

Photochemical Reactions of 1,3,3-Trimethylbicyclo[2.2.2]octa-5,7-dien-2-ones

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The photochemistry of 1,3,3-trimethylbicyclo[2.2.2]octa-5,7-dien-2-ones **1a–f** containing multiple chromophoric moieties under various conditions is described. Upon direct irradiation, dienones **1a–f** in benzene, acetonitrile, and methanol were found to aromatize through photoelimination of dimethylketene, which was trapped with 3-phenylprop-2-en-1-ol (**12**). Triplet sensitization of dienone **1a** in acetone and in acetone/acetophenone mixed solvents afforded aromatic compound **2a**, whilst bicyclic systems **1b–c** were found to be

unreactive on sensitization. In the cases of dienones **1d–f** in acetone, aromatic compounds **2d–f** and di- π -methane (DPM) photoproducts **3d–f** and **4f** were observed, but in the acetone/acetophenone mixed solvent system only DPM photoproducts were detected. Plausible mechanisms for these photochemical reactions are described.

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Introduction

Di- π -methane (DPM)^[1] and its variant oxadi- π -methane (ODPM)^[2] rearrangement processes are interesting reactions that occur from the excited states of 1,4-dienes and β,γ -unsaturated ketones, respectively; generally, their products are not readily accessible through ground-state chemical reactions. The merits of these reactions in the preparation of highly strained compounds have been recognized by synthetic chemists.^[1,2]

One of the striking attributes of the DPM and ODPM rearrangements, which share a common mechanistic pathway, is their dependence on reaction multiplicity and structure.^[1,2] In acyclic 1,4-diene systems, for instance, the DPM rearrangement is usually observed on singlet excitation (direct irradiation),^[1c,1d] whereas triplet excitation (sensitized irradiation) only produces *cis/trans* isomerization of the C–C double bond, due to the free-rotor effect.^[3] However, for sterically congested dienes, in which free rotation in the excited state is inhibited^[4] or in which the central sp^3 carbon atom, flanked by the two vinylic moieties, is substituted with electron-delocalizing groups,^[5] triplet di- π -methane rearrangements are observed. In the case of acyclic β,γ -unsaturated ketones, singlet excitation of unconstrained systems does not usually give rise to ODPM rearrangement, but competing photochemical processes such as the Norrish Type I reaction, decarbonylation, 1,3-acyl migration, and

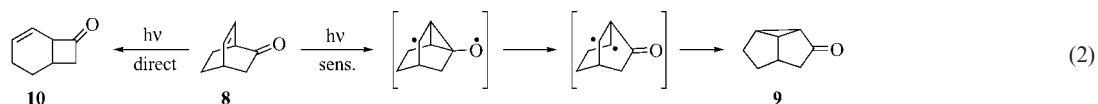
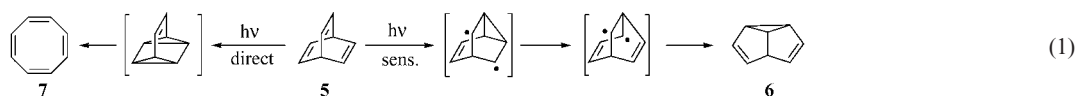
cycloaddition occur instead.^[2c] Like dienes, simple acyclic β,γ -enones easily undergo *cis/trans* isomerization under triplet-sensitized conditions,^[6] but β,γ -enones with bulky substituents^[2a] or with vinyl,^[7] phenyl,^[8] or oxo groups^[2c] conjugated to the alkene moiety may undergo ODPM reactions. In the case of bicyclic systems, in which conformational flexibility is more constrained, DPM and ODPM rearrangements are commonly observed under triplet-excitation conditions.^[1b,2b,2c] These general photoreactions have been well demonstrated in the photochemistry of bridged bicyclic systems such as barrelene (**5**) and bicyclo[2.2.2]oct-5-en-2-one (**8**), proceeding through biradicaloid intermediates^[2b,9] upon triplet excitation [Equations (1) and (2)]. In the presence of a sensitizer, barrelene generates the DPM photoproduct **6**, whereas the bicyclo[2.2.2]octenone **8** generates the ODPM photoproduct **9**. The ODPM rearrangement of bicyclic octenone **8** and its congeners is one of the most general reactions of this class of β,γ -enones,^[2] whilst in the case of substituted barrelene systems^[2b,10] the generality of DPM rearrangements is also found. Di- π and oxadi- π rearrangements during singlet excitation are not a common occurrence in many bicyclic systems, however, because cyclic systems have alternative photochemical reactions that can compete successfully.^[1,2] Barrelene undergoes an initial [2+2] cycloaddition, eventually producing cyclooctatetraene (**7**) on direct irradiation, whilst the bicyclic octenone **8** undergoes a 1,3-acyl shift on singlet excitation to form the cyclobutanone **10** (vide infra).

Although extensive investigations into the mechanistic intricacies of these fascinating rearrangement processes have been carried out,^[1,2] very few studies of the competitive behavior of DPM and ODPM reactions have been conducted.^[1a] It is of interest to investigate the photochemical behavior of substrates containing multiple chromophoric

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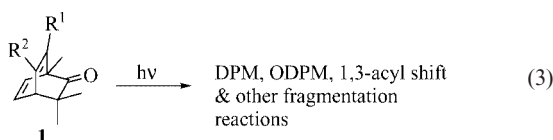
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groups: the photochemistry of such substrates could feature competition between DPM and ODPM rearrangements and interference by other photochemical processes.

Bicyclo[2.2.2]octadienones **1** are interesting substrates for photochemical investigations. Irradiation of bicyclo[2.2.2]octadienones, endowed with structural features required both for di- π -methane (DPM) and for oxadi- π -methane (ODPM) rearrangements, could in principle result in several products [Equation (3)].



Barring a few early reports,^[11–14] the competitive photochemistry of simple bicyclo[2.2.2]octadienones has not been studied in detail. Strikingly, with the exception of the bicyclic system **11**, which bears no substituents on the vinyl carbon atoms,^[12] all of the simple bicyclo[2.2.2]octadienones irradiated so far feature a vinyl bridge bearing methoxycarbonyl groups on both carbon atoms and all of them have preferentially undergone DPM rearrangements.^[11,13] This scenario clearly points to a lack of easy access to simple but diversely substituted bicyclo[2.2.2]octadienones. To this end we took 1,3,3-trimethylbicyclo[2.2.2]octadienones **1a–f** (Scheme 1) as our model dienone systems to study their photochemical reactions.



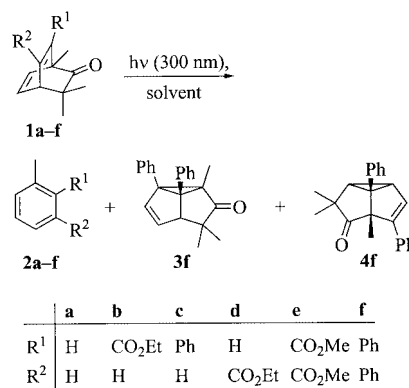
We envisaged that these compounds, which can be readily prepared in multigram quantities,^[15] should reveal important mechanistic aspects on the competitive nature of DPM and ODPM rearrangements and other photochemical processes. Here we report our findings.

Results

Direct Irradiation of Bicyclo[2.2.2]octadienones **1a–f**

Under direct irradiation conditions, bicyclo[2.2.2]octadienone **1a** in benzene, bubbled with argon for 1 h, and irra-

diated with 300 nm light in a Pyrex vessel for 72 h, afforded **2a** in 83% yield. When benzene was replaced with acetonitrile, which is a polar solvent, compound **2a** was obtained in 90% yield, but in methanol as solvent the photoproduct could only be obtained in 70% yield (Scheme 1; Table 1). Irradiation of **1b**, containing an ester moiety at the bridge carbon atom, in benzene for 72 h afforded **2b** in good yield (75%). Interestingly, **1b** in either acetonitrile or methanol



Scheme 1. Direct irradiation of bicyclo[2.2.2]octadienones **1a–f**.

Table 1. Percentage yields of photoproducts of 1,3,3-trimethylbicyclo[2.2.2]octa-5,7-dien-2-one derivatives **1a–f** in different solvent systems.

Reactant	Photoproduct (yield [%])				
	Direct irradiation ^[a]		Sensitized reaction ^[b]		
	Benzene	MeCN	MeOH	MeCOMe	MeCOMe/PhCOMe
1a ^[c]	2a (83)	2a (90)	2a (70)	2a (90)	2a (80)
1b	2b (75)	2b (86)	2b (84)	1b (80) ^[d]	1b (75) ^[d]
1c	2c (87)	2c (96)	2c (80)	1c (60) ^[d]	1c (70) ^[d]
1d	2d (88)	2d (89)	2d (97)	2d (19)	3d (60)
				3d (46)	
1e	2e (80)	2e (76)	2e (90)	2e (53)	3e (62)
				3e (11)	
1f	2f (69)	2f (73)	2f (65)	2f (33)	3f (58)
	3f (5)	3f (6)	3f (7)	3f (40)	4f (17)
	4f (10)	4f (12)	4f (8)	4f (4)	

[a] Reactants were irradiated at $\lambda = 300$ nm. [b] Reactants were irradiated in MeCOMe and MeCOMe/PhCOMe solvent systems at $\lambda = 300$ nm. [c] Photoproducts of **1a** were determined indirectly through the percentage yield of ketene trapped as allyl ester of 3-phenylprop-2-en-1-ol (**12**). [d] Recovered starting material.

produced **2b** in comparable yields of 86 and 84%, respectively. Under the same conditions as used with **1a**, the dienone **1c** (time_{irr} = 24 h) in benzene afforded the biphenyl **2c** in 87% yield, whilst replacement of benzene with acetonitrile afforded **2c** in 96% yield, but the yield dropped to 80% when methanol was used as solvent. We next irradiated the bicyclic dienone **1d** in benzene for 18 h, to obtain **2d** in 88% yield, and observed a similar result when **1d** was irradiated in acetonitrile under the same reaction conditions. In methanol, however, **1d** afforded **2d** in excellent yield (97%). In bicyclic system **1e**, containing two ester moieties at the bridge carbon atoms, irradiation in benzene for 4 h gave the *o*-phthalate **2e** in 80% yield, but this yield dropped to 76% in acetonitrile, whilst in methanol as solvent **2e** was generated in excellent yield (90%). In contrast to **1a–e**, the dienone **1f** exhibited different photochemical behavior, with direct irradiation of **1f** in the three solvents for 12 h affording **3f** (5–7%) and **4f** (8–12%) in small amounts, together with **2f** (65–73%) in considerable yields.

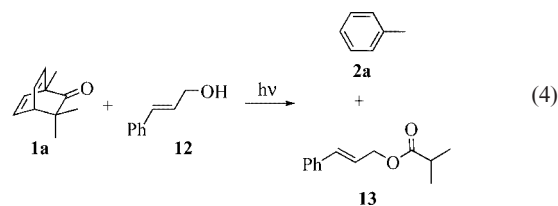
Sensitized Reactions of Bicyclo[2.2.2]octadienones **1a–f**

Acetone and acetophenone, serving as solvents and sensitizers, were used during triplet sensitization of **1a–f**. Irradiation of bicyclo[2.2.2]octadienone **1a** in acetone, bubbled under argon for 1 h and irradiated with 300 nm light for 48 h, afforded toluene (**2a**) in 90% yield (Table 1). Addition of acetophenone (10 equiv.) to the acetone solvent again furnished **2a** in good yield. When **1b** was subjected to similar reaction conditions, however, we recovered the starting material, with no characterizable photoproducts being detected, and a similar result was obtained when we irradiated the dienone **1c** in both solvent systems for 48 h. In stark contrast with **1b** and **1c**, the dienones **1d–f** in acetone afforded the substituted benzenes **2d–f** and the tricyclic oxo compounds **3d–f**, respectively, with the diphenyl derivative **1f** also producing a small amount of tricyclic ketone **4f**. When acetophenone (10 equiv.) was added to **1d–f** in acetone as solvent, **3d–f** were obtained in about 60% yields after illumination of the sample for 12–18 h, with the bicyclic dienone **1f** also furnishing the tricyclic ketone **4f** in 17% yield.

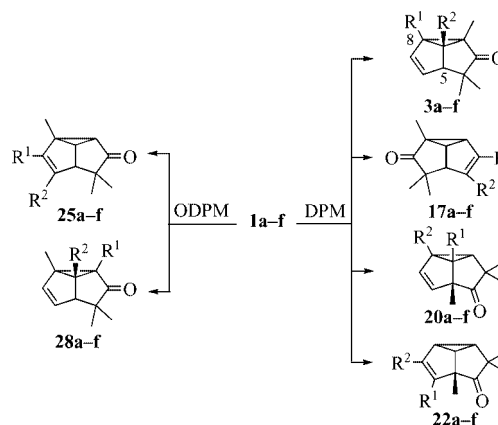
Discussion

Structural Determination of the Photoproducts

The structures of the photoproducts were determined mainly by spectroscopic methods and partly with the aid of chemical correlations. In the case of bicyclo[2.2.2]octadienone **1a**, the yields of toluene (**2a**) as a photoproduct after direct irradiation were calculated from the dimethylketene, which was trapped by 3-phenylprop-2-en-1-ol (**12**) to afford the ester **13** [Equation (4)]. Spectroscopic profiles of photoproducts **2b–f** were correlated with the reported spectra in the literature.^[16]

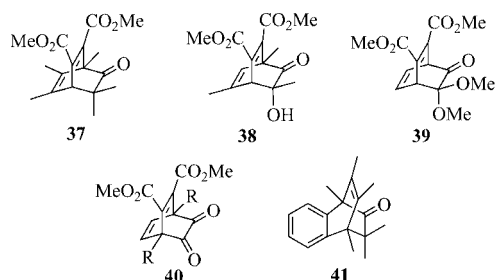


In principle, the reaction of each bicyclic dienone under sensitized conditions may formally afford six photoproducts through DPM and ODPM rearrangements (Scheme 2). In our bicyclic dienone systems **1a–f**, only the dienones **1d–f** generated the 1,2-shift rearrangement photoproducts, whilst **1a** was transformed into aromatic **2a** and the bicyclic systems **1b** and **1c** were recovered after prolonged irradiation. Of the six conceivable photoproducts of **1d**, the tricyclic ketone **3d** fits the ¹H NMR spectrum, which showed proton chemical shifts at $\delta = 3.49$ ppm due to coupling of the allylic hydrogen atom at C-5 with the vinylic hydrogen atom and at $\delta = 2.73$ ppm due to coupling of the second allylic hydrogen atom at C-8 with the vinylic hydrogen atom of the C–C double bond (see Experimental Section). On the basis of this spectral analysis, **1d** apparently underwent DPM rearrangement. The assignment of the lower δ value to the C-8 proton is based on the principle that the chemical shift for a highly strained ring is generally upfield; this observed value is consistent with reported δ values for tricyclic systems possessing structures similar to **1d**.^[12,13] The other conceived rearrangement photoproducts are ruled out as follows: (1) structures **17d**, **22d**, and **25d** should each only exhibit one vinylic proton chemical shift, (2) structure **20d** should not exhibit allylic proton coupling, and (3) structure **28d** should only exhibit one allylic proton coupling with the vinyl proton.

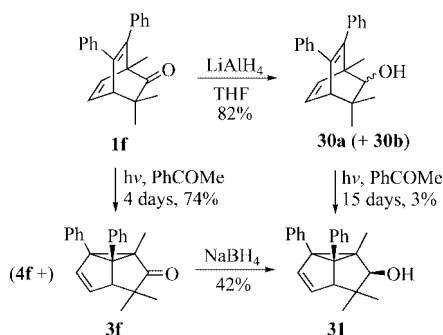


Scheme 2. Conceivable DPM and ODPM photoproducts of bicyclo[2.2.2]octadienones **1a–f**.

A clear-cut distinction can easily be made between **3e** and **3f** and the other conceivable DPM products. Vinylic proton chemical shifts, as are present in **3e** and **3f**, should not be observed in **17e**, **17f**, **22e**, or **22f**. For structures **20e** and **20f**, no allylic proton coupling with the vinyl proton would be expected.



The ^1H , ^{13}C , and DEPT NMR spectra of **3e** and **3f** each show the presence of a lone C–C double bond as part of an allylic moiety bearing one hydrogen atom on each of its three carbon atoms. Out of all the conceivable photoproducts, this kind of photochemical rearrangement is present only in **3e** and **3f** and in **28e** and **28f** (vide supra). However, from the striking similarity of the ^1H NMR spectra of **3e** and **3f** to that of **29**, reported by Yates and Stevens,^[13] we arrived at the conclusion that **3e** and **3f** are DPM rearrangement products. To ascertain which photorearrangement had actually been in operation, compound **1f** was reduced with LiAlH_4 to provide a 3:1 separable mixture of alcohols **30a** (major product) and **30b** (Scheme 3).



Scheme 3. Structural elucidation of tricyclo[3.3.0.0^{2,8}]octadienone **3f**.

The stereochemical assignment of the two alcohols is based solely on their NMR spectroscopic data. The ^1H NMR spectrum of bicyclo[2.2.2]octadienol **30a** showed a one-proton doublet at $\delta = 3.27$ ppm, assigned to the C-2 proton, and another one-proton doublet at $\delta = 3.46$ ppm for the bridgehead proton (Figure 1). In contrast with **30a**, bicyclo[2.2.2]octadienol **30b** showed a C-2 one-proton doublet at $\delta = 3.45$ ppm and a bridgehead proton doublet at $\delta = 3.51$ ppm. Proton couplings observed at $\delta = 3.27$ ppm and $\delta = 3.45$ ppm can be ascribed to the interaction of the C-2 proton with the hydroxylic proton, while those at $\delta = 3.46$ ppm and $\delta = 3.51$ ppm are attributable to the interaction of the bridgehead protons with the olefinic proton (see Experimental Section). The higher δ value for the C-2 proton in **30b** as compared with that in **30a** indicates the proximity of this hydrogen atom to the phenyl moiety, which can deshield the proton through its anisotropic effect.^[15,17] In the case of the C-4 bridgehead protons of the two isomers, which are directly below the second phenyl group, the

chemical shifts are almost the same, suggesting that changes occurring at C-2 can only be attributed to the proximity of the phenyl group at C-6.

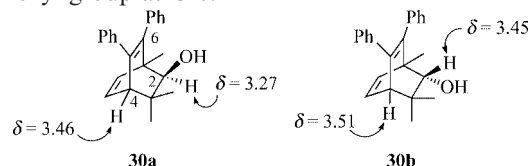
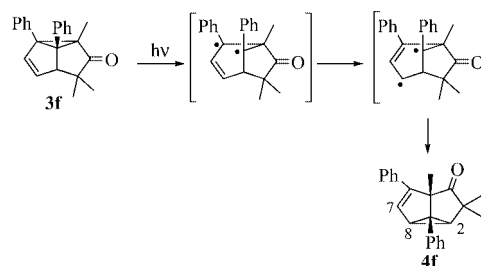


Figure 1. ^1H NMR chemical shifts of **30a** and **30b** at carbon atoms C-2 and C-4.

When an acetophenone solution of **30a** was irradiated with 350 nm light for 15 d, we obtained about a 3% yield of **31** and recovered most of the starting material (65%). Fortunately, **3f** furnished the same product **31** upon reduction with NaBH_4 as **30a** did upon irradiation. The preference for the borohydride to approach the *endo* face (concavity) of tricyclo[3.3.0.0^{2,8}]octenone **3f** during the reduction process is facilitated by the presence of the two adjacent methyl groups and of the bulky phenyl moieties on the *exo* side of the tricyclic ketone. These results not only confirm the assigned structures of **3e** and **3f** but also establish that **3e** and **3f** are formed through regiospecific DPM rearrangements of **1e** and **1f**, respectively. On the other hand, **4f** – with its ^1H NMR spectrum indicating the presence of a lone olefinic proton – could not have been formed by any of the six pathways outlined in Scheme 2 (vide supra). The ^{13}C NMR spectrum of **4f** indicates the presence of a vinylic C–C double bond, effectively ruling out the 1,3-acyl shift, whilst HRMS analysis shows all the mass units of **1f** intact. Apparently, **4f** should be a secondary photoproduct, and could have resulted from **3f** itself as shown in Scheme 4. To test this hypothesis, we irradiated **3f** in acetone/acetophenone mixed solvent with 300 nm light for 12 h, and we indeed obtained the photoproduct **4f** with a **3f/4f** ratio of 3.4:1. Even if we prolonged the irradiation time to 24 h we still obtained the same photoproduct ratio. In a separate experiment we investigated the irradiation of **4f** under the same reaction conditions as described above, and to our surprise we also obtained the same photoproduct ratio. The photoproducts **3f** and **4f** probably exist in a photostationary state.^[18]

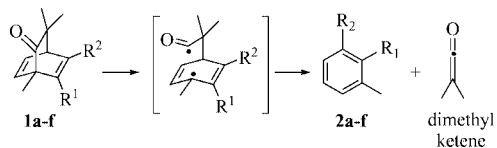


Scheme 4. Conceived photorearrangement of tricyclo[3.3.0.0^{2,8}]octenone **3f** to **4f**.

Mechanisms of Photoreactions

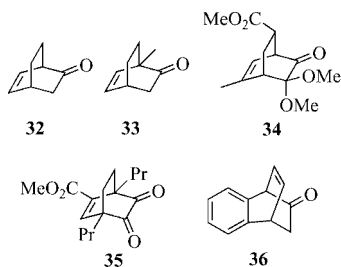
Clearly, a sharp contrast between direct and sensitized irradiation of 1,3,3-trimethylbicyclo[2.2.2]octa-5,7-dien-2-

ones **1a–f** can be seen. Upon direct irradiation of dienones **1a–f**, aromatic photoproducts and dimethylketene were obtained (Scheme 5), whilst we were unable to detect the 1,3-acyl shift products commonly observed in the photolysis of β,γ -unsaturated ketones.^[1c,2d] This kind of fragmentation pattern, which is also observed in several bicyclic dienone systems,^[11,19] is consistent with the general observation that intersystem crossing (ISC) in dienes and β,γ -unsaturated ketones is an inefficient process.^[19a,19b] An excited singlet state may be involved in the observed fragmentation pattern. In the case of **1f** the rearrangement products **3f** and **4f** were also detected, albeit in small amounts, suggesting that ISC of the excited singlet state of **1f** competes – although not effectively – with the relatively fast α -cleavage process.^[19c]



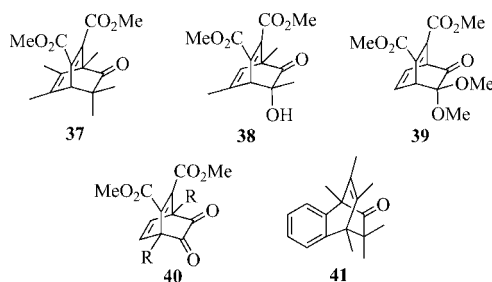
Scheme 5. Plausible photofragmentation of bicyclo[2.2.2]octa-dienones **1a–f** under direct irradiation conditions.

In agreement with the postulated mechanism (vide supra), a survey of the literature reveals interesting photochemical behavior in bicyclic systems containing vinyl and carbonyl chromophoric groups. Under direct irradiation conditions, the bicyclic systems **32–35**^[19a,20–23] underwent 1,3-acyl shift rearrangements to generate cyclobutanones, some of which subsequently collapsed to afford cyclohexadienes and ketenes on further irradiation. The benzodienone **36**, which exhibits similar photochemical behavior, generated naphthalene and ketene on extended irradiation.^[23]



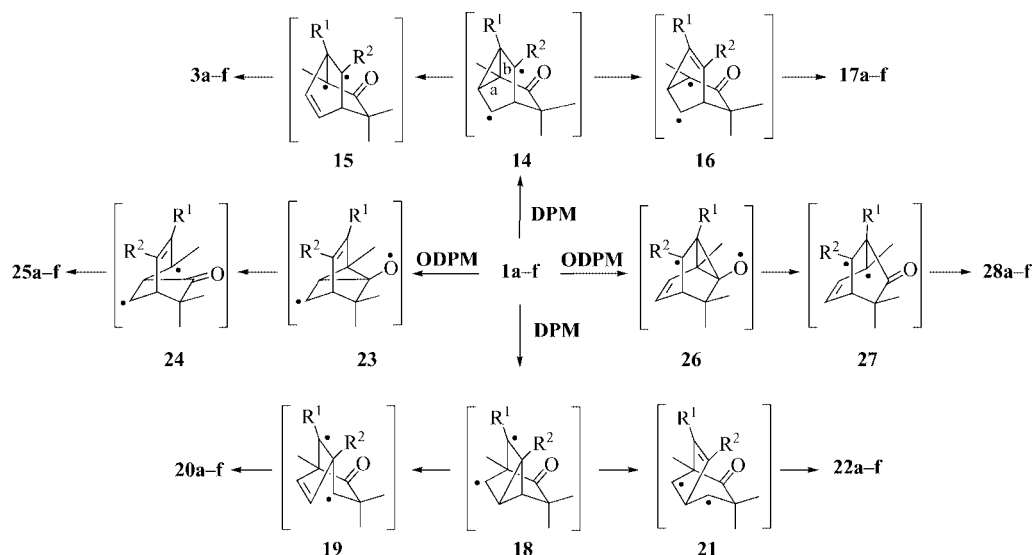
At the other end of the spectrum are the bicyclic systems **37–41**,^[11,19c,24] which did not generate the transient cyclobutanones; aromatic compounds were instead obtained on direct irradiation. In the case of benzodienone **41**, Murray and Hart^[19c] noted that irradiation of this compound in ether solution produced only benzene derivatives, with none of the 1,3-acyl shift products being detectable.

The photochemical behavior of dienones **1a–f** under direct irradiation conditions is quite consistent with the photochemical properties of bicyclic systems **37–41**. Apparently, the generation of aromatic products and the stability of ketenes have an important bearing on the mechanism of the reaction. Bicyclic dienones that are able to produce aromatic compounds through the loss of ketenes or other



stable entities do so readily during direct irradiation. If a biradicaloid intermediate (Scheme 5, vide supra) formed by Norrish Type I cleavage is assumed,^[25] the absence of 1,3-acyl shift rearrangement products in our dienone systems would suggest that the carbonyl orbital of the biradical overlaps weakly with the vinylic group and that the 1,3-acyl shift therefore becomes less competitive with the fragmentation process, resulting in the formation of stable aromatic products and ketene.^[26]

In the triplet-sensitized irradiation of bicyclo[2.2.2]octa-dienone **1a**, we obtained only the aromatic compound **2a** in both solvent systems. This is at variance with the results obtained by Luibrand et al.^[12] in their sensitized irradiation of bicyclic octenone **11**, which generated a DPM photoproduct. The presence of the methyl group at the bridgehead carbon atom may have enhanced the reactivity of the α -cleavage process that may occur during singlet (S_1 , n,π^*) or triplet (T_2 , n,π^*) excitation by stabilization of the incipient radical generated at the bridgehead carbon atom.^[2,20,26b] Interestingly, the bicyclodienones **1b** and **1c** did not undergo rearrangement under triplet-sensitization conditions. The failure of **1b** and **1c** to undergo DPM or ODPM can probably be ascribed either to rapid radiationless decay of the triplet excited state^[19a] or to lack of energy needed to reach the reaction surface.^[18] In the cases of dienones **1d–f**, DPM rearrangement products were observed under sensitized conditions. These results corroborate the work of Becker^[11] and Luibrand^[12] on their sensitized irradiation of dienones **38** and **11** (vide supra), respectively, in which only DPM products were obtained. The preference for DPM over ODPM rearrangement may be ascribed either to the weaker C=C bond, which can interact more easily than the stronger C=O bond with the triplet biradical during the bridging process^[11,27] or to the large difference in triplet energy between the sensitizer and the vinyl moiety.^[28] Nevertheless, the behavior of **1d–f** and the dienones **38** and **11** is in line with Zimmerman's^[29] suggestions and Luibrand's^[12] generalization that vinyl-vinyl bridging is preferred over vinyl-keto bridging. It is important to note that when bicyclodienones **1d–f** were irradiated in the presence of acetone as sensitizer, the aromatic compounds **2d–f** were also formed together with the DPM photoproducts **3d–f**, but that when a small amount of acetophenone was added to acetone, only the DPM photoproducts were obtained. This observation can be ascribed to residual direct light absorption by the dienones due to insufficient filtering of light by the acetone.^[20,30]



Scheme 6. Conceivable DPM and ODPM rearrangements of bicyclo[2.2.2]octadienones **1a–f**.

The generation of DPM photoproducts **3d–f** can be explained by presuming a stepwise mechanism (Scheme 6). Each dienone can potentially undergo four possible DPM pathways, resulting in four different products, but spectral analyses and chemical correlations of the photoproducts of **1a–f** show that only the dienones **1d–f** had undergone DPM rearrangements.

The regioselectivity of **1d–f** toward DPM rearrangement may be attributable to the stabilization of the cyclopropyldicarbonyl diradical in **15**, presumably through homoconjugative interaction of the carbonyl group with the cyclopropyl moiety, and the presence of electron-delocalizing substituents at C-5 (Figure 2). The odd-electrons at the bridge carbon atoms in **14_{1d–14_f}**, as shown in Figure 2, would be more stabilized by resonance than in **14_{1a–14_c}**.

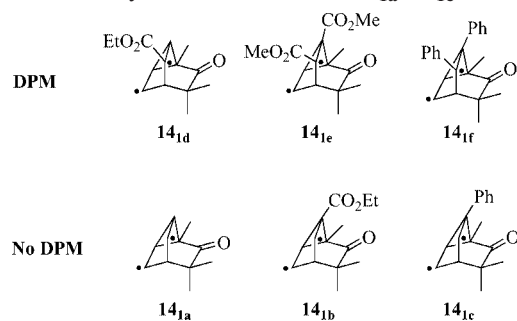
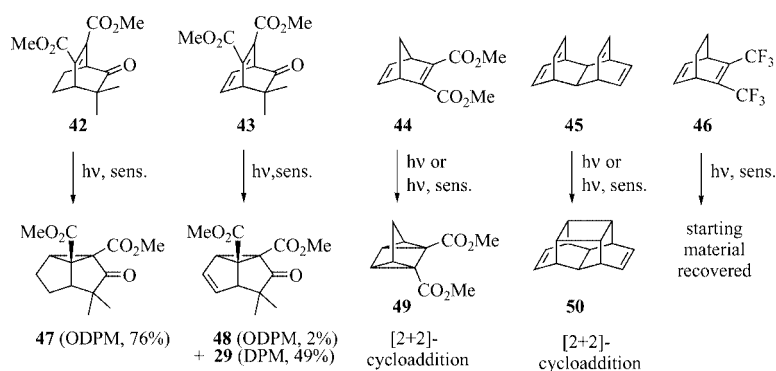


Figure 2. Conceived intermediates **14** of bicyclo[2.2.2]octadienones **1d–f**.

A question that immediately arises relates to which bond of the cyclopropyl moiety opens. Carbonyl carbon atoms of cyclopropyldicarbonyl species have been reported to be electron-rich,^[31] and dissipation of this electron density by breaking of the ring depends largely on its interaction with the odd-electrons in intermediate **14**. Apparently, the radical originating from the second vinyl group, which is less delocalized, interacts strongly with the cyclopropyl carbon atom; this breaks the a-bond of the cyclopropyl moiety to

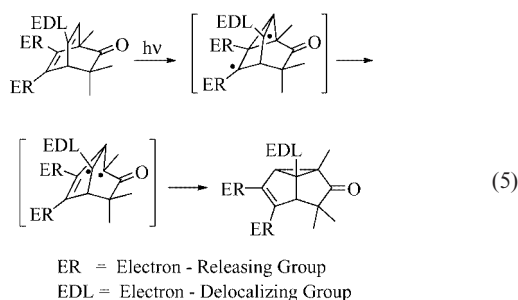
generate the stable diradicaloid species^[32] in intermediate **15** with the concomitant formation of the DPM products **3d–f** (Scheme 6, vide supra). Another important aspect of the regioselectivity of the process is the resonance contribution of the carbonyl group to the stability of the odd-electron centers in intermediate **15**. The interaction of the carbonyl orbital with the diradical intermediate lowers the energy of the reaction surface,^[18] thus enhancing the rate of DPM rearrangement. Other than in the cases of intermediates **15** and **16**, the radical centers of which are conjugated with the carbonyl group, none of the other conceived DPM and ODPM intermediates exhibits a similar resonance stability; the odd-electron centers are not adjacent to the carbon–oxygen π -bond. As explained above, intermediate **15**, on the pathway to photoproducts **3a–f**, should be more favored than intermediate **16**, on the pathway to photoproducts **17a–f**.

At this point it is interesting to discuss why we obtained a very low yield (3%) for the DPM rearrangement of bicyclic octadienol **30**, requiring 15 d of irradiation, whereas compound **1f** containing the carbonyl moiety, only needed 4 d of irradiation and provided the DPM photoproducts **3f** and **4f** in good yield (74%). This interesting observation suggests that the carbonyl group was participating in enhancing the rate and regioselectivity of the DPM rearrangement. A survey in the literature reveals interesting findings on the photochemical properties of several bicyclic systems (Scheme 7). Yates and Stevens^[13b] reported that bicyclo[2.2.2]octenone **42** generated ODPM photoproduct **47** in good yield (76%), whilst in a related study,^[13a] in which they investigated the photochemical behavior of bicyclic octadienone **43**, the ODPM product yield dropped to 2%, with DPM photoproduct **29** being obtained in good yield (49%). It has been suggested that this could be due to preemptive homoconjugative interaction of the diene moiety, but the authors interpreted their results in terms of stability of diradicaloid intermediates. Surprisingly, when the carbonyl group was missing, as in bicyclic systems **44** and **46**

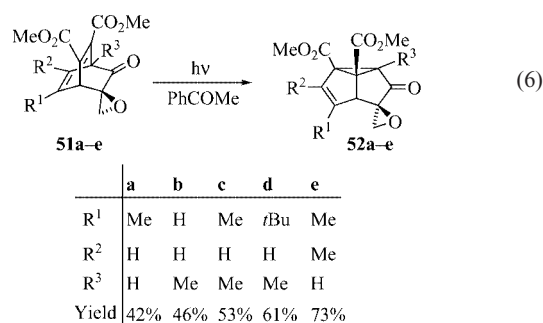
Scheme 7. Photoisomerization of bicyclic systems **42–44** and **46** and tetracyclic tetradecaene **45**.

and the tetracyclic tetradecaene **45**, no DPM product was observed under sensitized conditions. In the cases of the norbornadiene **44** examined by Ikezawa et al.^[33] and the tetracyclic tetradecaene **45** reported by Lin et al.,^[34] direct and sensitized irradiation of these compounds furnished the [2+2] cycloaddition photoproducts **49** and **50**, respectively. Unlike in the cases of compounds **44** and **45**, sensitized irradiation of bicyclic octadiene **46** resulted in the recovery of the starting material, whilst under direct irradiation conditions the quadricyclane derivative was observed.^[35] This interesting observation can be accounted for by the participation of the carbonyl group in enhancing the rate and controlling the regioselectivity of DPM rearrangement. As pointed out earlier, the carbonyl moiety may lower the energy of the reaction surface by delocalizing odd-electron centers adjacent to it, as in intermediate **15**. This kind of stabilization cannot be observed in the DPM rearrangement of the bicyclic octadienol **30a** to the tricyclic octenol **31**.

On the basis of the above analysis, we propose a model for our dienone systems **1a–f**. The attachment of electron-releasing (ER) groups at one vinyl group and of electron-delocalizing (EDL) groups at the second vinyl moiety may influence the regioselectivity and rate of the DPM rearrangement [Equation (5)].



The model presented in Equation (5) fits quite well with the findings of Becker and Ruge^[11] in their photochemical investigation of bicyclo[2.2.2]octadienones **51a–e** [Equation (6)].



That group noted that all the dienones produced DPM products under acetophenone-sensitized conditions. In these data, one can observe increases in the percentage yields of the photoproducts if alkyl (electron-releasing) groups are attached at R¹ and R² and methoxycarbonyl (electron-delocalizing) groups are attached at the second vinyl moiety. If a stepwise mechanism is assumed, constellations of these moieties in the designated sites of the bicyclic system ensure the stability of the biradical intermediates. The presence of the methyl group at the bridgehead carbon atom is also important, as this could participate in stabilizing the diradicaloid intermediate through C–H hyperconjugation.

Changes in solvent composition and properties commonly affect the routes of photochemical reactions,^[36–38] but such inversion of energy states is not apparent in our photochemical investigations of dienones **1a–f** in benzene, acetonitrile, and methanol solvent systems. We obtained the same kind of products in all the three solvents, though the variation in the percentage compositions of the products observed in these solvent systems is a manifestation of the different modes of solute–solvent interaction, such as dipole–dipole, polarization, and H-bonding.

Conclusions

We have succeeded in unraveling some of the mechanistic intricacies of photochemical processes of 1,3,3-trimethylbicyclo[2.2.2]octa-5,7-dien-2-one derivatives. Under direct irradiation conditions, the dienones **1a–f** generated aromatic

products and ketenes without undergoing 1,3-acyl shift rearrangement, and in addition, small amounts of DPM rearrangement products (**3f** and **4f**) were observed. In triplet-sensitized reactions, DPM photoproducts were detected along with aromatic compounds, which can be ascribed either to residual light absorption by the dienones or to excitation of dienones to higher triplet states. The stepwise mechanism and Luibrand's postulated interactions of the chromophoric groups can reasonably account for the photochemical behavior of **1d–f**. The regioselectivity of the DPM rearrangements in these bicyclic systems can probably be enhanced by specific constellations of electron-repelling and electron-delocalizing substituents at the vinyl moieties and attachment of an alkyl group at the bridgehead carbon atom. From a mechanistic point of view, it is tempting to conclude that the regioselectivities and rates of DPM rearrangements can be enhanced by the presence of a carbonyl moiety, stabilizing the incipient diradical intermediates.

Experimental Section

General Procedures: Unless stated otherwise, reagents were obtained from commercial sources and were used without further purification. The reduction reaction was performed under nitrogen. Reactions were monitored by thin-layer chromatography (0.25 mm silica gel plates, 60F-254) with 7% ethanolic phosphomolybdic acid [H_2SO_4 , CeSO_4 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$] as developing reagent. Standard column chromatography was conducted with 70–230 mesh silica gel. IR spectra were recorded as films on NaCl plates. Unless otherwise specified, ^1H NMR, ^{13}C NMR, and DEPT spectra were recorded in CDCl_3 , and chemical shifts are reported in δ [ppm] with the solvent resonance as the internal reference. High-resolution mass spectra (HRMS) were recorded with a JEOL JMS-HX 100 mass spectrometer. Photochemical reactions were carried out in spectroscopic grade solvents. All solutions of starting materials in specific solvents were purged with argon for 1 h. Irradiations of samples were performed in a Rayonet photoreactor with use of RPR 3500 ($\lambda = 350$ nm) or RPR 3000 ($\lambda = 300$ nm) lamps. UV spectra of the starting material were determined with a double-beam UV/Vis spectrophotometer. 1,3,3-Trimethylbicyclo[2.2.2]octa-5,7-dien-2-ones **1a–f** were prepared according to reported methods,^[15] and their UV spectra are given in the Supporting Information.

Irradiation of 1a: An argon-purged (1 h) solution of **1a** (75 mg, 0.46 mmol) and 3-phenylprop-2-en-1-ol (**12**, 309 mg, 2.3 mmol) in benzene (40 mL) was irradiated at 300 nm in a Pyrex vessel for 72 h, concentrated under reduced pressure (50 °C/0.05 Torr), and chromatographed on silica gel (hexanes/ethyl acetate, 20:1) to furnish **13**^[16a] (78 mg, 83%). Replacement of the solvent with acetonitrile and MeOH also afforded **13** (85 mg, 90% and 66 mg, 70%, respectively). In the procedure described above, a degassed solution of **1a** (75 mg, 0.46 mmol) and **12** (309 mg, 2.3 mmol) in acetone (40 mL) furnished **13** (85 mg, 90%) after irradiation for 48 h. A degassed solution of **1a** (70 mg, 0.43 mmol) and **12** (294 mg, 2.2 mmol) in acetophenone (10 equiv.) and acetone (40 mL) afforded **13** (70 mg, 80%).

Irradiation of 1b: A solution of **1b** (85 mg, 0.36 mmol) in benzene (35 mL), purged with Ar for 1 h, was irradiated at 300 nm in a Pyrex vessel for 72 h. The solvent was removed under reduced pres-

sure, and the crude product was separated on silica gel (hexanes/ethyl acetate, 7:1) to furnish **2b**^[16d] (44 mg, 75%). Replacement of the solvent with acetonitrile and methanol also resulted in **2b** (51 mg, 86% and 50 mg, 84%, respectively). In the procedure described above, a degassed solution of **1b** in acetone (35 mL) returned the starting material in 80% yield. A degassed solution of **1b** in acetone (35 mL) and acetophenone (10 equiv.) was irradiated for 48 h, and after workup and column chromatography, the starting material was recovered in 75% yield.

Irradiation of 1c: A degassed solution of **1c** (93 mg, 0.39 mmol) in benzene (40 mL) was irradiated for 24 h according to the procedure described for **1b**, furnishing **2c**^[16c] (57 mg, 87%) after workup and column chromatography (silica gel; hexanes/ethyl acetate, 30:1). Replacement of the solvent with acetonitrile and methanol also resulted in **2c** (63 mg, 96% and 52 mg, 80%, respectively). A degassed solution of **1c** (93 mg, 0.39 mmol) in acetone (40 mL) was irradiated for 48 h, and after workup and column separation, the starting material was recovered in 60% yield. In a similar procedure with a degassed solution of **1c** in acetone (40 mL) and acetophenone (10 equiv.), the starting material was recovered in 70% yield after irradiation for 48 h.

Irradiation of 1d: A degassed solution of **1d** (85 mg, 0.36 mmol) in benzene (35 mL), treated as described in the procedure for **1b**, afforded **2d**^[16b] (52 mg, 88%); $\text{time}_{\text{irr}} = 18$ h, column chromatography (silica gel; hexanes/ethyl acetate, 10:1). Replacement of the solvent with acetonitrile and methanol also resulted in **2d** (53 mg, 89% and 57 mg, 97%, respectively). A degassed solution of **1d** (85 mg, 0.36 mmol) in acetone (35 mL) furnished **2d** (11 mg, 19%) and **3d** (39 mg, 46%); $\text{time}_{\text{irr}} = 36$ h, column chromatography (silica gel, hexanes/ethyl acetate 10:1). Treatment of a degassed solution of **1d** (100 mg, 0.43 mmol) in acetone (40 mL) and acetophenone (10 equiv.) by the procedure described for **1b** furnished **3d** (60 mg, 60%); $\text{time}_{\text{irr}} = 18$ h, column chromatography (silica gel, hexanes/ethyl acetate 10:1).

Ethyl 2,4,4-Trimethyl-3-oxotricyclo[3.3.0.0^{2,8}]oct-6-ene-1-carboxylate (3d**):** ^1H NMR (400 MHz, CDCl_3 , 25 °C): $\delta = 5.76$ (dd, $J = 5.6, 2.4$ Hz, 1 H), 5.66 (dd, $J = 5.6, 2.4$ Hz, 1 H), 4.20 (q, $J = 7.2$ Hz, 2 H), 3.49 (d, $J = 2.4$ Hz, 1 H), 2.73 (d, $J = 2.4$ Hz, 1 H), 1.47 (s, 3 H), 1.27 (t, $J = 7.2$ Hz, 3 H), 1.19 (s, 3 H), 0.89 (s, 3 H) ppm. ^{13}C NMR (600 MHz, CDCl_3 , 25 °C): $\delta = 213.4, 170.3, 135.5, 128.2, 62.2, 60.8, 55.5, 54.5, 53.0, 48.9, 25.5, 17.4, 14.2, 13.9$ ppm. MS (EI, 70 eV): m/z (%) = 234 (17) [$\text{M}]^+$, 207 (11), 161 (53), 160 (27), 133 (100), 114 (23). IR (film): $\tilde{\nu} = 2970, 1731, 1446, 1229, 1383, 1221, 1104$ cm^{-1} . HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3$ [$\text{M}]^+$ 234.1256; found 234.1238.

Irradiation of 1e: Treatment of a degassed solution of **1e** (111 mg, 0.40 mmol) in benzene (40 mL) as described in the procedure for **1b** afforded **2e**^[16c] (67 mg, 80%); $\text{time}_{\text{irr}} = 4$ h, column chromatography (silica gel; hexanes/ethyl acetate, 4:1). Replacement of the solvent with acetonitrile and methanol also resulted in **2e** (63 mg, 76% and 75 mg, 90%, respectively). A degassed solution of **1e** (90 mg, 0.32 mmol) in acetone (30 mL) afforded **2e** (36 mg, 53%) and **3e** (10 mg, 11%); $\text{time}_{\text{irr}} = 12$ h, column chromatography (silica gel; hexanes/ethyl acetate, 4:1). Treatment of a degassed solution of **1e** (99 mg, 0.36 mmol) in acetone (35 mL) and acetophenone (10 equiv.) by the procedure described for **1b** afforded **3e** (61 mg, 62%); $\text{time}_{\text{irr}} = 12$ h; column chromatography (silica gel; hexanes/ethyl acetate, 4:1).

Dimethyl 2,4,4-Trimethyl-3-oxotricyclo[3.3.0.0^{2,8}]oct-6-ene-1,8-dicarboxylate (3e**):** ^1H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 5.87$ (d, $J = 5.5$ Hz, 1 H), 5.79 (dd, $J = 5.5, 2.3$ Hz, 1 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 3.50 (d, $J = 2.3$ Hz, 1 H), 1.64 (s, 3 H), 1.21 (s, 3 H), 0.94

(s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 212.0, 168.5, 166.7, 136.2, 128.1, 62.6, 58.1, 56.4, 55.3, 53.0, 52.4, 52.3, 25.1, 17.5, 11.1 ppm. IR (film): $\tilde{\nu}$ = 2964, 1736, 1442, 1229, 1057 cm^{-1} . MS (EI, 70 eV): m/z (%) = 278 (2) $[\text{M}]^+$, 191 (16), 177 (55), 149 (59), 135 (100). HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_5$ $[\text{M}]^+$ 278.1155; found 278.1156.

Irradiation of 1f: Treatment of a degassed solution of **1f** (100 mg, 0.32 mmol) in benzene (30 mL) as described in the procedure for **1b** furnished **2f**^[6f] (54 mg, 69%), **3f** (5 mg, 5%), and **4f** (10 mg, 10%); time_{irr} = 12 h, column chromatography (silica gel; hexanes/ethyl acetate, 15:1). Replacement of the solvent with acetonitrile and methanol resulted in **2f** (57 mg, 73% in acetonitrile; 51 mg, 65% in methanol), **3f** (6 mg, 6% in acetonitrile; 7 mg, 7% in methanol), and **4f** (12 mg, 12% in acetonitrile; 8 mg, 8% in methanol). Treatment of a degassed solution of **1f** (95 mg, 0.30 mmol) in acetone (30 mL) by the procedure described for **1b** furnished **2f**^[6f] (24 mg, 33%), **3f** (38 mg, 40%), and **4f** (4 mg, 4%); time_{irr} = 12 h, column chromatography (silica gel; hexanes/ethyl acetate, 15:1). Irradiation of **1f** (300 mg, 0.96 mmol) in acetone (90 mL) and acetophenone (10 equiv.) as described in the procedure for **1b** afforded **3f** (175 mg, 58%) and **4f** (50 mg, 17%); time_{irr} = 12 h, column chromatography (silica gel; hexanes/ethyl acetate, 15:1).

2,4,4-Trimethyl-1,8-diphenyltricyclo[3.3.0.0^{2,8}]oct-6-en-3-one (3f): ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.38–7.26 (m, 5 H), 7.15–7.13 (m, 3 H), 6.96–6.94 (m, 2 H), 5.89 (d, J = 5.5 Hz, 1 H), 5.82 (dd, J = 5.5, 2.4 Hz, 1 H), 3.36 (d, J = 2.4 Hz, 1 H), 1.39 (s, 3 H), 1.23 (s, 3 H), 0.99 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 216.2 (3-C), 139.0, 136.9, 135.6, 133.2, 129.5, 128.9, 128.6, 128.1, 126.9, 126.6, 64.9, 61.9, 59.3, 56.6, 51.1, 25.6, 17.9, 14.4 ppm. IR (film): $\tilde{\nu}$ = 3059, 1722, 1600, 1496, 1448 cm^{-1} . GC-MS (70 eV): m/z (%) = 314 (14) $[\text{M}]^+$, 244 (56), 229 (24), 165 (20), 83 (100). HRMS (EI): calcd. for $\text{C}_{23}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 314.1671; found 314.1668.

3,3,5-Trimethyl-1,6-diphenyltricyclo[3.3.0.0^{2,8}]oct-6-en-4-one (4f): ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.39–7.25 (m, 10 H), 6.15 (d, J = 2.6 Hz, 1 H), 2.49 (dd, J = 7.3, 2.6 Hz, 1 H), 2.18 (d, J = 7.3 Hz, 1 H), 1.41 (s, 3 H), 1.32 (s, 3 H), 1.08 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 216.4, 144.2, 138.8, 135.4, 130.3, 130.1, 128.3, 128.1, 127.4, 127.2, 127.1, 67.2, 55.5, 47.4, 40.5, 38.5, 29.3, 26.5, 14.2 ppm. IR (film): $\tilde{\nu}$ = 3025, 1728, 1601, 1493, 1448 cm^{-1} . MS (EI, 70 eV): m/z (%) = 314 (2) $[\text{M}]^+$, 244 (100), 165 (20), 105 (27), 77 (18). HRMS (EI): calcd. for $\text{C}_{23}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 314.1671; found 314.1641.

Reduction of 1f: A solution of LiAlH_4 in THF (3 mL, 3 mmol, 1.0 M) was added slowly to a cooled (0 °C) solution of **1f** (465 mg, 1.48 mmol) in dry THF (20 mL). The resulting mixture was stirred at 0 °C for 1 h, and the reaction mixture was diluted slowly with water (20 mL) and HCl (1 M, 20 mL) while stirring at 0 °C and was then extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with saturated NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. Column chromatography of the residue on silica gel with 15% ethyl acetate in hexanes as eluent afforded **30a** (284 mg, 61%) and **30b** (98 mg, 21%).

(2R*,4S*)-1,3,3-Trimethyl-5,6-diphenylbicyclo[2.2.2]octa-5,7-dien-2-ol (30a): ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.25–6.90 (m, 10 H), 6.60 (dd, J = 7.2, 6.0 Hz, 1 H), 6.08 (dd, J = 7.2, 1.6 Hz, 1 H), 3.46 (dd, J = 6.0, 1.6 Hz, 1 H), 3.27 (d, J = 7.2 Hz, 1 H), 1.46 (d, J = 7.2 Hz, 1 H), 1.31 (s, 3 H), 1.13 (s, 3 H), 1.03 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 143.9, 141.7, 140.1, 139.2, 138.2, 136.7, 129.8, 128.3, 127.8, 127.6, 126.1, 125.8, 83.1, 55.9, 52.2, 42.6, 31.6, 24.8, 19.5 ppm. IR (CHCl_3): $\tilde{\nu}$ = 3485, 3051, 1601, 1490, 1444, 1047 cm^{-1} . MS (70 eV): m/z (%) = 316 (0.2) $[\text{M}]^+$, 298

(1), 283 (1), 255 (1), 244 (100), 229 (80), 215 (18), 202 (17), 165 (21), 72 (1). HRMS (EI): calcd. for $\text{C}_{23}\text{H}_{24}\text{O}$ 316.1827; found 316.1824.

(2S*,4S*)-1,3,3-Trimethyl-5,6-diphenylbicyclo[2.2.2]octa-5,7-dien-2-ol (30b): ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.26–6.83 (m, 10 H), 6.77 (apparent t, dd, J = 6.3, 6.0 Hz, 1 H), 6.11 (dd, J = 6.0, 1.2 Hz, 1 H), 3.51 (dd, J = 6.3, 1.2 Hz, 1 H), 3.45 (d, J = 9.4 Hz, 1 H), 1.29 (s, 3 H), 1.22 (s, 3 H), 1.09 (d, J = 9.4 Hz, 1 H), 1.01 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ = 143.8, 141.9, 139.8, 138.8, 138.2, 136.5, 129.6, 128.1, 127.9, 127.6, 126.3, 126.0, 83.3, 56.1, 52.1, 43.2, 31.2, 25.3, 19.0 ppm. IR (CHCl_3): $\tilde{\nu}$ = 3415, 3051, 2960, 1600, 1491, 1451, 1062 cm^{-1} . MS (70 eV): m/z (%) = 316 (0.1) $[\text{M}]^+$, 298 (1), 283 (1), 252 (1), 244 (100), 229 (73), 215 (18), 202 (18), 165 (22), 72 (12). HRMS (EI): calcd. for $\text{C}_{23}\text{H}_{24}\text{O}$ 316.1827; found 316.1815.

Reduction of 3f: Compound **3f** (50 mg, 0.159 mmol) in THF (2 mL) and 2 drops of water were stirred in an ice bath for 15 min, NaBH_4 (40 mg, 1.05 mmol) was then added, and stirring was continued for 20 h. The resulting reaction mixture was treated with water (20 mL) and extracted with ethyl acetate (3 × 15 mL). The organic layer was washed with NaOH (5%) followed by saturated NaCl solution, dried (MgSO_4), and concentrated. The residue was subjected to column chromatography on silica gel with 20% ethyl acetate in hexanes as eluent to afford **31** (21 mg, 42%) as a colorless oil.

Irradiation of 30a: A degassed solution of **30a** (1.120 g, 3.50 mmol) in acetophenone (8 mL) was irradiated at 350 nm in a Pyrex vessel for 15 d. The solvent was removed under reduced pressure (50 °C/0.05 Torr) and the residue was chromatographed on silica gel (hexanes/ethyl acetate, 1:8) to furnish **31** (28 mg, 3%) and starting material (65%).

(3R*,5S*)-2,4,4-Trimethyl-1,8-diphenyltricyclo[3.3.0.0^{2,8}]oct-6-en-3-ol (31): ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 7.54–7.08 (m, 8 H), 6.94–6.91 (m, 2 H), 5.75 (dd, J = 5.5, 2.6 Hz, 1 H), 5.69 (d, J = 5.5 Hz, 1 H), 3.91 (s, 1 H), 3.05 (d, J = 2.6 Hz, 1 H), 1.34 (s, 3 H), 1.01 (s, 3 H), 1.00 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 141.3, 139.1, 134.4, 130.0, 130.0, 128.8, 128.0, 127.9, 126.0, 125.9, 80.7, 67.0, 58.5, 54.9, 54.0, 44.0, 21.6, 20.8, 14.9 ppm. IR (CHCl_3): $\tilde{\nu}$ = 3433, 3055, 2946, 1680, 1600, 1495, 1445, 1058 cm^{-1} . MS (70 eV): m/z (%) = 316 (37) $[\text{M}]^+$, 244 (100), 238 (8), 229 (15), 218 (17), 215 (17), 202 (12), 195 (16), 179 (20), 165 (16). HRMS (EI): calcd. for $\text{C}_{23}\text{H}_{24}\text{O}$ 316.1827; found 316.1833.

Supporting Information (see footnote on the first page of this article): UV spectra of **1a–f**, ^1H and ^{13}C NMR and DEPT spectra of **3d–f**, **4f**, **30a**, **30b**, and **31**.

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