Photochemical Vinylcyclopropane Rearrangements of 1-Substituted-3-(2,2-diphenylvinyl)-2,2-dimethylcyclopropanes to Cyclopentenes and Different Heterocycles

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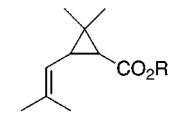
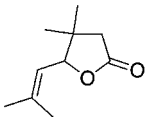
Introduction

[1,3]-Sigmatropic rearrangements of vinylcyclopropanes have been a subject of interest for many years.[1] The results obtained from studies in this area show that vinylcyclopropanes undergo three types of reorganization reactions under thermal and photochemical conditions including cis−trans isomerization, ring opening to pentadienes, and ring expansion to cyclopentenes.[1] A majority of past photochemical studies in this area concentrated on all-carbon systems. Only a few have focused on the influence of ring functionality on the photoreactivity of vinylcyclopropanes, and most of these were related to the photochemistry of pyrethroids.[2] The latter efforts have led to the discovery of a new vinylcyclopropane photorearrangement involving the conversion of (+)-*trans*-chrysanthemic acid (**1a**) to a racemic mixture of the four diastereoisomers of **1a** and the lactone **2**.[2b] The formation of **2** suggests the possibility that suitably substituted vinylcyclopropanes would undergo photorearrangements to yield a variety of heterocyclic products.



1a: R = H
1b: R = Et



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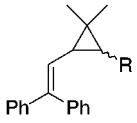

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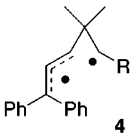

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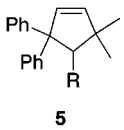

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3a, **4a**, **5a**: R = CO_2Et
3b, **4b**, **5b**: R = CO_2H
3c, **4c**, **5c**: R = CHO
3d, **4d**, **5d**: R = COMe
3e, **4e**, **5e**: R = CH=NOH
3f, **4f**: R = CH_2OH

This proposal has led to a study aimed at detecting novel ring-expansion photoreactions related to the conversion **1a** → **2**. A family of substances (**3**) related to **1a** were selected for this effort because diphenyl substitution at the vinyl unit in **3** should favor the generation of biradical intermediates **4** resulting from photoinduced homolytic cleavage of the allylic cyclopropane ring bonds. Furthermore, this type of substitution pattern should enable studies to be carried out under both direct, using Pyrex glass filtered-light (λ > 300 nm), and triplet-sensitized photoreaction conditions, employing sensitizers such as acetophenone or *m*-methoxyacetophenone.[3] The results of this investigation show that in most cases substituted vinylcyclopropanes **3** undergo cis−trans isomerization and rearrangement to cyclopentenes, which is the normal photochemical reactivity reported previously for this class of compounds. However, novel photorearrangements to produce 1,2-oxazine and different furan derivatives, and important differences in reactivity between the triplet-sensitized and the direct irradiations, have been observed for the first time in this study.

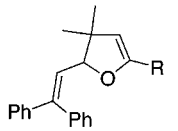
Results and Discussion

The vinylcyclopropanes **3** were readily synthesized by standard procedures starting with ethyl chrysanthemate (**1b**). Ozonolysis of **1b** yields ethyl 3-formyl-2,2-dimethyl-1-cyclopropanecarboxylate which is transformed to **3a** by Horner−Emmons olefination with diethyl diphenylmethylphosphonate. Hydrolysis of the ester group in **3a** yields the acid **3b**. LAH reduction of **3a** gives the alcohol **3f** which is oxidized to the aldehyde **3c** using PCC. Condensation of **3c** with hydroxylamine hydrochloride affords the oxime **3e**. Finally, ketone **3d** is obtained by conversion of **3b** into the corresponding acid chloride followed by reaction with Me_2CuLi. All of the substrates **3a**−**f** were obtained as a 1:2 mixture of cis:trans isomers.

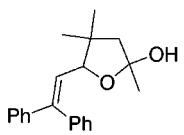
Triplet-Sensitized Irradiations. The photochemical behavior of these substances was first investigated by using triplet-sensitized conditions (*m*-methoxyacetophenone for **3a**−**d** and **3f** and acetophenone for **3e**). Irradiation of a solution of *m*-methoxyacetophenone and **3a** in CH_2Cl_2 followed by column chromatography on silica gel gave recovered **3a** (74%, 1:1 mixture of cis:trans isomers) and cyclopentene **5a** (19%). The structure of **5a** was established by conventional analytical and spectroscopic methods.

A reasonable pathway explaining both the isomerization and bond reorganization processes begins with triplet state homolytic cleavage yielding the delocalized biradical **4a**. Rotation and recombination in **4a** leads to trans−cis isomerization while alternative radical recombination of **4a** provides **5a**.

Compound **3b** behaves similarly under triplet-sensitized photoreaction conditions affording the cyclopentene derivative **5b** (17%) and recovered starting material (80%, 1:1 mixture of cis:trans isomers). Ring expansion to cyclopentene derivatives along with trans−cis isomerizations also occur in the triplet reactions of the carbonyl derivatives **3c** and **3d**. However, compounds **3c** and **3d** also undergo novel rearrangements to produce furan derivatives **6a** and **7**, respectively. Thus, aldehyde **3c**



6a: R = H
6b: R = Me



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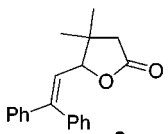

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(1) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229, and references cited herein.

(2) (a) Sasaki, T.; Eguchi, S.; Ohno, M. *J. Org. Chem.* **1968**, *33*, 676. (b) Sasaki, T.; Eguchi, S.; Ohno, M. *J. Org. Chem.* **1970**, *35*, 790. (c) Ueda, K.; Matsui, M. *Tetrahedron* **1971**, *27*, 2771. (d) Ruzo, L. O.; Holmstead, R. L.; Casida, J. E. *Tetrahedron Lett.* **1976**, *35*, 3045. (e) Ruzo, L. O.; Casida, J. E. *J. Chem. Soc., Perkin Trans. 1* **1980**, 728.

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

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affords recovered starting material (46%, 1:1 mixture of cis:trans isomers), cyclopentene **5c** (20%), and dihydrofuran **6a** (31%). The structure of **6a** was assigned on the basis of analytical and spectroscopic data. Similarly, ketone **3d** yields starting material (25%, 1:1 mixture of cis:trans isomers), cyclopentene **5d** (13%), and the tetrahydrofuran **7** (13%) as an inseparable mixture of two diastereoisomers. The identity of **7** was established on the basis of conventional analytical and spectroscopic techniques. Of particular value in this respect was the comparison of the ^{1}H and ^{13}C NMR spectra of compounds **6a** and **7** that shows clearly the structural similarities between these two compounds, namely, the presence of a diphenylvinyl unit, a dimethyl-substituted quaternary carbon, and a furan ring.

The formation of **6a** can be explained by carbon−oxygen bonding within the delocalized biradical intermediate **4c** while **7** most likely arises by nucleophilic addition of water to the initial photoproduct dihydrofuran **6b**.[4]

Oxime **3e** was obtained as a mixture of the four possible diastereoisomers. ^{1}H NMR analysis demonstrated that the ratio of cis:trans isomers was 1:2 and that the ratio of (*Z:E*)-oxime isomers was 1:1 for the cis isomer and 3:1 for the trans isomer. Triplet-sensitized (acetophenone) irradiation of this isomeric mixture afforded recovered **3e** (48%, 1:2 mixture of the cis:trans pair of (*Z*)-oxime isomers and cyclopentene **5e** (20%). No products resulting from carbon−nitrogen bonding within the intermediate biradical **4e** were obtained in this case.

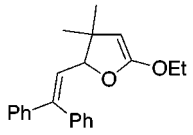
To establish the influence of the stabilization of the biradical intermediates **4**, effected by conjugation of the radical site with the functional groups at position 1 of the cyclopropane ring, the study was extended to the alcohol **3f**. Irradiation of **3f**, under the same conditions used for compounds **3a**−**d**, yielded a complex mixture of highly polar compounds that were not identified and 60% of recovered starting material as an unchanged mixture of diastereoisomers. This result shows that the stabilization of the intermediate biradical **4**, by conjugation with the functional group originally present in position 1 of the cyclopropane ring, plays an important role in promoting the recombination of the corresponding intermediate **4** to the starting cyclopropane and to the five-membered-ring carbocyclic or heterocyclic products. The distribution of photoproducts, their isolated yields, and the ratio of cis:trans isomers in the recovered starting materials, for the triplet-sensitized irradiations of compounds **3**, are presented in Table 1.

Direct Irradiations. The photochemical reactivity of vinylcyclopropanes **3** was also probed by use of direct irradiation conditions. Irradiation of **3a** by using Pyrex glass filtered light (λ > 300 nm) affords recovered **3a** (65%) as a 1:1 mixture of stereoisomers and a new product (19%) that was identified by conventional spectroscopic methods as the 2-furanone **8**. The formation of **8** is rationalized by carbon−oxygen bonding within the delocalized biradical intermediate **4a** to yield the dihydrofuran derivative **9** followed by addition of water to give **10** and ethanol elimination to afford **8**.[4] Compound **3b** behaves similarly on direct irradiation yielding the lactone **8** in 15% yield along with the starting cyclopropane **3b** (75%, 1:1 mixture of diastereoisomers). However, under these conditions, aldehyde **3c** does not give the dihydrofuran **6a** observed in the triplet-sensitized irradiation but rather affords cyclopentene **5c** (24%) and the cyclopropane **3c** (30%), as an unchanged 1:2 mixture of diastereoisomers. In contrast, on direct irradiation ketone **3d** does not gives the cyclopentene derivative **5d** observed in the triplet-sensitized reaction but produces the tetrahydrofuran **7** (19%) and recovered starting material (34%) as an unchanged mixture of diastereoisomers.

Table 1. Product Distribution in the Photoreactions of 3a−f

substr[a]	irradn condns[b]	isolated products (yield, %)	cis:trans ratio of recovered **3**
3a	A	**5a** (19), **3a** (74)	1:1
3a	B	**3a** (65), **8** (19)	1:1
3b	A	**5b** (17), **3b** (80)	1:1
3b	B	**3b** (75), **8** (15)	1:1
3c	A	**5c** (20), **3c** (46), **6a** (31)	1:1
3c	B	**5c** (24), **3c** (30)	1:2
3d	A	**5d** (13), **3d** (25), **7** (13)	1:1
3d	B	**3d** (34), **7** (19)	1:2
3e	C	**5e** (20), **3e** (48)	1:2
3e	B	**5e** (9), **3e** (47), **12** (6)	2:1
3f	A	**3f** (60)	1:2
3f	B	**3f** (40), **14** (20)	1:6

[a] Compounds **3** were obtained and irradiated as a 1:2 mixture of cis:trans isomers. [b] Method A: *m*-methoxyacetophenone sensitized. Method B: direct irradiation. Method C: acetophenone sensitized.



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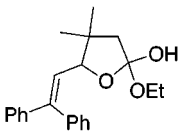

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It is interesting that neither the aldehyde **3c** nor the ketone **3d** undergo trans:cis isomerization upon direct irradiation. This suggests the possibility of a concerted pathway for these reactions.

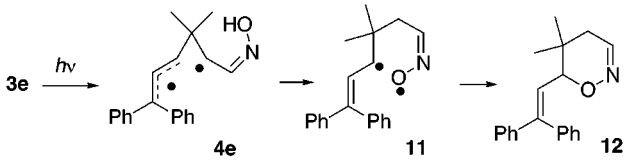
Direct irradiation of the diastereomeric oximes **3e** yields starting material (47%, 2:1 mixture of the cis:trans pair of (*Z*)-oxime isomers), the cyclopentene **5e** (9%), and a new substance (6%) that we identified as the 5,6-dihydro-4*H*-1,2-oxazine **12**.[5] The formation of **12** is best explained by a mechanism involving hydrogen abstraction in biradical intermediate **4e**, via a five-membered transition state, to produce an iminoxyl radical **11** that undergoes cyclization by carbon−oxygen bonding to afford **12** (Scheme 1).

Finally, direct irradiation of a 1:2 mixture of cis:trans isomers of **3f**, in which the biradical intermediate **4f** is not stabilized by additional conjugation, gives recovered **3f** (40%, 1:6 cis:trans ratio) and the conjugated diene **14** (20%). The identity of **14** was established on the basis of analytical and spectroscopic data. This result is surpris-

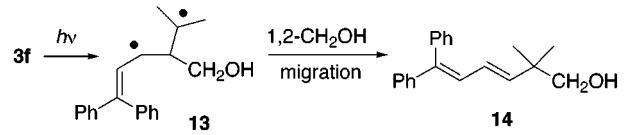
(4) (a) There are precedents of electrophilic additions to the electron-rich double bond present in dihydrofurans under very mild conditions (ref 4b). In this instance the addition of water must occur during isolation. We believe that this takes place during the elimination of the solvent by rotary evaporation since the ^{1}H NMR spectra of the oily residue obtained shows the presence of addition product. (b) Sargent, M. V.; Dean, F. M. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 4, p 653.

(5) (a) The identity of **12** was established by comparison of its spectroscopic data with those reported (ref 5b) for similar 1,2-oxazines obtained in the DCA-sensitized irradiation of γ,δ-unsaturated oximes. (b) Armesto, D.; Austin, M. K.; Griffiths, O. J.; Horspool, W. M.; Carpintero, M. *J. Chem. Soc., Chem. Commun.* **1996**, 2715.

Scheme 1



Scheme 2



ing because production of **14** formally involves the 1,2-migration of a CH_2OH group. As far as we are aware, 1,2-migrations of alkyl groups have not been reported previously in the photochemistry of vinylcyclopropanes. A mechanism involving homolytic bond fission of the cyclopropyl 2,3-bond to yield the biradical **13** followed by 1,2-migration of the CH_2OH group is proposed to account for this result (Scheme 2). The distribution of photoproducts, their isolated yields, and the ratio of cis:trans isomers in the recovered starting materials, for the direct irradiations of compounds **3**, are collected in Table 1.

Conclusions

The results of this study indicate that there is a marked influence of substitution at the 1-position on the photochemical reactivity of 1-substituted-2-vinylcyclopropanes **3**. In addition, the nature of the excited state also plays an important role in the photochemical reactivity of these systems (see Table 1). Thus, the predominant triplet reactivity of **3a**−**d** is trans−cis isomerization. However, in the irradiation of **3e**, under these conditions, only isomerization around the C−N double bond is observed. Triplet-sensitized irradiations of compounds **3a**−**e** also afford the corresponding cyclopentene derivatives **5a**−**e**. In addition to ring expansion to form cyclopentenes, the carbonyl derivatives **3c** and **3d** also react to yield furan derivatives **6a** and **7**, respectively. The photoreactivity of **3** under direct irradiation conditions shows important differences with those displayed under triplet sensitization conditions. Thus, while **3a** and **3b** undergo trans−cis isomerization under direct and sensitized conditions, cyclopropanes **3c** and **3d** do not isomerize on direct irradiation. Rather, **3c** yields the cyclopentene **5c**, exclusively, while **3d** rearranges to the furan **7**, only. Compounds **3e** and **3f** undergo isomerization at the cyclopropane ring only on direct irradiation but not on triplet sensitization. The furanone **8** is obtained in the direct irradiation of derivatives **3a** and **3b** while the corresponding cyclopentenes **5a** and **5b** are formed in the triplet-sensitized reactions. Cyclopropane **3e** affords the cyclopentene derivative **5e** exclusively on sensitized irradiation while a mixture of **5e** and the 1,2-ozaxine **12** is obtained on direct irradiation. Finally, the cyclization to cyclopentene derivatives and heterocycles, such as 1,2 oxazines, and different furan derivatives is favored when the biradical intermediate **4** is stabilized by conjugation with a substituent at the 1-position. In the absence of such stabilization, as in **3f**, a different reaction pathway is followed yielding the conjugated diene **14**.

Although it is difficult to explain at this point the differences observed in the excited-state reactivity of the cyclopropanes **3**, especially those resulting from the competition between alternative cyclization of the intermediate biradicals, it is clear that suitably substituted vinylcyclopropanes can be used as accessible starting materials for the synthesis of cyclopentene derivatives and different types of heterocyclic compounds.[6] Further studies are underway to determine the factors that control the competition between the alternative reaction paths as well as the scope of these new photochemical reactions.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. UV/vis spectra were recorded in CH_2Cl_2 solution. Column chromatography was performed using silica 60 (40−63 μm) from Merck. Commercially available starting materials and reagents were purchased from Aldrich. The photolyses were carried out in a quartz immersion well apparatus with a Pyrex filter and a 400-W medium-pressure Hg arc lamp. Solutions of the compounds and the sensitizer (in the sensitized irradiations) in dry CH_2Cl_2 (420 mL) were purged for 1 h with argon and irradiated under a positive pressure of argon. After completion of the irradiation, the solvent (and acetophenone or *m*-methoxyacetophenone in sensitized irradiations) was removed under reduced pressure, and the products were separated by flash column chromatography on silica gel.

Ethyl 3-(2,2-Diphenylvinyl)-2,2-dimethyl-1-cyclopropanecarboxylate (3a). This compound was synthesized in two steps from ethyl chrysanthemate according to the following procedure: ethyl chrysanthemate (20 g, 0.102 mol) in CH_2Cl_2 (200 mL) was ozonized at −78 °C over 2 h. The reaction mixture was then purged with N_2, and triphenylphosphine (28 g, 0.107 mol) in CH_2Cl_2 (50 mL) was added. The mixture was warmed to room temperature and concentrated under reduced pressure. Hexane (100 mL) was added, and the precipitate was removed by filtration and washed with hexane and ether. The combined extracts were evaporated, and the crude product was distilled under reduced pressure yielding ethyl 3-formyl-2,2-dimethyl-1-cyclopropanecarboxylate (15.5 g, 90%) as a 1:2 mixture of cis:trans isomers: bp 50 °C (0.8 mm); IR (neat) 1730, 1710 cm^{-1}; ^1H NMR (250 MHz) δ 1.20−1.40 (3 s and 1 t, 8 H, cis and trans), 1.50 (s, 1 H, cis), 1.85 (dd, J = 6.6, 8.7 Hz, 0.33 H, cis), 2.13 (d, J = 8.7 Hz, 0.33 H, cis), 2.46 (m, 1.33 H, trans), 4.16 (m, 2 H, cis and trans), 9.58 (d, J = 3.6 Hz, 0.66 H, trans), 9.75 (d, J = 6.6 Hz, 0.33 H, cis); ^{13}C NMR (75 MHz) δ 14.3, 15.0 (cis), 20.6 (trans), 21.0 (trans), 28.3 (cis), 29.8 (cis), 33.2 (trans), 34.5 (trans), 36.5 (cis), 40.8 (cis), 42.0 (trans), 61.1, 169.8, 198.8 (trans), 200.8 (cis); MS m/z 171 (M^+ + 1, 5), 170 (M^+, 4), 141 (15), 107 (6), 51 (100). Anal. Calcd for $C_9H_{14}O_4$ (acid): C, 58.1; H, 7.3. Found: C, 58.34; H, 7.49.[7] To a stirred solution of diethyl diphenylmethylphosphonate[8] (13.4 g, 44 mmol) in dry DME (30 mL) under argon and at 0 °C was added n-BuLi (25.5 mL 1.6 M in hexane). The resulting red solution was stirred for 1 h at 0 °C, and then ethyl 3-formyl-2,2-dimethyl-1-cyclopropanecarboxylate (4.7 g, 27 mmol) in DME (20 mL) was added. The reaction mixture was stirred at 0 °C for 40 min before being quenched with H_2O and extracted with ether. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to dryness. Flash chromatography using hexane/Et_2O (8:2) yielded **3a** (8.5 g, 96%) as an oil and as a 1:2 mixture of cis:trans isomers: IR (neat) 1720 cm^{-1}; ^1H NMR (300 MHz) δ 1.14 (s, 1 H, cis), 1.22 (s, 2 H, trans), 1.25 (t, 3 H), 1.27 (s, 2 H, trans), 1.38 (s, 1 H, cis), 1.62 (d, J = 5.4 Hz, 0.66 H, trans), 1.68 (d, J = 8.7 Hz, 0.33 H, cis), 1.83 (app t, J = 9.0 Hz, 0.33 H, cis), 2.10 (dd, J = 5.4, 8.7 Hz, 0.66 H, trans), 4.10 (m, 2 H), 5.74 (d, J = 8.7 Hz, 0.66 H, trans), 6.50 (d, J = 9.4 Hz, 0.33 H, cis), 7.21−7.34 (m, 10 H); ^{13}C NMR (63 MHz) δ 14.5, 15.2 (cis), 20.1 (trans), 22.7 (trans), 28.1 (cis), 28.4 (cis), 29.9 (trans), 32.7 (cis), 34.1

(6) Yields have not been optimized.

(7) This aldehyde undergoes spontaneous oxidation in the presence of atmospheric oxygen. The combustion analysis quoted herein corresponds to the carboxylic acid resulting from the oxidation of the aldehyde.

(8) Zimmerman, H. E.; Khun, R. T. *Tetrahedron* **1978**, 34, 1775.

(cis), 34.6 (trans), 36.1 (trans), 60.1 (cis), 60.4 (trans), 123.9−144.0, 171.5 (cis) 171.8 (trans); MS *m/z* 320 (M^+, 26), 247 (100), 167 (60), 152 (18); UV (CH_2Cl_2) λ_{max} 265 nm (ϵ 167 00 l mol^{-1} cm^{-1}). Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.5; H, 7.5. Found: C, 82.20; H, 7.42.

3-(2,2-Diphenylvinyl)-2,2-dimethyl-1-cyclopropanecarboxylic Acid (3b). A solution of KOH (1 g, 12.5 mmol) and ethyl 3-(2,2-diphenylvinyl)-2,2-dimethyl-1-cyclopropanecarboxylate (**3a**) (1 g, 3.1 mmol) in ethanol absolute (180 mL) was refluxed for 24 h. The solvent was evaporated to dryness, and the crude product was dissolved in water. The solution was washed with ether to remove unreacted starting material, and the aqueous layer was acidified with a 20% HCl solution and extracted with ether. The organic phases were dried ($MgSO_4$), filtered, and concentrated to dryness. Flash chromatography of the residue using hexane/Et_2O (7:3) yielded **3b** (812 mg, 89%) as an oil and as a 1:2 mixture of cis:trans isomers: IR (neat) 3100−2900, 1700 cm^{-1}; ^1H NMR (250 MHz) δ 1.14 (s, 1 H, cis), 1.24 (s, 2 H, trans), 1.28 (s, 2 H, trans), 1.39 (s, 1 H, cis), 1.63 (d, J = 5.3 Hz, 0.66 H, trans), 1.68 (d, J = 8.7 Hz, 0.33 H, cis), 1.95 (app t, J = 9.2 Hz, 0.33 H, cis), 2.13 (dd, J = 8.7, 5.3 Hz, 0.66 H, trans), 5.73 (d, J = 8.7 Hz, 0.66 H, trans), 6.43 (d, J = 9.8 Hz, 0.33 H, cis), 7.15−7.40 (m, 10 H), 10.81 (br s, 1 H, cis and trans); ^{13}C NMR (63 MHz) δ 14.9 (cis), 15.2 (trans), 20.2 (trans), 22.7 (cis), 28.3 (trans), 29.3 (cis), 30.9 (trans), 32.3 (cis), 34.9 (cis), 35.5 (trans), 123.1−144.4, 177.7 (cis), 178.0 (trans); MS *m/z* 292 (M^+, 71), 275 (2), 247 (83), 205 (93), 165 (39), 91 (100); UV (CH_2Cl_2) λ_{max} 269 nm (ϵ 3400).

2-(2,2-Diphenylvinyl)-3-(hydroxymethyl)-1,1-dimethylcyclopropane (3f). To a stirred suspension of LAH (0.74 g, 19 mmol) in Et_2O (75 mL) under argon was added a solution of the ester **3a** (7.74 g, 24 mmol) in anhydrous Et_2O (25 mL) dropwise. The mixture was stirred at room temperature for 1 h. The reaction was quenched with water and filtered. The ether layer was separated, dried ($MgSO_4$), filtered, and concentrated to dryness. Flash chromatography of the residue using hexane/Et_2O (9:1) afforded **3f** (6.5 g, 97%) as a oil and as a 1:2 mixture of cis:trans isomers: IR (neat) 3350, 1620 cm^{-1}; ^1H NMR (300 MHz) δ 0.90 (m, 0.66 H, trans), 1.10 (s, 1 H, cis), 1.11 (s, 2 H, trans), 1.19 (s, 1 H, cis), 1.20 (s, 2 H, trans), 1.46 (m, 1.33 H, cis and trans), 3.46 (m, 1 H), 3.67 (m, 0.66 H), 3.82 (dd, J = 7.7, 2.2 Hz, 0.33 H), 5.77 (d, J = 8.8 Hz, 0.66 H, trans), 5.84 (d, J = 9.8 Hz, 0.33 H, cis), 7.18−7.40 (m, 10 H), (OH signal not observed); ^{13}C NMR (63 MHz) δ 15.9 (cis), 20.9 (trans), 23.2 (trans), 23.4 (cis), 24.4 (trans), 28.5 (cis), 29.0 (cis), 31.3 (trans), 33.3 (cis), 36.6 (trans), 63.2 (trans), 66.0 (cis), 125.4−143.7; MS m/z 278 (M^+, 17), 247 (100), 167 (20); UV (CH_2Cl_2) λ_{max} 266 nm (ϵ 15 100).

3-(2,2-Diphenylvinyl)-2,2-dimethyl-1-cyclopropanecarbaldehyde (3c). The alcohol **3f** (6 g, 21 mmol) and PCC (7 g, 32 mmol) were allowed to react in CH_2Cl_2 (50 mL) at room temperature for 4 h. The crude reaction mixture was filtered through silica gel and the solvent evaporated to dryness. Flash chromatography of the residue using hexane/Et_2O (95:5) give aldehyde **3c** (4.1 g, 69%) as an oil and as a 1:2 mixture of cis:trans isomers: IR (neat) 1700, 1660 cm^{-1}; ^1H NMR (300 MHz) δ 1.16 (s, 1H, cis), 1.28 (s, 2H, trans), 1.31 (s, 2H, trans), 1.47 (s, 1H, cis), 1.82 (m, 1H, cis and trans), 2.15 (app t, J = 9.0 Hz, 0.33 H, cis), 2.37 (dd, J = 5.1, 9.0 Hz, 0.66 H, trans), 5.75 (d, J = 9.0 Hz, 0.66 H, trans), 6.36 (d, J = 9.6 Hz, 0.33 H, cis), 7.20−7.50 (m, 10 H), 9.23 (d, J = 5.6 Hz, 0.66 H, trans), 9.64 (d, J = 5.7 Hz, 0.33 H, cis); ^{13}C NMR (63 MHz) δ 16.0 (cis), 21.3 (trans), 22.5 (trans), 28.5 (cis), 32.1 (cis), 32.2 (trans), 36.4 (trans), 38.2 (cis), 42.8 (cis), 45.9 (trans), 122.5−145.1, 200.2 (trans), 201.3 (cis); MS m/z 276 (M^+, 5), 247 (100), 191 (28), 165 (31); UV (CH_2Cl_2) λ_{max} 268 nm (ϵ 13 600).

3-(2,2-Diphenylvinyl)-2,2-dimethyl-1-cyclopropanecarbaldehyde Oxime (3e). Aldehyde **3c** (2.1 g, 7.6 mmol), hydroxylamine hydrochloride (0.8 g, 0.01 mol), and pyridine (0.78 g, 0.01 mol) were heated at reflux in ethanol (50 mL) for 1 h. After conventional workup, column chromatography of the crude product on silica gel using hexane/Et_2O (9:1) gave the oxime **3e** (1.8 g, 83%) as an oil and as a 1:2 mixture of cis:trans isomers. The cis isomer was obtained as a 1:1 mixture of the (*Z*:*E*)-oxime isomers and the trans isomer as a 3:1 mixture of (*Z*:*E*)-oxime isomers: IR (neat) 3100−2800, 1610 cm^{-1}; ^1H NMR (300 MHz) δ 1.01, 1.02, 1.05, 1.15, 1.16, 1.17, 1.19, 1.32, (8 s, 6 H), 1.50−1.80 (m, 1.33 H, cis and trans of (*Z*)- and (*E*)-oxime isomers), 2.15−2.25 (m, 0.66 H, cis and trans of (*Z*)- and (*E*)-oxime isomers), 5.64 (d, J = 8.7 Hz, 0.17 H, cis of (*E*)-oxime isomer), 5.70 (d, J = 9.3 Hz, 0.5 H, trans of (*Z*)-oxime isomer), 5.77 (d, J = 9.6 Hz, 0.17 H, cis of (*Z*)-oxime isomer), 5.78 (d, J = 9.0 Hz, 0.17 H, trans of (*E*)-oxime isomer), 6.20 (d, J = 8.7 Hz, 0.5 H, trans of (*Z*)-oxime isomer), 6.58 (d, J = 9.0 Hz, 0.17 H, cis of (*Z*)-oxime isomer), 7.00 (d, J = 8.3 Hz, 0.17 H, cis of (*E*)-oxime isomer), 7.10−7.27 (m, 10.17 H, trans of (*E*)-oxime isomer), 7.80, 8.00, 8.25, (br s, 1 H, cis and trans of (*Z*)- and (*E*)-oxime isomers); ^{13}C NMR (63 MHz) δ 16.8 (trans), 22.3 (trans), 22.4 (cis), 22.5 (cis), 26.2, 26.7 (trans), 27.0, 27.8 (cis), 28.0, 30.2 (cis), 30.9, 32.6 (trans), 33.4, 34.0 (trans), 34.1, 35.7 (cis), 124.2−149.0, 150.0, 151.1, 151.8, 152.5 (cis and trans); MS *m/z* 291 (M^+, 1), 273 (32), 75 (100); UV (CH_2Cl_2) λ_{max} 299 nm (ϵ 15 300).

1-Acetyl-3-(2,2-diphenylvinyl)-2,2-dimethylcyclopropane (3d). This compound was synthesized in two steps from the acid **3b** according to the following procedure: the acid **3b** (590 mg, 2.02 mmol) and thionyl chloride (1 mL) were heated at reflux for 20 min. The residual thionyl chloride was removed under reduced pressure yielding 3-(2,2-diphenylvinyl)-2,2-dimethylcyclopropane-1-carbonyl chloride (627 mg, 100%) as an oil and as a 1:2 mixture of cis:trans isomers, which was used without further purification: IR (neat) 1785 cm^{-1}; ^1H NMR (300 MHz) δ 1.22 (s, 1 H, cis), 1.27 (s, 2 H, trans), 1.37 (s, 2 H, trans), 1.39 (s, 1 H, cis), 2.23−2.37 (m, 2 H, cis and trans), 5.76 (d, J = 8.4 Hz, 0.66 H, trans), 6.20 (d, J = 8.7 Hz, 0.33 H, cis), 7.20−7.43 (m, 10 H). To a stirred suspension of CuI (407 mg, 2.42 mmol) in anhydrous Et_2O (100 mL) under argon and at −40 °C was added MeLi (3.3 mL, 1.6 M in ether). The mixture was stirred for 30 min, and then 3-(2,2-diphenylvinyl)-2,2-dimethyl-1-cyclopropanecarbonyl chloride (627 mg, 2.02 mmol) in Et_2O (100 mL) was added. The reaction was kept at −40 °C for 30 min, allowed to warm at 0 °C, and stirred for 30 min before being quenched with a saturated NH_4Cl solution and extracted with ether. The combined organic phases were dried, filtered, and concentrated to dryness. Flash chromatography of the residue using hexane/Et_2O (95:5) afforded **3d** (374 mg, 64%) as a oil and as a 1:2 mixture of cis:trans isomers: IR (neat) 1705, 1680 cm^{-1}; ^1H NMR (300 MHz) δ 1.15 (s, 2 H, trans), 1.18 (s, 1H, cis), 1.30 (s, 2H, trans), 1.35 (s, 1H, cis), 1.95 (d, J = 5.7 Hz, 0.66 H, trans), 2.04 (m, 0.66 H, cis), 2.19 (s, 2H, trans), 2.20−2.30 (m, 0.66 H, trans, with overlapping singlet at 2.28, 1 H, cis), 5.78 (d, J = 8.4 Hz, 0.66 H, trans), 6.50 (m, 0.33 H, cis), 7.18−7.45 (m, 10 H); ^{13}C NMR (63 MHz) δ 14.7 (cis), 19.5 (trans), 22.9 (trans), 28.7 (cis), 31.3 (cis), 32.5 (trans), 33.5 (cis), 33.6 (trans), 36.1 (trans), 37.6 (cis), 40.4 (cis), 44.5 (trans), 123.6−144.3, 205.5 (trans), 206.0 (cis); MS *m/z* 290 (M^+, 2), 247 (100), 167 (19); UV (CH_2Cl_2) λ_{max} 227 nm (ϵ 4200).

***m*-Methoxyacetophenone-Sensitized Irradiation of 3a.** Compound **3a** (400 mg, 1.25 mmol), as a 1:2 mixture of cis:trans isomers, and *m*-methoxyacetophenone (600 mg, 4 mmol) were irradiated for 3 h. Flash chromatography using hexane/Et_2O (9:1) gave 298 mg (74%) of **3a**, as a 1:1 mixture of cis:trans isomers, and 75 mg (19%) of ethyl 2,2-dimethyl-5,5-diphenyl-3-cyclopentene-1-carboxylate (**5a**) as a oil. Further elution with Et_2O afforded 12 mg (3%) of highly polar material. Compound **5a**: IR (neat) 1755 cm^{-1}; ^1H NMR (300 MHz) δ 1.03 (t, J = 7.0 Hz, 3 H), 1.13 (s, 3 H), 1.23 (s, 3 H), 3.76 (s, 1H), 3.86 (m, 2 H), 5.78 (d, J = 5.6 Hz, 1 H), 6.18 (d, J = 5.6 Hz, 1 H), 7.13−7.43 (m, 10 H); ^{13}C NMR δ 14.1, 24.7, 30.2, 48.5, 59.9, 62.7, 64.9, 126.0−148.6, 171.9; MS *m/z* 320 (M^+, 50), 247 (100), 191 (32).

***m*-Methoxyacetophenone-Sensitized Irradiation of 3b.** Compound **3b** (575 mg, 1.97 mmol), as a mixture 1:2 of cis:trans isomers, and *m*-methoxyacetophenone (4.4 g, 29.2 mmol) were irradiated for 4 h. Flash chromatography using hexane/Et_2O (95:5) gave 96 mg (17%) of 2,2-dimethyl-5,5-diphenyl-3-cyclopentene-1-carboxylic acid (**5b**) as a oil and 459 (80%) of **3b**, as a 1:1 mixture of cis:trans isomers. Further elution with Et_2O afforded 20 mg (3%) of highly polar material. Compound **5b**: IR (neat) 3100−2900, 1700 cm^{-1}; ^1H NMR (300 MHz) δ 1.15 (s, 3 H), 1.20 (s, 3 H), 3.77 (s, 1 H), 5.78 (d, J = 5.6 Hz, 1 H), 6.10 (d, J = 5.6 Hz, 1 H), 7.00−7.50 (m, 10 H) (COOH signal not observed); ^{13}C NMR (63 MHz) δ 28.4, 30.0, 48.4, 62.1, 65.0, 123.2−148.2, 177.4; MS *m/z* 292 (M^+, 20), 275 (10), 247 (100).

***m*-Metoxyacetophenone-Sensitized Irradiation of 3c.** Compound **3c** (398 mg, 1.4 mmol), as a 1:2 mixture of cis:trans isomers, and *m*-methoxyacetophenone (3 g, 22 mmol) were

irradiated for 1 h. Flash chromatography using hexane/Et_2O (95:5) gave 123 mg (31%) of 2-(2,2-diphenylvinyl)-3,3-dimethyl-2,3-dihydrofuran (**6a**), 80 mg (20%) of 2,2-dimethyl-5,5-diphenyl-3-cyclopentene-1-carbaldehyde (**5c**), and 184 mg (46%) of **3c** as a 1:1 mixture of cis:trans isomers. Compound **6a**: IR (neat) 1610 cm^{-1}; ^1H NMR (300 MHz) δ 1.00 (s, 3 H), 1.17 (s, 3 H), 4.53 (d, J = 10.0 Hz, 1 H), 4.86 (d, J = 2.7 Hz, 1 H), 6.24 (d, J = 10.0 Hz, 1 H), 6.25 (d, J = 2.7 Hz, 1 H), 7.20−7.41 (m, 10 H); ^{13}C NMR (63 MHz) δ 24.1, 27.8, 42.8, 87.6, 112.6, 124.2, 127.3−129.8, 139.0, 141.6, 143.3, 146.0; MS m/z 276 (M^+, 9), 247 (100), 191 (19), 167 (11); HRMS m/z (M^+) calcd for $C_{20}H_{20}O$ 276.1509, found 276.1519. Compound **5c**: IR (neat) 1720 cm^{-1}; ^1H NMR (300 MHz) δ 1.17 (s, 3 H), 1.21 (s, 3 H), 3.41 (d, J = 5.8 Hz, 1 H), 5.90 (d, J = 5.5 Hz, 1 H), 6.22 (d, J = 5.5 Hz, 1 H), 7.20−7.37 (m, 10 H), 9.27 (d, J = 5.8 Hz, 1 H); ^{13}C NMR (63 MHz) δ 23.7, 30.1, 49.7, 64.2, 66.2, 126.3−147.9, 206.5; MS m/z 277 (M^+ + 1, 45), 276 (M^+, 45), 247 (100), 207 (74).

***m*-Methoxyacetophenone-Sensitized Irradiation of 3d.** Compound **3d** (117 mg, 0.40 mmol), as a mixture 1:2 cis:trans isomers, and *m*-metoxyacetophenone (109 mg, 0.95 mmol) were irradiated for 1 h. Flash chromatography using hexane/Et_2O (98:2) gave 29.8 mg (25%) of starting **3d** as a 1:1 mixture of cis:trans isomers, 14.6 mg (13%) of 4-acetyl-3,3-dimethyl-5,5-diphenyl-1-cyclopentene (**5d)** as a oil, 15 mg (13%) of 5-(2,2-diphenylvinyl)-2-hydroxy-2,4,4-trimethyltetrahydrofuran (**7**) as a white solid, and a 2:1 mixture of the two possible diastereoisomers **A** and **B**. Further elution with Et_2O afforded 9 mg (5%) of highly polar material. Compound **5d**: IR (neat) 1680 cm^{-1}; ^1H NMR (300 MHz) δ 1.00 (s, 3 H), 1.26 (s, 3 H), 2.19 (s, 3 H), 3.79 (s, 1 H), 5.73 (d, J = 5.6 Hz, 1 H), 6.26 (d, J = 5.6 Hz, 1 H), 7.13−7.35 (m, 10 H); ^{13}C NMR (63 MHz) δ 24.2, 30.0, 32.1, 48.3, 61.0, 63.7, 123.6−148.8, 201.5; MS m/z 290 (M^+, 8), 247 (100), 205 (30). Compound **7:** mp 120−122 °C (hexane); IR (KBr) 3450−3350 cm^{-1}; ^1H NMR (300 MHz) δ 0.91 (s, 1 H, **B**-isomer), 0.93 (s, 2 H, **A**-isomer), 1.09 (s, 2 H, **A**-isomer), 1.25 (s, 1 H, **B**-isomer), 1.53 (AB system, J = 14.7 Hz, 1.33 H, **A**-isomer), 1.56 (s, 2 H, **A**-isomer), 1.72 (d, J = 13.2 Hz, 0.33 H, **B**-isomer), 1.88 (s, 1 H, **B**-isomer), 1.96 (d, J = 13.2 Hz, 0.33 H, **B**-isomer), 2.29 (br s, 0.66 H, **A**-isomer), 2.57 (br s, 0.33 H, **B**-isomer), 4.15 (d, J = 10.1 Hz, 0.33 H, **B**-isomer), 4.42 (d, J = 9.8 Hz, 0.66 H, **A**-isomer), 6.07 (d, J = 9.8 Hz, 0.66 H, **A**-isomer), 6.25 (d, J = 10.1 Hz, 0.33 H, **B**-isomer), 7.20−7.45 (m, 10 H); ^{13}C NMR (63 MHz) δ 23.5, 23.8, 25.8, 27.2, 29.3, 29.4, 42.9, 43.8, 53.1, 53.9, 83.1, 85.7, 103.7, 104.7, 124.6−146.4; MS m/z 291 (M^+ −17, 4), 250 (33), 209 (100), 167 (13). Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.8; H, 7.8. Found: C, 81.99; H, 7.70.

Acetophenone-Sensitized Irradiation of 3e. The mixture of the four diastereoisomers obtained in the synthesis of compound **3e** (407 mg, 1.4 mmol) and acetophenone (7 g, 59 mmol) were irradiated for 1 h. Flash chromatography using hexane/Et_2O (9:1) gave 83 mg (20%) of 2,2-dimethyl-5,5-diphenyl-3-cyclopentene-1-carbaldehyde oxime (**5e**) as an oil, and as a 6:5 mixture of (*Z*:*E*)-isomers, and 194 mg (48%) of the (*Z*)-isomer of the starting oxime **3e** as a 1:2 mixture of cis:trans isomers. Further elution with Et_2O afforded 76 mg (15%) of highly polar material. Compound **5e**: IR (neat) 3220, 1650, 1620 cm^{-1}; ^1H NMR (300 MHz) δ 0.81 (s, 1.35 H, (*E*)-isomer), 0.85 (s, 1.65 H, (*Z*)-isomer), 1.08 (s, 1.35 H, (*E*)-isomer), 1.15 (s, 1.65 H, (*Z*)-isomer), 3.50 (d, J = 10.2 Hz, 0.45 H, (*E*)-isomer), 4.44 (d, J = 9.3 Hz, 0.55 H, (*Z*)-isomer), 5.80 (d, J = 5.7 Hz, 0.55 H, (*Z*)-isomer), 5.83 (d, J = 5.7 Hz, 0.45 H, (*E*)-isomer), 6.02 (d, J = 5.7 Hz, 1 H, (*Z*:*E*)-isomers), 6.22 (d, J = 9.3 Hz, 0.55 H, (*Z*)-isomer), 6.85 (d, J = 10.2 Hz, 0.45 H, (*E*)-isomer), 7.03−7.35 (m, 10 H), 8.20 (br s, 0.45 H, (*E*)-isomer), 8.80 (br s 0.55 H, (*Z*)-isomer); ^{13}C NMR (63 MHz) δ 23,5 (*E*)-isomer), 23.8 (*Z*)-isomer), 29.1 (*E*)-isomer), 29.7 (*Z*)-isomer), 49.2 (*E*)-isomer), 49.5 (*Z*)-isomer), 49.9 (*Z*)-isomer), 55.7 (*E*)-isomer), 63.6 (*E*)-isomer), 65.1 (*Z*)-isomer), 126.1−148.4, 152.9 (*Z*)-isomer), 153.4 (*E*)-isomer); MS m/z 291 (M^+, 32), 274 (100), 193 (53), 167 (35); HRMS m/z (M^+) calcd for $C_{20}H_{21}NO$ 291.1619, found 291.1618.

***m*-Methoxyacetophenone-Sensitized Irradiation of 3f.** Compound **3f** (205 mg, 0.73 mmol) as a 1:2 mixture of cis:trans isomers and *m*-methoxyacetophenone (362 mg, 2.4 mmol) were irradiated for 4 h. Flash chromatography using hexane/Et_2O (95:5) as eluent gave 123 mg (60%) of starting material **3f** as a 1:2 mixture of cis:trans isomers. Further elution with Et_2O afforded 82 mg (30%) of highly polar material.

Direct Irradiation of 3a. Compound **3a** (308 mg, 0.9 mmol) as a 1:2 mixture of cis:trans isomers was irradiated for 8 h. Flash chromatography using hexane/Et_2O (9:1) gave 201 mg (65%) of the ester **3a**, as a 1:1 mixture of cis:trans isomers, and 60 mg (19%) of 5-(2,2-diphenylvinyl)-4,4-dimethyltetrahydro-2-furanone (**8**). Further elution with Et_2O afforded 35 mg (11%) of highly polar material. Compound **8**: IR (neat) 1775 cm^{-1}; ^1H NMR (300 MHz) δ 1.02 (s, 3 H), 1.19 (s, 3H), 2.36 (AB system, J = 16.7 Hz, 2 H), 4.63 (d, J = 10.2 Hz, 1 H), 6.07 (d, J = 10.2 Hz, 1 H), 7.20−7.40 (m, 10 H); ^{13}C NMR (63 MHz) δ 22.4, 25.3, 40.6, 44.3, 85.9, 120.9−149.0, 176.2; MS m/z 292 (M^+, 24), 207 (100), 165 (27).

Direct Irradiation of 3b. Compound **3b** (426 mg, 1.45 mmol) as a mixture 1:2 of cis:trans isomers was irradiated for 10 h. Flash chromatography using hexane/Et_2O (9:1) gave 64 mg (15%) of **8** and 320 mg (75%) of recovered starting material **3b** as a 1:1 mixture of cis:trans isomers. Further elution with Et_2O afforded 41.8 mg (10%) of highly polar material.

Direct Irradiation of 3c. Compound **3c** (288 mg, 1.1 mmol) as a 1:2 mixture of cis:trans isomers was irradiated for 10 h. Flash chromatography using hexane/Et_2O (95:5) gave 70 mg (24%) of 2,2-dimethyl-5,5-diphenyl-3-cyclopentene-1-carbaldehyde (**5c**) as a oil and 85 mg (30%) of recovered starting material **3c** as a 1:2 mixture of cis:trans isomers. Further elution with Et_2O afforded 111 mg (30%) of highly polar material.

Direct Irradiation of 3d. Compound **3d** (141 mg, 0.49 mmol) as a 1:2 mixture of cis:trans isomers was irradiated for 3 h 30 min. Flash chromatography using hexane/Et_2O (9:1) gave 48 mg (34 %) of **3d** as a 1:2 mixture of cis:trans isomers and 26 mg (19%) of 5-(2,2-diphenylvinyl)-2-hydroxy-2,4,4-trimethyltetrahydrofuran (**7**) as a white solid and as a 2:1 mixture of the two possible diastereoisomers **A** and **B**. Further elution with Et_2O afforded 45 mg (30%) of highly polar material.

Direct Irradiation of 3e. The mixture of the four diastereoisomers obtained in the synthesis of compound **3e** (344.5 mg, 1.2 mmol) was irradiated for 8 h. Flash chromatography using hexane/Et_2O (95:5) gave 66.1 mg (20%) of a 1:1 mixture of cis:trans isomers of aldehyde **3c**, resulting from partial hydrolysis of the starting oxime, 30.7 mg (9%) of 2,2-dimethyl-5,5-diphenyl-3-cyclopentene-1-carbaldehyde oxime (**5e**) as an oil and as a 1:2 mixture of (*Z*:*E*) isomers, 21 mg (6%) of 6-(2,2-diphenylvinyl)-5,5-dimethyl-5,6-dihydro-4*H*-1,2-oxazine (**12**) as a oil, and 93 mg (27%) of **3e** as a 2:1 mixture of cis:trans isomers of the (*Z*)-oxime. Further elution with Et_2O afforded 100 mg (28%) of highly polar material. Compound **12**: IR (neat) 1655 cm^{-1}; ^1H NMR (300 MHz) δ 0.83 (s, 3 H), 1.10 (s, 3 H), 1.90 (d, J = 3.0 Hz, 2 H), 4.08 (d, J = 10.0 Hz, 1 H), 6.07 (d, J = 10.0 Hz, 1 H), 7.14 (t, J = 3.0 Hz, 1 H), 7.26−7.40 (m, 10 H); ^{13}C NMR (63 MHz) δ 21.1, 26.4, 29.0, 36.6, 80.8, 121−129.7, 147.2; MS m/z 291 (M^+, 9), 247 (75), 209 (100), 165 (56).

Direct Irradiation of 3f. Compound **3f** (220 mg, 0.78 mmol) as a 1:2 mixture of cis:trans isomers was irradiated for 10 h 30 min. Flash chromatography using hexane/Et_2O (95:5) gave 42 mg (20%) of (*E*)-2,2-dimethyl-6,6-diphenyl-3,5-hexadien-1-ol (**14**) as a oil and 88 mg (40%) of recovered starting material **3f** as a 1:6 mixture of cis:trans isomers. Further elution with Et_2O afforded 80 mg (30%) of highly polar material. Compound **14**: IR (neat) 3620−3590 cm^{-1}; ^1H NMR (300 MHz) δ 0.99 (s, 6 H), 3.34 (d, J = 5.4 Hz, 2 H), 5.84 (d, J = 15.3 Hz, 1 H), 6.20 (dd, J = 15.3, 10.5 Hz, 1 H), 6.67 (d, J = 10.5 Hz, 1 H), 7,21−7,46 (m, 10 H), (OH signal not observed); ^{13}C NMR (63 MHz) δ 23.9, 39.1, 71.8, 127.0−142.8; MS m/z 278 (M^+, 21), 261 (10), 260 (4), 247 (100), 152 (75).

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Supporting Information Available: ^1H NMR spectra for all compounds lacking analyses (16 pages). See any current masthead page for ordering and Internet access information.

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