 (11)

in common that an allylic radical system closes 1,3 and bonds at the central allylic carbon either with hydrogen to form photoproduct **5** (eq 11) or with a carbon odd-electron center to form photoproduct **6** (eq 12). There are three variations of the mechanism affording photoproduct **6**, and these are given in eq 12a, 12b, and 12c. The mechanism in eq 12b accounts for the major pathway affording regioisomer **6′**, while the mechanisms in eq 12a and 12c lead to the minor regioisomer **6″**. The mechanism in eq 12b involves scission of bond *b*, while the minor mechanisms in eq 12a and 12c involve fission of bond *a* or bond *c*. The former alternative (i.e. eq 12a) proceeds via the more delocalized diradical **33**. Another reason for this preference is that the mechanism is precisely parallel to that in eq 12b which is known to occur.



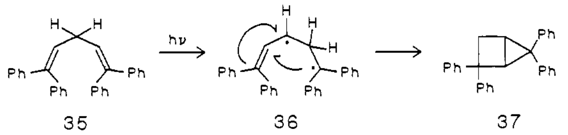
(12a)

(12b)

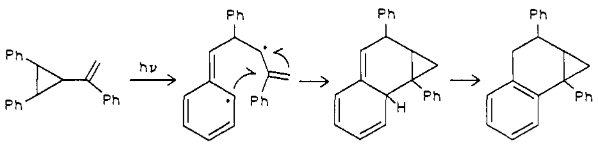
(12c)

Considering further the mechanisms leading to photoproducts **5** and **6**, as outlined in eq 11 and 12, we find each rearrangement to consist of two basic processes, each of which, alone, is mechanistically unusual. The 1,3-closure, even if electronically excited, of an allylic radical to a cyclopropyl radical species is endothermic and unlikely; the arrows corresponding to this process are labeled i in eq 11 and 12. Equally, delivery of a hydrogen atom or an odd-electron bearing carbon to the central carbon of an allylic radical moiety, labelled ii in these equations, is mechanistically unlikely.

However, if the subprocesses corresponding to electron redistributions i and ii occur together, then the mechanisms become acceptable. Nevertheless, there is minimal precedent for mechanisms of this type. One example[21a] is shown in eq 13 and another[21b] in eq 14.[22] Both are seen to involve bonding between terminal carbons of an allylic radical moiety in addition to attack of an odd-electron carbon on the central atom of that allylic system.

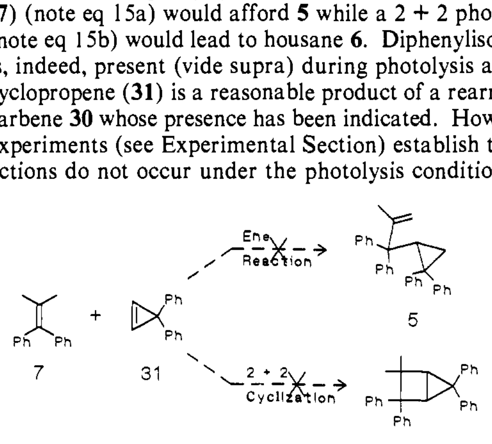


35 36 37 (13)



38 39 40 41 (14)

It needs to be noted that a further possible mechanism exists for formation of isopropenylcyclopropane **5** and housane **6**. An ene reaction of diphenylcyclopropene (**31**) with diphenylisobutylene (**7**) (note eq 15a) would afford **5** while a 2 + 2 photocyclization (note eq 15b) would lead to housane **6**. Diphenylisobutylene (**7**) is, indeed, present (vide supra) during photolysis and diphenylcyclopropene (**31**) is a reasonable product of a rearrangement of carbene **30** whose presence has been indicated. However, control experiments (see Experimental Section) establish that these reactions do not occur under the photolysis conditions.



(15a)

(15b)

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(18) Dürr, H. *Chem. Ber.* **1970**, *103*, 369–379.

(19) (a) For an excellent review see: Hixson, S. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol. 4, Chapter 3. (b) Kristinsson, H.; Griffin, G. W. *Tetrahedron Lett.* **1966**, 3259–3265, report some very early examples. (c) Meinwald, J.; Seeley, D. A. *Tetrahedron Lett.* **1970**, 3739–3742, 3743–3746. (d) Hulrich, L.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1970**, *53*, 1323–1330.

(20) (a) It was originally noted that first-order degeneracies provide a mechanism for radiationless decay.[20b] (b) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1566–1567.

(21) (a) Zimmerman, H. E.; Pincock, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2957–2963. (b) Zimmerman, H. E.; Flechtner, T. W. *J. Am. Chem. Soc.* **1970**, *92*, 7178–7183.

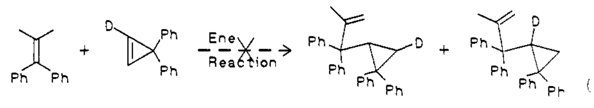
(22) (a) Two examples of bicyclopentane formation that may proceed via similar mechanisms are given in ref 22c,d. (b) Jorgenson, M. J. *J. Am. Chem. Soc.* **1969**, *91*, 6432–6443. (c) Kristinsson, H.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 5970–5971.

Table I. Quantum Yield Results

reactant	additive	solvent	wavelength (nm)	quantum yield[a]	product
(diphenylvinyl)cyclopropane **1**	none	*t*-BuOH	280	0.0053	diene **4**
				0.0073	allyl CP **5**
				0.0034	housane **6**
				0.0055	propene**7**
				0.00042	indene **8**
(diphenylvinyl)cyclopropane **1**	thioxanthone	CH_3CN	366	<0.0008	
(dicyanovinyl)cyclopropane **2**	none	*t*-BuOH	280	0.017	propenyl hexadiene **13**
				0.0076	pentadiene **14**
				0.0079	hexadiene **15**
(dicyanovinyl)cyclopropane **2**	none	CH_3CN	366	0.018	propenyl hexadiene **13**
(dicyanovinyl)cyclopropane **2**	thioxanthone	CH_3CN	366	0.058	*E*-phenyl butadiene **25a**
				0.064	*Z*-phenyl butadiene **25b**

[a] Error of ±10%.

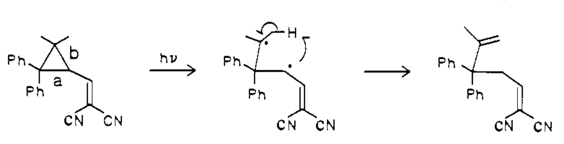
Further convincing evidence against this mechanism in formation of allylcyclopropane **5** is that, in the reaction of the labeled (diphenylvinyl)cyclopropane **1**-*d*, the deuterium would be scrambled as a consequence of the equivalence of the two hydrogens in diphenylcyclopropene (**31**). Note eq 16.



(16)

7 31-d 5-d 5-d'

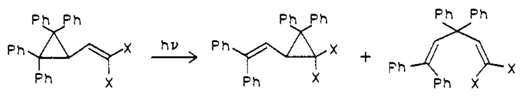
Mechanisms for the Singlet (Dicyanovinyl)cyclopropane Rearrangements. Structural Aspects. The photochemistry of (dicyanovinyl)cyclopropane **2** in eq 5 is seen to afford three products in the less polar solvents employed. Photoproduct **13** clearly arises in a process analogous to that observed for formation of photoproduct **4** in the (diphenylvinyl)cyclopropane reaction. Again, we observe fission of that bond (here *b*) giving rise to the less stabilized diradical **42** of two alternatives. Note eq 17.



(17)

2 42 13

The remaining two photoproducts, **14** and **15**, are considerably less usual. These may be viewed as "reverse di-π-methane rearrangements". There appear to be only two examples of this type.[6,7] Note eq 18.

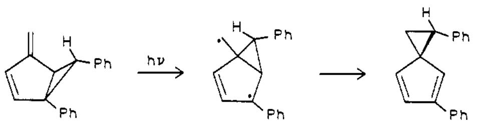


(18)

43 a,b 44 a,b 45 a,b

a X= CN
b X= CO_2CH_3

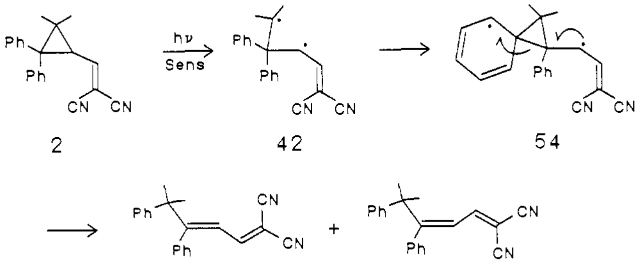
The reaction is also related to the "bicycle rearrangement"[23] in which the out-of-plane three-ring carbon of a bicyclo[*n*.1.0] excited singlet moves along the surface of an *n*-sized ring. The reaction name derives from the fact that one can picture the sp^5 orbitals of this carbenoid carbon of the three-membered ring as bicycle wheels that move stereospecifically along the surface of the π-system of the *n*-ring. Note eq 19.



(19)

46 47 48

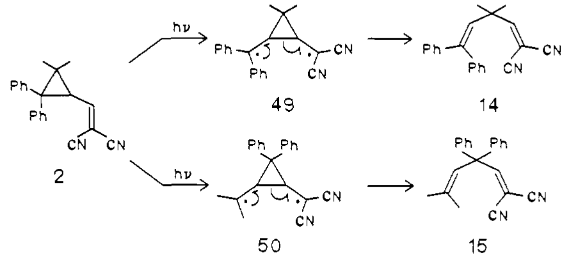
Scheme III. Mechanism for the Sensitized Phenyl Migration Reaction



2 42 54

25a 25b

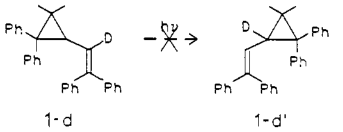
In contrast to the examples of eq 18[6,7] and related cases[24] the present example in eq 20 involves bicycling only to the adjacent bond. In our previous investigations on bicycle rearrangements, it was suggested[7,24b,c] that the S_0 cyclopropyldicarbinyl diradical intermediate species opens to the di-π-methane system, thus precluding further bicycling. In contrast, the S_1 diradicals are able to continue bicycling to more remote bonds. The mechanism for the present photochemistry is depicted in eq 20.



(20)

2 49 14 50 15

Relative to bicycling still another interesting conclusion may be drawn. Thus in the photochemistry of (diphenylvinyl)cyclopropane **1**, one might envisage a degenerate rearrangement in which the isopropylidene group bicycled from one end of a diphenylbutadiene moiety to the other. However, the photolysis of the deuteriated reactant **1**-*d* revealed no scrambling of the deuterium label of the reactant. Note eq 21.



(21)

1-d 1-d'

Mechanism for the Triplet (Dicyanovinyl)cyclopropane Phenyl Migration Reaction. Among the most unique reactions encountered in our study was the phenyl migration reaction that resulted from the sensitized photolysis of (dicyanovinyl)cyclopropane **2**. The mechanism depicted in Scheme III. In view of the sensi-

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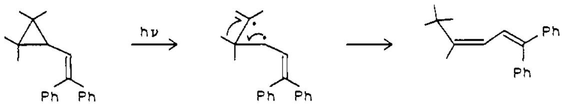
[23] Zimmerman, H. E. *Chimia* **1982**, *32*, 423–428.

[24] (a) Zimmerman, H. E.; Juers, D. F.; McCall, J. M.; Schröder, B. *J. Am. Chem. Soc.* **1971**, *93*, 3662–3674. (b) Zimmerman, H. E.; Cutler, T. P. *J. Org. Chem.* **1978**, *43*, 3283–3303. (c) Zimmerman, H. E.; Factor, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 3538–3548.

tization, the reaction begins with the triplet of reactant (i.e. ^{3}**2***). One estimate for the triplet energy of the dicyanovinyl chromophore is 60 kcal/mol,[6] and this moiety then provides the locus for initial triplet excitation. Three-ring opening to afford diradical **42** follows the general principle that σ bonds conjugated with excited π-moieties are subject to fission. Formation of diradical **42** is followed by interesting regioselectivity in which a central phenyl group migrates to the less delocalized radical center, namely the dimethyl-substituted one.

A further point is that the initially formed triplet diradical **42** may intersystem cross to S_0 either initially, prior to migration, or more likely during the process of migration (e.g. in the phenyl-bridged species **54**).

This reaction is nearly without precedent. One example was reported in which a methyl group undergoes a 1,2-shift in a 1,3-diradical singlet.[4f] Note eq 22. A more recent one involved migration of a *p*-methoxycumenyl moiety, again, in a singlet 1,3-diradical.[25] The literature seems to hold no examples of phenyl migration in an acyclic triplet 1,3-diradical.[26a–f]



51 52 53 (22)

Source of the Regioselectivity of Three-Ring Opening. A final consideration regards the observation of a preference for opening of bond *b* in cyclopropanes **1** and **2** despite the fission of bond *a* leading to a more delocalized diradical. We note that the quantum efficiencies throughout are of the order of 0.1 or less. This suggests that three-ring bond opening is reversible and one of the factors may be a relative dearth of pathways available to the more stable diradical **33**. An additional factor seems likely to be involved. This is seen in Figure 2 which gives a Newman projection diagram of two conformations for (diphenylvinyl)cyclopropane **1** and (dicyanovinyl)cyclopropane **2**. The conformations are those in which the vinyl π-system overlaps[26g,h] with the three-ring banana bonds as the 1,3-diradicals are formed. It is seen that there is more steric interference between the phenyl groups at C-1 of the three-membered ring and the X groups (cyano or phenyl) in conformer I. Thus conformer II leading to the less stabilized of the two alternative diradicals is likely to be responsible for product formation.

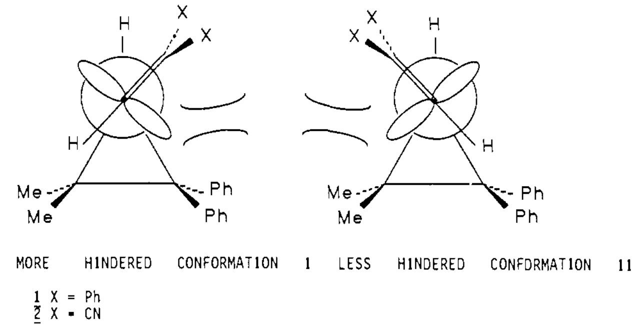


Figure 2.

Conclusion. Despite the intensive study of cyclopropane photochemistry over the decades, it is seen that unusual reactivity is still to be found. The diradical behavior involved is both multifaceted and unusual.

Experimental Section[27–29]

2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (1). To a 0 °C solution of 2.82 g (9.27 mmol) of diethyl diphenylmethylphosphonate[30] in 35.0 mL of DME was added 6.20 mL (9.30 mmol) of 1.5 M *n*-butyllithium in hexane. After the mixture was stirred for 0.5 h, 1.40 g (5.59 mmol) of 3,3-dimethyl-2,2-diphenylcyclopropanecarboxaldehyde[30] in 10.0 mL of DME was added and the mixture was warmed to room temperature and stirred for 1 h. Neutral workup[27] gave 1.76 g of a slightly yellow oil. Recrystallization from ethanol gave 1.36 g (60.7%) of 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane as white needles, mp 135–137 °C (lit.[3c] mp 139–141.5 °C).

Exploratory Direct Photolysis of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (1). A solution of 74.0 mg (0.185 mmol) of 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane in 150 mL of *tert*-butyl alcohol was photolyzed through a Corex filter for 1 h. Concentration in vacuo gave 76.8 mg of a yellow oil that was chromatographed on a 20 × 20 cm preparative thick-layer plate, eluting eight times with 4% benzene in pentane. The most rapidly moving band, band 1, contained 7.1 mg (18.4%) of 2-methyl-1,1-diphenyl-1-propene[31] as a colorless oil. Band 2 contained 1.0 mg (2.8%) of 3-phenylindene as an oil.[32] Band 3 contained 20.3 mg (27.4%) of allylcyclopropane **5** as an oil. Recrystallization from pentane gave 18.9 mg (25.5%) of 2-(2-methyl-1,1-diphenyl-2-propene)-1,1-diphenylcyclopropane as a white solid, mp 138–140 °C. Band 4 gave 14.7 mg (19.9%) of diene **4** as an oil. Recrystallization from ethanol gave 12.3 mg (16.6%) of 5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene as a white solid, mp 106–108 °C. Band 5 gave 10.7 mg (14.5%) of bicyclopentane **6** as an oil. Recrystallization from ethanol gave 8.3 mg (11.2%) of 3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane as a white solid, mp 153–155 °C.

The spectral data for 5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (**4**) were the following: IR (CHCl$_3$) 3060, 3030, 2980, 2940, 2900, 1630, 1590, 1485, 1435, 1070, 1030 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.39–6.82 (m, 10 H, arom), 5.97 (t, 1 H, J = 6.7 Hz, =CH), 5.08 (s, 1 H, =C*H*H), 4.93 (s, 1 H, =CH*H*), 3.13 (d, 2 H, J = 6.7 Hz, CH$_2$), 1.60 (s, 3 H, CH$_3$); UV (95% EtOH) λ_{max} 257 nm (ϵ 15400); MS, m/e 400.2190 (calcd for C$_{31}$H$_{28}$, m/e 400.2191).

Anal. Calcd for C$_{31}$H$_{28}$: C, 92.95; H, 7.05. Found: C, 93.17; H, 7.13.

The spectral data for 2-(2-methyl-1,1-diphenyl-2-propenyl)-1,1-diphenylcyclopropane (**5**) were the following: IR (CHCl$_3$) 3085, 3060, 3020, 3010, 2955, 2930, 2860, 1600, 1495, 1445, 1250 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.32–6.67 (m, 20 H, arom), 5.48 (s, 1 H, =C*H*H), 5.15 (s, 1 H, =CH*H*), 2.99 (dd, 1 H, J = 7.4, 9.5 Hz, cyclopropyl CH), 1.55 (s, 3 H, CH$_3$), 1.40 (dd, 1 H, J = 5.1, 7.4 Hz, cyclopropyl C*H*H), 1.27 (dd, 1 H, J = 5.1, 9.5 Hz, cyclopropyl CH*H*); UV (95% EtOH) λ_{max}

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(25) Zimmerman, H. E.; Kamath, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 900–911.

(26) (a) But note the examples of benzo migration in minor amounts on irradiation and thermolysis of pyrazolines.[26b–f] (b) Adam, W.; Carballeira, N.; De Lucchi, O. *J. Am. Chem. Soc.* **1980**, *102*, 2107–2108. (c) Adam, W.; De Lucchi, O. *J. Am. Chem. Soc.* **1980**, *10*, 2109–2110. (d) Adam, W.; De Lucchi, O. *J. Org. Chem.* **1981**, *46*, 4137–4138. (e) Adam, W.; De Lucchi, O.; Peters, E.; von Schnering, H. G. *J. Am. Chem. Soc.* **1982**, *104*, 5747–5753. (f) Adam, W.; Kron, J.; Rosenthal, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 7074–7081. (g) Overlap effects in vinylcyclopropanes have been discussed: Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 1411–1412. (h) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 3647–3649.

(27) Melting points were determined on 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. 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) 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. Analyses were performed with a 0.6 × 60 cm polished stainless steel column packed with 4–6 μm porous silica beads.[28] Neutral workup refers to quenching the reaction with water, ether extraction, washing the organic layer with water and brine, drying, filtering, and concentration in vacuo. Acidic workup included a 10% aqueous hydrochloric acid wash after ether extraction. Basic workup included a 10% aqueous sodium hydroxide wash after ether extraction. Basic–Acidic workup used sequential base and acid washes after ether extraction. Exploratory photolyses were done with a Hanovia 450-W medium-pressure mercury lump equipped with the appropriate 2-mm filter. All photolyses were purged with purified nitrogen[29] both prior to and during photolysis. Acetonitrile, benzene, and *tert*-butyl alcohol were distilled from calcium hydride. Dichloromethane was purified by distillation from phosphorous 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. Hexane used for HPLC was washed with nitric acid and sulfuric acid (1:1), water, aqueous saturated sodium bicarbonate, and brine, dried over calcium chloride, passed through alumina, and distilled from calcium hydride.

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

(29) Meites, L.; Meites, T. *Anal. Chem.* **1948**, *20*, 984–985.

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

(31) Brodhag, A.; Hauser, C. R. *J. Am. Chem. Soc.* **1955**, *77*, 3024–3031.

(32) Laus, G.; Tourwe, D.; van Binst, G. *Heterocycles* **1984**, *22*, 311–331.

258 (ϵ 1030), 263 (1200), 270 (1100), 277 nm (640); MS, *m/e* 400.2190 (calcd for $C_{31}H_{28}$, *m/e* 400.2191).

Anal. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05. Found: C, 92.58; H, 7.19.

The spectral data for 3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]-pentane (**6**) were the following: IR ($CHCl_3$) 3085, 3060, 3015, 2960, 2925, 2870, 1595, 1580, 1490, 1425 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.48–6.74 (m, 20 H, arom), 3.10 (d, 1 H, J = 6.0 Hz, CH), 2.30 (d, 1 H, J = 6.0 Hz, CH), 1.04 (s, 3 H, CH_3), 0.83 (s, 3 H, CH_3). A NOE difference measurement[33] with irradiation of the methyl group at δ 0.83 led to an ca. 13% increase in the methine signal at δ 2.30. Irradiation of the methyl group at δ 1.04 led to an ca. 3% enhancement of the methine signal at δ 2.30. No enhancement of the methine at δ 3.10 was observed in either experiment. On the basis of these observations the methine at δ 2.30 is assigned as the proton on C-4 of the bicyclopentane and the methine at δ 3.10 is assigned as the proton on C-1 of the bicyclopentane; MS, *m/e* 400.2156 (calcd for $C_{31}H_{28}$, *m/e* 400.2191).

Anal. Calcd for $C_{31}H_{28}$: C, 92.95; H, 7.05. Found: C, 93.22; H, 6.98.

3,3,6,6-Tetraphenyl-5-hexen-2-one (11). To a refluxing solution of 0.285 g (2.54 mmol) of potassium *tert*-butoxide in 125 mL of *tert*-butyl alcohol was added 0.378 g (1.80 mmol) of 1,1-diphenylacetone in one portion. The solution was refluxed for 30 min, 0.500 g (1.83 mmol) of 1-bromo-3,3-diphenyl-2-propene[34] in 15.0 mL of *tert*-butyl alcohol was added to the refluxing solution, and the solution was stirred at 60 °C for 1 h.[35] Removal of solvent in vacuo followed by neutral workup[27] gave 0.560 g of a yellow oil that was crystallized from hexane to give 0.405 g (55.9%) of 3,3,6,6-tetraphenyl-5-hexen-2-one as a white solid, mp 131–133 °C.

The spectral data were the following: IR ($CHCl_3$) 3060, 3040, 3010, 2980, 1700, 1485, 1435, 1350, 1185, 1155, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.38–6.66 (m, 10 H, arom), 5.87 (t, 1 H, J = 7.3 Hz, =CH), 3.14 (d, 2 H, J = 7.3 Hz, CH_2), 2.01 (s, 3 H, CH_3); MS, *m/e* 402.1984 (calcd for $C_{30}H_{26}O$, *m/e* 402.1984).

Anal. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51. Found: C, 89.30; H, 6.56.

2-Methyl-3,3,6,6-tetraphenyl-5-hexen-2-ol. To a solution of 15.0 mL (15.0 mmol) of 1 M methyllithium in ether and 300 mL of benzene was added 3.00 g (7.46 mmol) of 3,3,6,6-tetraphenyl-5-hexen-2-one in 100 mL of benzene. After the mixture was stirred for 1 h at room temperature, acidic workup[27] gave 3.10 g of a colorless foam, which was chromatographed on a 4 × 60 cm silica gel column: fraction 1, 2.0 L of 1% ether in hexane, 0.89 g (30.0%) of the starting ketone; fraction 2, 4.0 L of 2% ether in hexane, 1.59 g of the alcohol as a colorless oil. Recrystallization from methanol/water gave 1.25 g (40.0%) of 2-methyl-3,3,6,6-tetraphenyl-5-hexen-2-ol as a white solid, mp 111–113 °C.

The spectral data were the following: IR ($CHCl_3$) 3540, 3060, 3000, 2980, 2880, 1610, 1500, 1455, 1215, 1120 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.62–6.85 (m, 10 H, arom), 5.86 (t, 1 H, J = 6.7 Hz, =CH), 3.23 (d, 2 H, J = 6.7 Hz, CH_2), 1.92 (s, 1 H, OH), 1.14 (s, 6 H, CH_3); MS, *m/e* 418.2295 (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, 89.08; H, 7.42.

5-Methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (4). To a 0 °C solution of 2.23 g (5.35 mmol) of 2-methyl-3,3,6,6-tetraphenyl-5-hexen-2-ol in 75.0 mL of pyridine was added 36.2 g (236 mmol) of phosphorous oxychloride. The solution was heated to 80 °C for 3.5 h and poured onto ice. Acidic workup[27] gave 1.87 g of an oil that was recrystallized from ethanol to give 1.34 g (62.5%) of 2-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene as a white solid, mp 106–108 °C. The spectral data were identical with those found for the material produced from the photolysis of (diphenylvinyl)cyclopropane **1**.

Lithium–Liquid Ammonia Reduction of 2-(2-Methyl-1,1-diphenyl-2-propenyl)-1,1-diphenylcyclopropane (5). To 20 mL of anhydrous ammonia at −78 °C was added 19 mg (2.7 mmol) of lithium. A solution of 55 mg (0.14 mmol) of 2-(2-methyl-1,1-diphenyl-2-propenyl)-1,1-diphenylcyclopropane in 5.0 mL of THF was then added at −78 °C and the solution was stirred for 20 min. Quenching the reaction with ammonium chloride, evaporation of the ammonia, and neutral workup[27] gave 61 mg of an oil that was chromatographed on a 1 × 60 cm silica gel column: elution with 300 mL of 1% ether in hexane gave 48 mg (85%) of 2-methyl-3,3,6,6-tetraphenyl-1-hexene (**12**) as a colorless oil.

The spectral data were the following: IR (neat) 3075, 3045, 3015, 2940, 2860, 1630, 1600, 1495, 1450, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.31–7.04 (m, 20 H, arom), 4.97 (bs, 2 H, =CH_2), 3.73 (t, 1 H, J = 7.6 Hz, CH), 2.19 (m, 2 H, CH_2), 1.81 (m, 2 H, CH_2), 1.51 (s, 3 H, CH_3); MS, *m/e* 402.2345 (calcd for $C_{31}H_{30}$, *m/e* 402.2348).

Anal. Calcd for $C_{31}H_{30}$: C, 92.49; H, 7.51. Found: C, 92.18; H, 7.88.

2-Methyl-3,3,6,6-tetraphenyl-1-hexene (12). To 20 mL of anhydrous ammonia at −78 °C was added 43 mg (6.2 mmol) of lithium. A solution of 101 mg (0.25 mmol) of 2-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene in 5.0 mL of THF was then added at −78 °C, followed by stirring for 5 min. Quenching with ammonium chloride, evaporation of the ammonia, and neutral workup[27] gave 105 mg of an oil that was chromatographed on a 20 × 20 cm preparative thick-layer plate, eluting three times with 1% ether in pentane. The fastest moving band (R_f 0.7) gave 5.0 mg (84.4%) of 2-methyl-3,3,6,6-tetraphenyl-1-hexene as a colorless oil. The spectral data were identical with those found for the material produced from the lithium–liquid ammonia reduction of allylcyclopropane **5**.

Single-Crystal X-ray Structure of 3,3-Dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (6). Crystals of 3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane were prepared by slow crystallization from methanol. X-ray data were collected with Mo Kα radiation on a Nicolet (Syntex) P-1 diffractometer from a parallelepiped shaped crystal of dimensions 0.90 × 0.20 × 0.35 mm. Unit cell parameters were obtained by least-squares refinement of 25 reflections (17.0° < 2θ < 24.3°). Data were collected in the (hkl) range (−10, −12, 0) to (10, 12, 15) with 3 reflections monitored every 100. A total of 3085 unique data was collected, with 2206 of $F > 3\sigma(F)$. Lorentz and polarization corrections were applied and the structure solved under $P\bar{1}$ symmetry by direct methods with SHELXS86.[36] Hydrogen atoms were located from difference Fourier syntheses and full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Refinement of 404 parameters converged to $R_1(F)$ = 0.064 and $R_w(F)$ = 0.067. Results and structural parameters are available as Supplementary Material.

3-(1,1-Dideuteriomethanol)-2,2-dimethyl-1,1-diphenylcyclopropane. To a suspension of 63.0 mg (1.50 mmol) of lithium aluminum deuteride in 4.0 mL of THF was added 258 mg (0.97 mmol) of 3,3-dimethyl-2,2-diphenyl-1-cyclopropanecarboxylic acid[30] in 4.0 mL of THF. After being stirred for 18 h at room temperature, the solution was refluxed for 1 h, quenched with magnesium sulfate heptahydrate, and filtered. Neutral workup[27] gave 262 mg of an oil that was chromatographed on a 2 × 40 cm silica gel column; elution with 1.5 L of 10% ether in pentane gave 225 mg of the alcohol as an oil which crystallized on standing. Recrystallization from hexane gave 200 mg (81.4%) of 3-(1,1-dideuteriomethanol)-2,2-dimethyl-1,1-diphenylcyclopropane as a white solid, mp 94–95 °C.

The spectral data were the following: IR ($CHCl_3$) 3685, 3620, 3460, 3020, 2975, 2950, 2920, 2435, 2400, 1220 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.42–7.04 (m, 10 H, arom), 1.64 (s, 1 H, CH), 1.35 (s, 1 H, OH), 1.21 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3); MS, *m/e* 254.1645 (calcd for $C_{18}H_{18}D_2O$, *m/e* 254.1640).

3,3-Dimethyl-2,2-diphenylcyclopropanecarboxaldehyde-d_1 (3-d). To a solution of 1.0 mL of pyridine and 10.0 mL of dichloromethane was added 0.566 g (5.66 mmol) of chromium trioxide.[37] The solution was stirred for 30 min, and 0.200 g (0.79 mmol) of 3-(1,1-dideuteriomethanol)-2,2-dimethyl-1,1-diphenylcyclopropane in 2.0 mL of dichloromethane was added. After being stirred for 2 h, the solution was decanted and the residue was washed with ether. Basic–acidic workup[27] of the resulting solution gave 0.204 g of a white solid, mp 120–125 °C. Recrystallization from hexane gave 0.171 g (86.1%) of 3,3-dimethyl-2,2-diphenylcyclopropanecarboxaldehyde-d_1, mp 128–130 °C.

The spectral data were the following: IR ($CHCl_3$) 3025, 3015, 2955, 2925, 2115, 1675, 1495, 1445, 1155, 1025 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.41–7.08 (m, 10 H, arom), 2.29 (s, 1 H, CH), 1.55 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3); MS, *m/e* 251.1418 (calcd for $C_{18}H_{17}DO$, *m/e* 251.1420).

3-(1-Deuterio-2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (1-d). To a 0 °C solution of 0.265 g (0.871 mmol) of diethyl diphenylmethylphosphonate[30] in 5.0 mL of DME was added 1.30 mL (0.87 mmol) of 1.5 M n-butyllithium in hexane. After the mixture was stirred for 0.5 h, 0.159 g (0.633 mmol) of 3,3-dimethyl-2,2-diphenylcyclopropanecarboxaldehyde-d_1 in 3.0 mL of DME was added, and the mixture was warmed to room temperature and stirred for 3 h. Neutral workup[27] gave 0.330 g of a yellow oil that was chromatographed on a 2 × 30 cm silica gel column; elution with 1.5 L of pentane gave 0.186 g

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of the vinylcyclopropane as a colorless oil. Recrystallization from hexane gave 0.166 g (65.1%) of 3-(1-deuterio-2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclopropane as a white solid, mp 135–137 °C.

The spectral data were the following: IR ($CHCl_3$) 3080, 3055, 3020, 2980, 2400, 1600, 1495, 1450, 1220, 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.57–6.96 (m, 20 H, arom), 2.12 (s, 1 H, CH), 1.29 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3); MS, *m/e* 401.2258 (calcd for $C_{31}H_{27}D$, *m/e* 401.2254).

Exploratory Direct Photolysis of 3-(1-Deuterio-2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (1-*d*). A solution of 70.0 mg (0.174 mmol) of 3-(1-deuterio-2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclopropane in 150 mL of *tert*-butyl alcohol was photolyzed through a Corex filter for 1 h. Concentration in vacuo gave 75.1 mg of a yellow oil that was chromatographed on a 20 × 20 cm preparative thick-layer plate, eluting ten times with 4% benzene in pentane. The most rapidly moving band, band 1, contained 7.5 mg (21%) of 2-methyl-1,1-diphenyl-1-propene[34] as a colorless oil. Band 2 contained 1.2 mg (3.5%) of a 1.85:1 mixture of 2-deuterio-3-phenylindene and 1-deuterio-3-phenylindene.[31,13] Band 3 contained 18.3 mg (26.4%) of allylcyclopropane **5**-*d*. Recrystallization from pentane gave 15.0 mg (21.4%) of 3-deuterio-2-(2-methyl-1,1-diphenyl-2-propene)-1,1-diphenylcyclopropane as a white solid, mp 138–141 °C. Band 4 gave 14.0 mg (20.1%) of diene **4**-*d*. Recrystallization from ethanol gave 11.1 mg (15.9%) of 2-deuterio-5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene as a white solid, mp 101–103 °C. Band 5 gave 10.0 mg (14.4%) of a 5.6:1 mixture of 4-deuterio-3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (**6′**) and 1-deuterio-3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (**6″**) as a colorless oil.

The spectral data for 3-deuterio-5-methyl-2-(2-methyl-1,1-diphenyl-2-propene)-1,1-diphenylcyclopropane (**5**-*d*) were the following: IR ($CHCl_3$) 3085, 3060, 3035, 3010, 2955, 2930, 2860, 1600, 1495, 1445 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.36–6.69 (m, 20 H, arom), 5.50 (s, 1 H, =C*H*H), 5.16 (s, 1 H, =CH*H*), 2.99 (d, 1 H, *J* = 9.5 Hz, CH), 1.54 (s, 3 H, CH_3), 1.27 (d, 1 H, *J* = 9.5 Hz, CHD); MS, *m/e* 401.2269 (calcd for $C_{31}H_{27}D$, *m/e* 401.2254).

The spectral data for 2-deuterio-5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (**4**-*d*) were the following: IR ($CHCl_3$) 3060, 3000, 2920, 2840, 2400, 1600, 1490, 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.36–6.86 (m, 20 H, arom), 5.08 (s, 1 H, =C*H*H), 4.93 (s, 1 H, =CH*H*), 3.13 (s, 2 H, CH_2), 1.60 (s, 3 H, CH_3); MS, *m/e* 401.2259 (calcd for $C_{31}H_{27}D$, *m/e* 401.2254).

The spectral data for the mixture of 1- and 4-deuterio-3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (**6″**, **6′**) were the following: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.61–6.70 (m, 20 H, arom), 3.10 (s, 0.85 H, $CH(Ph)_2$), 2.27 (s, 0.15 H, $CH(C(CH_3)_2)$), 1.04 (s, 3 H, CH_3), 0.83 (s, 3 H, CH_3); MS, *m/e* 401.2248 (calcd for $C_{31}H_{27}D$, *m/e* 401.2254).

Irradiation of 3,3-Diphenylcyclopropene (31) and 2-Methyl-3,3-diphenyl-2-propene (7). A solution of 79.0 mg (0.41 mmol) of 3,3-diphenylcyclopropene[38] and 75.0 mg of 2-methyl-3,3-diphenyl-2-propene[31] in 150 mL of *tert*-butyl alcohol was photolyzed through a Corex filter for 1.5 h. Concentration in vacuo gave 0.151 g of an oil that was chromatographed on a 1 × 30 cm basic alumina column: fraction 1, 200 mL of hexane, nil; fraction 2, 50 mL of hexane, 77.0 mg of 2-methyl-3,3-diphenyl-2-propene and a trace of 1,1-diphenylallene; fraction 3, 75 mL of hexane, 69.0 mg of 3,3-diphenylcyclopropene, 3-phenylindene, and 1,1-diphenylallene in a 28:5:1 ratio, respectively.

3-(2,2-Dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (2). A mixture of 2.22 g (8.87 mmol) of 3,3-dimethyl-2,2-diphenylcyclopropanecarboxaldehyde,[30] 0.710 g (10.8 mmol) of malononitrile, 0.246 g (2.76 mmol) of β-alanine, and 4.0 mL of acetic acid in 50 mL of benzene was refluxed for 14 h, with water being azeotropically removed by a Dean-Stark trap. Neutral workup[27] gave 3.69 g of a yellow oil, which was chromatographed on a 3 × 40 cm silica gel column: fraction 1, 1 L of 1% ether in hexane, nil; fraction 2, 1 L of 2% ether in hexane, 2.35 g of the vinylcyclopropane, mp 145–146 °C. Recrystallization from ethanol gave 2.21 g (83.5%) of 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane as a white solid, mp 141–143 °C.

The spectral data were the following: IR ($CHCl_3$) 3020, 2950, 2230, 1590, 1490, 1450, 1170, 1155, 1110, 870 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.45–7.12 (m, 10 H, arom), 6.95 (d, 1 H, *J* = 11.7 Hz, =CH), 2.75 (d, 1 H, *J* = 11.7 Hz, CH), 1.40 (s, 3 H, CH_3), 1 21 (s, 3 H, CH_3); UV (95% EtOH) λ_{max} 227 (ε 17 200), 288 nm (14 300); MS, *m/e* 298.1478 (calcd for $C_{21}H_{18}N_2$, *m/e* 298.1470).

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08. Found: C, 84.21; H, 6.33.

Exploratory Direct Photolysis of 3-(2,2-Dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (2) in *tert*-Butyl Alcohol. A solution of 149 mg (0.50 mmol) of 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane in 150 mL of *tert*-butyl alcohol was photolyzed through a Pyrex filter for 1 h. Concentration in vacuo gave 156 mg of a yellow oil that was chromatographed on a 1 × 130 cm silica gel column eluting with 5% ether in hexane; 44-mL fractions were taken. Fractions 65–80 gave 20 mg (13%) of hexadiene **15** as an oil. Recrystallization from hexane gave 10 mg (6.7%) of 1,1-dicyano-5-methyl-3,3-diphenyl-1,4-hexadiene (**15**) as a white solid, mp 114–116 °C. Fractions 81–93 gave 27 mg (18%) of 1,1-dicyano-5-methyl-3,3-diphenyl-1,4-hexadiene (**13**) as an oil. Fractions 94–119 gave 82 mg (55%) of a 5:1 mixture of the starting vinylcyclopropane and hexadiene **13**. Recrystallization from ethanol gave 51 mg (34%) of the starting vinylcyclopropane as a white solid, mp 141–143 °C. Fractions 120–153 gave 24 mg (16%) of pentadiene **14** as an oil. Recrystallization from hexane gave 14 mg (9.4%) of 1,1-dicyano-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**14**) as fine needles, mp 88–89 °C.

The spectral data for 1,1-dicyano-5-methyl-4,4-diphenyl-1,5-hexadiene (**13**) were the following: IR (neat) 3080, 3040, 2960, 2920, 2230, 1640, 1600, 1495, 1450, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz), δ 7.55–7.20 (m, 10 H, arom), 7.14 (t, 1 H, *J* = 7.1 Hz, $CH{=}C(CN)_2$), 5.18 (s, 1 H, =C*H*H), 4.97 (s, 1 H, =CH*H*), 3.54 (d, 2 H, *J* = 7.1 Hz, CH_2), 1.61 (s, 3 H, CH_3); MS, *m/e* 298.1469 (calcd for $C_{21}H_{18}N_2$, *m/e* 298.1470).

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08. Found: C, 84.39; H, 6.34.

The spectral data for 1,1-dicyano-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**14**) were the following: IR ($CHCl_3$) 3020, 2960, 2230, 1600, 1490, 1460, 1445, 1370, 1230, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.52–7.13 (m, 10 H, arom), 6.81 (s, 1 H, $CH{=}C(CN)_2$), 6.30 (s, 1 H, $CH{=}C(Ph)_2$), 1.48 (s, 6 H, CH_3); UV (95% EtOH) λ_{max} 253 nm (ε 16 900); MS, *m/e* 298.1471 (calcd for $C_{21}H_{18}N_2$, *m/e* 298.1470).

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08. Found: C, 84.75; H, 6.41.

The spectral data for 1,1-dicyano-5-methyl-3,3-diphenyl-1,4-hexadiene (**15**) were the following: IR ($CHCl_3$) 2970, 2930, 2860, 2240, 1595, 1495, 1450, 1390, 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.97 (s, 1 H, $CH{=}C(CN)_2$), 7.40–7.12 (m, 10 H, arom), 6.07 (dd, 1 H, *J* = 1.3, 1.1 Hz, $\mathit{CH}{=}C(CH_3)_2$), 1.90 (d, 3 H, *J* = 1.3 Hz, CH_3), 1.30 (d, 3 H, *J* = 1.1 Hz, CH_3); UV (95% EtOH) λ_{max} 263 nm (ε 4200); MS, *m/e* 298.1471 (calcd for $C_{21}H_{18}N_2$, *m/e* 298.1470).

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08. Found: C, 84.19; H, 6.24.

Exploratory Direct Photolysis of 3-(2,2-Dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (2) in Benzene. A solution of 23.2 mg (0.078 mmol) of 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane in 150 mL of benzene was photolyzed through a Pyrex filter for 1.0 h. Concentration in vacuo gave 25.4 g of a yellow oil that was shown to be a 15:8:1.1:1 mixture of starting material: 1,1-dicyano-5-methyl-4,4-diphenyl-1,5-hexadiene (**13**), 1,1-dicyano-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**14**), and 1,1-dicyano-5-methyl-3,3-diphenyl-1,4-hexadiene (**15**), respectively, by NMR analysis.

Exploratory Direct Photolysis of 3-(2,2-Dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (2) in Acetonitrile. A solution of 46 mg (0.15 mmol) of 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane in 150 mL of acetonitrile was photolyzed through a Pyrex filter for 2.5 h. Concentration in vacuo gave 48 mg of a yellow oil that was chromatographed on a 20 × 20 cm preparative thick-layer plate, eluting twice with 3% ether in pentane. The major band (R_f 0.4) gave 38 mg (83%) of 1,1-dicyano-5-methyl-4,4-diphenyl-1,5-hexadiene (**13**) as a slightly yellow oil.

Exploratory Direct Photolysis of 3-(2,2-Dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (2) in Methanol. A solution of 28 mg (0.094 mmol) of 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane in 150 mL of methanol was photolyzed through a Pyrex filter for 1.0 h. Concentration in vacuo gave 29 mg of a yellow oil that was shown to be a 2:5 mixture of 1,1-dicyano-5-methyl-4,4-diphenyl-1,5-hexadiene (**13**) and starting material by NMR.

Exploratory Sensitized Photolysis of 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (2). A solution of 68.9 mg (0.23 mmol) of 3-(2,2-dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane and 10.0 mL (80.8 mmol) of acetophenone in 150 mL of acetonitrile was photolyzed through a Pyrex filter for 20 min. Concentration in vacuo and removal of the acetophenone (45 °C (0.30 mm Hg)) gave 81.2 mg of a yellow oil that was chromatographed on a 20 × 20 cm preparative thick-layer plate, eluting once with 5% ether in pentane. The top band gave (R_f 0.3) 64.1 mg of a colorless oil, which was a 6.9:1 mixture of the (E) and (Z) hexadienes (**25a**, **25b**) by NMR analysis. Fractional crystallization from hexane gave 33.9 mg (49.2%) of (*E*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene as clear plates, mp 107–109 °C, and 6.1 mg (8.9%) of (*Z*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene as a white solid, mp 153–155 °C.

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The spectral data for (*E*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene (**25a**) were the following: IR ($CHCl_3$) 3080, 3060, 3020, 2970, 2230, 1590, 1495, 1230, 1190 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.50–7.14 (m, 8 H, arom), 7.08 (d, 1 H, J = 11.7 Hz, $CH{=}C(CN)_2$), 6.95 (d, 1 H, J = 11.7 Hz, $CH{=}C(Ph)$), 6.53 (m, 2 H, arom), 1.53 (s, 6 H, CH_3); UV (95% EtOH) λ_{max} 316 nm (ϵ 22300); MS, *m/e* 298.1479 (calcd for $C_{21}H_{18}N_2$, *m/e* 298.1470).

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08. Found: C, 84.23; H, 6.25.

The spectral data for (*Z*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene (**25b**) were the following: IR ($CHCl_3$) 3060, 3040, 3000, 2960, 2220, 1585, 1490, 1460, 1440, 1180 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.48–7.23 (m, 10 H, arom), 7.08 (d, 1 H, J = 12.5 Hz, $CH{=}C(CN)_2$), 6.39 (d, 1 H, J = 12.5 Hz, $CH{=}C(Ph)$), 1.48 (s, 6 H, CH_3); MS, *m/e* 298.1478 (calcd for $C_{21}H_{18}N_2$, *m/e* 298.1470).

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08. Found: C, 84.78; H, 6.28.

2-Methyl-3,3-diphenyl-5-hexen-2-ol (16). To a solution of 46.0 mL (46.0 mmol) of 1 M methyllithium in ether and 200 mL of benzene was added 6.00 g (24.0 mmol) of 3,3-diphenyl-5-hexen-2-one[35] in 30.0 mL of benzene. After the mixture was stirred for 5 h at room temperature, acidic workup[27] gave 5.22 g of an oil, which was chromatographed on a 4 × 65 cm silica gel column: fraction 1, 1.5 mL of 10% ether in hexane, 2.26 g (37.7%) of the starting ketone; fraction 2, 1.0 L of 20% ether in hexane, 3.26 g (51.0%) of 2-methyl-3,3-diphenyl-5-hexen-2-ol as a colorless oil.

The spectral data were the following: IR (neat) 3560, 3460, 3300, 2960, 2860, 1640, 1600, 1500, 1450, 1390, 1375, 1165, 930 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.59–7.15 (m, 10 H, arom), 5.54 (m, 1 H, $=CH$), 5.13 (dd, 1 H, J = 17.2, 1.9 Hz, $=C\mathit{H}$), 4.94 (dd, 1 H, J = 10.0 Hz, 1.9 Hz, $=CH\mathit{H}$), 3.20 (d, 2 H, J = 6.6 Hz, CH_3), 2.17 (s, 1 H, OH), 1.30 (s, 6 H, CH_3); MS, *m/e* 266.1673 (calcd for $C_{19}H_{22}O$, *m/e* 266.1671).

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.80; H, 8.13.

4-Hydroxy-4-methyl-3,3-diphenylpentan-1-al Lactol (17). Into a −78 °C solution of 1.94 g (7.28 mmol) of 2-methyl-3,3-diphenyl-5-hexen-2-ol in 15.0 mL of methanol was bubbled 15.0 mmol of ozone. The reaction mixture was stirred at −78 °C for 15 min and then purged with nitrogen; 6.0 mL of dimethyl sulfide[39] was added at −78 °C and the reaction mixture was warmed to room temperature and stirred for 1 h. The excess dimethyl sulfide was removed by purging the solution with nitrogen. Neutral workup[27] gave 1.83 g of a white solid, mp 114–130 °C. Recrystallization from hexane gave 1.56 g (79.6%) of 4-hydroxy-4-methyl-3,3-diphenylpentan-1-al lactol as a white solid, mp 154–156 °C.

The spectral data were the following: IR ($CHCl_3$) 3580, 3380, 2980, 2920, 1490, 1460, 1440, 1385, 1370, 1080, 1025 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.46–6.95 (m, 10 H, arom), 5.88 (m, 1 H, J = 6.3, 5.0, 3.5 Hz, $C\mathit{H}OH$), 3.69 (d, 1 H, J = 3.5 Hz, OH), 2.95 (m, 2 H, J = 5.0, 6.3, 13.7 Hz, CH_2), 1.36 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3); MS, *m/e* 268.1456 (calcd for $C_{18}H_{20}O_2$, *m/e* 268.1463).

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.43; H, 7.52.

2-Methyl-3,3-diphenylpentan-2,5-diol. To a suspension of 0.228 g (6.01 mmol) of lithium aluminum hydride in 30.0 mL of THF was added 1.56 g (5.81 mmol) of 4-hydroxy-4-methyl-3,3-diphenylpentan-1-al lactol in 20.0 mL of THF. The solution was stirred for 2.5 h, quenched with magnesium sulfate heptahydrate, and filtered. Neutral workup[27] gave 1.42 g of a white foam, which was crystallized from hexane to give 1.37 g (86.9%) of 2-methyl-3,3-diphenylpentan-2,5-diol as a white solid, mp 144–143 °C.

The spectral data were the following: IR ($CHCl_3$) 3600, 3360, 3000, 1500, 1450, 1170, 1040 cm^{-1}; ^1H NMR (acetone-d_6, 200 MHz) δ 7.52–7.10 (m, 10 H, arom), 5.09 (s, 1 H, tertiary OH), 4.27 (t, 1 H, J = 4.8 Hz, $CH_2O\mathit{H}$), 3.19 (m, 2 H, CH_2O), 2.58 (m, 2 H, CH_2), 1.23 (s, 6 H, CH_3); MS, *m/e* (M + 1) 270.1619 (calcd for $C_{18}H_{22}O_2$, *m/e* 270.1620).

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.64; H, 8.05.

1-Acetoxy-4-methyl-3,3-diphenylpentan-4-ol (18). A mixture of 0.94 g (3.48 mmol) of 2-methyl-3,3-diphenylpentan-2,5-diol, 15.0 mL of acetic anhydride, and 30.0 mL of pyridine was stirred at room temperature for 14 h. Neutral workup[27] gave 1.34 g of a yellow oil that was chromatographed on a 2 × 40 cm silica gel column; elution with 1.5 L of 10% ether in hexane gave 1.07 g of an oil. Recrystallization from hexane gave 1.03 g (94.5%) of 1-acetoxy-4-methyl-3,3-diphenylpentan-4-ol as a white solid, mp 104–106 °C.

The spectral data were the following: IR ($CHCl_3$) 3600, 3460, 3000, 1730, 1500, 1390, 1375, 1250, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.61–7.14 (m, 10 H, arom), 3.85 (t, 2 H, J = 7.1 Hz, CH_2O), 2.65 (t, 2 H, J = 7.1 Hz, CH_2), 2.25 (s, 1 H, OH), 1.95 (s, 3 H, CH_3CO), 1.25 (s, 6 H, CH_3); MS, *m/e* 312.1725 (calcd for $C_{20}H_{24}O_3$, *m/e* 312.1725).

Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.88; H, 8.20. Found: C, 77.11; H, 7.92.

1-Acetoxy-4-methyl-3,3-diphenyl-4-pentene. To 0.94 g (3.01 mmol) of 1-acetoxy-4-methyl-3,3-diphenylpentan-4-ol in 50.0 mL of pyridine at 0 °C was added 7.20 g (60.3 mmol) of thionyl chloride. After being stirred 3 h at 0 °C the solution was poured onto ice. Acidic workup[27] gave 0.91 g of a yellow oil that was chromatographed on a 3 × 40 cm silica gel column; elution with 750 mL of 2.5% ether in hexane gave 0.88 g (99.3%) of 1-acetoxy-4-methyl-3,3-diphenyl-4-pentene as a colorless oil.

The spectral data were the following: IR (neat) 3080, 3050, 3020, 2860, 1735, 1490, 1440, 1370, 1240, 1035 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.45–7.16 (m, 10 H, arom), 5.11 (s, 1 H, $=C\mathit{H}H$), 5.07 (s, 1 H, $=CH\mathit{H}$), 3.86 (t, 2 H, J = 7.8 Hz, CH_2OAc), 2.63 (t, 2 H, J = 7.8 Hz, CH_2), 1.93 (s, 3 H, OAc), 1.59 (s, 3 H, CH_3); MS, *m/e* 294.1620 (calcd for $C_{20}H_{22}O_2$, *m/e* 294.1620).

Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.61; H, 7.53. Found: C, 82.01; H, 7.87.

4-Methyl-3,3-diphenyl-4-penten-1-ol (19). To a suspension of 0.164 g (4.32 mmol) of lithium aluminum hydride in 20.0 mL of THF was added 0.885 g (3.01 mmol) of 1-acetoxy-4-methyl-3,3-diphenyl-4-pentene in 20.0 mL of THF. After the mixture was stirred for 6 h at room temperature the reaction was quenched with magnesium sulfate heptahydrate and filtered. Neutral workup[27] gave 0.740 g (97.3%) of 4-methyl-3,3-diphenyl-4-penten-1-ol as a colorless oil.

The spectral data were the following: IR ($CHCl_3$) 3320, 3080, 3050, 3020, 2960, 2890, 1640, 1600, 1490, 1450, 1380, 1035, 910 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.43–7.20 (m, 10 H, arom), 5.07 (s, 2 H, $=CH_2$), 3.46 (t, 2 H, J = 7.4 Hz, CH_2O), 2.59 (t, 2 H, J = 7.4 Hz, CH_2), 1.65 (s, 3 H, CH_3); MS, *m/e* 252.1513 (calcd for $C_{18}H_{20}O$, *m/e* 252.1514).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.94; H, 8.14.

4-Methyl-3,3-diphenyl-4-penten-1-al. To a suspension of 0.294 g (1.36 mmol) of pyridinium chlorochromate[40] in 1.0 mL of dichloromethane was added 0.199 g of 4-methyl-3,3-diphenyl-4-penten-1-ol in 1.0 mL of dichloromethane. The solution was stirred for 2 h, diluted with ether, and filtered through Florisil. The filtrate was concentrated in vacuo to give 0.178 g (89.9%) of 4-methyl-3,3-diphenyl-4-penten-1-al as a colorless oil.

The spectral data were the following: IR (neat) 3040, 3020, 2960, 2920, 2840, 2740, 1710, 1635, 1595, 1440, 1030, 900 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 9.45 (t, 1 H, J = 2.5 Hz, CHO), 7.37–7.15 (m, 10 H, arom), 5.16 (d, 1 H, $=C\mathit{H}H$), 4.90 (s, 1 H, $=CH\mathit{H}$), 3.27 (d, 2 H, J = 2.5 Hz, CH_2), 1.66 (s, 3 H, CH_3); MS, *m/e* 250.1351 (calcd for $C_{18}H_{18}O$, *m/e* 250.1358).

1,1-Dicyano-5-methyl-4,4-diphenyl-1,5-hexadiene (13). A mixture of 95.0 mg (0.38 mmol) of 4-methyl-3,3-diphenyl-4-penten-1-al, 89.0 mg (1.35 mmol) of malononitrile, and 125 mg (1.33 mmol) of potassium fluoride dihydrate in 1.0 mL of *N*,*N*-dimethylformamide and 1.0 mL of ethylene glycol was stirred for 3 h.[41] Neutral workup[27] gave 85.0 mg of a yellow oil that was chromatographed on a 20 × 20 cm preparative thick-layer plate and eluted once with 10% ether in pentane. The major band (R_f 0.4) gave 56.0 mg (49.4%) of the 1,1-dicyano-5-methyl-4,4-diphenyl-1,5-hexadiene as a slightly yellow oil. The spectral data were identical with those found for the material produced from the direct photolysis of (dicyanovinyl)cyclopropane **2**.

1,1-Dicyano-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (14). A mixture of 3.13 g (12.51 mmol) of 3,3-dimethyl-5,5-diphenyl-butan-1-al,[4f] 0.865 g (13.09 mmol) of malononitrile, 0.351 g (3.94 mmol) of β-alanine, and 6.0 mL of acetic acid in 100 mL of toluene was refluxed for 8 h, with water being azeotropically removed by a Dean-Stark trap. Neutral workup[27] gave 4.05 g of a yellow oil. Recrystallization from hexane gave 1.77 g (47.6%) of 1,1-dicyano-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene[11b] as fine needles, mp 88–89 °C. The spectral data were identical with those found for the material produced from the direct photolysis of (dicyanovinyl)cyclopropane **2**.

1-(Tetrahydropyranyloxy)-3-hydroxy-2,2-diphenylpropane (22). A mixture of 4.00 g (17.5 mmol) of 2,2-diphenylpropan-1,3-diol,[42] 0.438 g (1.74 mmol) of pyridinium *p*-toluenesulfonate, and 1.61 g (19.2 mmol) of 3,4-dihydro-2*H*-pyran in 75.0 mL of dichloromethane was stirred for

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18 h at room temperature.[43] Neutral workup[27] gave 5.58 g of a colorless oil that was chromatographed on a 3 × 50 cm silica gel column: fraction 1, 2 L of 5% ether in hexane, 1.34 g (19.3%) of the bis-THP ether; fraction 2, 3 L of 10% ether in hexane, 3.25 g (59.4%) of 1-(tetrahydropyranyloxy)-3-hydroxy-2,2-diphenylpropane as a colorless oil; fraction 3, 2 L 10% ether in hexane, 0.26 g (6.5%) of the starting diol. Fraction 1 was recrystallized from hexane to give 1.14 g (16.4%) of 1,3-bis(tetrahydropyranyloxy)-2,2-diphenylpropane as a white solid, mp 84–86 °C.

The spectral data for 1-(tetrahydropyranyloxy)-3-hydroxy-2,2-diphenylpropane (**22**) were as follows: IR (neat) 3440, 3060, 3020, 3000, 2900, 2840, 1600, 1490, 1450, 1130, 1070, 1025 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.38–7.11 (m, 10 H, arom), 4.58 (m, 1 H, OCHO), 4.34 (d, 1 H, J = 9.8 Hz, (Ph)$_2$CC*H*H), 4.30 (m, 2 H, CH$_2$OH), 4.16 (d, 1 H, J = 9.8 Hz, (Ph)$_2$CCH*H*), 3.71 (m, 1 H, C*H*HO), 3.44 (m, 1 H, CH*H*O), 3.06 (t, 1 H, J = 6.7 Hz, OH), 1.80–1.35 (m, 6 H, CH$_2$); MS, *m/e* 312.1698 (calcd for $C_{20}H_{24}O_3$, *m/e* 312.1725).

Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.83; H, 7.74. Found: C, 76.44; H, 7.74.

The spectral data for 1,3-bis(tetrahydropyranyloxy)-2,2-diphenylpropane were the following: IR (CHCl$_3$) 3000, 2940, 2870, 1150, 1140, 1130, 1080, 1070, 1039 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.33–7.13 (m, 10 H, arom), 4.60 (dd, 1 H, J = 2.5, 3.0 Hz, OCHO), 4.56 (dd, 1 H, J = 2.7, 3.1 Hz, OCHO), 4.41 (d, 1 H, J = 9.7 Hz, (Ph)$_2$CCHH), 4.39 (d, 1 H, J = 9.6 Hz, (Ph)$_2$CCHH), 3.97 (d, 1 H, J = 9.7 Hz, (Ph)$_2$CCHH), 3.93 (d, 1 H, J = 9.7 Hz, (Ph)$_2$CCHH), 3.69–3.33 (m, 4 H, CHHO), 1.81–1.36 (m, 12 H, CH$_2$); MS, *m/e* 396.2298 (calcd for $C_{25}H_{32}O_4$, *m/e* 306.2300).

Anal. Calcd for $C_{25}H_{32}O_4$: C, 75.73; H, 8.13. Found: C, 75.46; H, 7.96.

3-(Tetrahydropyranyloxy)-2,2-diphenylpropan-1-al. To a suspension of 1.07 g (4.96 mmol) of pyridinium chlorochromate[40] and 0.088 g (1.07 mmol) of sodium acetate in 7.0 mL of dichloromethane was added 1.04 g (3.33 mmol) of 1-(tetrahydropyranyloxy)-3-hydroxy-2,2-diphenylpropane in 3.0 mL of dichloromethane. The solution was stirred for 14 h, diluted with ether, and filtered through Florisil. The filtrate was concentrated in vacuo to give 0.842 g (81.5%) of 3-(tetrahydropyranyloxy)-2,2-diphenylpropan-1-al as a colorless oil.

The spectral data were the following: IR (CHCl$_3$) 3020, 3000, 2940, 2860, 2720, 1725, 1490, 1450, 1070, 1030, 1020 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 9.91 (s, 1 H, CHO), 7.39–7.14 (m, 10 H, arom), 4.59 (s, 1 H, OCHO), 4.53 (d, 1 H, J = 9.9 Hz, (Ph)$_2$CC*H*H), 4.17 (d, 1 H, J = 9.9 Hz, (Ph)$_2$CCH*H*), 3.42 (bs, 2 H, CH$_2$O), 1.78–1.32 (m, 6 H, CH$_2$); MS, *m/e* 310.1573 (calcd for $C_{20}H_{23}O_3$, *m/e* 310.1569).

1-(Tetrahydropyranyloxy)-5-methyl-2,2-diphenyl-3-pentene (23). To a solution of 4.64 g (10.73 mmol) of isopropyltriphenylphosphonium iodide in 12.0 mL of toluene was added 15.75 mL (10.50 mmol) of 1.5 M *n*-butyllithium in hexane. After the solution was stirred for 45 min, 3.01 g (9.70 mmol) of 3-(tetrahydropyranyloxy)-2,2-diphenylpropan-1-al in 10.0 mL of toluene was added, and the mixture was stirred for 3 h and quenched with saturated aqueous ammonium chloride. Neutral workup[27] gave 3.66 g of a yellow oil that was chromatographed on a 4 × 50 cm silica gel column: elution with 600 m of 5% ether in hexane gave 1.50 g (46.0%) of 1-(tetrahydropyranyloxy)-5-methyl-2,2-diphenyl-3-pentene as a colorless oil.

The spectral data were the following: IR (CHCl$_3$) 3080, 3025, 3010, 2920, 2860, 1660, 1445, 1125, 1070, 1035 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.65–7.13 (m, 10 H, arom), 5.90 (dd, 1 H, J = 1.1, 1.2 Hz, =CH), 4.51 (bs, 1 H, OCHO), 4.31 (d, 1 H, J = 9.9 Hz, (Ph)$_2$CC*H*H), 3.84 (d, 1 H, J = 9.9 Hz, (Ph)$_2$CCH*H*), 3.60 (m, 1 H, OC*H*H), 3.41 (m, 1 H, OCH*H*), 1.80 (d, 3 H, J = 1.2 Hz, CH$_3$), 1.55 (m, 6 H, CH$_3$), 1.14 (d, 3 H, J = 1.1 Hz, CH$_3$); MS, *m/e* (M + 1) 377.2160 (calcd for $C_{23}H_{29}O_2$, *m/e* 337.2167).

Anal. Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.21; H, 8.29.

5-Methyl-2,2-diphenyl-3-penten-1-ol. A mixture of 1.50 g (4.46 mmol) of 1-(tetrahydropyranyloxy)-5-methyl-2,2-diphenyl-3-pentene and 0.254 g (1.01 mmol) of pyridinium *p*-toluenesulfonate in 12.0 mL of ethanol was stirred at 60 °C for 18 h.[43] Neutral workup[27] gave 1.11 g of an oil that was chromatographed on a 3 × 40 cm silica gel column: fraction 1, 500 mL of hexane, 0.090 g (6.0%) of the starting material; fraction 2, 600 mL of 5% ether in hexane gave 0.921 g (81.8%) of 5-methyl-2,2-diphenyl-3-penten-1-ol as a colorless oil.

The spectral data were the following: IR (neat) 3420, 3050, 3020, 2960, 2920, 2870, 1600, 1490, 1450, 1060 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.41–7.18 (m, 10 H, arom), 5.86 (dd, 1 H, J = 1.2, 1.3 Hz, =CH), 4.12 (d, 2 H, J = 6.9 Hz, CH$_2$), 1.82 (d, 3 H, J = 1.2 Hz, CH$_3$), 1.54 (t, 1 H, J = 6.9 Hz, OH), 1.13 (d, 3 H, J = 1.3 Hz, CH$_3$); MS, *m/e* 252.1499 (calcd for $C_{18}H_{20}O$, *m/e* 252.1514).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.38; H, 7.90.

5-Methyl-2,2-diphenyl-3-penten-1-al (24). To a suspension of 0.403 g (1.60 mmol) of pyridinium chlorochromate[40] in 2.0 mL of dichloromethane was added 0.173 g (0.69 mmol) of 5-methyl-2,2-diphenyl-3-penten-1-ol in 2.0 mL of dichloromethane. The solution was stirred for 2 h, diluted with ether, and filtered through Florisil. The filtrate was concentrated in vacuo to give 0.154 g (89.9%) of 5-methyl-2,2-diphenyl-3-penten-1-al as a colorless oil.

The spectral data were the following: IR (neat) 3040, 3010, 2950, 2900, 2880, 2830, 2710, 1715, 1655, 1590, 1275 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 9.76 (s, 1 H, CHO), 7.62–7.11 (m, 10 H, arom), 5.88 (dd, 1 H, J = 0.8, 1.1 Hz, =CH), 1.88 (d, 3 H, J = 1.1 Hz, CH$_3$), 1.29 (d, J = 0.8 Hz, CH$_3$); MS, *m/e* 250.1355 (calcd for $C_{18}H_{18}O$, *m/e* 250.1358).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.04; H, 7.49.

1,1-Dicyano-5-methyl-3,3-diphenyl-1,4-hexadiene (15). A mixture of 0.773 g (3.09 mmol) of 5-methyl-2,2-diphenyl-3-penten-1-al, 0.225 g (3.41 mmol) of malononitrile, 0.102 g (1.14 mmol) of β-alanine, and 1.5 mL of acetic acid in 50 mL of toluene was refluxed for 5 h, with water being azeotropically removed by a Dean-Stark trap. Neutral workup[27] gave 0.798 g of a red oil, which was chromatographed on a 3 × 40 cm silica gel column: fraction 1, 1 L of 1% ether in hexane, nil; fraction 2, 1 L of 1% ether in hexane, 0.402 g of the diene as an oil. Recrystallization from hexane gave 0.366 g (47.3%) of 1,1-dicyano-5-methyl-3,3-diphenyl-1,4-hexadiene as a white solid, mp 114–116 °C. The spectral data were identical with those found for the material produced from the direct photolysis of (dicyanovinyl)cyclopropane **2**.

***tert*-Butyl 3-Hydroxy-4-methyl-3,4-diphenylpentanoate.** To a solution of 13.9 mmol of lithium diisopropyl amide, prepared by the addition of 9.30 mL (14.0 mmol) of 1.5 M *n*-butyllithium in hexane to 2.10 mL (15.0 mmol) of diisopropylamine in 30 mL of ether at −78 °C, a solution of 1.90 mL (14.1 mmol) of *tert*-butyl acetate in 10 mL of ether was added. The solution was stirred at −78 °C for 1 h and allowed to warm to room temperature. A solution of 2.08 g (9.27 mmol) of 2-methyl-1,2-diphenyl-1-propanone[31] in 10 mL of ether was added dropwise, and the solution was stirred for 1 h. Acidic workup[27] gave 3.62 g of a yellow oil, which was chromatographed on a 3 × 45 cm silica gel column; elution with 2 L of 1% ether in hexane gave 2.74 g of the alcohol as an oil. Recrystallization from cold hexane gave 1.96 g (62.0%) of *tert*-butyl 3-hydroxy-4-methyl-3,4-diphenylpentanoate as a white solid, mp 58–60 °C.

The spectral data were the following: IR (neat) 3540, 3460, 3080, 2960, 2920, 2880, 1735, 1705, 1395, 1370, 1150 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.37–7.12 (m, 10 H, arom), 4.44 (s, 1 H, OH), 3.09 (d, 1 H, J = 15.4 Hz, C*H*H), 2.48 (d, 1 H, J = 15.4 Hz, CH*H*), 1.38 (s, 3 H, CH$_3$), 1.31 (s, 3 H, CH$_3$), 1.10 (s, 9 H, C(CH$_3$)$_3$); MS, *m/e* (M + 1) 341.2113 (calcd for $C_{22}H_{29}O_3$, *m/e* 341.2117).

Anal. Calcd for $C_{22}H_{29}O_3$: C, 77.61; H, 8.29. Found: C, 77.55; H, 8.26.

***tert*-Butyl 3-Acetoxy-4-methyl-3,4-diphenylpentanoate (27).** A solution of 2.08 g (6.11 mmol) of *tert*-butyl 3-hydroxy-4-methyl-3,4-diphenylpentanoate, 40.0 mL of *N*,*N*-dimethylaniline, and 9.0 mL (0.13 mmol) of acetyl chloride in 30 mL of chloroform was refluxed for 2 days.[44] Acidic workup[27] of the blue solution gave 2.23 g of the acetate as a yellow oil, which was chromatographed on a 3 × 45 cm column: elution with 3 L of 2% ether in hexane gave 1.76 g (75.3%) of *tert*-butyl 3-acetoxy-4-methyl-3,4-diphenylpentanoate as a colorless oil.

The spectral data were the following: IR (CHCl$_3$) 3080, 2970, 2930, 1730, 1450, 1390, 1370, 1250, 1150, 1045, 1030 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.22 (m, 8 H, arom), 6.66 (m, 2 H, arom), 3.57 (d, 1 H, J = 15.8 Hz, C*H*H), 3.45 (d, 1 H, J = 15.8 Hz, C*H*H), 2.18 (s, 3 H, OAc), 1.47 (s, 3 H, CH$_3$), 1.45 (s, 3 H, CH$_3$), 1.40 (s, 9 H, C(CH$_3$)$_3$); MS, *m/e* (M + 1) 383.2236 (calcd for $C_{24}H_{31}O_4$, 383.2222).

Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.53; H, 8.05.

***tert*-Butyl (*Z*)- and (*E*)-4-Methyl-3,4-diphenyl-2-pentenoate.** A solution of 0.377 g (3.36 mmol) of potassium *tert*-butoxide in 8.0 mL of *tert*-butyl alcohol was added dropwise to a refluxing solution of 1.18 g (3.08 mmol) of *tert*-butyl 3-acetoxy-4-methyl-3,4-diphenylpentanoate in 20.0 mL of *tert*-butyl alcohol and the solution was refluxed for 0.5 h. Acidic workup[27] gave 0.864 g of a yellow oil, which was chromatographed on a 3 × 80 cm silica gel column: fraction 1, 2.0 L of 1% ether in pentane, 0.051 g (5.2%) of *tert*-butyl (*Z*)-4-methyl-3,4-diphenyl-2-pentenoate as a colorless oil; fraction 2, 2.0 L of 3% ether in pentane, 0.708

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g of the *E* isomer. Recrystallization from hexane gave 0.540 g (71.4%) of *tert*-butyl (*E*)-4-methyl-3,4-diphenyl-2-pentenoate as a white solid, mp 57–59 °C.

The spectral data for *tert*-butyl (*E*)-4-methyl-3,4-diphenyl-2-pentenoate (**28a**) were the following: IR (neat) 3040, 3020, 2970, 2930, 2870, 1720, 1690, 1370, 1320, 1240, 1150 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.34–7.05 (m, 8 H, arom), 6.59 (m, 2 H, arom), 6.02 (s, 1 H, =CH), 1.45 (s, 6 H, CH$_3$), 1.12 (s, 9 H, C(CH$_3$)$_3$); MS, *m/e* 322.1941 (calcd for $C_{22}H_{26}O_2$, *m/e* 322.1933).

Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 82.06; H, 7.98.

The spectral data for *tert*-butyl (*Z*)-4-methyl-3,4-diphenyl-2-pentenoate (**28b**) were the following: IR (neat) 3040, 3010, 2960, 2920, 1720, 1490, 1360, 1270, 1150, 770 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.54–7.06 (m, 10 H, arom), 5.63 (s, 1 H, =CH), 1.48 (s, 6 H, CH$_3$), 1.24 (s, 9 H, C(CH$_3$)$_3$); MS, *m/e* 322.1954 (calcd for $C_{22}H_{26}O_2$, *m/e* 322.1933).

Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 82.26; H, 8.28.

(*E*)-4-Methyl-3,4-diphenyl-2-penten-1-ol. To a −78 °C solution of 0.565 g (1.75 mmol) of *tert*-butyl (*E*)-4-methyl-3,4-diphenyl-2-pentenoate in 20.0 mL of toluene was added 7.0 mL (7.0 mmol) of 1.0 M diisobutyl aluminum hydride in hexane. The solution was stirred for 1 h at −78 °C and for 1 h at room temperature and was then quenched with saturated ammonium chloride. Acidic workup[27] gave 0.451 g of a yellow oil, which was chromatographed on a 2 × 40 cm silica gel column; elution with 2.5 L of 10% ether in pentane gave 0.427 g of the alcohol. Recrystallization from hexane gave 0.351 g (79.4%) of (*E*)-4-methyl-3,4-diphenyl-2-penten-1-ol as a white solid, mp 64–65 °C.

The spectral data were the following: IR (CHCl$_3$) 3600, 3400, 3040, 2980, 2950, 2850, 1590, 1220, 1030, 1010 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.42–6.95 (m, 8 H, arom), 6.59 (m, 2 H, arom), 5.91 (t, 1 H, J = 6.6 Hz, =CH), 3.84 (d, 2 H, J = 6.6 Hz, CH$_2$), 1.44 (s, 6 H, CH$_3$). A NOE difference measurement[33] with irradiation of the δ 1.44 methyl groups led to an ca. 25% increase in the δ 5.91 vinyl signal; MS, *m/e* 252.1506 (calcd for $C_{18}H_{20}O$, *m/e* 252.1514).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.58; H, 8.02.

(*Z*)-4-Methyl-3,4-diphenyl-2-penten-1-ol. To a −78 °C solution of 60.0 mg (0.19 mmol) of *tert*-butyl (*Z*)-4-methyl-3,4-diphenyl-2-pentenoate in 3.0 mL of toluene was added 1.0 mL (1.0 mmol) of 1.0 M diisobutyl aluminum hydride in hexane. The solution was stirred for 1 h at −78 °C and for 1 h at 25 °C and was then quenched with saturated ammonium chloride. Acidic workup[27] gave 50.0 mg of a colorless oil, which was crystallized from hexane to give 37.5 mg (78.9%) of (*Z*)-4-methyl-3,4-diphenyl-2-penten-1-ol as a white solid, mp 69–71 °C.

The spectral data were the following: IR (CHCl$_3$) 3600, 3000, 2960, 2920, 2860, 1600, 1495, 1470, 1450, 1040, 1020 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.53–7.17 (m, 10 H, arom), 5.43 (t, 1 H, J = 6.8 Hz, =CH), 3.64 (d, 2 H, J = 6.8 Hz, CH$_2$), 1.37 (s, 6 H, CH$_3$). A NOE difference measurement[33] with irradiation of the δ 1.37 methyl groups led to an ca. 7% increase in the δ 5.43 methylene signal; MS, *m/e* 252.1521 (calcd for $C_{18}H_{20}O$, *m/e* 252.1514).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.51; H, 8.12.

(*E*)-4-Methyl-3,4-diphenyl-2-penten-1-al. To a suspension of 0.771 g (3.58 mmol) of pyridinium chlorochromate[40] in 2.0 mL of dichloromethane was added 0.398 g (1.58 mmol) of (*E*)-3,4-diphenyl-4-methyl-2-penten-1-ol in 3.0 mL of dichloromethane. The solution was stirred for 1 h, diluted with ether, and filtered through Florisil. The filtrate was concentrated in vacuo to give 0.388 g (98.1%) of (*E*)-4-methyl-3,4-diphenyl-2-penten-1-al as a colorless oil.

The spectral data were the following: IR (CHCl$_3$) 3040, 3000, 2960, 2830, 2730, 1670, 1605, 1590, 1170, 1120 cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.18 (d, 1 H, J = 7.8 Hz, CHO), 7.38–7.10 (m, 8 H, arom), 6.67 (m, 2 H, arom), 6.33 (d, 1 H, J = 7.8 Hz, =CH), 1.49 (s, 6 H, CH$_3$); MS, *m/e* 250.1353 (calcd for $C_{18}H_{18}O$, *m/e* 250.1358).

Anal. Calcd from $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.13; H, 7.44.

(*Z*)-4-Methyl-3,4-diphenyl-2-penten-1-al. To a solution of 0.50 mL of pyridine and 4.0 mL of dichloromethane was added 72.0 mg (0.72 mmol) of chromium trioxide.[37] The solution was stirred for 10 min, and 9.7 mg (0.038 mmol) of (*Z*)-3,4-diphenyl-4-methyl-2-penten-1-ol in 2.0 mL of dichloromethane was added. After being stirred for 15 min, the solution was decanted and the residue washed with ether. Basic–acidic workup[27] of the resulting solution gave 9.0 mg (93%) of (*Z*)-4-methyl-3,4-diphenyl-2-penten-1-al as a colorless oil.

The spectral data were the following: IR (CHCl$_3$) 3010, 2960, 2920, 2860, 2740, 1665, 1490, 1470, 1260, 1130 cm^{-1}; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 9.36 (d, 1 H, J = 8.2 Hz, CHO), 7.56–7.17 (m, 10 H, arom), 5.78 (d, 1 H, J = 8.2 Hz, =CH), 1.53 (s, 6 H, CH$_3$); MS, *m/e* 250.1355 (calcd for $C_{18}H_{18}O$, *m/e* 250.1358).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.22; H, 7.44.

(*E*)-1,1-Dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene (25a). A mixture of 0.215 g (0.86 mmol) of (*E*)-4-methyl-3,4-diphenyl-2-penten-1-al, 0.181 g (2.74 mmol) of malononitrile, and 0.161 g (1.71 mmol) of potassium fluoride dihydrate in 1.0 mL of *N*,*N*-dimethylformamide and 1.0 mL of ethylene glycol was stirred for 4 h.[41] Neutral workup[27] gave 0.250 g of a yellow oil that was chromatographed on a 20 × 20 cm preparative thick-layer plate, eluting once with 20% ether/pentane. Band 1 (R_f 0.5) gave 0.236 g of a colorless oil that was crystallized from hexane to give 0.194 g (75.6%) of (*E*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene as a white solid, mp 107–109 °C. The spectral data were identical with those found for the material produced from the sensitized photolysis of (dicyanovinyl)cyclopropane **2**.

(*Z*)-1,1-Dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene. A mixture of 20.0 mg (0.080 mmol) of (*Z*)-4-methyl-3,4-diphenyl-2-penten-1-al, 17.0 mg (0.26 mmol) of malononitrile, and 38.0 mg (0.40 mmol) of potassium fluoride dihydrate in 0.50 mL of *N*,*N*-dimethylformamide and 0.50 mL of ethylene glycol was stirred for 1.5 h.[41] Neutral workup[27] gave 26.6 mg of a yellow oil, which was crystallized from hexane to give 17.0 mg (68.5%) of (*Z*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene as a white solid, mp 153–155 °C. The spectral data were identical with those found for the material produced from the sensitized photolysis of (dicyanovinyl)cyclopropane **2**.

Photolysis Equipment for Quantum Yield Determinations. Quantum yields were performed on the "Wisconsin Black Box"[14] or the microoptical[14] bench. Light output was measured with a digital actinometer[15] calibrated by ferrioxalate actinometry.[16] For "Black Box" runs the following filter solution combination was used: (a) 2.0 M nickel sulfate in 5% sulfuric acid, (b) 0.8 M cobalt sulfate in 5% sulfuric acid, and (c) 2.46 × 10^{-3} M bismuth trichloride in 40% hydrochloric acid (this combination gave a transmission maximum at 285 nm (32% transmission) and was opaque above 325 nm and below 250 nm). 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 366 nm.

Summary of Direct Quantum Yield Results for 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (1). All runs were performed on the "Black Box"[14] in 740 mL of *tert*-butyl alcohol. All runs were analyzed by HPLC (7.5% dichloromethane in hexane), with triphenylmethane as the internal standard, and NMR with 4,4′-dimethoxybenzophenone as the internal standard. The quantum yields of appearance for 5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (**4**), 2-(2-methyl-1,1-diphenyl-2-propene)-1,1-diphenylcyclopropane (**5**), 3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (**6**), 2-methyl-3,3-diphenyl-2-propene (**7**), and 3-phenylindene (**8**) were determined to be 0.0053, 0.0073, 0.0034, 0.0055, and 0.00042, respectively.

Summary of Sensitized Quantum Yield Results for 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (1). The run was performed on the microbench[14] in 43.0 mL of acetonitrile with thioxanthone as sensitizer. A solution of 22.5 mg (0.056 mmol) of 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane and 3.0 mg (0.014 mmol) of thioxanthone in 43.0 mL of acetonitrile was photolyzed on the microbench until 0.6908 mEinstein had been absorbed. Concentration in vacuo gave a slightly yellow solid that contained only the starting vinylcyclopropane and sensitizer by NMR. The mixture was chromatographed on a 20 × 20 cm preparative thick-layer plate, eluting twice with pentane. The most rapidly moving band (R_f 0.2) gave 21.4 mg (95.1%) of the vinylcyclopropane as a white solid, mp 130–132 °C, $\Phi < 0.0008$.

Summary of Direct Quantum Yield Results for 3-(2,2-Dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (2) in *tert*-Butyl Alcohol. All runs were performed on the "Black Box"[14] in 740 mL of *tert*-butyl alcohol. All runs were analyzed by HPLC (5% ether in hexane), with naphthalene as the internal standard. The quantum yields of appearance for 1,1-dicyano-5-methyl-4,4-diphenyl-1,5-hexadiene (**13**), 1,1-dicyano-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene (**14**), and 1,1-dicyano-5-methyl-3,3-diphenyl-1,4-hexadiene (**15**) were determined to be 0.017, 0.0076, and 0.0079, respectively.

Summary of Direct Quantum Yield Results for 3-(2,2-Dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (2) in Acetonitrile. All runs were performed on the "Black Box"[14] in 740 mL of acetonitrile. All runs were analyzed by NMR with 4,4′-dimethoxybenzophenone as the internal standard. The quantum yield of appearance for 1,1-dicyano-5-methyl-4,4-diphenyl-1,5-hexadiene (**13**) was determined to be 0.018.

Summary of Sensitized Quantum Yield Results for 3-(2,2-Dicyanovinyl)-2,2-dimethyl-1,1-diphenylcyclopropane (2). All runs were performed on the microbench[14] in 43.0 mL of acetonitrile with thioxanthone as sensitizer. All runs were analyzed by NMR with 4,4′-dimethoxybenzophenone as the internal standard. The quantum yields of appearance for (*E*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene (**25a**) and (*Z*)-1,1-dicyano-5-methyl-4,5-diphenyl-1,3-hexadiene (**25b**) were determined to be 0.058 and 0.064, respectively.

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Supplementary Material Available: Tables of crystal data collection parameters, positional parameters, interatomic distances, bond angles, and anisotropic and isotropic temperature factors for **6** and direct quantum yield results for **1** and **2** (8 pages). Ordering information is given on any current masthead page.

Competitive Catalysis and Quenching by Amines of Photo-Smiles Rearrangement as Evidence for a Zwitterionic Triplet as the Proton-Donating Intermediate

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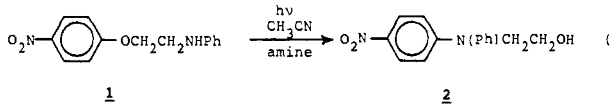
Abstract: Ten amine bases are observed to catalyze the photo-Smiles rearrangement of 4-$O_2NC_6H_4OCH_2CH_2NHPh$ in acetonitrile. Plots of (quantum yield)$^{-1}$ vs [amine]$^{-1}$ are linear for all ten bases, but the intercepts representing limiting quantum yields range from a low of 1.81 ($\Phi_{\mathrm{lim}} = 0.55$) for pyridine to a high of 16.3 ($\Phi_{\mathrm{lim}} = 0.061$) for 1,4-diazabicyclo[2.2.2]octane. The differing intercepts imply that the amines quench as well as catalyze the reaction, and the linear double reciprocal plots can result only if the quenching and catalysis involve the same intermediate in the mechanism. The expected properties of zwitterion diradical, $^-O_2\dot{N}C_6H_4OCH_2CH_2\dot{N}^+HPh$, are consistent with all findings for the proton-donating and quenchable intermediate; the N-protonated Meisenheimer complex does not appear to be an intermediate leading to photoproduct. The reaction is sensitized by a triplet donor, is not quenched by triplet energy acceptors having E_T in the range of 50-60 kcal/mol, but is quenched by 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide ($E_T \sim 40$ kcal/mol). The derived rate constants for deprotonation by the amines make a nonlinear plot according to the Brønsted Catalysis Law. The Brønsted β reaches 0.6 in the strength-dependent regime, and the plot shows a maximal rate of 10^9 M^{-1} s^{-1} at a pK_a (acetonitrile) of 14, which corresponds closely to the predicted pK_a of the zwitterion diradical. The amine quenching mechanisms proposed involve electron exchange for tertiary amines and hydrogen abstraction-electron transfer for primary amines.

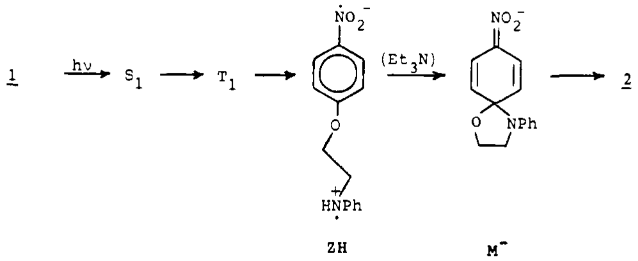
The photo-Smiles rearrangement of 2-(4-nitrophenoxy)-1-anilinoethane (**1**) (eq. 1) reported by Mutai and co-workers[1-4] interests us because the reaction is "accelerated" by triethylamine and is regioselective for the attachment para to the nitro group. In contrast, photo-Smiles rearrangement of 2-(nitrophenoxy)-ethylamine,[5-7] which is general base catalyzed, requires attachment of the rearranging side chain meta to the nitro group. We have concluded[6,8] as have Mutai and co-workers[9,10] that this regioselectivity difference reflects a mechanistic difference, the latter reaction proceeding by heterolytic nucleophilic attack while the former proceeds by intramolecular electron transfer and radical coupling.



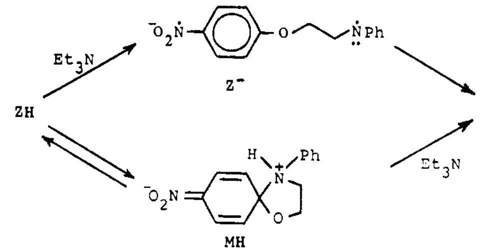
(1)

Nanosecond flash photolysis studies of the photorearrangement of **1** by Mutai and co-workers[2] established several mechanistic features, as shown by Scheme I. Involvement of the nitrophenyl

Scheme I



Scheme II



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