JOC Article

Photochemistry of Bicyclo[2.2.2]oct-7-ene-2,5-diones and the Corresponding 5-Hydroxyimino and 5-Methylene Derivatives

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Synthesis and photochemistry of several title compounds **1**−**3** containing multiple chromophoric systems are described. The Diels−Alder reactions of 2,6,6-trimethylcyclohexa-2,4-dienone (**5**) with acetylenes **6a**−**d** provided the adducts **7a**−**d**, which upon hydrolysis furnished the desired bicyclo-[2.2.2]octenediones **1a**−**d**. Oximes **2a**−**d** were prepared from diones **1a**−**d** by treatment with hydroxylamine hydrochloride in pyridine. 5-Methylenebicyclo[2.2.2]oct-7-en-2-ones **3a**−**d** were obtained via chemoselective Wittig reaction of the corresponding diones **1a**−**d**. Bicyclo[2.2.2]-octenediones **1a**−**c** underwent chemoselective oxa-di-π-methane rearrangement under sensitized conditions and suffered formal ketene extrusion upon direct irradiation. Direct irradiation of **1d** afforded **11d** via formal ketene extrusion but under sensitization it remained unchanged. Oximes **2a**−**d** suffered ketene extrusion upon direct irradiation and *E*/*Z* isomerization under sensitized conditions. On the other hand, 5-methylenebicyclo[2.2.2]oct-7-en-2-ones **3a**−**d** generally underwent 1,3-acyl shift. The plausible courses of all these photochemical processes are discussed.

Introduction

The di-π-methane (DPM) rearrangement (Zimmerman rearrangement) and its oxa- and aza-variants are general organic photochemical reactions with fascinating mechanistic complexity in conjuction with remarkable consistency and beauty.[1,2] Extensive studies on these rearrangements helped unravel most of the mechanistic intricacies and structural limitations. These reactions exhibit reasonable levels of generality and possess considerable synthetic potential unlike several other organic photochemical reactions. The oxa-di-π-methane (ODPM) rearrangement,[1−4] in particular, has been employed as one of the key synthetic steps in the total syntheses of several complex natural products[4] showing that it could be a dependable synthetic reaction. The aza-di-π-methane rearrangement (ADPM), a relatively new member of the group, is beginning to show its potential.[5]

The other possible side reactions, viz., cis−trans isomerization, 1,3-acyl migration, ketene extrusion, decarbonylation, etc., are often encountered even when the substrate contains a chromophoric system necessary for one of the DPM rearrangements.[6] It is therefore interesting to study the photochemical behavior of substrates containing multiple chromophoric systems required for the DPM rearrangements. Photochemistry of such substrates could feature intramolecular competition between various DPM rearrangements as well as interference by other processes. However, intramolecular competitive photochemistry associated with these reactions is relatively less investigated.[1] The factors responsible for the chemoselectivity of DPM rearrangement were identified and some generalizations were made about the preferences of vinyl−vinyl bridging, benzo−vinyl bridging, and free rotation.[7,8] While the chemoselectivity of ODPM rearrangement needs more examples for clear under-

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(1) Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065−3112.

(2) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531−551. (b) Dauben, W. G.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73−114. (c) Schuster, D. I. In *Rearrangements of Enones in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 167−279. (d) Zimmerman, H. E. In *Rearrangements of Enones in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 131−166. (e) Zimmerman, H. E. *Org. Photochem.* **1991**, *11*, 1−36. (f) Demuth, M. *Org. Photochem.* **1991**, *11*, 37−109. (g) Armesto, D. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Soon, P.-S., Eds.; CRC Press: New York, 1995; pp 915−930.

(3) (a) Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820−836. (b) Schaffner, K.; Demuth, M. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, Germany, 1986; Vol. 4 p 61.

(4) For some notable applications of ODPM rearrangement in the total synthesis of natural products, see: (a) Yates, P.; Stevens, K. E. *Tetrahedron* **1981**, *37*, 4401−4410. (b) Demuth, M.; Hinsken, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 973−975. (c) Mehta, G.; Subrahmanyam, D. *J. Chem. Soc., Chem. Commun.* **1985**, 768−769. (d) Liao, C.-C.; Wei, C.-P. *Tetrahedron Lett.* **1989**, *30*, 2255−2256. (e) Paquette, L. A.; Kang, H.-J.; Ra, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 7387−7395. (f) Yen, C.-F.; Liao, C.-C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4090−4093.

(5) Armesto, D.; Caballero, O.; Amador, U. *J. Am. Chem. Soc.* **1997**, *119*, 12659−12660.

(6) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1−74.

(7) (a) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 6096−6108. (b) Zimmerman, H. E.; Bender, C. O. *J. Am. Chem. Soc.* **1970**, *92*, 4366−4376.

(8) (a) Luibrand, R. T.; Fujinari, E. M. *J. Org. Chem.* **1980**, *45*, 958−960. (b) Mariano, P. S.; Ko, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 1766−1776.

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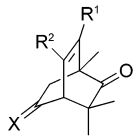


1a-d - 3a-d

1 X= O, **2** X= NOH, **3** X= CH_2

	a	b	c	d
R^1	CO_2Et	CO_2Me	Ph	Ph
R^2	H	CO_2Me	H	Ph

FIGURE 1. Multiple chromophoric systems with common alkene moiety.

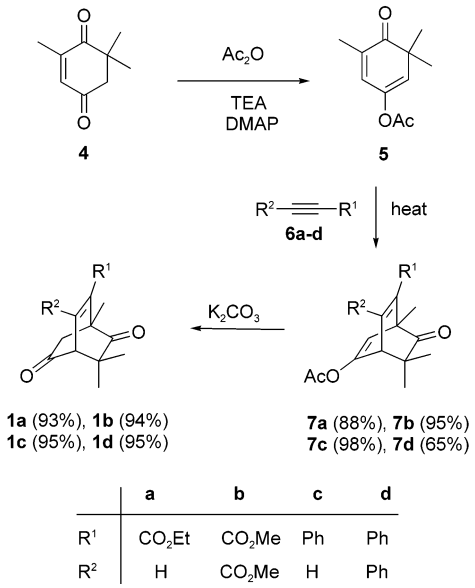
standing,[9,10] and that of ADPM rearrangement is yet to be encountered. Although some studies that dealt with intramolecular competition of DPM with ODPM or ADPM rearrangement appeared in the literature,[11−13] there was not a single case that dealt with intramolecular competition between ODPM and ADPM rearrangements. Bicyclo[2.2.2]octenediones and its derivatives are good systems for studying various competitive processes.

As part of our continuing studies on the photochemistry of bicyclo[2.2.2]octene derivatives,[13,14] we have contemplated a study of the photochemical behavior of compounds **1**−**3** containing multiple chromophoric systems that share a common alkene moiety (Figure 1). The objective is to study the chemoselectivity of the ODPM rearrangement and to determine the influence of interfering chromophoric systems on it. Such studies could possibly provide insights into intramolecular competition between ODPM, ADPM, and DPM rearrangements and other reactions. It should be mentioned that the photochemistry of a few bicyclo[2.2.2]octenediones was reported earlier.[9,10] On the other hand, the photochemical reactions of compounds **2** were never studied. Nevertheless, we have prepared compounds **1**−**3** starting from 4-ketoisophorone (**4**) and then subjected them to irradiation under various conditions, and herein we present the details.

Results and Discussion

Preparation of Compounds 1−3. Bicyclo[2.2.2]-octene-2,5-diones **1a**−**d** were selected as substrates for examining the chemoselectivity of ODPM rearrangement and also as precursors for compounds **2a**−**d** and **3a**−**d**. Although there are some reports for the preparation of bicyclo[2.2.2]octene-2,5-diones,[9,10,15] no straightforward general procedures exist. Parent bicyclo[2.2.2]octene-2,5-dione was prepared from hydroquinone in 16% yield.[9,15] Yates and co-workers prepared dimethyl 6,6-dimethyl-5,7-dioxobicyclo[2.2.2]oct-2-ene-2,3-dicarboxylate by the treatment of 5,5-dimethyl-2-cyclohexene-1,4-dione with a large excess of isopropenyl acetate and dimethyl acetylenedicarboxylate.[10] We have recently developed an efficient procedure for multigram scale preparation of **1a**−**d**,[16] which involves (a) the conversion of **4** to **5**,[17] (b) the Diels−Alder reactions of **5** with acetylenes **6a**−**d** to afford adducts **7a**−**d**, and (c) the hydrolysis of **7a**−**d** with K_2CO_3 in EtOH or MeOH at 0 °C (Scheme 1). The selection of enediones **1a**−**d** as the precursors for **2**−**3** has much to do with the anticipated difference in the reactivity of the two keto groups, a feature quite critical for future manipulations.

SCHEME 1

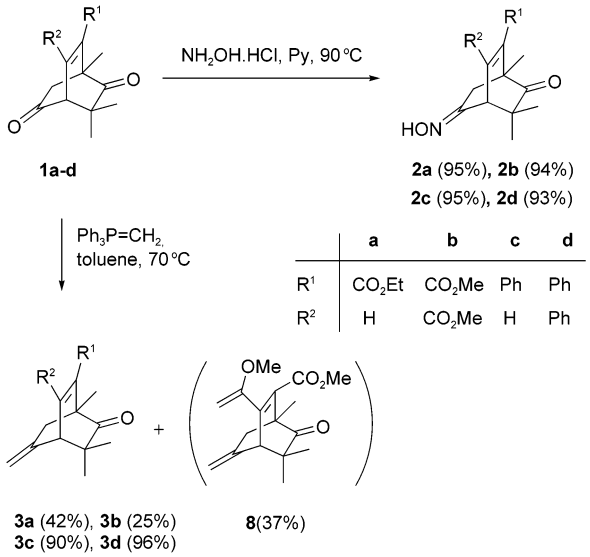


	a	b	c	d
R^1	CO_2Et	CO_2Me	Ph	Ph
R^2	H	CO_2Me	H	Ph

Stereochemically pure oximes **2a**−**d** were synthesized in excellent yields from compounds **1a**−**d** by treatment with hydroxylamine hydrochloride in pyridine at 90 °C. Importantly, these imine formation reactions proceeded in a highly chemoselective manner as desired; no trace of oximes resulting from the sterically hindered ketone was discernible in any of these reactions. The oximes **2a**−**d** were assigned the *E*-configuration based on the following assumption. The chemical shift of C-4 methine hydrogen and methylene hydrogens on C-6 would be influenced by the proximity of the oxygen atom of oximes or their derivatives, a common feature for such compounds.[18] It was indeed found to be the case. Comparison

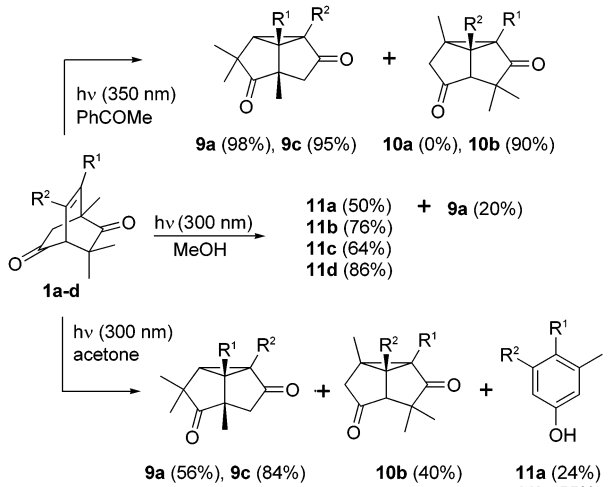
(9) Demuth, M.; Ritterskamp, P.; Weigt, E.; Schaffner, K. *J. Am. Chem. Soc.* **1986**, *108*, 4149−4154.
(10) Yates, P.; Burnell, J.; Freer, V. J.; Sawyer, J. F. *Can. J. Chem.* **1987**, *65*, 69−77.
(11) (a) Becker, H.-D.; Ruge, B. *J. Org. Chem.* **1980**, *45*, 2189−2195. (b) Hart, H.; Murray, R. K. *Tetrahedron Lett.* **1969**, 379−382. (c) Givens, R. S.; Oettle, W. F.; Coffin, R. L.; Carlson, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 3957−3962. (d) Van der veen, R. H.; Kruk, C.; Cerfontain, H. *J. Am. Chem. Soc.* **1983**, *105*, 4367−4374. (e) Nitta, M.; Sugiyama, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1127−1132. (f) Hassner, A.; Middlemiss, D.; Murray-Rust, J.; Murray-Rust, P. *Tetrahedron* **1982**, *16*, 2539−2546. (g) Luibrand, R. T.; Broline, B. M.; Charles, K. A.; Drues, R. W. *J. Org. Chem.* **1981**, *46*, 1874−1877.
(12) (a) Nitta, M.; Inoue, O.; Tada, M. *Chem. Lett.* **1977**, 1065. (b) Nitta, M.; Kasahara, I.; Kobayashi, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1275−1276. (c) Armesto, D.; Ortiz, M. J.; Ramos, A.; Horspool, W. M.; Mayoral, E. P. *J. Org. Chem.* **1994**, *59*, 8115−8124.
(13) (a) Liao, C.-C. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Soon, P.-S., Eds.; CRC Press: New York, 1995; pp 194−203. (b) Liao, C.-C.; Hsieh, H.-P.; Lin, S.-Y. *J. Chem. Soc., Chem. Commun.* **1990**, 545−547. (c) Liao, C.-C.; Yang, P.-H. *Tetrahedron Lett.* **1992**, *33*, 5521−5524.
(14) (a) Hwang, J.-T.; Liao, C. C. *Tetrahedron Lett.* **1991**, *32*, 6583−6586. (b) Hsu, D.-S.; Rao, P. D.; Liao, C.-C. *Chem. Commun.* **1999**, 1795−1796. (c) Lee, T.-H.; Rao, P. D.; Liao, C.-C. *Chem. Commun.* **1999**, 801−802.
(15) Weitemeyer, C.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 686−687.
(16) Yang, M.-S.; Chang, S.-Y.; Lu, S.-S.; Rao, P. D.; Liao, C.-C. *Synlett* **1999**, 225−227.
(17) Soukup, M.; Lukac, T.; Roessler, Z. F.; Steiner, K.; Widmer, E. *Helv. Chim. Acta* **1989**, *72*, 365−369.

SCHEME 2



	a	b	c	d
R1	CO_2Et	CO_2Me	Ph	Ph
R2	H	CO_2Me	H	Ph

SCHEME 3



	a	b	c	d
R1	CO_2Et	CO_2Me	Ph	Ph
R2	H	CO_2Me	H	Ph

of ^{1}H NMR spectra of the pure oximes and the purified mixture of oximes obtained from irradiation in acetone or acetophenone (vide infra) clearly showed that the C-4 methine hydrogen in *Z*-oximes suffers considerable downfield shift (>1.0 ppm). Even though less pronounced, the C-6 methylene hydrogens suffered an upfield shift in *Z*-oximes as expected.

Preparation of compounds **3a**−**d** was accomplished by heating compounds **1a**−**d** with the preformed ylide ($Ph_3P{=}CH_2$) in toluene at 70 °C for 2 h. While **1a** afforded **3a (**42%) in moderate yield, **1b** provided compound **8** (37%) as the major product along with the desired compound **3b** in only 25% yield. Efforts to improve the yield of **3a** and **3b** were unsuccessful. However, compounds **1c** and **1d** furnished the desired compounds **3c** and **3d,** respectively, in high yields (Scheme 2). Oximation and Wittig olefination of **1a**−**d** also took place exclusively at the unhindered keto group to afford the corresponding oximes **2a**−**d** and methylenic compounds **3a**−**d**, respectively.

Photochemistry of Compounds 1−**3.** Since the photochemistry of compounds **1**−**3** was never thoroughly investigated, it was decided to carry out both sensitized and direct irradiations. While acetophenone and acetone were used as solvents as well as sensitizers for the sensitized irradiation, methanol, acetonitrile, or benzene were employed as solvents for the direct irradiation experiments.

Bicyclo[2.2.2]octenediones 1a−**d.** Compound **1a** provided **9a** in 98% yield upon acetophenone-sensitized irradiation for 8.5 h exhibiting remarkably high chemoselectivity. No trace of **10a** could be observed. Under the same conditions, in total difference with **1a**, compound **1b** furnished **10b** exclusively in 90% yield upon irradiation for 144 h.[10] Interestingly, **1c** upon irradiation for 6.5 h provided **9c** (95%) as the only discernible product much like **1a**. The formation of ODPM products **9a**,**c** and **10b** under sensitized conditions occurs from the π,π^* triplet excited state. In stark contrast with **1a**−**c**, the dione **1d** was found to be insensitive to light during 84 h of exposure in acetophenone (Scheme 3). This may be due to localization of the triplet excited-state energy in the stilbene moiety,[19] which may not have sufficient energy (E_T = 49.3 kcal/mol) for rearrangement to occur.

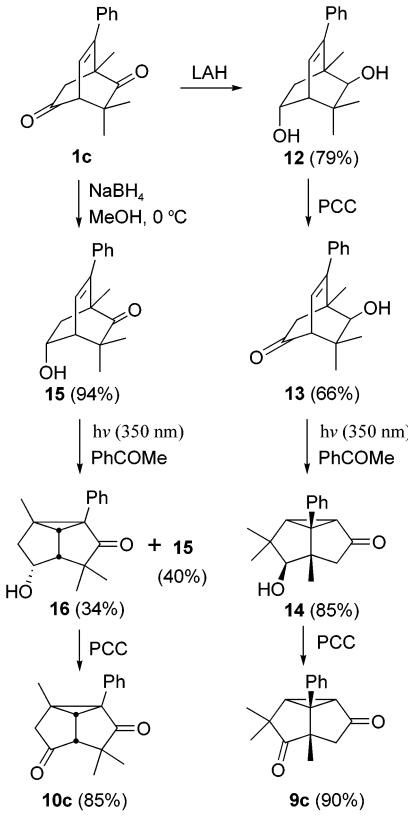
Compound **1a** furnished a 1:2 mixture of phenol **11a** and ODPM product **9a** upon irradiation for 8 h in acetone. On the other hand, upon irradiation for 53 h in acetone, **1b** provided phenol **11b** as the major product in 55% yield and the ODPM product **10b** in 40% yield. Interestingly, **1c** underwent ODPM rearrangement quite efficiently to provide compound **9c** in 84% yield as the only discernible product. However, **1d** furnished phenol **11d** in 58% yield as the sole isolable product when irradiated in acetone. Except for **1a**, which provided a mixture of **11a** (50%) and ODPM product **9a** (20%), the other three substrates **1b**−**d** upon direct irradiation in methanol furnished phenols **11b**−**d** in 76, 64, and 86% yields, respectively. The phenols **11a**−**d** presumably resulted from initial Norrish type I α-cleavage followed by elimination of dimethylketene formally via the n,π^* singlet excited state. In the case of **1a**, the intersystem crossing is in competition with the singlet excited state to form **9a**.[3]

Structure Elucidation of Compounds 9a and 9c. The assignment of the structure of photoproduct **9a** was based on the following facts. HRMS and elemental analysis of the photoproduct indicated the presence of all the mass units as in **1a**. Its ^{13}C NMR spectrum showed the absence of olefinic carbons revealing that the actual product is not due to a 1,3-acyl shift. Of the two possible ODPM products **9a** and **10a**, the actual product was shown to be the former. ^{1}H, ^{13}C NMR and DEPT spectra of the photoproduct indicated the presence of a geminally coupled methylene unit (J = 18.4 Hz) and a pair of vicinal methine hydrogens (J = 9.6 Hz), which are present in both proposed structures **9a** and **10a**. The high J value of methine hydrogens, typical for methine hydrogens of the cyclopropane moiety of the tricyclo[3.3.0.0^{2,8}]octane

(18) Karabatsos, G. J.; Krumel, K. L. *Tetrahedron* **1967**, *23*, 1079−1095.

(19) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker Inc.: New York, 1993; p 46.

SCHEME 4



system, confirms the structure of **9a** as the photoproduct of **1a**. Noticeably, the ^{1}H NMR spectrum of **9a** has considerable similarity to that of **9c** and lacks similarity to those of **10b** or **10c**. Furthermore, **9a** was found to be insensitive to 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) unlike **10b**, which undergoes opening of the cyclopropane ring under such conditions.[10]

In addition to the spectroscopic methods, the structure of compound **9c** was determined by its synthesis via a totally conceivable route (Scheme 4). Reduction of **1c** with LAH provided diol **12** as a single isomer. Oxidation of diol **12** with PCC occurred at the less-hindered hydroxyl group to provide hydroxy ketone **13**. Irradiation of an acetophenone solution of **13** at 350 nm provided ODPM product **14** through the π,π^* triplet excited state in 85% yield. Oxidation of **14** with PCC furnished a diketone whose spectral data were found to be identical with those of **9c**. This chemical transformation clearly establishes the structure of **9c** as assigned. Furthermore, the other conceivable ODPM product **10c** of **1c**, albeit not obtained, was also synthesized in accordance with Scheme 4. Reduction of **1c** with $NaBH_4$ in MeOH at 0 °C occurred at the less hindered ketone to provide hydroxy ketone **15** as a single isomer. Hydroxy ketone **15** upon irradiation in acetophenone at 350 nm undergoes π,π^* triplet excitation to furnish the ODPM product **16**, which on further treatment with PCC furnished **10c**, whose spectral data were found to be quite different from those of **9c**.

The assigned relative stereochemistry of diol **12** and hydroxy ketone **15** is based on NOE experiments. Significant NOE enhancements were observed in the signals corresponding to H_a, H_b, and H_c when the signal at δ 3.94 corresponding to H_e of compound **12** was irradiated.

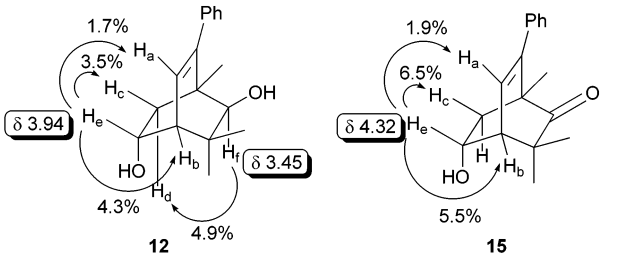
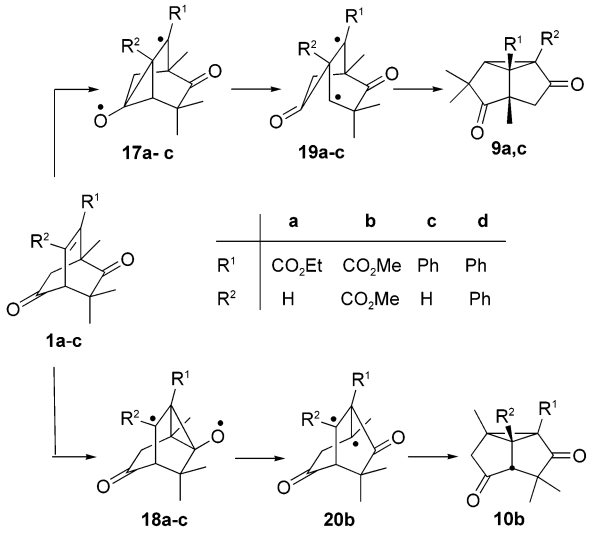


FIGURE 2. ^{1}H NMR studies of NOE (%) for **12** and **15**.

SCHEME 5

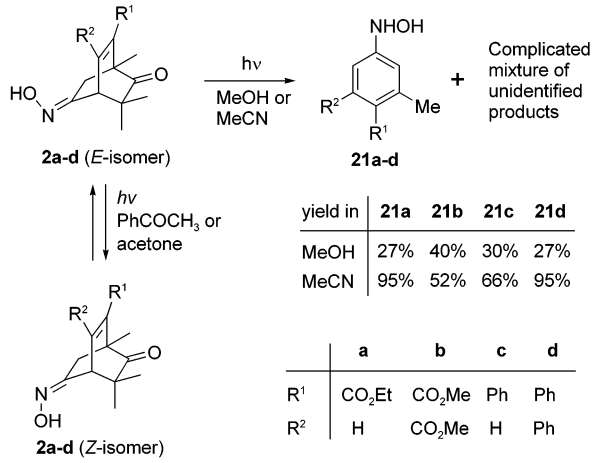


Similarly, about 4.9% of NOE enhancement was observed in the signal corresponding to H_d when the signal at δ 3.45 corresponding to H_f of compound **12** was irradiated. The proximity of various hydrogens indicated by these NOE experiments clearly confirms the assigned relative stereochemistry of diol **12**. On the other hand, the NOE enhancement for the signal corresponding to H_b, when the signal at δ 4.32 corresponding to H_e of **15** was irradiated, confirms the assigned relative configuration.

Origin of Chemoselectivity. The enediones **1a**−**d** can in principle undergo ODPM rearrangement at two sites. It is pertinent to mention that only five examples of chemoselective ODPM rearrangement have been reported to date.[1,9,10] Acetophenone-sensitized reactions of **1a**−**c** have proceeded in a highly chemoselective manner. The selectivity in the case of **1a** and **1c** is due to the higher stability of the two possible tertiary diradicals **17a** and **17c** leading to **9a** and **9c** compared to the other possible secondary diradicals **18a** and **18c** (R^2 = H), respectively (Scheme 5).

On the other hand, the behavior of **1b** is intriguing, and it is hard to explain its remarkable chemoselectivity in producing **10b**. It is important to mention that Yates and co-workers reported identical results in the case of **1b**, however, they did not offer any explanation.[10] While the resonance effect in both **17b** and **18b** is comparable, the cleavage of the cyclopropane ring in **17b** leads to a secondary radical **19b** whereas the collapse of **18b** produces relatively stable tertiary radical **20b** (Scheme 5). Attention should be drawn to Demuth's explanation for the chemoselectivity of 3,3,6-trimethylbicyclo[2.2.2]-oct-7-ene-2,5-dione that was based on steric factors.[9]

SCHEME 6



yield in	21a	21b	21c	21d
MeOH	27%	40%	30%	27%
MeCN	95%	52%	66%	95%

	a	b	c	d
R^1	CO_2Et	CO_2Me	Ph	Ph
R^2	H	CO_2Me	H	Ph

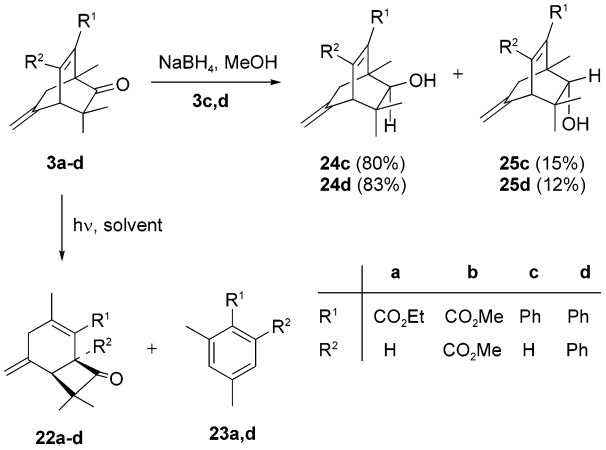
Since no visible steric factors could be attributed for the chemoselectivity observed in the case of **1b**, it may be concluded that the relative stability of the diradicals **19b** and **20b** guides the reaction. However, the possibility of some undetermined structural features being responsible for the observed chemoselectivity in **1b** cannot be ruled out.

5-(*N*-Hydroxy)iminobicyclo[2.2.2]octene-2-ones 2a−d. We have earlier reported several examples of intramolecular competition between DPM and ADPM rearrangements.[20] It was conceived that each of compounds **2a**−**d** containing chromophoric groups necessary for both ODPM and ADPM rearrangements would provide an opportunity to observe intramolecular competition between ODPM and ADPM rearrangements, a scenario with no precedent. Although β,γ-unsaturated oximes generally exhibit reluctance to react in ADPM mode due to single electron transfer, encouraged by the recent success of Armesto and co-workers[21] we have decided to study the photochemistry of oximes **2a**−**d**.

Nonetheless, when **2a**−**d** were subjected to acetophenone- or acetone-sensitized irradiation only *E*/*Z* isomerization was observed (Scheme 6). On the other hand, upon direct irradiation in benzene, methanol, or acetonitrile, oximes **2a**−**d** suffered formally ketene extrusion and afforded phenylhydroxyamine derivatives **21a**−**d** with a complicated mixture of unidentified products. The formation of **21a**−**d** could be expected from the n,π^* singlet excited state. Among these solvents used, acetonitrile was the best. One possible reason for the failure of **2a**−**d** to undergo either ODPM or ADPM rearrangement in sensitized conditions could be the dissipation of π,π^* triplet energy through the free rotation of the C=N bond, leading to *E*/*Z* isomerization.[22]

5-Methylenebicyclo[2.2.2]octen-2-ones 3a−d. Compounds **3a**−**d** were found to be unreactive toward ir-

SCHEME 7



	a	b	c	d
R^1	CO_2Et	CO_2Me	Ph	Ph
R^2	H	CO_2Me	H	Ph

yield in	22a	22b	22c	22d	23a	23d
Acetone	16%	17%	8%	36%	-	-
MeOH	34%	19%	21%	20%	2%	35%

radiation in acetophenone at 350 nm and >90% starting materials were recovered after 36 h of exposure. The results of the irradiation of **3a**−**d** in acetone and methanol are given in Scheme 7. Interestingly, compounds **3a**−**d** did not provide products resulting from either DPM or ODPM rearrangements upon the direct as well as the sensitized irradiation. While in acetone, **3a**−**d** furnished substantial amounts of the corresponding 1,3-acyl shift products **22a**−**d**; in methanol, the 1,3-acyl shift had become a more efficient process from the n,π^* singlet excited state as one would expect. However, **3d** furnished **22d** along with benzene derivative **23d** in 35% resulting from formal elimination of ketene when irradiated in methanol via the n,π^* singlet excited state. Similar observations were made in the case of **3a.** The photolytes of **3a** and **3d** could be separated into individual compounds. In the case of **3b** and **3c**, the photoproducts **22b** and **22c** could not be obtained in the pure form despite expenditure of considerable efforts.

The compounds **3a**−**d** did not undergo DPM rearrangements characteristic of β,γ-unsaturated ketones or 1,4-dienes under sensitized conditions probably due to dissipation of triplet energy through free rotation of the methylene group.[23] Although such behavior is not totally unexpected under the sensitized conditions because of the dissipation of triplet energy, **3a**−**d** were anticipated to undergo DPM rearrangement upon direct irradiation in the excited singlet state without undergoing a 1,3-acyl shift. It was therefore decided to examine the photochemical reactions of the corresponding alcohols **24c**,**d**. Accordingly, the ketone **3c** was reduced with $NaBH_4$ to isomeric alcohols *syn*-**24c** and *anti*-**25c**, which were separated and irradiated under both direct and sensitized conditions; however, the starting materials were recovered. Similar observations were made in the cases of *syn*-**24d** and *anti*-**25d** derived from **3d** (Scheme 7). It may be pertinent to mention that Ipaktschi and others had shown that in cases of bicyclo[2.2.1]heptene and bicyclo-

(20) (a) Chou, C.-H.; Peddinti, R. K.; Liao, C.-C. *Heterocycles* **2001**, *54*, 61−64 and references therein. (b) Liao, C.-C.; Peddinti, R. K. *Acc. Chem. Res.* **2002**, *35*, 856−866.

(21) Armesto, D.; Ramos, A.; Ortij, M. J.; Horspool, W. M.; Mancheno, M. J.; Caballero, O.; Mayoral, E. P. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1535−1541.

(22) (a) Armesto, D.; Langa, F.; Martin, J. A. F.; Perej-Ossorio, R. *J. Chem. Soc., Perkin Trans. 1* **1987**, 743−746. (b) Pratt, A. C.; Abdul-Majid, Q. *J. Chem. Soc., Perkin Trans. 1* **1987**, 359−364. (c) Armesto, D.; Horspool, W. M.; Langa, F. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1874−1875.

(23) (a) Swenton, J. S.; Crumrine, A. R.; Walker, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 1406−1407. (b) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 1407−1409 and 1409−1410. (c) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 1411−1412.

[3.2.2]nonatriene systems, the exocyclic double bond can participate in DPM rearrangement.[24] However, upon direct irradiation **3a**−**d** underwent a 1,3-acyl shift and ketene elimination reactions albeit with difficulty.

Structure Determination of Photoproducts 22a−**d.** The structure of photoproduct **22d** was assigned on the basis of spectral study. Its IR spectrum indicated the presence of a highly strained cyclic ketone (1770 cm^{-1}). The ^{13}C and DEPT spectra clearly indicate the presence of an olefinic methylene unit, an aliphatic methylene unit and a tetrasubstituted C−C double bond. The HRMS analysis indicated the presence of all mass units as in **3d**. These features can only exist in the assigned structure of **22d**. However, it was further confirmed by its single-crystal X-ray diffraction analysis.[25]

Similar observations were made in the structure assignment of **22a**. The ^{13}C and DEPT spectra clearly indicate the presence of olefinic and aliphatic methylene units and a tetrasubstituted C−C double bond. Its HRMS analysis indicated the presence of all mass units intact and the IR spectrum showed the presence of a highly strained cyclic ketone (1776 cm^{-1}). On the basis of these facts and the information provided by its ^1H NMR spectrum, the structure of **22a** was confirmed. As the photoproducts **22b** and **22c** were not obtained in their pure states, their structures were deduced on the basis of their ^1H NMR spectral data which were similar to those of **22a** and **22d** in this series.

Conclusion

In summary, we have developed an efficient procedure for the preparation of bicyclo[2.2.2]octenediones **1a**−**d** and their derivatives **2a**−**d** and **3a**−**d**. Compounds **1a**−**c** underwent highly chemoselective ODPM rearrangement under acetophenone-sensitization to yield **9a**,**c** and **10b** as major products. In the case of **1c**, the chemoselectivity of the ODPM rearrangement is less due to the higher stability of two possible diradicals **17a** and **17c** compared to the other possible diradicals **18a** and **18c**, respectively, whereas **1d** was unreactive due to the localization of triplet excited state energy, which may not be sufficient for rearrangement. We observed only *E*/*Z* isomerization in oximes **2a**−**d** under acetophenone- or acetone-sensitized irradiation. Compounds **3a**−**d**, which are also β,γ-unsaturated ketones, did not undergo either DPM or ODPM rearrangement but undergo a 1,3-acyl shift in acetone leading to the formation of products **22a**−**d**. In addition to 1,3-acyl shift products **22a** and **22d**, benzene derivatives **23a** and **23d** due to ketone extrusion were also obtained on direct irradiation of **3a** and **3d**, respectively.

Experimental Section

The general procedure for the preparation of compounds **1a**−**d** and the spectral analysis of compound **1a** and **1b** was reported earlier.[16,10]

(1*S,4*R**)-1,3,3-Trimethyl-7-phenylbicyclo[2.2.2]oct-7-ene-2,5-dione (1c).** Mp 122−123 °C; IR (neat) 3020, 2972, 1730, 1722, 1590, 1489, 1454 cm^{-1}; ^1H NMR (400 MHz) δ 7.32−7.34 (m, 3H), 7.06−7.08 (m, 2H), 6.31 (d, J = 6.4 Hz, 1H), 3.25 (d, J = 6.4 Hz, 1H), 2.44 (d, J = 19 Hz, 1H), 2.31 (d, J = 19 Hz, 1H), 1.26 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (100 MHz) δ 213, 207.4, 147.7, 137.1, 128.4, 128.0, 127.8, 61.8, 53.4, 42.8, 42.5, 26.3, 25.2, 16.1; MS (EI, 70 eV) *m*/*z* (rel intensity) 254 (M^+, 78), 211 (21), 185 (88), 183 (100), 169 (45), 156 (92), 141 (55), 115 (63), 91 (31), 77 (23), 70 (22); HRMS (EI) calcd for $C_{17}H_{18}O_2$ 254.1306, found 254.1315. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.27; H, 7.19.

(1*S,4*R**)-1,3,3-Trimethyl-7,8-diphenylbicyclo[2.2.2]oct-7-ene-2,5-dione (1d).** Mp 133−134 °C; IR (neat) 3040, 2972, 1726, 1493, 1444, 1384 cm^{-1}; ^1H NMR (400 MHz) δ 7.23−7.26 (m, 3H), 7.10−7.13 (m, 3H), 6.98−7.0 (m, 2H), 6.90−6.91 (m, 2H), 3.58 (s, 1H), 2.56 (d, J = 19.2 Hz, 1H), 2.41 (d, J = 19.2 Hz, 1H), 1.32 (s, 3H), 1.22 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz) δ 213.1, 207.6, 140.9, 139.1, 137.9, 136, 129.3, 128.2, 128.1, 127.9, 127.4, 127.3, 67.7, 53.5, 43, 42.8, 25.5, 25.1, 16.6; MS (EI, 70 eV) *m*/*z* (rel intensity) 330 (M^+, 69), 261 (48), 245 (18), 232 (100), 215 (25), 77 (6); HRMS (EI) calcd for $C_{23}H_{22}O_2$ 330.1620, found 330.1615. Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.57; H, 6.75.

(1*S,4*R**)-1,3,3-Trimethyl-5-hydroxyimino-7-ethoxycarbonylbicyclo[2.2.2]oct-7-en-2-one (2a).** A mixture of **1a** (2.50 g, 10 mM) and hydroxylamine hydrochloride (0.83 g, 12 mM) in pyridine (20 mL) was heated at 90 °C for 12 h with stirring under nitrogen. Then the reaction mixture was cooled to room temperature. The reaction mixture was diluted with ether and washed sequentially with 6 N HCl, saturated $NaHCO_3$ solution, and brine. The ether layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was recrystallized (hexanes and ether) to obtain **2a** (2.51 g, 95%) as colorless crystals. Mp 126−127 °C (from hexanes−ether); IR (film) 3417, 2978, 1722, 1708 cm^{-1}; ^1H NMR (300 MHz) δ 8.84 (s, 1H), 7.32 (d, J = 6.8 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.34 (d, J = 6.8 Hz, 1H), 2.61, 2.37 (AB q, J = 18.8 Hz, 2H), 1.50 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.12 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (75 MHz) δ 212.9, 164.0, 157.9, 142.7, 135.9, 60.9, 50.9, 50.4, 43.2, 34.9, 26.3, 25.2, 16.0, 14.1; MS (EI, 70 eV) *m*/*z* (rel intensity) 265 (M^+, 27), 248 (15), 220 (35), 248 (15), 95 (71), 136 (29), 122 (100); HRMS (EI) calcd for $C_{14}H_{19}NO_4$ (M^+) 265.1315, found 265.1315. Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.24; H, 7.31; N, 5.39.

(1*S,4*R**)-1,3,3-Trimethyl-5-hydroxyimino-7,8-bis(methoxycarbonyl)bicyclo[2.2.2]oct-7-en-2-one (2b).** Oxime **2b** (2.47 g, 94%) was obtained as colorless crystals by heating a mixture of **1b** (2.50 g, 8.51 mM) and hydroxylamine hydrochloride in pyridine following the procedure described for **2a**. Mp 119−121 °C (hexanes−ether); IR (film) 3435, 2973, 1729, 1710 cm^{-1}; ^1H NMR (300 MHz) δ 8.46 (br s, 1H), 3.82 (s, 4H), 3.79 (s, 3H), 2.68, 2.43 (ABq, J = 18.8 Hz, 2H), 1.29 (s, 3H), 1.11 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (75 MHz) δ 211.2, 165.9, 162.8, 156.4, 145.6, 132.8, 52.6, 52.4, 51.8, 49.6, 42.7, 33.9, 25.1, 24.6, 13.9; MS (EI, 70 eV) *m*/*z* (rel intensity) 309 (M^+, 13), 278 (21), 260 (31), 239(51), 208 (100), 195 (60), 180 (46); HRMS (EI) calcd for $C_{15}H_{19}NO_6$ (M^+) 309.1213, found 309.1215. Anal. Calcd for $C_{15}H_{19}NO_6$: C, 58.25; H, 6.19; N, 4.53. Found: C, 58.25; H, 6.15; N, 4.51.

(1*S,4*R**)-1,3,3-Trimethyl-5-hydroxyimino-7-phenylbicyclo[2.2.2]oct-7-en-2-one (2c).** Oxime **2c** (2.50 g, 95%) was obtained as colorless crystals by heating a mixture of **1c** (2.50 g, 9.84 mM) and hydroxylamine hydrochloride in pyridine according to the procedure described for **2a**. Mp 187−189 °C (hexanes−ether); IR (film) 3392, 2978, 1718 cm^{-1}; ^1H NMR (300 MHz) δ 9.10 (br s, 1H), 7.32−7.04 (m, 5H), 6.37 (d, J = 6.6 Hz, 1H), 3.33 (d, J = 6.6 Hz, 1H), 2.71, 2.53 (AB q, J = 18.7 Hz, 2H), 1.25 (s, 3H), 1.18 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (75 MHz) 214.3, 159.6, 146.3, 137.6, 130.9, 128.1, 127.6, 52.6, 50.4, 43.8, 35.1, 26.6, 25.2, 16.5; MS (EI, 70 eV) *m*/*z* (rel intensity) 269 (M^+, 30), 253 (10), 224 (10), 199 (100), 167 (22);

(24) (a) Ipaktschi, J. *Chem. Ber.* **1972**, *105*, 1840−1853. (b) Goldschmidt, Z.; Gutman, U. *Tetrahedron* **1974**, *30*, 3327−3331. (c) Goldschmidt, Z.; Worchel, A. *Tetrahedron Lett.* **1973**, 3621−3622 and 3622−3623. (d) Goldschmidt, Z.; Kende, A. S. *Tetrahedron Lett.* **1971**, 4625−4628. (e) Mariano, P. S.; Ko, J.-K. *J. Am. Chem. Soc.* **1973**, *95*, 8670−8678.

(25) CCDC deposition No. 206677.

HRMS (EI) calcd for $C_{17}H_{19}NO_2$ (M^+) 269.1417, found 269.1407. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.84; H, 7.12; N, 5.25.

(1*S,4*R**)-1,3,3-Trimethyl-5-hydroxyimino-7,8-diphenylbicyclo[2.2.2]oct-7-en-2-one (2d).** Oxime **2d** (2.48 g, 93%) was obtained as colorless crystals by heating a mixture of **1d** (2.50 g, 7.58 mM) and hydroxylamine hydrochloride in pyridine following the procedure described for oxime **2a**. Mp 187−189 °C (hexanes−ether); IR (film) 3241, 2972, 1718 cm^{-1}; ^1H NMR (300 MHz) δ 10.03 (br s, 1H), 7.26−6.93 (m, 10H), 3.67 (s, 1H), 2.87, 2.65 (AB q, J = 18.9 Hz, 2H), 1.31 (s, 3H), 1.17 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (75 MHz) 214.6, 159.6, 140.8, 139.6, 138.3, 136.3, 129.4, 128.1, 127.8, 127.1, 127.0, 56.2, 52.8, 44.0, 35.3, 25.6, 25.0, 16.9; MS (EI, 70 eV) *m*/*z* (rel intensity) 345 (M^+, 30), 329 (21), 288 (33), 275 (100), 258 (56), 232 (18), 215 (19); HRMS (EI) calcd for $C_{23}H_{23}NO_2$ (M^+) 345.1730, found 345.1722. Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71; N, 4.05. Found: C, 80.13; H, 6.66; N, 4.09.

Representative Procedure for the Preparation of Compounds 3a−d. (1*S,4*S**)-1,3,3-Trimethyl-5-methylene-7-ethoxycarbonylbicyclo[2.2.2]oct-7-en-2-one (3a).** To a solution of **1a** (1.16 g, 4.64 mM) in toluene (50 mL) was added with stirring a solution of $Ph_3P{=}CH_2$ (14. 6 mM), prepared prior to the Wittig reaction by adding potassium *tert*-amyl oxide in toluene (80 mL) to a solution of Ph_3MePBr in toluene (40 mL) and then heating at 70 °C for 1 h in toluene (120 mL). The resulting mixture was heated at 70 °C for 2 h with vigorous stirring under nitrogen. Then the reaction mixture was allowed to cool to room temperature, 1.0 M HCl was added, and the reaction mixture was extracted with ether. The combined organic layers were washed with saturated $NaHCO_3$ followed by brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by column chromatography (EtOAc/hexanes 1:9) on silica gel to obtain **3a** (0.48 g, 42%) as a colorless solid. Mp 61−62 °C (from ethyl acetate−hexanes); IR (film) 2975, 1722 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.21 (d, J = 6.6 Hz, 1H), 4.75 (d, J = 1.2 Hz, 1H), 4.60 (d, J = 1.2 Hz, 1H), 3.92−3.95 (m, 2H), 2.61 (d, J = 6.6 Hz, 1H), 1.99 (dd, J = 17.2, 3.7 Hz, 1H), 1.98 (dd, J = 17.2, 3.7 Hz, 1H), 1.68 (s, 3H), 0.95 (s, 3H), 0.93 (t, J = 6.2 Hz, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 213.6, 164.9, 146.0, 144.4, 134.7, 110.2, 61.1, 55.7, 52.1, 43.5, 39.6, 27.1, 25.9, 17.4, 14.8; MS (EI, 70 eV) *m*/*z* (rel intensity) 248 (M^+, 1), 203 (19), 178 (91), 133 (13), 105 (100); HRMS (EI) calcd for $C_{15}H_{20}O_3$ 248.1412, found 248.1403. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.54; H, 8.12. Found: C, 72.43; H, 8.13.

(1*S,4*R**)-1,3,3-Trimethyl-5-methylene-7,8-bis(methoxycarbonyl)bicyclo[2.2.2]oct-7-en-2-one (3b).** Compound **3b** (0.40 g, 25%) was obtained as a slightly yellowish oil along with compound **8** (0.50 g, 37%), when **1b** (1.37 g, 4.66 mM) was treated with preformed $Ph_3P{=}CH_2$ (7.37 mM) in toluene following the procedure described for **3a**. **3b**: IR (film) 2961, 1728 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 4.90 (dd, J = 2.9, 2.0 Hz, 1H), 4.61 (dd, J = 2.9, 2.0 Hz, 1H), 3.61 (s, 1H), 3.46 (s, 3H), 3.29 (s, 3H), 2.11 (dd, J = 17.2, 2.0 Hz, 1H), 1.93 (dd, J = 17.2, 2.0 Hz, 1H), 1.31 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 212.5, 166.7, 164.2, 145.3, 143.4, 135.7, 111.1, 55.1, 53.0, 52.6, 52.4, 43.3, 38.8, 26.2, 25.4, 15.3; MS (EI, 70 eV) *m*/*z* (rel intensity) 292 (M^+, 4), 222 (23), 204 (25), 191 (70), 178 (24), 163 (100), 145 (64); HRMS (EI) calcd for $C_{16}H_{20}O_5$ 292.1311, found 292.1310. Compound **8**: IR (film) 2964, 1726 cm^{-1}; ^1H NMR (400 MHz) δ 4.99 (s, 2H), 4.96 (dd, J = 2.0, 1.6 Hz, 1H), 4.84 (dd, J = 2.0, 1.6 Hz, 1H), 3.68 (s, 3H), 3.12 (s, 1H), 2.42 (dd, J = 16.9, 2.0 Hz, 1H), 2.33 (dd, J = 16.9, 2.0 Hz, 1H), 1.89 (s, 3H), 1.22 (s, 3H), 1.09 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz) δ 213.9, 167.0, 148.2, 143.3, 141.7, 128.6, 114.9, 109.2, 57.8, 51.3, 50.1, 42.9, 38.3, 25.1, 24.7, 20.7, 14.9; MS (EI, 70 eV) *m*/*z* (rel intensity) 290 (M^+, 1), 274 (26), 204 (32), 145 (91), 84 (100); HRMS (EI) calcd for $C_{17}H_{22}O_4$ 290.1518, found 290.1518.

(1*S,4*S**)-1,3,3-Trimethyl-5-methylene-7-phenylbicyclo[2.2.2]oct-7-en-2-one (3c).** Compound **3c** (1.96 g, 90%) was obtained as a colorless oil by treating **1c** (2.20 g, 8.65 mM) with preformed $Ph_3P{=}CH_2$ (25.94 mM) in toluene according to the procedure described for **3a**. IR (film) 2925, 1719, 1651 cm^{-1}; ^1H NMR (400 MHz) δ 7.22−7.26 (m, 3H), 7.02−7.04 (m, 2H), 6.36 (d, J = 6.4 Hz, 1H), 4.94 (d, J = 1.2 Hz, 1H), 4.81 (d, J = 1.2 Hz, 1H), 3.02 (d, J = 6.4 Hz, 1H), 2.38 (t, J = 2.2 Hz, 2H), 1.15 (s, 3H), 1.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 144.9, 143.3, 138.3, 133.3, 128.2, 127.7, 127.0, 107.9, 54.7, 52.6, 43.6, 38.9, 26.7, 25.1, 16.5; MS (EI, 70 eV) *m*/*z* (rel intensity) 252 (M^+, 4), 182 (100), 167 (65), 152 (6); HRMS (EI) calcd for $C_{18}H_{20}O$ 252.1520, found 252.1520.

(1*S,4*R**)-1,3,3-Trimethyl-5-methylene-7,8-diphenylbicyclo[2.2.2]oct-7-en-2-one (3d).** Compound **3d** (0.41 g, 96%) was obtained as colorless crystals by treating **1d** (0.43 g, 1.32 mM) with preformed $Ph_3P{=}CH_2$ (4.14 mM) in toluene following the procedure described for **3a**. Mp 101−102 °C (from ether); IR (film) 2970, 1717 cm^{-1}; ^1H NMR (400 MHz) δ 6.90−7.20 (m, 10H), 5.12 (d, J = 1.2 Hz, 1H), 4.94 (d, J = 1.2 Hz, 1H), 3.40 (s, 1H), 2.52 and 2.56 (ABq, J = 17.0 Hz, 2H), 1.26 (s, 3H), 1.14 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (100 MHz) δ 216.0, 144.9, 143.1, 139.4, 137.2, 136.9, 129.6, 128.0, 127.9, 127.8, 127.7, 126.7, 126.5, 108.2, 61.1, 52.8, 43.8, 39.1, 25.8, 24.9, 17.0; MS (EI, 70 eV) *m*/*z* (rel intensity) 328 (M^+, 25), 258 (100), 243 (65), 181 (7), 165 (10); HRMS (EI) calcd for $C_{24}H_{24}O$ 328.1827, found 328.1823. Anal. Calcd for $C_{24}H_{24}O$: C, 87.80; H, 7.32. Found: C, 87.79; H, 7.30.

Irradiation of 1a−d in Acetophenone/Acetone/Methanol: Irradiation of 1a. A solution of **1a** (0.1 g, 0.4 mM) in freshly distilled acetophenone (2 mL) in a Pyrex vessel was irradiated for 8.5 h at 350 nm. Removal of acetophenone under reduced pressure (50 °C at 0.05 Torr) followed by column chromatography of the residue on silica gel with 20% ethyl acetate in hexanes afforded **9a** (98 mg, 98%) as a colorless oil.

A solution of **1a** (0.05 g, 0.20 mM) in acetone (5 mL) in a Pyrex vessel was irradiated for 8 h at 300 nm. Removal of acetone on a rotavapor followed by column chromatography of the residue on silica gel with 2.5% methanol in chloroform as eluent furnished **9a** (28 mg, 56%) and phenol **11a** (9 mg, 24%).

A solution of **1a** (0.05 g, 0.20 mM) in methanol (5 mL) in a Pyrex vessel was irradiated for 15 h at 300 nm. Removal of methanol on a rotavapor followed by column chromatography of the residue on silica gel with 2.5% methanol in chloroform as eluent furnished **9a** (10 mg, 20%) and phenol **11a** (16 mg, 50%).

Ethyl (1*S,2*S**,5*S**,8*S**)-5,7,7-Trimethyl-3,6-dioxotricyclo[3.3.0.0^{2,8}]octane-1-carboxylate (9a).** IR (film) 2930, 1733, 1457 cm^{-1}; ^1H NMR (400 MHz) δ 4.15 (q, J = 7.6 Hz, 2H), 2.72 (d, J = 9.6 Hz, 1H), 2.64 (d, J = 18.4 Hz, 1H), 2.54 (d, J = 9.6 Hz, 1H), 2.14 (d, J = 18.4 Hz, 1H), 1.55 (s, 3H), 1.23 (t, J = 7.6 Hz, 3H), 1.21 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz) δ 220.8, 207.7, 169.3, 61.2, 55.4, 53.1, 46.4, 46.3, 43.8, 43.4, 26.4, 22.9, 17.7, 14.0; MS (EI, 70 eV) *m*/*z* (rel intensity) 250 (M^+, 6), 222 (28), 194 (100), 179 (38), 165 (33), 121 (78); HRMS (EI) calcd for $C_{14}H_{18}O_4$ 250.1205, found 250.1216.

Ethyl 4-Hydroxy-2-methylbenzoate (11a). Mp 88−89 °C (from EtOAc−hexanes); IR (film) 3293, 2950, 1690, 1600 cm^{-1}; ^1H NMR (400 MHz) δ 7.89 (dd, J = 5.0, 2.8 Hz, 1H), 6.70 (d, J = 5.0 Hz, 1H), 6.69 (d, J = 2.8 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 2.57 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz) δ 167. 6, 158.9, 143.3, 133.2, 121.9, 118.3, 112.6, 60.6, 22.1, 14.3; MS (70 eV) *m*/*z* (rel intensity) 180 (M^+, 31), 152 (10), 135 (100), 107 (20), 77 (32), 29 (17); HRMS (EI) calcd for $C_{10}H_{12}O_3$ 180.0786, found 180.0791. Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.66, H, 6.71.

Irradiation of 1b. A solution of **1b** (0.49 g, 1.66 mM) in freshly distilled acetophenone (5 mL) in a Pyrex vessel was irradiated for 6 d at 350 nm. Removal of acetophenone under reduced pressure (50 °C at 0.05 Torr) followed by recrystallization of the residue in dichloromethane−hexanes afforded **10b** (0.44 g, 90%) as colorless crystals.

A solution of **1b** (0.05 g, 0.17 mM) in acetone (5 mL) in a Pyrex vessel was irradiated for 53 h at 300 nm. Removal of acetone on a rotavapor followed by column chromatography of the residue on silica gel with 50% ethyl acetate in hexanes furnished **10b** (20 mg, 40%) and phenol **11b** (21 mg, 55%).

A solution of **1b** (0.05 g, 0.17 mM) in methanol (5 mL) in a Pyrex vessel was irradiated for 72 h at 300 nm. Removal of methanol on a rotavapor followed by column chromatography of the residue on silica gel with 25% ethyl acetate in hexanes furnished phenol **11b** (29 mg, 76%).

Dimethyl (1*S,2*R**,5*S**,8*S**)-4,4,8-Trimethyl-3,6-dioxotricyclo[3.3.0.0^{2,8}]octane-1,2-dicarboxylate (10b).**[10] Mp 109−110 °C (from CH_2Cl_2−hexanes); IR (film) 2964, 1745, 1737, 1715 cm^{-1}; ^{1}H NMR (400 MHz) δ 3.78 (s, 3H), 3.77 (s, 3H), 3.18 (s, 1H), 2.44 (s, 2H), 1.65 (s, 3H), 1.32 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (75 MHz) δ 210.2, 207.7, 167.7, 164.3, 60.2, 55.6, 52.9, 52.6, 47.4, 44.0, 40.7, 25.7, 21.8, 17.4, 16.7; GCMS (12 eV) *m*/*z* (rel intensity) 294 (M$^+$, 3), 235 (11), 193 (100), 175 (15), 105 (16), 70 (26); HRMS (EI) calcd for $C_{15}H_{18}O_6$ 294.1103, found 294.1106. Anal. Calcd for $C_{15}H_{18}O_6$: C, 61.22; H, 6.16. Found: C, 61.26; H, 6.21.

Dimethyl 5-Hydroxy-3-methylphthalate (11b). Mp 67−68 °C (from hexanes); IR (film) 3379, 2954, 1735, 1720 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.19 (d, J = 2.4 Hz, 1H), 6.81 (d, J = 2.4 Hz, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz) δ 170.7, 166.7, 156.6, 137.9, 129.9, 126.7, 121.1, 114.3, 52.6, 52.6, 19.2, GCMS (12 eV) *m*/*z* (rel intensity) 224 (M$^+$, 12), 193 (100), 163 (8), 134 (68), 77 (27); HRMS (EI) calcd for $C_{11}H_{12}O_5$ 224.0685, found 224.0683.

Irradiation of 1c. A solution of **1c** (0.10 g, 0.39 mM) in freshly distilled acetophenone (3 mL) in a Pyrex vessel was irradiated for 6.5 h at 350 nm. Removal of acetophenone under reduced pressure (50 °C at 0.05 Torr) followed by recrystallization of the residue in ethyl acetate−hexanes (1:3) afforded **9c** (95 mg, 95%) as colorless crystals

A solution of **1c** (0.05 g, 0.2 mM) in acetone (5 mL) in a Pyrex vessel was irradiated for 10 h at 300 nm. Removal of acetone on a rotavapor followed by column chromatography of the residue on silica gel with 25% ethyl acetate in hexanes furnished **9c** (42 mg, 84%).

A solution of **1c** (0.05 g, 0.20 mM) in methanol (5 mL) in a Pyrex vessel was irradiated for 18 h at 300 nm. Removal of methanol on a rotavapor followed by column chromatography of the residue on silica gel with 20% ethyl acetate in hexanes furnished phenol **11c** (23 mg, 64%).

(1*R,2*S**,5*S**,8*R**)-5,7,7-Trimethyl-1-phenyltricyclo[3.3.0.0^{2,8}]octane-3,6-dione (9c).** Mp 119−120 °C (from EtOAc−hexanes); IR (film) 2970, 1735, 1731 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.33−7.39 (m, 3H), 7.26−7.28 (m, 2H), 2.69 (dd, J = 18, 1.7 Hz, 1H), 2.48 (d, J = 9.5 Hz, 1H), 2.36 (dd, J = 9.5, 1.7 Hz, 1H), 2.28 (d, J = 18 Hz, 1H), 1.42 (s, 3H), 1.20 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (75 MHz) δ 222.3, 210.8, 136.4, 130.1, 128.7, 128.1, 55.1, 54.7, 49.7, 46.6, 44.4, 42.8, 26.8, 23.3, 18.0; MS (EI, 70 eV) *m*/*z* (rel intensity) 254 (M$^+$, 42), 198 (41), 185 (61), 183 (100), 169 (24), 156 (38), 141 (27); HRMS (EI) calcd for $C_{17}H_{18}O_2$ 254.1306, found 254.1309. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.14; H, 7.15.

3-Methyl-4-phenylphenol (11c). IR (film) 3371, 3020, 1610 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.27−7.38 (m, 5H), 7.10 (dd, J = 3.0, 10.6 Hz, 1H), 6.74 (d, J = 10.6 Hz, 1H), 6.73 (d, J = 3.0 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (75 MHz) δ 154.6, 141.5, 136.9, 134.6, 130.9, 129.0, 127.9, 126.4, 116.9, 112.7, 20.5; GCMS (12 eV) *m*/*z* (rel intensity) 184 (M$^+$, 100), 165 (33), 155 (24), 144 (20); HRMS (EI) calcd for $C_{13}H_{12}O$ 184.0888, found 184.0886.

Irradiation of 1d. A solution of **1d** (0.10 g, 0.39 mM) in freshly distilled acetophenone (3 mL) in a Pyrex vessel was irradiated for 84 h at 350 nm. TLC and ^{1}H NMR analysis indicated no reaction. **1d** (84 mg, 84%) was recovered after removal of acetophenone under reduced pressure (50 °C at 0.05 Torr).

A solution of **1d** (0.05 g, 0.15 mM) in acetone (5 mL) in a Pyrex vessel was irradiated for 10 h at 300 nm. Removal of acetone on a rotavapor followed by column chromatography of the residue on silica gel with 15% ethyl acetate in hexanes as eluent furnished phenol **11d** (23 mg, 58%).

A solution of **1d** (0.05 g, 0.15 mM) in methanol (5 mL) in a Pyrex vessel was irradiated for 48 h at 300 nm. Removal of methanol on a rotavapor followed by column chromatography of the residue on silica gel with 15% ethyl acetate in hexanes as eluent furnished phenol **11d** (34 mg, 86%).

3-Methyl-4,5-diphenylphenol (11d). Mp 107−108 °C (from CH_2Cl_2−pentane); IR (film) 3399, 1604 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.09−7.18 (m, 6H), 6.98−7.03 (m, 4H), 6.78 (d, J = 2.4 Hz, 1H), 6.74 (d, J = 2.4 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (75 MHz) δ 154.3, 142.8, 141.7, 140.0, 138.1, 133.1, 130.8, 129.6, 127.5, 127.3, 126.0, 126.0, 115.9, 114.4, 21.2; MS (EI, 70 eV) *m*/*z* (rel intensity) 260 (M$^+$, 100), 245 (24), 215 (27), 152 (13), 77 (13); HRMS (EI) calcd for $C_{19}H_{16}O$ (M$^+$) 260.1201, found 260.1214. Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.63; H, 6.12.

(1*S,2*S**,4*R**,5*R**)-1,3,3-Trimethyl-7-phenylbicyclo[2.2.2]oct-7-ene-2,5-diol (12).** To a solution of **1c** (0.10 g, 0.39 mM) in dry THF (10 mL) was added a solution of LAH (4 mL, 4 mM, 1 M in THF) at 0 °C. The contents of the flask were stirred for 4 h at 0 °C. Then the reaction was quenched carefully with a 0.5 M solution of sodium potassium tartrate and extracted with ethyl acetate. The combined ethyl acetate layers were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel with 40% ethyl acetate in hexanes as eluent to obtain diol **12** (80 mg, 79%) as a colorless oil. IR (film) 3406, 3040, 2934, 1636 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.24−7.33 (m, 3H), 7.18−7.20 (m, 2H), 6.22 (d, J = 7.6 Hz, 1H), 3.94 (ddd, J = 2.6, 6.0, 10.0, Hz, 1H), 3.45 (s, 1H), 2.32 (dd, J = 2.6, 7.6 Hz, 1H), 1.93 (dd, J = 10.0, 13.2 Hz, 1H), 1.83 (br, 2H), 1.43 (s, 3H), 1.34 (dd, J = 6.0, 13.9 Hz, 1H), 1.13 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (75 MHz) δ 145.2, 140.5, 132.1, 128.1, 126.6, 85.3, 71.4, 51.3, 43.5, 40.7, 39.6, 31.1, 25.8, 21.2; MS (EI, 70 eV) *m*/*z* (rel intensity) 258 (M$^+$, weak), 186 (100), 171 (95), 169 (34), 157 (20); HRMS (EI) calcd for $C_{17}H_{22}O_2$ (M$^+$) 258.1620, found 258.1620.

(1*R,4*S**,5*S**)-5-Hydroxy-4,6,6-trimethyl-8-phenylbicyclo[2.2.2]oct-7-en-2-one (13).** PCC (0.18 g, 0.83 mM) and Celite (0.18 g) were mixed in CH_2Cl_2 (5 mL) in a round-bottom flask. To this mixture was added a solution of **12** (0.18 g, 0.7 mM) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was stirred for 70 min at that temperature. Then dry ether was added and the mixture was filtered through a pad of florisil. Removal of solvents followed by column chromatography (EtOAc/hexane 1:5) of the residue afforded the hydroxy ketone **13** (117 mg, 66%) as a colorless oil. IR (film) 3427, 2960, 1712, 1643 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.28−7.35 (m, 3H), 7.19−7.21 (m, 2H), 6.14 (d, J = 6.4 Hz, 1H), 3.54 (s, 1H), 2.85 (d, J = 6.4 Hz, 1H), 2.12 (d, J = 18.8 Hz, 1H), 2.04 (d, J = 18.8 Hz, 1H), 1.80 (br, 1H), 1.20 (s, 3H), 1.14 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (75 MHz) δ 190.5, 149.5, 139.3, 128.1, 127.8, 127.1, 125.6, 82.8, 62.3, 46.3, 44.2, 41.2, 30.2, 23.0, 20.7; GCMS (12 eV) *m*/*z* (rel intensity) 256 (M$^+$, 6), 199 (4), 184 (100), 169 (15), 156 (15); HRMS calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1454.

(1*R,2*S**,5*S**,6*S**,8*R**)-Hydroxy-5,7,7-trimethyl-1-phenyltricyclo[3.3.0.0^{2,8}]octan-2-one (14).** A solution of **13** (0.04 g, 0.16 mM) in freshly distilled acetophenone (2 mL) in a Pyrex vessel was irradiated for 8 h at 350 nm. Removal of acetophenone under reduced pressure (50 °C at 0.05 Torr) followed by column chromatography of the residue on silica gel with 15% ethyl acetate in hexanes afforded **14** (34 mg, 85%) as colorless crystals. Mp 172−173 °C (CH_2Cl_2−hexanes); IR (film) 3475, 2963, 1705 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.26−7.37 (m, 5H), 3.53 (s, 1H), 2.51 (d, J = 19 Hz, 1H), 2.41 (d, J = 19 Hz, 1H), 2.27 (d, J = 9.8 Hz, 1H), 2.04 (d, J = 9.8 Hz, 1H), 1.77 (br, 1H), 1.36 (s, 3H), 1.18 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (75 MHz) δ 214.2, 137.7, 130.4, 128.1, 127.3, 92.9, 57.0, 53.6, 53.6, 49.6, 46.0, 44.7, 26.7, 26.4, 20.9; GCMS (12 eV) *m*/*z* (rel intensity)

256 (M^+, weak), 199 (3), 186 (15), 185 (66), 184 (100); HRMS calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1456. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.64; H, 7.87. Found: C, 79.54; H, 7.88.

5,7,7-Trimethyl-1-phenyltricyclo[3.3.0.0^{2,8}]octane-3,6-dione (9c). Oxidation of **14** (47 mg, 0.18 mM) with PCC (60 mg, 0.28 mM) in CH_2Cl_2 (5 mL) following the procedure described for diol **12** afforded **9c** (42 mg, 90%) as a colorless solid.

(1*S,4*R**,5*R**)-5-Hydroxy-1,3,3-trimethyl-7-phenylbicyclo[2.2.2]oct-7-en-2-one (15).** To a solution of **1c** (0.20 g, 0.78 mM) in methanol (10 mL) was added $NaBH_4$ (0.12 g, 3.17 mM) at 0 °C and the mixture was stirred for 70 min. Then water was added and extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel with use of a 1:2 mixture of ethyl acetate and hexanes as eluent to obtain alcohol **15** (190 mg, 94%) as a colorless oil. IR (film) 3445, 2970, 1709 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.27−7.32 (m, 3H), 7.03−7.05 (m, 2H), 6.31 (d, J = 7.1 Hz, 1H), 4.32 (ddd, J = 10.2, 6.0, 2.6 Hz, 1H), 2.76 (dd, J = 7.1, 2.6 Hz, 1H), 2.23 (dd, J = 13.9, 10.2 Hz, 1H), 1.77 (br, 1H), 1.66 (dd, J = 13.9, 6.0 Hz, 1H), 1.42 (s, 3H), 1.21 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (75 MHz) δ 216.8, 142.9, 138.2, 134.1, 128.1, 128.0, 127.8, 127.2, 70.1, 51.1, 50.8, 43.4, 38.6, 29.9, 26.3, 16.6; MS (EI, 70 eV) *m*/*z* (rel intensity) 256 (M^+, 29), 211 (18), 186 (72), 171 (69), 169 (100), 88 (20); HRMS calcd for $C_{17}H_{20}O_2$ 256.1464, found 256.1456.

(1*R,2*S**,5*R**,6*R**,8*S**)-6-Hydroxy-4,8,8-trimethyl-2-phenyltricyclo[3.3.0.0^{2,8}]octan-3-one (16).** A solution of **15** (0.13 g, 0.50 mM) in acetophenone (5 mL) in a Pyrex vessel was irradiated at 350 nm for 5 d. Removal of acetophenone under reduced pressure (50 °C at 0.05 Torr) followed by column chromatography of the residue on silica gel with 15% ethyl acetate in hexanes as eluent afforded **16** (44 mg, 34%) as colorless crystals. Substrate **15** (50 mg, 40%) was also recovered. Mp 124−125 °C (from EtOAc−hexanes); IR (film) 3440, 2947, 1715 cm^{-1}; ^{1}H NMR (400 MHz) δ 7.32 (m, 3H), 7.26 (m, 2H), 4.52 (ddd, J = 11.0, 8.2, 5.2 Hz, 1H), 2.57 (d, J = 5.2 Hz, 1H), 2.54 (ddd, J = 5.2, 5.2, 1.7 Hz, 1H), 2.06 (ddd, J = 13.0, 8.2, 1.7 Hz, 1H), 1.68 (dd, J = 13.0, 11.0 Hz, 1H), 1.60 (br, 1H), 1.24 (s, 3H), 1.11 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (75 MHz) δ 215.8, 134.5, 129.0, 127.9, 126.7, 78.8, 52.2, 51.4, 50.6, 38.2, 37.7, 35.6, 28.7, 20.2, 18.5; GCMS (12 eV) *m*/*z* (rel intensity) 256 (M^+, 32), 228 (66), 213 (76), 210 (30), 195 (100), 169 (65), 157 (23); HRMS calcd for $C_{17}H_{20}O_2$ 256.1464, found 256.1458.

(1*R,2*S**,5*R**,8*S**)-4,8,8-Trimethyl-2-phenyltricyclo-[3.3.0.0^{2,8}]octane-3,6-dione (10c).** To a solution of **16** (39 mg, 0.15 mM) in CH_2Cl_2 (3 mL) were added PCC (66 mg, 0.3 mM) and Celite (66 mg). The mixture was stirred vigorously for 40 min at room temperature. The reaction mixture was diluted with anhydrous ether and filtered through a pad of florisil. Removal of solvents under reduced pressure followed by recrystalization of residue in EtOAc−hexanes (1:5) afforded **10c** (33 mg, 85%) as a colorless solid. Mp 138−139 °C (from EtOAc−hexanes); IR (film) 2961, 1735, 1727; ^{1}H NMR (400 MHz) δ 7.36 (m, 5H), 2.89 (d, J = 5.2 Hz, 1H), 2.78 (dd, J = 5.2, 2.4 Hz, 1H), 2.47 (d, J = 19.2 Hz, 1H), 2.39 (dd, J = 19.2, 2.4 Hz, 1H), 1.23 (s, 3H), 1.03 (s, 3H), 0.95 (s. 3H); ^{13}C NMR (100 MHz) δ 214.0, 212.6, 134.1, 129.0, 128.4, 127.4, 58.6, 54.2, 51.7, 42.9, 35.9, 34.7, 26.5, 20.2, 17.5; GCMS (12 eV) *m*/*z* (rel intensity) 254 (M^+, 9), 226 (23), 211 (100), 183 (18), 169 (17), 83 (23); HRMS calcd for $C_{17}H_{18}O_2$ 254.1308, found 254.1330. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.21; H, 7.12.

Irradiation of 2a−d in Acetophenone and Acetone. Solutions of **2a**−**d** in acetophenone or acetone in Pyrex vessels were irradiated for several hours with a Hanovia 450W Hg-Arc lamp. ^{1}H NMR analysis of the crude reaction mixtures after removal of solvent indicated only *E*/*Z* isomerization (Scheme 6). However, the *E*/*Z* isomers could not be separated by various conventional techniques.

Irradiation of Oxime 2a. A solution of **2a** (0.025 g, 0.094 mM) in methanol (6.5 mL) was irradiated for 4 h with a Hanovia 450W Hg-Arc lamp. Methanol was removed on a rotavapor under reduced pressure. The residue was first subjected to column chromatography (EtOAc/hexanes 1:3) to obtain **21a** along with some impurities. Pure **21a** (5 mg, 27%) was obtained by preparative thin-layer chromatography on silica gel with 20% ethyl acetate in benzene.

A solution of **2a** (0.025 g, 0.094 mM) in acetonitrile (6.5 mL) was irradiated for 4 h at 300 nm. Removal of acetonitrile on a rotavapor followed by column chromatography (EtOAc/hexanes 1:3) of the residue furnished *N*-hydroxyaniline derivative **21a** (18 mg, 95%).

Ethyl 2-Methyl-4-(*N*-hydroxy)aminobenzoate (21a). IR (film) 3468, 3377, 2984, 1691 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.83 (dd, J = 6.7, 2.4 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 6.47 (d, J = 6.7 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.98 (br, 2H), 2.53 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz) δ 167.3, 149.8, 142.9, 133.0, 119.1, 117.1, 114.5, 59.9, 22.3, 14.4; MS (EI, 70 eV) *m*/*z* (rel intensity) 195 (M^+, 1), 179 (30), 151 (7), 134 (100), 106 (20); HRMS (EI) calcd for $C_{10}H_{13}NO_3$ 195.0896, found 195.0895.

Irradiation of Oxime 2b. A solution of **2b** (0.025 g, 0.081 mM) in methanol (5.5 mL) was irradiated for 4 h with a Hanovia 450W Hg-Arc lamp. Methanol was removed on a rotavapor under reduced pressure. The residue was first subjected to column chromatography (EtOAc/hexane 1:3) to obtain **21b** along with some impurities. Pure **21b** (7 mg, 40%) was obtained by preparative thin-layer chromatography on silica gel with 20% ethyl acetate in benzene.

A solution of **2b** (0.025 g, 0.081 mM) in acetonitrile (5.5 mL) was irradiated for 4 h at 300 nm. Removal of acetonitrile on a rotavapor followed by column chromatography (EtOAc/hexanes 1:3) of the residue furnished *N*-hydroxyaniline derivative **21b** (10 mg, 52%).

Dimethyl 3-Methyl-5-(*N*-hydroxy)aminophthalate (21b). IR (film) 3469, 3377, 2952, 1719, 1708 cm^{-1}; ^{1}H NMR (300 MHz) δ 6.97 (d, J = 2.0 Hz, 1H), 6.60 (d, J = 2.0 Hz, 1H), 3.92 (br, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz) δ 169.8, 167.1, 147.3, 137.7, 130.5, 124.1, 119.4, 113.1, 52.3, 52.1, 19.5; MS (EI, 70 eV) *m*/*z* (rel intensity) 239 (M^+, 1), 223 (34), 207 (5), 192 (100), 191 (27), 149 (11), 133 (50); HRMS (EI) calcd for $C_{11}H_{13}NO_5$ 239.0794, found 239.0779.

Irradiation of Oxime 2c. A solution of **2c** (0.035 g, 0.13 mM) in methanol (8.7 mL) was irradiated for 4 h with a Hanovia 450W Hg-Arc lamp. Methanol was removed on a rotavapor under reduced pressure. The residue was first subjected to column chromatography (EtOAc/hexanes 1:3) to obtain **21c** along with some impurities. Pure **21c** (7 mg, 30%) was obtained by preparative thin-layer chromatography on silica gel with 20% ethyl acetate in benzene.

A degassed solution of **2c** (0.035 g, 0.094 mM) in acetonitrile (8.7 mL) was irradiated for 4 h at 300 nm. Removal of acetonitrile on a rotavapor followed by column chromatography (EtOAc/hexanes 1:3) of the residue furnished *N*-hydroxyaniline derivative **21c** (17 mg, 66%).

5-Hydroxylamino-2-phenyltoluene (21c). IR (film) 3460, 3373, 3055, 2964 cm^{-1}; ^{1}H NMR (300 MHz) δ 7.42−7.30 (m, 5H), 7.06 (d, J = 7.9 Hz, 1H), 6.62 (d, J = 2.5 Hz, 1H), 6.59 (dd, J = 7.9, 2.5 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (75 MHz) δ 145.5, 142.0, 136.3, 132.6, 130.8, 129.4, 127.9, 126.1, 116.8, 112.6, 20.5; MS (EI, 70 eV) *m*/*z* (rel intensity) 199 (M^+, 2), 183 (10), 167 (40), 152 (30); HRMS (EI) calcd for $C_{13}H_{13}NO$ 199.0998, found 199.1001.

Irradiation of Oxime 2d. A solution of **2d** (0.035 g, 0.101 mM) in methanol (6.8 mL) was irradiated for 4 h with a Hanovia 450W Hg-Arc lamp. Methanol was removed on a rotavapor under reduced pressure. The residue was first subjected to column chromatography (EtOAc/hexanes 1:3) to obtain **21d** along with some impurities. Pure **21d** (10 mg, 27%) was obtained by preparative thin-layer chromatography on silica gel with 20% ethyl acetate in benzene.

A solution of **2d** (0.035 g, 0.101 mM) in acetonitrile (6.8 mL) was irradiated for 4 h at 300 nm. Removal of acetonitrile on a rotavapor followed by column chromatography (EtOAc/hexanes 1:3) of the residue furnished *N*-hydroxyaniline derivative **21d** (12 mg, 95%).

2,3-Diphenyl-5-hydroxyaminotoluene (21d). IR (film) 3455, 3369, 3022, 2957 cm^{-1}; ^1H NMR (300 MHz) δ 7.18−7.00 (m, 10H), 6.65 (d, J = 2.3 Hz, 1H), 6.61 (d, J = 2.3 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (75 MHz) δ 145.1, 142.6, 142.2, 140.4, 137.6, 131.3, 131.1, 129.7, 127.5, 127.3, 126.0, 125.8, 115.8, 114.4, 21.2; MS (EI, 70 eV) *m*/*z* (rel intensity) 275 (M^+, 2), 235 (100), 220 (45), 178 (23); HRMS (EI) calcd for $C_{19}H_{17}NO$ 275.1311, found 275.1301.

Irradiation of 3a−d. A solution of **3a** (0.05 g, 0.20 mM) in freshly distilled acetophenone (2 mL) in a Pyrex vessel was irradiated for 36 h at 350 nm. Removal of acetophenone under reduced pressure (50 °C at 0.05 Torr) followed by column chromatography (silica gel, 10% ethyl acetate in hexanes) of the residue afforded **3a** (45 mg, 90%) as colorless crystals. Under similar conditions **3b**, **3c**, and **3d** also gave corresponding starting material only.

A solution of **3a** (0.05 g, 0.2 mM) in acetone (5 mL) in a quartz vessel was irradiated for 24 h at 300 nm. Removal of acetone on a rotavapor followed by column chromatography (silica gel, 10% ethyl acetate in hexanes) of the residue furnished **3a** (35 mg, 70%) and **22a** (8 mg, 16%).

A solution of **3a** (0.05 g, 0.20 mM) in methanol (5 mL) in a quartz vessel was irradiated for 24 h at 300 nm. Removal of methanol on a rotavapor followed by column chromatography (silica gel, 10% ethyl acetate in hexane) of the residue furnished **3a** (23 mg, 46%), **22a** (17 mg, 34%), and benzene derivative **23a** (1 mg, 2%).

Ethyl (1*S,6*R**)-3,7,7-Trimethyl-5-methylene-8-oxobicyclo[4.2.0]oct-2-ene-2-carboxylate (22a).** IR (film) 2961, 1776, 1709 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 4.81 (d, J = 10.4 Hz, 1H), 4.77 (d, J = 1.9 Hz, 1H), 4.66 (d, J = 1.9 Hz, 1H), 4.02−4.09 (m, 2H), 2.54, 2.59 (ABq, J = 18.4 Hz, 2H), 2.54 (d, J = 10.4 Hz, 1H), 2.08 (s, 3H), 1.01 (t, J = 7.0 Hz, 3H), 0.99 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 212.0, 167.1, 150.9, 142.6, 121.8, 113.7, 62.5, 61.0, 58.2, 43.9, 42.8, 26.0, 22.9, 17.9, 14.9; MS (EI, 70 eV) *m*/*z* (rel intensity) 248 (M^+, 28), 228 (33), 196 (81), 168 (33), 101 (100); HRMS calcd for $C_{15}H_{20}O_3$ 248.1413, found 248.1419.

Ethyl 2,4-Dimethylbenzoate (23a). IR (film) 2956, 1715 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.85 (d, J = 6.8 Hz, 1H), 7.26 (s, 1H), 7.04 (d, J = 6.8 Hz, IH), 4.35 (q, J = 7.1 Hz, 2H), 2.90 (s, 3H), 2.57 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); MS (EI, 70 eV) *m*/*z* (rel intensity) 178 (M^+, 4), 150 (6), 144 (29), 132 (100), 116 (62), 104 (59); HRMS calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0992.

Irradiation of 3b. A solution of **3b** (0.05 g, 0.17 mM) in acetone (5 mL) in a quartz vessel was irradiated for 12 h at 300 nm. Removal of acetone on a rotavapor followed by column chromatography (silica gel, 10% ethyl acetate in hexanes) of the residue furnished **3b** (22 mg, 44%) and **22b** (8.5 mg, 17%).

A solution of **3b** (0.05 g, 0.17 mM) in methanol (5 mL) in a quartz vessel was irradiated for 12 h at 300 nm. Removal of methanol on a rotavapor followed by column chromatography (silica gel, 10% ethyl acetate in hexanes) of the residue furnished **3b** (13 mg, 26%) and **22b** (9.5 mg, 19%).

Dimethyl (1*R,6*R**)-3,7,7-Trimethyl-5-methylene-8-oxobicyclo[4.2.0]oct-2-ene-1,2-dicarboxylate (22b).** ^1H NMR (400 MHz, C_6D_6) δ 4.78 (s, 1H), 4.65 (s, 1H), 3.43 (s, 3H), 3.42, 3.35 (ABq, J = 21.1 Hz, 2H), 3.25 (s, 3H), 2.11 (dd, J = 17.2, 2.0 Hz, 1H), 1.93 (dd, J = 17.2, 2.0 Hz, 1H), 1.21 (s, 3H), 1.17 (s, 3H), 0.99 (s, 3H).

Irradiation of 3c. A solution of **3c** (0.05 g, 0.2 mM) in acetone (5 mL) in a quartz vessel was irradiated for 12 h at 300 nm. Removal of acetone on a rotavapor followed by column chromatography (silica gel, 10% ethyl acetate in hexanes) of the residue furnished a 10:1 mixture of **3c** (40 mg, 80%) and **22c** (4 mg, 8%).

A solution of **3c** (0.05 g, 0.20 mM) in methanol (5 mL) in a quartz vessel was irradiated for 12 h at 300 nm. Removal of methanol on a rotavapor followed by column chromatography (silica gel, 10% ethyl acetate in hexanes) of the residue furnished a 3:1 mixture of **3c** (31 mg, 62%) and **22c** (10.5 mg, 21%).

(1*S,6*R**)-2-Phenyl-3,7,7-trimethyl-5-methylenebicyclo[4.2.0]oct-2-en-8-one (22c).** ^1H NMR (400 MHz, C_6D_6) δ 7.02−7.29 (m, 5H), 4.95 (d, J = 1.2 Hz, 1H), 4.76 (d, J = 1.2 Hz, 1H), 4.12 (d, J = 6.4 Hz, 1H), 2.68 and 2.58 (ABq, J = 18.2 Hz, 2H), 2.64 (d, J = 6.4 Hz, 1H), 1.57 (s, 3H), 1.01 (s, 6H).

Irradiation of 3d. A solution of **3d** (0.05 g, 0.15 mM) in acetone (5 mL) in a quartz vessel was irradiated for 24 h at 300 nm. Removal of acetone on a rotavapor followed by column chromatography (silica gel, 5% ethyl acetate in hexanes) of the residue furnished **3d** (25 mg, 50%) and **22d** (18 mg, 36%).

A solution of **3d** (0.05 g, 0.15 mM) in methanol (5 mL) in a quartz vessel was irradiated for 24 h at 300 nm. Removal of methanol on a rotavapor followed by column chromatography (silica gel, 5% ethyl acetate in hexanes) of the residue furnished **3d** (5 mg, 10%), **22d** (10 mg, 20%), and benzene derivative **23d** (14 mg, 35%).

(1*R,6*S**)-1,2-Diphenyl-3,7,7-trimethyl-5-methylenebicyclo[4.2.0]oct-2-en-8-one (22d).** Mp 110−111 °C (from hexanes); IR (film) 2963, 1770 cm^{-1}; ^1H NMR (400 MHz) δ 7.16−7.07 (m, 8H), 6.58−6.56 (m, 2H), 5.20 (d, J = 1.2 Hz, 1H), 5.08 (d, J = 1.2 Hz, 1H), 3.26 (s, 1H), 3.22, 3.17 (ABq, J = 21.1 Hz, 2H), 1.54 (s, 3H), 1.37 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz) δ 213.1, 142.6, 140.2, 138.9, 132.2, 130.9, 129.9, 127.8, 127.3, 126.4, 126.3, 113.3, 71.6, 60.7, 53.6, 37.8, 24.8, 21.4, 20.2; MS (EI, 70 eV) *m*/*z* (rel intensity) 328 (M^+, 7), 258 (100), 243 (76), 228 (7), 165 (11); HRMS calcd for $C_{24}H_{24}O$ 328.1827, found 328.1827. Anal. Calcd for $C_{24}H_{24}O$: C, 87.80; H, 7.32. Found: C, 87.72; H, 7.27.

2,3-Diphenyl-1,5-dimethylbenzene (23d). IR (film) 3024, 2919 cm^{-1}; ^1H NMR (400 MHz) δ 7.01−7.19 (m, 12H), 2.40 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 143.5, 142.6, 141.7, 138.8, 137.7, 137.2, 131.7, 131.0, 130.9, 129.5, 128.8, 128.6, 127.3, 127.1, 21.5, 21.4; MS (EI, 70 eV) *m*/*z* (rel intensity) 258 (M^+, 100), 243 (17), 228 (11); HRMS calcd for $C_{20}H_{18}$ 258.1409, found 258.1402.

Reduction of 3c. To a solution of **3c** (0.25 g, 0.99 mM) in methanol (10 mL) was added $NaBH_4$ (0.12 g, 3.14 mM) at room temperature and the mixture was stirred for 70 min. Then water was added and extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel with use of a 1:10 mixture of ethyl acetate and hexanes as eluent to obtain *syn*-**24c** (0.20 g, 80%) as a colorless oil along with *anti*-**25c** (0.04 g, 15%).

(1*S,2*S**,4*S**)-1,3,3-Trimethyl-5-methylene-7-phenylbicyclo[2.2.2]oct-7-en-2-ol (24c).** IR (film) 3512, 3064, 2935, 1650 cm^{-1}; ^1H NMR (400 M Hz) δ 7.19−7.30 (m, 5H), 6.28 (d, J = 6.6 Hz, 1H), 4.78 (dd, J = 2.0, 1.8 Hz, 1H), 4.67 (dd, J = 2.0, 1.8 Hz, 1H), 3.27 (s, 1H), 2.65 (d, J = 6.6 Hz, 1H), 2.15 (dd, J = 17.0, 2.0 Hz, 1H), 2.10 (dd, J = 17.0, 2.0 Hz, 1H), 1.50 (br, 1H), 1.15 (s, 3H), 1.08 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz) 147.2, 145.0, 140.5, 131.5, 128.3, 127.7, 126.6, 106.0, 84.0, 55.0, 45.2, 40.7, 39.6, 30.3, 23.2, 21.0; MS (EI, 70 eV) *m*/*z* (rel intensity) 254 (M^+, 1), 182 (100), 167 (67), 84 (55), 49 (73); HRMS calcd for $C_{18}H_{22}O$ 254.1670, found 254.1669.

(1*S,2*R**,4*S**)-1,3,3-Trimethyl-5-methylene-7-phenylbicyclo[2.2.2]oct-7-en-2-ol (25c).** IR (film) 3459, 2948, 1649 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.00−7.15 (m, 5H), 6.03 (d, J = 6.4 Hz, 1H), 4.83 (dd, J = 1.6,1.2 Hz, 1H), 4.76 (dd, J = 2.0,1.6 Hz, 1H), 3.07 (d, J = 1.2 Hz, 1H), 2.53 (dd, J = 16.8,1.2 Hz, 1H), 2.43 (d, J = 6.4 Hz, 1H), 1.80 (ddd, J = 16.8, 2.0, 1.2 Hz, 1H), 0.99 (s, 3H), 0.96 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz) δ 149.2, 148.1, 141.6, 131.8, 129.3, 128.7, 127.5, 106.6, 81.1, 55.8, 45.5, 38.1, 34.4, 31.9, 24.9, 20.9; MS (EI, 70 eV) *m*/*z* (rel intensity) 254 (M^+, 1), 181 (77), 167 (100), 152 (17), 128 (12); HRMS calcd for $C_{18}H_{22}O$ 254.1670, found 254.1657.

Reduction of 3d. *syn*-**24d** (0.251 g, 83%) was obtained as a colorless oil along with *anti*-**25d** (0.036 g, 12%) on column chromatography (silica gel, EtOAc/hexanes 1:10) by treating **3d** (0.30 g, 0.92 mM) with $NaBH_4$ (0.12 g, 3.2 mM) in methanol (10 mL) stirring at room temperature according to the procedure described for the reduction of **3c**.

(1*S,2*S**,4*R**)-1,3,3-Trimethyl-5-methylene-7,8-diphenylbicyclo[2.2.2]oct-7-en-2-ol (24d).** IR (neat) 3470, 2949, 1649, 1598, 1492, 1451 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.21−6.86 (m, 10H), 4.96 (dd, J = 2.1, 1.6 Hz, 1H), 4.80 (dd, J = 2.1, 1.6 Hz, 1H), 3.06 (d, J = 4.4 Hz, 1H), 3.00 (s, 1H), 2.13 (dd, J = 17.2, 2.1 Hz, 1H), 1.99 (dd, J = 17.2, 2.1 Hz, 1H), 1.19 (br s, 1H), 1.03 (s, 3H), 0.98 (s, 6H); ^{13}C NMR (100 MHz) δ 147.3, 140.7, 140.6, 139.5, 139.0, 129.8, 128.3, 127.7, 127.6, 127.5, 127.4, 126.1, 125.9, 106.2, 83.4, 61.1, 45.5, 40.6, 40.0, 30.2, 23.0, 21.4; MS (EI, 70 eV) *m*/*z* (rel intensity) 330 (M^+, 7), 258 (100), 243 (77), 228 (16), 215 (8), 181 (9), 165 (18), 141 (4), 115 (8), 91 (9); HRMS (EI) calcd for $C_{24}H_{26}O$ 330.1984, found 330.1980.

(1*S,2*R**,4*R**)-1,3,3-Trimethyl-5-methylene-7,8-diphenylbicyclo[2.2.2]oct-7-en-2-ol (25d).** IR (neat) 3476, 2944, 1648, 1452 cm^{-1}; ^1H NMR (400 MHz) δ 7.17−6.99 (m, 10H), 4.92 (dd, J = 2.3, 2.0 Hz, 1H), 4.77 (dd, J = 2.3, 2.0 Hz, 1H), 3.45 (dd, J = 3.9, 1.8 Hz, 1H), 2.99 (s, 1H), 2.57 (ddd, J = 16.8, 2.3, 2.3 Hz, 1H), 2.00 (dd, J = 16.8, 1.8 Hz, 1H), 1.55 (br s, 1H), 1.14 (s, 3H), 1.02 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 149.3, 142.3, 141.6, 141.4, 140.3, 130.6, 129.4, 128.9, 128.6, 127.2, 127.0, 106.8, 80.9, 62.2, 45.9, 38.2, 34.5, 31.8, 24.7, 21.4; MS (EI, 70 eV) *m*/*z* (rel intensity) 330 (M^+, 6), 292 (5), 258 (100), 243 (75), 228 (15), 215 (8), 181 (6), 165 (13), 115 (4), 57 (6); HRMS (EI) calcd for $C_{24}H_{26}O$ 330.1984, found 330.1967.

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Supporting Information Available: General experimental procedure, table of yields of photoproducts, ^1H and ^{13}C NMR and DEPT spectra for **1a**−**d, 2a**−**d**, **3a**−**d**, **8**, **9a**,**c**, **10b**,**c**, **11a**−**d**, **12**−**16**, **21a**−**d**, **22a**,**d**, **23d**, **24c**,**d**, and **25c**,**d**; NOE spectra for compounds **12** and **15**; and X-ray crystal data for compound **22d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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