

Photoinduced Cycloaddition and Ene Reactions of 2,7-Cyclooctadienone: Experimental and Computational Studies of a Cyclopentyl Oxyallyl Intermediate

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Abstract: The photochemical reactions of cyclooctadienone **6** have been studied as a mode of entry to a cyclopentyl–oxyallyl system. Irradiation of *cis,cis*-2,7-cyclooctadienone **6** results in isomerization to *cis,trans*-2,7-cyclooctadienone **24**. The strained dienone **24** is stable at $-70\text{ }^{\circ}\text{C}$, but undergoes conrotatory cyclization at temperatures above $-30\text{ }^{\circ}\text{C}$ to the *cis*-bicyclo[3.3.0]oxyallyl system **25**. The density functional theory (DFT) structural optimizations for **6**, **24**, and **25** at the 6-31G* B3LYP level yielded energies, selected geometric parameters, and charge/spin population data. The oxyallyl intermediate reacts with vinyl ethers in a stepwise fashion to give bridged and fused tricyclic products with defined stereochemistry at the ring junctures. Simple alkenes react with **25** in a concerted ene reaction to give bicyclic products. An explanation is offered to harmonize the traditional zwitterionic view of oxyallyl systems with the current computational assessment of oxyallyls as diradical species.

Introduction

Over their long history oxyallyl compounds have been invoked as intermediates in a wide range of reactions including the Favorskii rearrangement,¹ isomerization and cycloaddition reactions of cyclopropanones,² reductive-elimination of α,α' -dibromoketones,³ and photochemical reactions of cross-conjugated dienones (most notably 4,4-dialkyl-2,5-cyclohexadienones).⁴ The past few years have seen a revival of interest in the chemistry of oxyallyl compounds. Recent experimental and theoretical studies have been directed at clarifying the electronic ground state (singlet or triplet) and reactivity of oxyallyl intermediates (zwitterion or diradical), determining the energy separation between oxyallyls and their related cyclopropanones,^{5–7} attempting to directly observe an oxyallyl compound^{8–10} and harnessing oxyallyls intermediates to develop new synthetic transformations.¹¹

Several years ago we initiated a program designed to explore the effects of oxa-substitution on the stability and reactivity of radical and non-Kekule systems.¹² As part of this program, we sought to generate and observe a simple oxyallyl system to provide evidence for its existence, to test the theoretical predictions (ground-state spin multiplicity, zwitterion or diradical), and to explore potential new reactions of these high energy systems. To address these issues we sought to find a photochemical entry to oxyallyl systems that would permit investigation over a range of temperatures and conditions. One of the potential impediments to observing a simple oxyallyl system and intercepting it with a bimolecular reaction is the expected instability of acyclic oxyallyl systems relative to the covalent cyclopropanone isomer. Experimental and computational studies place simple acyclic oxyallyl compounds 21–27 kcal/mol higher in energy than the related cyclopropanone isomer.^{13–15} In addition, the parent oxyallyl system **1** has been computed to sit

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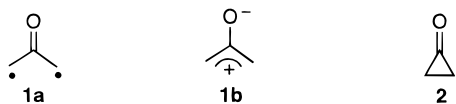
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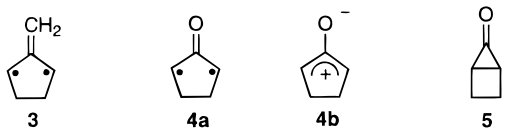
in a broad shallow well with a 0.33 kcal/mol E_a for ring closure to cyclopropanone **2**.¹³ These data may explain the lack of direct



spectroscopic evidence identifying a simple oxyallyl intermediate and raise the question of whether cyclic oxyallyl species are trappable intermediates or transition states in the reactions of cyclopropanones.

Sorensen and Sun have recently reported the preparation of several sterically congested *cis*-2,3-dialkyl-substituted cyclopropanones.^{10b,c} These compounds were prepared in an attempt to decrease or reverse the energy difference between oxyallyl and cyclopropanone isomers and permit the direct observation of an oxyallyl compound. Low-temperature NMR line-broadening experiments on *cis*-2,3-di-(2,3,3-trimethylbutyl)cyclopropanone indicate that the cyclopropanone and oxyallyl isomers are in dynamic equilibrium with a ΔG^\ddagger of 9.8 kcal/mol. This substantial decrease in the oxyallyl–cyclopropanone energy separation led Sorensen and Sun to estimate that 1 M solutions of *cis*-2,3-di-(2,3,3-trimethylbutyl)cyclopropanone may contain nanomolar concentrations of the oxyallyl isomer. Despite this dramatic success, the equilibrium concentrations were too low to allow direct spectroscopic observation of the oxyallyl isomer.

An alternative strategy to stabilize a diradical species with respect to its covalent isomer has been employed in the study of trimethylenemethane (TMM). Berson and co-workers have shown that confining the diradical within a five-member ring greatly increased the lifetime of TMM **3** and permitted detailed chemical and physical study of this transient species.¹⁶ The highly strained covalent isomer, 5-methylenebicyclo[2.1.0]pentane, was found to be less stable than the triplet diradical isomer **3**. Ab initio MO calculations suggest that this strategy should also be applicable to oxyallyl–cyclopropanone pairs. Calculations by Ichimura et al. find that the energy-ordering of cyclopropanone and oxyallyl is reversed from acyclic systems with cyclopentyl oxyallyl **4** lying ~ 3 kcal/mol below the cyclopropanone isomer **5**.⁶ Encouraged by these results we targeted the photochemical generation of cyclopentyl–oxyallyl systems for study.



Two papers published in 1968, one by Crandall and Haseltine and one by Noyori and Kato suggested that irradiation of cyclooctadienone **6** provided entry to a cyclopentyl–oxyallyl compound.^{17,18} Both groups showed that irradiation of **6** in hydroxylic solvents produced 2-substituted *cis*-bicyclo[3.3.0]octanones **7**. In addition, Crandall and Haseltine also showed

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Scheme 1

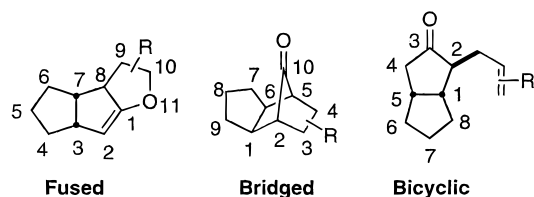
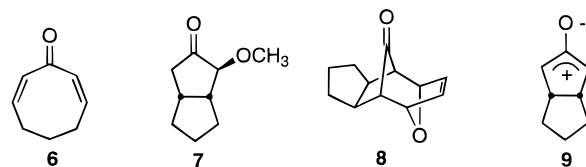


Table 1. Photoproducts from the Irradiation of **6** in the Presence of Vinyl Ethers

entry	R ¹	R ²	R ³	R ⁴	yield (%)	
					fused	bridged
a	OEt	H	H	H	51	19
b	OMe	Me	H	H	39	34
c	OEt	OEt	H	H	49 ^a	24
d	OMe	OMe	Me	Me	30	14
e	OMe	OMe	OMe	OMe	23	45

^a Fused product hydrolyzed on silica gel. Yield estimated from isolated yield of **19c** and fused/bridged ratio of **11c** and **12c** as determined by GC of crude reaction mixture.

that irradiation of **6** in the presence of furan produced cycloadduct **8**. Both groups proposed that the zwitterionic oxyallyl **9** was the reactive intermediate being captured.



We have extended the studies of Crandall and Haseltine and Noyori and Kato. In our initial report we showed that irradiation of **6** in the presence of ethyl vinyl ether or methoxypropene produced tricyclic 1:1 adducts consistent with the trapping of an oxyallyl intermediate.¹⁹ This was the first example of the trapping of a simple (nonmetal complexed) oxyallyl compound with a mono-alkene.²⁰ Here we present a full account of our work along with mechanistic evidence consistent with a polar diradical oxyallyl intermediate.


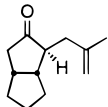

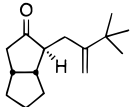

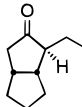
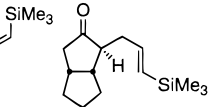
Results

Irradiation of hexane or dichloromethane solutions of **6** in the presence of an excess olefin produced, in general, 3 families of 1:1 adducts containing the *cis*-bicyclo[3.3.0]octane ring system: fused, bridged, and bicyclic (Scheme 1). The family of 1:1 adducts produced was dependent on the electron density of the π -systems of the olefin trap. Electron-rich vinyl ethers (Table 1) furnished good yields of bridged and fused adducts, whereas simple alkenes (Table 2) resulted in modest yields of bicyclic products. Acyclic dienes gave 4 + 3 adducts commonly attributed to capture of oxyallyl intermediates (Table 3). No $[2\pi + 2\pi]$ enone–alkene cycloadducts were seen even when the vinyl ethers were used as solvent and no dimers of **6** were observed in the absence of trapping reagents.


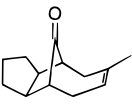

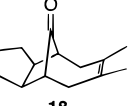
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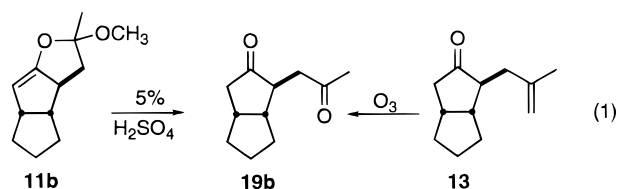
Table 2. Photoproducts from Irradiation of **6** in the Presence of Alkenes

Alkene	Bicyclic Photoproducts	Yield (%)
	 13	15
	 14	12
	 15	14 ^a , 10 ^b
	 16	

^a Yield of **15**. ^b Yield of **16**.**Table 3.** Photoproducts from Irradiation of **6** in the Presence of Acyclic Dienes

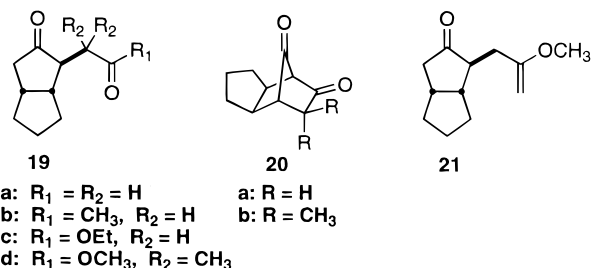
Diene	Photoproduct	Yield (%)
	 17	50
	 18	55

Structures of Photoproducts with Vinyl Ethers. The structures of the bridged and fused adducts (Table 1, entries a–e) were identified by spectral data (¹H and ¹³C NMR, decoupling experiments, IR and MS) and chemical transformation. In general, the bridged and fused products were separated by flash chromatography on silica gel. The characteristic feature in the ¹H NMR for the fused compounds is a narrow triplet at $\delta \sim 4.4$ ($J = 3$ Hz) for the vinyl ether proton at C-2. The triplet arises from the coincidental equality of the vicinal and allylic couplings as established by decoupling experiments. The highly polarized vinyl ether olefinic carbons are also readily apparent in the ¹³C NMR with the β -carbon showing the expected strong upfield shift at $\delta \sim 95$ and the quaternary α -carbon the strong downfield shift $\delta \sim 160$.²¹ The fused adducts **11a** and **11b** were isolated as a mixture of C-10 epimers. The observation of only one fused adduct (Table 1 entries c, d, and e), where no epimers at C-10 are possible, is consistent with this assignment. The epimeric mixtures were not readily separable by flash chromatography on silica gel, but NMR signals could be assigned to a particular diastereomer in **11a** by examining samples with different epimeric compositions. The fused compounds **11** were readily hydrolyzed by treatment with 5% H₂SO₄ to give the dicarbonyl compounds **19**. Formation of the cyclopentanone ring



was clearly apparent by the ¹³C NMR cyclopentanone carbonyl resonance at $\delta \sim 220$ along with acyclic keto or carboxy carbonyls absorptions in the IR and ¹³C NMR. The diastereomeric mixtures of fused adducts **11a** and **11b** hydrolyzed to form single dicarbonyl compounds with no evidence of the epimer at C-2. Vinyl ether **11c** was especially sensitive to hydrolysis, and passage through a silica gel column resulted in the isolation of the keto ester **19c**. However, the presence of **11c** was ascertained by GC–MS, ¹H NMR (vinyl ether triplet at δ 4.45), and ¹³C NMR (vinyl ether carbons at δ 159.7 and δ 95.0) examination of the crude photolysis mixture.

With the exception of entry e in Table 1, the bridged products were produced in an amount less than that of the accompanying fused isomers. The bridged products were identified by comparison of their IR and ¹³C NMR spectra with spectra from 7-norbornanone systems.²² The ¹³C carbonyl shifts ranged from δ 216–213 for compounds **12a–d**, (**12e** was δ 209.8) in agreement with the reported values of other 7-norbornanone systems. In addition the ¹³C NMR spectrum of **12e** displayed 8 signals in line with its C₃ symmetry. The carbonyl IR absorptions of compounds **12a–d** (1763–1771 cm⁻¹) compared quite well with values for substituted 7-norbornanones (1768–1770 cm⁻¹). In the case of ethyl vinyl ether and methoxypropene, only one of the possible endo/exo bridged isomers were isolated. MM2 structures for endo and exo isomers of **12a** were calculated using PCMODEL.²³ The coupling constants derived from these calculated structures predict the methine proton at C-3 in the exo isomer as a ddd, with $J = 9.6, 3.8, 1.0$ Hz, and the endo isomer as ddd, with $J = 9.6, 6.2, 3.6$ Hz. The downfield methine ether proton in **12a** was observed at δ 3.6 as a dd, $J = 8.8, 2.5$ Hz. Although we were unable to resolve the small third coupling constant, these data are most consistent with the ethoxy substituent being in the exo position. GC–MS analysis of the crude reaction mixtures in runs a and b showed a small amount of an isomeric compound in the region of the bridged product, which was likely the other C-3 epimer. Hydrolysis of keto ketals **12c** and **12d** with 5% H₂SO₄ produced the expected diketones **20a** and **20b** in good yields.



The reaction with methoxypropene (Table 1, entry b) also produced a small amount of the bicyclic product **21**. This product almost escaped detection because it was a minor component that had a GC retention time coincident with bridged product **12b**, and it readily hydrolyzed to diketone **19b**. Flash chromatography of the crude reaction mixture gave impure

(21) Rojas, A. C.; Crandall, J. K. *J. Org. Chem.* **1975**, *40*, 2225–2229.(22) Lightner, D. A.; Crist, G. V.; Kalyanam, N.; May, L. M.; Jackman, D. *J. Org. Chem.* **1985**, *50*, 3867–3878.

(23) PCMODEL, Gajewski, J. J.; Gilbert, K. E. Serena Software, 1992.

samples that exhibited spectroscopic data consistent with structure **21** (terminal vinyl ether methylene singlets at δ 4.10 and 4.14, methoxy singlet at δ 3.13). Repeated attempts at purification resulted in hydrolysis to diketone **19b**.

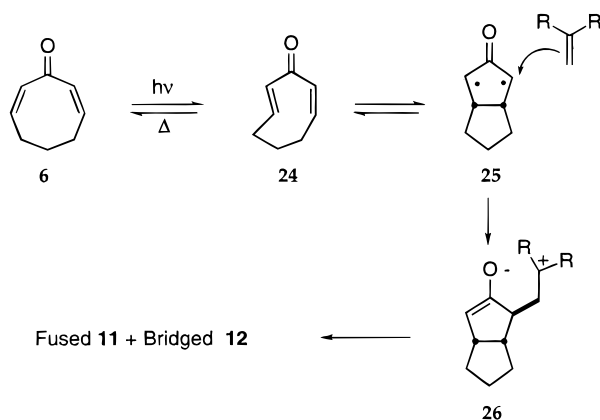
Structure of Photoproducts with Simple Alkenes. Irradiation of **6** in the presence of simple alkenes proceeds in fair yield to produce bicyclic products (Table 2). These compounds all contain distinctive ^{13}C NMR cyclopentanone carbonyl resonance at $\delta \sim 220$ and 2 alkene-carbon resonances. The terminal methylene groups in **13** and **14** are clearly seen in the DEPT spectrum at δ 112.3 and 107.3, respectively, and in the ^1H NMR at $\delta \sim 4.8$. Ozonolysis of bicyclic adduct **13** produced diketone **19b** which was identical to the product produced from hydrolysis of fused adduct **11b**. This result provides a key structural linkage between the fused products from the vinyl ether reactions and the bicyclic products in the reactions with the simple alkenes. These results reinforce the structural and stereochemical assignments in both series.

Surprisingly, the reaction with allyltrimethylsilane produced two keto alkenes in comparable amounts. One possibility was that the two isomers were C-2 endo/exo epimers. MM2 calculations predict that the C-2 exo isomer is ~ 3 kcal/mol more stable than the endo epimer. Treatment of a solution containing **15** and **16** with NaHCO_3 resulted in no change in the composition of the mixture. Including D_2O resulted in the gradual incorporation of three deuteriums without any change in the ratio of the ketoalkenes. These results indicate that the two keto alkenes are not C-2 epimers and both isomers have the alkenyl group in the more stable exo position. The position of the double bond in the propenyl side chain was confirmed by ozonolysis. Treatment of **15** and **16** with O_3 gave keto aldehyde **19a** which was identical to the product isolated from the hydrolysis of **11a**. The distinctive $J_{\text{H,H}}$ coupling constants observed across the double bond of the *cis* (14.0 Hz) and *trans* (18.4 Hz) silylalkenes unambiguously allow the assignment of the *cis* product **15** as the major isomer formed.²⁴

The assignment of the exo stereochemistry at C-2 in the bicyclic products was further reinforced by the excellent correlation of the ^{13}C NMR chemical shifts for the ring carbons with calculated values obtained using Whitesell and Matthews' empirically derived rules for the *cis*-bicyclo[3.3.0]octane ring system.²⁵ From an analysis of 15 monosubstituted *cis*-bicyclo[3.3.0] systems, they derived rules that allowed them to predict the ^{13}C chemical shift of 36 polyfunctionalized bicyclo[3.3.0]octanes with an average absolute error in chemical shift per compound of 0.7 ppm (SD = 0.6). Observed errors per carbon were ± 2.5 ppm. Using this method we calculated the ^{13}C chemical shifts of the ring carbons of exo-(**22**) and endo-2-methylbicyclo[3.3.0]octan-3-one (**23**) as models for the bicyclic products in our study. The ^{13}C chemical shifts for the ring carbons in the isobutylene adduct **13** had an average absolute error of 1.2 ppm when compared with the exo structure and 2.7 ppm when compared with the endo. The values for the bridgehead carbons (C-1 and C-5) showed the largest discrepancy (-2.4 and -2.5 ppm). The ^{13}C shifts of the ring carbons for **15**, **16**, and **19a-d** were very similar to the values observed for **13**. These data are all consistent with 2-exo substitution.

Structure of Photoproducts with Dienes. Crandall and Haseltine have previously shown that irradiation of **6** in the presence of conjugated cyclic dienes gives 4 + 3 cycloadducts. Reactions with acyclic dienes isoprene and 2,3-dimethyl-1,3-

Scheme 2



butadiene proceeded in an analogous manner producing adducts **17** (55% yield) and **18** (50%). The products were identified by spectroscopic analysis and comparison with spectroscopic data from related systems.^{10a,26} GC-MS shows some minor isomeric products (<5%) present in both reactions which may result from reaction with only one double bond. These products were not characterized.

Storable Reactive Intermediate. Crandall and Haseltine noted in their initial studies that irradiation of **6** at -78 °C followed by addition of furan in the dark gave the same tricyclic adduct **8** observed when the irradiation was carried out in the presence of furan.¹⁷ Following these studies, **6** was irradiated at -78 °C in CH_2Cl_2 for 1 h, and then ethyl vinyl ether was added in the dark. The reaction mixture was warmed to room temperature and analyzed. Adducts **11a** and **12a** were formed in about the same ratio as that seen when the photochemical reactions were carried out in the presence of trap. These experiments indicate that a storable ground-state species is on the reaction pathway. To determine the identity of the intermediate, **6** was irradiated at -78 °C in CD_2Cl_2 and then examined at -70 °C by ^{13}C NMR. Eight new signals appeared at δ 196.5, 160.6, 152.0, 140.4, 127.9, 38.8, 33.1, 32.2. The new signals were about $1/10$ as strong as three of the five signals (δ 193.7, 142.8, 135.2, 27.2, 24.8) displayed by dienone **6**, suggesting that the photoisomer was formed in about 20% under these conditions. Increasing the irradiation time did not increase the relative intensity of the new signals, implying that a photostationary state had been reached. The NMR data require that **6** is isomerized to a compound of lower symmetry and that this compound contains four olefinic carbons, three alkyl carbons, and one carbonyl group. These data are in accord with the photochemical conversion of **6** to *cis,trans*-2,7-cyclooctadienone, **24**. The *cis,trans*-dienone **24** was stable at -70 °C for at least 2 h and began to slowly disappear at temperatures above -30 °C.

Discussion

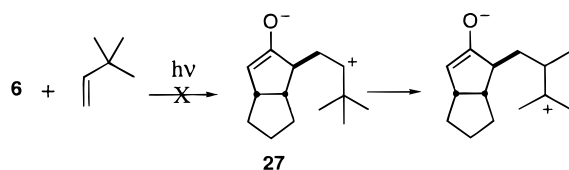
Formation of Bridged and Fused Adducts. Scheme 2 shows a mechanistic hypothesis to explain the formation of 1:1 adducts of **6** with vinyl ethers. The reaction sequence is initiated by the photochemical isomerization of **6** to produce the strained *cis,trans*-dienone **24**. At temperatures above -30 °C, **24** undergoes thermal conrotatory cyclization to produce *cis*-bicyclo[3.3.0]oxyallyl compound **25**. B3LYP/6-31G* calculations place **24** 15.0 kcal/mol higher in energy than **6** and only 12.1 kcal/mol below the singlet state of oxyallyl **25**. These

(24) Colvin, E. W. *Silicone in Organic Synthesis*; R. E. Krieger Publishing Co.: Malabar, FL, 1981; pp 60-61, 78.

(25) Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1977**, *42*, 3878-3882.

(26) Onove, H.; Moritani, I.; Murahasi, S. I. *Tetrahedron Lett.* **1973**, 121-124.

Scheme 3

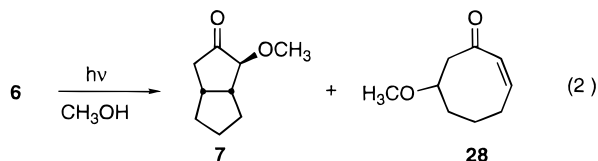


calculations show that it is energetically permissible for the cyclization of **24** to **25** to be occurring at temperatures as low as $-30\text{ }^{\circ}\text{C}$, providing that the cyclization transition state lies within ~ 5 kcal/mol of oxyallyl **25**. Orbital symmetry considerations require the cycloaddition reaction between **25** and vinyl ether proceed in a stepwise manner.^{6a} The initial bond formation occurs by preferential attack on the sterically more accessible convex face of the *cis*-bicyclo[3.3.0]octane ring system. The resultant zwitterionic intermediate **26** is formed with defined stereochemistry at three contiguous chiral centers. Zwitterion **26** partitions to give intramolecular O- or C-alkylation of the pseudo-enolate producing the fused and bridged series of products.

Additional support for the stepwise mechanism came from examination of the stereochemistry of the cycloaddition when **6** was irradiated in the presence of *cis*-1,2-dimethoxyethylene. A stepwise mechanism could produce a maximum of seven cycloadducts (four fused, three bridged), whereas a concerted pathway could produce a maximum of four cycloadducts (two bridged, two fused). Examination of the crude product mixture by GC-MS showed the presence of six cycloadducts, implying that the reaction followed the stepwise pathway.

In an effort to demonstrate the formation of zwitterionic intermediate **26** proposed in Scheme 2, **6** was irradiated in the presence of *tert*-butylethylene. It was reasoned that the putative intermediate **27** would undergo 2° to 3° carbocation rearrangement prior to cyclization, permitting a distinction between radical and ionic mechanisms (Scheme 3). After prolonged irradiation, no 1:1 adducts were observed. Apparently, *tert*-butylethylene is not reactive enough to trap **25**. Use of 2,3,3-trimethyl-1-butene as a trap resulted in the formation of the "normal" bicyclic adduct **14** without any skeletal rearrangement.

The strained dienone **24** can be intercepted with alcohols to give conjugate addition products.¹⁷ Irradiation of **6** in methanol gives a 1.3:1 ratio of **7** to **28** as the primary products. The



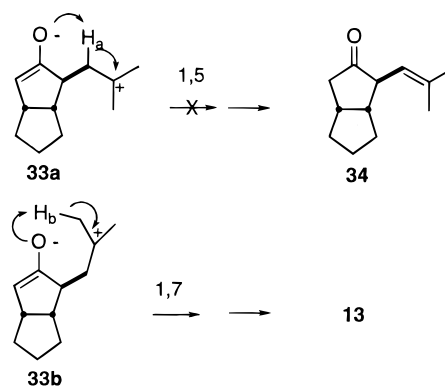
bicyclic keto ether **7** is produced by capture of oxyallyl **25** and the monocyclic keto ether results from capture of **24**. *trans*-2-Cyclooctenones and *trans*-2-cycloheptenones are well-known to react with alcohols at the β -enone carbon.²⁷ It is interesting to note that *trans*-2-cyclooctenone also reacts with dimethoxyethylene to give [2 + 2] cycloadducts.^{28,29} This reaction is believed to proceed in a stepwise manner with the initial bond formation taking place at the β -enone carbon. In contrast, no

(27) Hart, H.; Chen, B.; Jeffares, M. *J. Org. Chem.* **1979**, *44*, 2722–2726 and references therein.

(28) (a) Eaton, P. E.; Lin, K. *J. Am. Chem. Soc.* **1964**, *86*, 2087–2088. (b) Corey, E. J.; Bass, J. D.; LeMathieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570–5583.

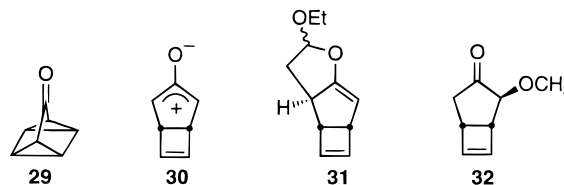
(29) (a) Corey, E. J.; M. T.; LeMahieu, R. A.; Libit, L. *J. Am. Chem. Soc.* **1965**, *87*, 2051–2052. (b) Eaton, P. E.; Lin, K. *J. Am. Chem. Soc.* **1965**, *87*, 2052–2054.

Scheme 4



[2 + 2] adducts are observed in the photochemical reactions of **6** with vinyl ethers, even when ethyl vinyl ether or methoxypropene was used as solvent. Vinyl ethers are not reactive enough nucleophiles to directly attack the *cis,trans*-dienone **24** at the β -position and trap the more reactive oxyallyl **25**.

Additional support for the intermediacy of an oxyallyl species in the photoinduced reactions of **6** can be found in the work of Hirano et al.⁹ They reported that photoisomerization of quad-racyclanone **29** gave rise to oxyallyl **30** which was trapped by ethyl vinyl ether and methanol to produce, respectively, fused adduct **31** and keto ether **32**. The similarity in the photoproducts derived from the structurally disparate **6** and **29** strongly suggests that both reactions involve a cyclopentyl oxyallyl intermediate.^{9b}



Formation of Bicyclic Products. Mechanistic parsimony (three products from one intermediate) initially attracted us to propose that the bicyclic products were also derived from zwitterionic intermediate **33** (Scheme 4) via an intramolecular proton transfer. However, the regiochemistry and stereochemistry of the double bond in the bicyclic products was not adequately explained by the stepwise mechanism. In principle zwitterionic intermediate **33** could suffer internal elimination by either 1,5 or 1,7 proton transfer to give, respectively, keto alkene **34** or **13**. However, only the 1,7 product was produced. Noyori observed a similar "1,7" product in the reaction of isobutylene with an oxyallyl-Fe(II) complex.³⁰ In this case they argued against the stepwise mechanism on the grounds that an ionic intermediate similar to **33** would eliminate preferentially via a five-membered cyclic transition state to give the more highly substituted alkene, e.g., **34**.

The surprising observation of large amounts of the sterically congested *cis*-silylalkene **15** in the reaction with **6** and allyltrimethylsilane provides an additional window on the formation of the bicyclic products. All mechanistic pathways leading to the *cis*-silylalkene **15** will suffer from *s-cis* steric congestion of the SiMe₃ group with the allyl carbon chain. Therefore, to make this pathway competitive, the alternative "trans pathway" must be subjected to a specific destabilizing interaction with the bicyclo[3.3.0] ring system. In evaluating the stepwise mechanism two conformations (pro-*cis* and pro-*trans*) were considered

(30) Noyori, R.; Shimizu, F.; Hayakawa, Y. *Tetrahedron Lett.* **1978**, 2091–2094.

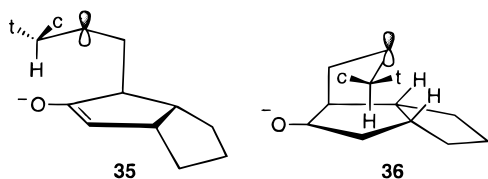
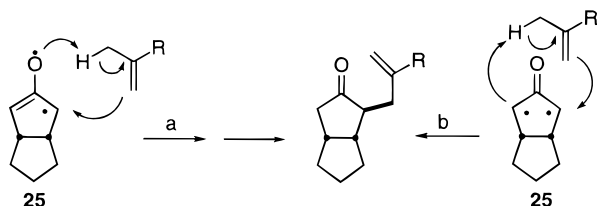


Figure 1. Possible conformations in the stepwise formation of bicyclic adducts. The internal elimination step involves proton transfer to the enolate at either O- (**35**) or C- (**36**). A substituent at "t" will end up at the trans position in the product, and a substituent at "c" will end up at the cis position.

Scheme 5



for proton transfer to each end of the enolate system (Figure 1).³¹ In all four of these pathways, the proton being abstracted is aligned parallel with the p-orbital of the adjacent carbocation. A qualitative analysis of these alternatives was carried out using hand-held molecular models. The trans pathway is clearly favored when the proton is transferred to the oxygen end of the enolate (**35**). In this case the SiMe₃ group points away from the bicyclic ring (**35**, t = SiMe₃, c = H). The cis and trans pathways look more competitive when the proton is transferred to the carbon end of the enolate (**36**). Here the conformation leading to the trans product (**36**, t = SiMe₃, c = H) points the SiMe₃ group toward the bridgehead of the bicyclic ring system. This interaction may raise the energy of the trans pathway enough to balance the developing s-cis steric interaction in the alternative conformation, leading to the cis product (**36**, c = SiMe₃, t = H). However, for this to explain the observed product distribution there needs to be a strong bias for the proton to be transferred to the carbon end of the enolate. Proton transfer should be a highly exothermic step with an early transition state. This should make the strength of the base site (C vs O) and the stability of the products (ketone vs enol) relatively unimportant factors. Therefore, there should be little bias favoring transfer from **36**, and it is unlikely that the stepwise mechanism would produce large amounts of *trans*-silylalkene **16**. In addition, if zwitterion **33** were on the reaction pathway, one might have expected intramolecular transfer of the trimethylsilyl group to be competitive with proton transfer. Analysis of the crude reaction mixture by GC-MS failed to detect any adducts that lacked the trimethylsilyl group.

Alternatively, the bicyclic adducts may be formed by a concerted ene reaction between oxyallyl **25** and alkenes. Again, there are two possible pathways for the ene reaction which differ by whether the proton is transferred to the oxygen (Scheme 5, path a) or carbon end (Scheme 5, path b) of oxyallyl **25**. Frontier MO analysis predicts that the ene reaction will proceed selectively following path b. The LUMO of the oxyallyl system has a node passing along the central carbon-oxygen bond which results in bonding interactions with the alkene HOMO at the carbon ends of oxyallyl (Figure 2). Examination of the two approaches of allyltrimethylsilane and **25**, along path b (Scheme 5), leading to the *cis*- and *trans*-ketoalkene products **15** and

(31) This analysis was for "pseudochair" transition states. The alternative "pseudoboat" transition states appeared to favor the trans product in all cases.

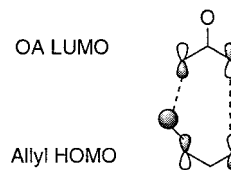
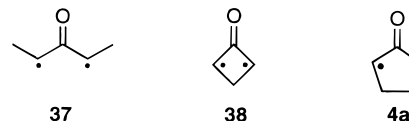


Figure 2. Frontier MO analysis of the ene reaction between oxyallyl and propene.

16, show interactions that are similar to that discussed in the stepwise mechanism involving transfer of the proton to carbon (Figure 1, **36**). Once again the conformation leading to the trans product **16** has the SiMe₃ pointed toward the bridgehead. This specific interaction should make formation of the *cis*-ketoalkene **15** competitive with the formation of **16** and provides the best explanation for the observed product distribution.

Electronic Nature of Oxyallyl Systems. The proper description of the electronic structure of oxyallyls remains a vexing question. Historically oxyallyls have been written as zwitterions, and most experimental studies still refer to the ionic structure despite the fact that the parent system has been repeatedly calculated to be a ground-state triplet as far back as 1968.³² Recent high-level calculations have found that the triplet of **1** is preferred by ~1–2 kcal/mol over the lowest singlet.⁵ Borden and co-workers have also found that alkyl substitution drops the singlet state of 1,3-dimethoxyoxyallyl **37**, ~5 kcal/mol below the triplet.

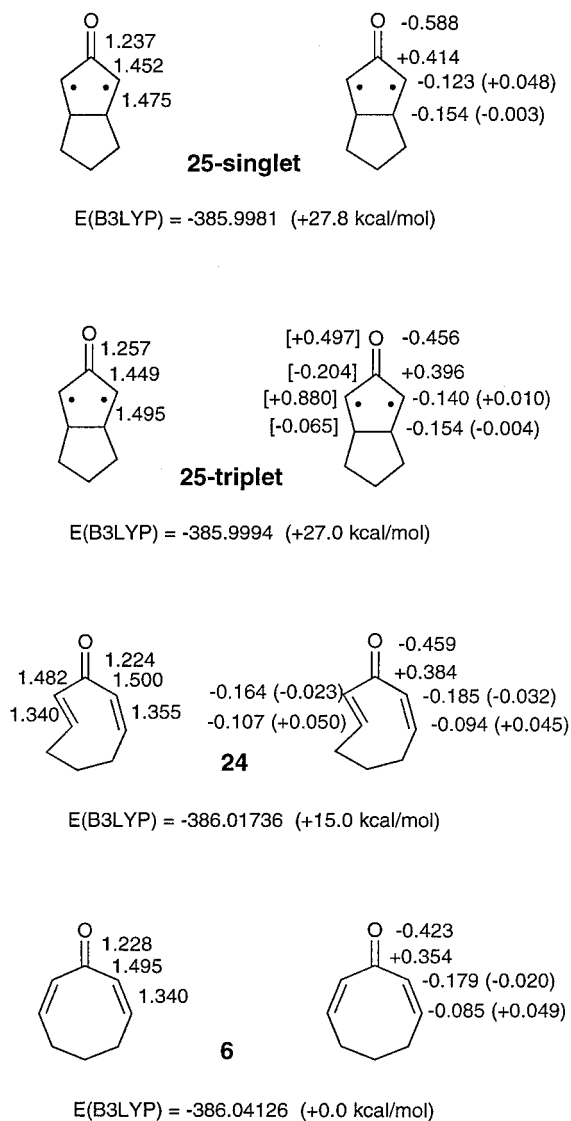


The structure calculated for 1,3-dimethyl oxyallyl **37** has a short C=O bond, indicating a high degree of π -bonding. The unpaired electron spin density resides largely on the α -carbons for the triplet state of **37**. There is some contribution from zwitterionic resonance structures that slightly polarizes the π -electron density. However, the diradical resonance structure **37** was reported to represent the electron distribution best. Qualitatively similar results were reported by some of us for the cyclic oxyallyl analogues **4a** and **38**,^{6a} both of which were found to have diradicaloid rather than zwitterionic electronic structures at the ab initio SCF-CI level of theory. Natural orbital analysis of singlet **4a** further revealed this state to be a polarized diradicaloid,^{6a} with a dipole moment of 5.01 D and frontier MO occupation numbers of 1.55 and 0.40; a "pure" diradical would have occupation numbers of 1.00. Further comparisons of these systems to the bicyclic oxyallyl **25** will be made below as appropriate.

The density functional theory (DFT) structural optimizations for **6**, **24**, and **25** at the 6-31G* B3LYP level yielded energies, selected geometric parameters, and charge/spin population data shown in Figure 3.³³ Full sets of Cartesian coordinates are given in the supporting material. DFT is known to give useful descriptions of structure and spin density distribution for states that are well described as a single configuration, but are more

(32) Hoffmann, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 1475–1485.

(33) All calculations were carried out using the program Gaussian94, Revision D.4: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian Inc.: Pittsburgh, 1995.



GEOMETRY DATA

POPULATION DATA

Figure 3. Selected DFT results for **6**, **24**, and **25**. All computations were carried out using RB3LYP/6-31G* wave functions except for triplet **25**, which used UB3LYP/6-31G*. Bond lengths are in angstroms, population numbers are from the Mulliken analysis (population numbers in parentheses are heavy atom populations with hydrogen contributions added). Population numbers in brackets [] for triplet **25** are Mulliken spin density results.

problematic for states that are highly multiconfigurational. Fortunately, the singlet states of oxyallyls are known to be less multiconfigurational than numerous other biradicaloid species, and we feel that use of DFT in these computations is justified on this basis. As we shall show below, the results obtained are quite in accord with previous results for related systems at multiconfigurational and SCF-configuration interaction level of ab initio theory.

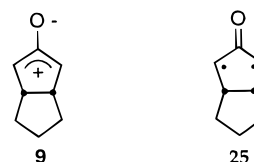
The triplet and singlet states of oxyallyl **25** are nearly degenerate, with the triplet state about 0.8 kcal/mol below the singlet at this level of theory. Similarly, parent oxyallyl **1** at the same level of DFT theory also has nearly degenerate triplet and singlet state (to within 1 kcal/mol). Such differences in DFT-computed state energies are so small, that it is best simply to classify the states as nearly degenerate. As described above,

the same situation has been computed for the parent oxyallyl system at the highest levels of ab initio theory used to date.

Both oxyallyl states lie about 26 kcal/mol higher than the *cis,cis*-diene **6**. The *cis,trans*-diene **24** lies between these, about 15 kcal/mol above the *cis,cis* isomer, due to the strained E-geometry double bond in **24**. Despite its considerably higher energy, **24** shows a very similar Mulliken charge density distribution to that of the *cis,cis* isomer, except for a slightly higher charge separation in the carbonyl bond. Individual bond lengths are similar in these geometric isomers, including the carbonyl bond length.

By comparison, the computed differences in Mulliken charge density distributions and geometric parameters between the triplet and singlet states of oxyallyl **25** are significant. The triplet state shows more geometric delocalization, with a longer C=O length (1.257 Å in the triplet versus 1.237 Å in the singlet). The shorter C=O length in the singlet state is consistent with a stronger π -bond, and with strong charge separation. The singlet state has Mulliken charges on the carbonyl oxygen and carbon of -0.59 and +0.42, respectively, by comparison to the corresponding values of -0.46 and +0.40 in the triplet state. A similar increase of carbonyl charge separation and decrease in bond length was observed in our earlier, ab initio study of analogue **4a**.^{6a} The spin density distribution in the triplet state of **25** shows most of the spin density to reside on the α -carbons, with considerably less on the carbonyl group, again similar to the previous results for **4a**.

Although several computations^{5,6,13} have shown oxyallyl systems to have nearly degenerate triplet and singlet states, experimental evidence has not unequivocally supported observation of any triplet oxyallyl state. The chemistry attributable to oxyallyls has been most consistent with singlet reactivity in other studies as well as this one.^{9,10,14,15,34,35} For this reason, we confine discussion of oxyallyl **25** to the singlet state. The summation of computational evidence from previous and present studies indicates that the oxyallyl should not be drawn as zwitterionic form **9**, but rather as a carbonyl-linked diradical form **25** having a strongly polarized C=O bond. The charge distributions in Figure 3 show negative charge distributions on the α -positions of singlet **25** (or a near-zero charge if the hydrogen atom contributions are summed into the heavy atoms), an observation that counterindicates resonance form **9** with its positive charge in that position. In addition, resonance form **9** suggests a long C—O bond length, as expected for a true “oxy-allyl” type structure. However, the computations for **25**, in accord with those for the parent oxyallyl and for monocyclic analogue **4a**, show a C=O bond that only 0.01 Å longer than that in the corresponding cyclic dienones. Thus, the reactivity patterns of **25** must be explained in terms other than those suggested, by assuming that the zwitterionic nature of resonance form **9** is the sole representation of oxyallyl.



To test the accuracy of the diradical description of oxyallyl, Borden and co-workers carried out a combined ab initio MO and Monte Carlo study of the effect of solvent on the disrotatory ring opening of monocyclic cyclopropanones to acyclic oxyallyls.¹³ The calculations show small changes in the dipole moment in going from cyclopropanone to oxyallyl ($\Delta\mu \approx 0.7-$

0.9 D) and therefore predict small solvent effects on the rate of ring opening. The results of the computational studies were in good agreement with Greene's investigations on the stereomutation of enantiometrically enriched *trans*-2,3-di-*tert*-butylcyclopropanone.¹⁴ Greene studied the rate of racemization in 5 solvents at 80 °C and found that the rate increased 12-fold when the solvent was changed from isooctane to acetonitrile. The solvent effects are significantly less than expected for a true zwitterionic intermediate, and the close agreement between the computational and experimental studies was presented as strong support for the diradical description of oxyallyl. Recent experimental studies on the effect of solvent on the ring opening of cyclopropanones by Sorensen and Sun^{10c} are also in qualitative agreement with the computational studies.³⁶

The electronic character of putative oxyallyl intermediates as revealed in bimolecular trapping reactions is less clear-cut. Either a zwitterionic or a diradical oxyallyl intermediate could be invoked to explain the concerted cycloadditions with dienes or the concerted ene reactions with allyl systems. However, the reactions with alkenes and alcohols suggest that oxyallyls have substantial zwitterionic character. The stepwise photoinduced reactions of **6** show a strong preference for electron-rich alkenes. Yields of trapped products are consistently higher and reactions are faster with vinyl ethers compared to simple alkenes. Haseltine has also reported that no adducts are produced when **6** is irradiated in the presence of electron-deficient π -systems found in 1,2-dichloroethylene and dimethylacetylenedicarboxylate.^{17b} Turro and co-workers have also reported that oxyallyl cycloaddition products were formed when 2,2-dimethylcyclopropanone was treated with dienes, but no adducts were observed when *cis*-1,2-dichloroethylene, maleic anhydride, or diethyl azodicarboxylate were employed as traps.² In contrast, electron-deficient alkenes such as maleic anhydride are known to react quantitatively with the isoelectronic trimethylenemethane diradical.¹⁶ These results are consistent with a zwitterionic oxyallyl acting as an electron acceptor.

Perhaps a more convincing argument for a zwitterionic oxyallyl can be made from the reactions of oxyallyls with alcohols. Formation of α -alkoxy ketones has been observed in a variety of photochemical reactions that are believed to involve oxyallyls, including the photolysis of quadracyclanone,⁹ irradiation of 4,4-dialkyl-cyclohexa-2,5-dienones,⁴ and irradiation of pyranones.^{11c-e} In fact it is the observation of the alkoxyketones that has been cited as evidence for a zwitterionic intermediate. A radical reaction between oxyallyl **25** and methanol would be expected to involve CH abstraction which is very unlikely to lead to the observed methoxyketone **7**.

It is possible to harmonize the computational description of the diradical oxyallyl with the experimentalist view of a zwitterionic oxyallyl by taking a dynamic view of the bimolecular reactions. It is clear from the computational studies that the electronic distribution in oxyallyls is sensitive to substitution. Placing alkyl groups on the α -carbon changes the ground state from triplet to singlet and increases the polarization. Therefore, it is reasonable to expect that in the bimolecular reactions with alkenes and alcohols the polarization in the diradical oxyallyl will continue to increase as a "nucleophilic" trapping reagent approaches. The SOMO1–SOMO2 separation should increase, forcing the two unpaired electrons into the lower orbital as the incoming pair of electrons from the trapping reagent flows into

the vacated oxyallyl orbital. This would give rise directly to zwitterionic intermediates such as **26**. The net effect is that the polarized diradical reacts operationally like a zwitterion. Therefore, while it is mechanistically convenient to view oxyallyls as zwitterions, care should be taken to not consider this Lewis structure a complete and proper description of the electron distribution.

Summary. Irradiation of *cis,cis*-2,7-cyclooctadienone **6** results in isomerization to *cis,trans*-2,7-cyclooctadienone **24**. The strained dienone **24** is stable at -70 °C, but undergoes conrotatory cyclization at temperatures above -30 °C to the *cis*-bicyclo[3.3.0]oxyallyl system **25**. The oxyallyl intermediate reacts with vinyl ethers in a stepwise fashion to give bridged and fused tricyclic products with defined stereochemistry at the ring junctures. Simple alkenes react with **25** in a concerted ene reaction to give bicyclic products. These studies are consistent with the description of cyclic oxyallyl systems as polarized singlet diradicals which are susceptible to nucleophilic capture.

Experimental Section

Gas chromatography (GC) was performed on a Hewlett-Packard model 5890 (Series II) equipped with either a 10-m OV101 capillary column (0.2 mm) or a 15-m OV17 capillary column (0.2 mm). Preparative GC was performed on a 5 ft \times 0.25 in. packed OV101 column unless otherwise stated. Low resolution GC-mass spectra were recorded on a Hewlett-Packard 5890A GC coupled with a Hewlett-Packard 5970 mass selective detector. High-resolution mass spectral analysis was performed at MAIF, Department of Chemistry, Case Western Reserve University and at the Mass Spectrometry Center at the Department of Chemistry, University of Pennsylvania. NMR Spectroscopy was performed on a Bruker AC-200 operating at 200 MHz for ¹H NMR and at 50 MHz for ¹³C NMR. All spectra were recorded using CDCl₃ as solvent, and the data are presented as follows: chemical shift δ (multiplicity, J Hz, integration).

General Procedure for Irradiation of Cyclooctadienone with Olefins. Cyclooctadienone^{37,38} was dissolved in either benzene, hexanes, or methylene chloride (2–10 mg/mL) in a Pyrex vessel. All solvents were dried and distilled prior to use. A large excess of the vinyl ether or alkene or diene was added, and the solutions were irradiated using either a Rayonet photochemical reactor equipped with sixteen 350-nm lamps or with a 450-W mercury vapor lamp (Hanovia) filtered by uranium glass ($\lambda \geq 350$ nm). All irradiations were conducted under a nitrogen atmosphere. A reflux condenser was attached to the photolysis vessel for the irradiations performed in the Rayonet. The photoreactions were followed by GC, and the reactions were stopped when all of the cyclooctadienone was consumed. The photolysis mixtures were concentrated by rotary evaporation, and the residues were dissolved in a 1:1 mixture of hexanes and ethyl ether and passed through a pad of silica gel to remove polymeric materials. The crude mixtures were concentrated and purified by flash chromatography on silica gel.

Irradiation of Cyclooctadienone with Ethyl Vinyl Ether. Cyclooctadienone (1 g, 8.2 mmol) was dissolved in 150 mL of benzene along with 25 mL of ethyl vinyl ether (distilled from sodium). The sample was irradiated for 7 h in a Rayonet photochemical reactor. The solvent was removed, and the flash chromatography (5:1, hexanes:ether) gave 1.12 g (70%) of products. The major product was a diastereomeric mixture of the fused adducts.

11a: ¹H NMR 5.58 (dd $J = 4.6, 7.4$, 1H), 4.40 (t $J = 3.0$, 1H), 3.84 (dq $J = 7.1, 9.5$, 1H), 3.55 (dq $J = 7.1, 9.5$, 1H), 3.18 (m, 1H), 2.6 (m, 1H), 2.5 (m, 1H), 2.28 (dddd $J = 0.6, 4.5, 7.6, 12.7$, 1H), 1.21 (t $J = 7.1$, 3H), 1.8–1.3 (m, 7H); ¹H NMR 5.48 (d $J = 5.3$, 1H), 4.40 (t $J = 3.0$, 1H), 3.77 (dq $J = 7.1, 9.5$, 1H), 3.45 (dq $J = 7.1, 9.5$, 1H), 3.18 (m, 1H), 3.0 (m, 1H), 2.5 (m, 1H), 2.0 (ddd $J = 0.5, 7.3, 12.1$, 1H), 1.18 (t $J = 7.1$, 3H), 1.8–1.3 (m, 7H); ¹³C NMR 160.8 (162.9), 113.2 (111.6), 94.6 (94.4), 65.6 (63.9), 52.2 (52.8), 51.7 (49.6), 46.2

(34) Turro, N. J.; Hammond, W. B. *Tetrahedron* **1968**, *24*, 6017.

(35) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242–248.

(36) However, Cordes and Berson have reported solvent effects on the ring opening of a spiro cyclopropanone, which do not follow the computational studies. See ref 15.

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(46.7), 37.6 (37.4), 32.9 (32.7), 32.1 (31.7), 26.8 (26.7), 14.0 (14.9); IR 1681 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$ (M^+) 194.1306, obsd 194.1307.

The minor product was the bridged adduct **12a**: ^1H NMR 3.6 (dd $J = 8.8, 2.5$, 1H), 3.41 (m, 2H), 2.20–1.8 (m, 6H), 1.8–1.5 (m, 3H), 1.4–1.05 (m, 6H); ^{13}C NMR 216.2, 76.0, 64.1, 49.7, 44.2, 43.0, 38.1, 34.7, 31.7, 31.6, 26.5, 15.3; IR 1768, 1732 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{O}_2$ (M^+) 194.1306, obsd 194.1308.

Hydrolysis of Fused Adduct 11a. **11a** (450 mg) was dissolved in 40 mL of ether and rapidly stirred with 15 mL of 5% H_2SO_4 for 3 h. The organic layer was separated and washed with bicarbonate, water, and brine, dried over sodium sulfate, and concentrated. Flash chromatography furnished keto aldehyde **19a**: ^1H NMR 9.76 (s, 1H), 2.85 (dd $J = 4.1, 18.2$, 1H), 2.73–2.45 (m, 3H), 2.35 (m, 2H), 2.20 (dd $J = 3.3, 17.7$, 1H), 2.05–1.50 (m, 5H), 1.40 (dt $J = 6.8, 12.5$, 1H); ^{13}C NMR 219.7, 200.1, 48.5, 46.0, 43.8, 43.5, 37.6, 33.4, 32.1, 25.4; IR 1735, 1729 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2$ (M^+) 166.0994, obsd 166.0993.

Irradiation of Cyclooctadienone with Methoxypropene. Cyclooctadienone (202 mg) was dissolved in 50 mL of methoxypropene and irradiated for 12 h in the Rayonet. Flash chromatography (5:1, hexanes/ether) furnished 235 mg (73% yield) of products. The major product was a diastereomeric mixture of the fused adducts.

11b: ^1H NMR 4.45 (t $J = 3.0$, 1H), 3.36 (s, 1.5H), 3.31 (s, 1.5H), 3.2 (m, 1H), 3.10 (m, 0.5 H), 2.70 (m, 0.5 H), 2.55 (m, 1 H), 2.14 (dd $J = 7.3, 11.8, 0.5$ H), 2.02 (dd $J = 7.9, 12.1, 0.5$ H), 1.90–1.30 (m, 7H), 1.53 (s, 1.5 H), 1.49 (s, 1.5 H); ^{13}C NMR 161.3 (163.0), 116.7, (118.1), 94.0, (94.3), 52.0 (52.0), 51.3, (51.9), 49.5 (50.0), 46.7 (46.8), 40.2 (43.2), 32.7 (32.8), 31.9 (32.1), 26.6 (26.9), 22.2 (24.5); IR 1682 cm^{-1} ; MS m/e 194 (10, M^+), 179 (26), 123 (10), 105 (10), 91 (15), 85 (13), 79 (13), 77 (12), 72 (38), 53 (16), 43 (100); HRMS (CI- NH_3) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_2$ ($\text{M} + \text{H}$) 195.1385, obsd 195.1364.

Bridged Adduct 12b: ^1H NMR 3.15 (s, 3H), 2.25–1.75 (m, 12H), 1.35 (s, 3H); ^{13}C NMR 215.4, 76.7, 53.9, 49.7, 46.0, 43.3, 41.1, 36.1, 31.7, 31.6, 26.4, 19.6; MS m/e 194 (10, M^+), 179 (26), 123 (10), 105 (10), 91 (15), 85 (13), 79 (13), 72 (38), 53 (16), 43 (100); IR 1763, 1734 cm^{-1} ; HRMS (CI- NH_3) calcd for $\text{C}_{12}\text{H}_{22}\text{NO}_2$ ($\text{M} + \text{NH}_4$) 212.1650, obsd 212.1638.

Hydrolysis of Fused Adduct 11b. Fused photoproduct (65 mg) was dissolved in 20 mL of diethyl ether along with 10 mL of 5% H_2SO_4 and rapidly stirred at room temperature for 1.5 h. The organic layer was separated and washed with bicarbonate, water, and brine, dried over sodium sulfate, and concentrated to give 31 mg of diketone **19b**: ^1H NMR 2.83 (dd $J = 4.3, 18.0$, 1 H), 2.71–2.46 (m, 3H), 2.39–2.20 (m, 3 H), 2.16 (s, 3H), 1.40 (dt $J = 7.0, 12.6$, 1H); ^{13}C NMR 220.5, 206.5, 49.6, 46.0, 43.7, 43.4, 37.6, 33.4, 32.2, 30.0, 25.4; IR 1737, 1722 cm^{-1} ; HRMS calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ (M^+) 180.1150, obsd 180.1152.

Irradiation of Cyclooctadienone with 1,1-Diethoxyethylene. Cyclooctadienone (1 g, 8.2 mmol) and 1,1-diethoxyethylene (4 g, 34 mmol)³⁹ were dissolved in 35 mL of methylene chloride and 50 mL of hexanes and irradiated for 7 h with a mercury vapor lamp. GC analysis indicated the presence of two main products. Flash chromatography (9:2, hexanes/ethyl ether) resulted in the hydrolysis of the fused product and a second flash column (5:1 hexanes/ethyl acetate) was required to separate the products.

Fused adduct 11c: as seen by GC-MS in crude m/e 238 (63, M^+), 209 (54), 164 (81), 136 (100), 135 (85), 107 (71), 79 (83), 55 (68), 41 (72).

Ethyl ester 19c: (49%) ^1H NMR 4.1 (q, 2H), 2.65–2.25 (m, H), 2.0–1.45 (m, H), 1.15 (t, 3H); ^{13}C NMR 219.8, 172.1, 60.6, 50.4, 45.9, 43.7, 37.6, 34.2, 33.5, 25.5, 14.1, IR 1729 cm^{-1} , MS m/e 210 (2, M^+), 165 (22), 136 (27), 123 (100), 67 (34), 55 (27) 41 (34); HRMS (CI- NH_3) calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3$ ($\text{M} + \text{H}$) 211.1334, obsd 211.1324.

Bridged adduct 12c: (24%) ^1H NMR 3.73–3.24 (m, 4H), 2.43 (m, 1H), 2.19 (m, 2H), 2.08 (s, 1H), 1.98 (d $J = 5.3$, 1H), 1.88 (m, 2H), 1.71–1.55 (m, 3H), 1.43–1.02 (m, 2H), 1.19 (dt $J = 7.1, 0.8$, 3H), 1.12 (dt $J = 7.1, 0.9$, 3H); ^{13}C NMR 213.4, 101.9, 57.5, 56.0,

54.3, 47.2, 43.0, 39.6, 34.8, 31.7, 31.2, 26.4, 15.2, 15.1; IR 1771, 1732 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{22}\text{O}_3$ (M^+) 238.1569, obsd 238.1578.

Hydrolysis of Bridged Adduct 12c. Bridged adduct **12c** (30 mg) was dissolved in 2 mL of acetone and 0.5 mL of chloroform. Water (~50 mL) and pyridinium tosylate (~2 mg) were added, and the reaction mixture was stirred for 4 h. The reaction mixture was passed through a pad of MgSO_4 and silica gel, and the diketone **20a** was isolated by flash chromatography (13:2, hexanes/ethyl acetate). ^1H NMR 2.65 (d, H), 2.6 (s, H), 2.58–2.48 (m, H), 2.15–1.95 (m, H), 1.63 (s, H), 1.6–1.1 (m, H); ^{13}C NMR 209.6, 205.2, 61.7, 48.8, 46.8, 42.5, 38.4, 31.6, 31.5, 26.5; IR 1792, 1743 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2$ (M^+) 164.0837, obsd 164.0839.

Irradiation of Cyclooctadienone with 1,1-Dimethoxy-2-methyl-1-propene. Cyclooctadienone (0.5 g, 4.1 mmol) and 1,1-dimethoxy-1-propene (2.4 g, 20 mmol)⁴⁰ were dissolved in 80 mL of methylene chloride and irradiated for 9 h with the Hanovia lamp. Flash chromatography (9:2 hexanes/ethyl ether) furnished two products in a combined 44% yield.

Fused adduct 11d: ^1H NMR 4.38 (t $J = 3.0$ Hz, 1H), 3.33 (s, 3H), 3.28 (s, 3H), 3.07 (m, 1H), 2.71 (dt $J = 2.7, 6.5$, 1H), 2.51 (m, 1H), 1.7–1.3 (m, 6H), 1.08 (s, 3H), 0.87 (s, 3H); ^{13}C NMR 157.5, 128.4, 94.9, 61.9, 51.8, 51.2, 49.2, 45.7, 40.3, 33.1, 32.9, 26.5, 22.1, 16.9; IR 1689 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{22}\text{O}_3$ (M^+) 238.1569, obsd 238.1574.

Bridged adduct 12d: ^1H NMR 3.17 (s, 3H), 3.16 (s, 3H), 2.39 (m, 2H), 1.95 (d $J = 1.32$, 1H), 1.81 (m, 2H), 1.54 (m, 1H), 1.43 (d $J = 1.25$, 1H), 1.4–0.09 (m, 3H), 1.12 (s, 3H), 1.04 (s, 3H); ^{13}C NMR 213.3, 104.4, 62.1, 55.9, 51.6, 51.4, 45.5, 35.7, 35.0, 71.8, 31.5, 26.3, 25.4, 20.8; IR 1770 cm^{-1} ; HRMS calcd for $\text{C}_{14}\text{H}_{22}\text{O}_3$ (M^+) 238.1569, obsd 238.1563.

Hydrolysis of Fused Adduct 11d. Fused adduct **11d** (50 mg) was dissolved in 5 mL of diethyl ether and vigorously stirred with 5 mL of 5% H_2SO_4 for 3 h. The organic layer was washed with bicarbonate and brine, dried over MgSO_4 , and concentrated to a yellow oil. Flash chromatography furnished keto ester **19d**: ^1H NMR 3.63 (s, 3H), 2.45 (m, 2H), 2.25 (dd $J = 1.8, 7.1$, 1H) 1.95 (m, 5H), 1.65–1.15 (m, 4H), 1.21 (s, 3H), 1.13 (s, 3H); ^{13}C NMR 220.6, 177.5, 61.4, 51.9, 45.3, 44.8, 42.97, 37.7, 35.1, 34.0, 26.1, 24.5, 22.1; IR 1739, 1477 cm^{-1} ; HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{O}_3$ (M^+) 224.1412, obsd 224.1405.

Hydrolysis of Bridged Adduct 12d. Bridged adduct **12d** (121 mg) was dissolved in an ether (5 mL), 5% sulfuric acid (5 mL) mixture. The mixture was stirred vigorously for 3 h. The organic layer was washed with bicarbonate and brine, dried over MgSO_4 , and concentrated to give diketone **20b**.

20b: ^1H NMR 2.67 (m, 1H), 2.48 (brs, 1H), 2.40 (m, 1 H), 2.04 (brs, 1H), 2.05 (m, 2H), 1.7 (m, 1H), 1.5–1.15 (m, 3H), 1.24 (s, 3H), 1.06 (s, 3H); ^{13}C NMR 211.9, 210.9, 61.8, 59.8, 52.3, 39.6, 36.6, 32.0, 31.4, 26.6, 24.5, 18.1; IR 1779, 1738 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$ (M^+) 192.1150, obsd 192.1149.

Irradiation of Cyclooctadienone with Tetramethoxyethylene. Cyclooctadienone (0.5 g, 4.1 mmol), and tetramethoxyethylene (2.0 g, 14 mmol)⁴¹ were dissolved in 70 mL of methylene chloride and photolyzed for 6 h with Hanovia lamp. The two photoproducts (combined yield 68%) were separated by flash chromatography (5:2, hexanes/ethyl ether).

Fused adduct 11e: ^1H NMR 4.55 (t $J = 3.2$, 1H), 3.47 (s, 3H), 3.46 (s, 3H), 3.40 (s, 3H), 3.31 (s, 3H), 3.14 (m, 1H), 2.96 (t $J = 2.5$, 1H), 1.82–1.28 (m, 7H); ^{13}C NMR 155.1, 124.0, 104.2, 96.8, 58.4, 52.5, 52.3, 50.9, 50.3, 40.3, 33.2, 32.3, 27.0; HRMS calcd for $\text{C}_{14}\text{H}_{22}\text{O}_5$ (M^+) 270.1467, obsd 270.1451.

Bridged adduct 12e: ^1H NMR 3.32 (s, 6H), 3.31 (s, 6H), 2.52 (t $J = 4.8$, 2H), 2.22 (s, 2H), 1.98–1.79 (m, 2H), 1.59 (m, 1H), 1.41–0.9 (m, 3H); ^{13}C NMR 209.8, 105.5, 56.2, 51.4, 51.3, 34.7, 31.3, 26.2; CH analysis calcd C 62.20, H 8.20; obsd, C 62.39, H 8.23.

Irradiation of Cyclooctadienone with *cis*-1,2-Dimethoxyethylene. A mixture of *cis*- and *trans*-1,2-dimethoxyethylene was prepared as described in the literature.⁴² A pure sample of *cis*-1,2-dimethoxyethylene was prepared by preparative GC on a 15% OV-17 column (5 ft \times 1/4

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in., column temperature 50 °C, 8 min). *cis*-1,2-Dimethoxyethylene (590 μ L) and cyclooctadienone (300 μ L) were dissolved in 15 mL of dry methylene chloride and irradiated for 10 h. Analysis of the crude reaction mixture by GC–MS showed the presence of six products with M^+ at 210 *m/e* corresponding to 1:1 adducts.

Irradiation of Cyclooctadienone with Isobutylene. Cyclooctadienone (610 mg, 5 mmol) and isobutylene (~25 mL, ~150 mmol) were dissolved in 250 mL of benzene and photolyzed for 40 h at –5 °C with the Hanovia lamp. Flash chromatography (6:1, hexanes/diethyl ether) produced the bicyclic adduct **13** (15% yield) and an unidentified 1:1 photoproduct (impure, <5% yield).

Bicyclic adduct 13: ^1H NMR 4.76 (brs, 1H), 4.70 (brs, 1H), 2.57–(m, 1H), 2.49–2.25 (m, 2H), 2.20–1.78 (m, 5H), 1.78–1.52 (m, 3H), 1.68 (s, 3H); ^{13}C NMR 222.0, 143.1, 112.3, 52.6, 45.9, 43.9, 39.2, 37.3, 33.6, 33.1, 25.6, 21.9; IR 1729, 1650; HRMS (CI–NH₃) calcd for C₁₂H₁₉O (*M* + *H*) 179.1436, obsd 179.1443.

Ozonolysis of Bicyclic Adduct 13. Ketoalkene **13** (70 mg) was dissolved in 10 mL of methanol and ozonized at –78 °C. The ozonide was decomposed by the addition of dimethyl sulfide at –78 °C. The mixture was kept at –78 °C for 45 min and then warmed to 0 °C for 1 h. The solvent was removed, and the oily residue was purified by flash chromatography (1:2, hexanes/diethyl ether) to give 20 mg of the diketone **19b**. This sample was identical (^1H NMR, ^{13}C NMR, GC–MS) to the compound produced by the hydrolysis of fused adduct **11b**.

Irradiation of Cyclooctadienone with Allyltrimethylsilane. Cyclooctadienone (1 g, 8.2 mmol) and allyltrimethylsilane (7 g, 61 mmol) were dissolved in 125 mL of methylene chloride and irradiated for 9 h in the Rayonet. The isomeric keto alkenes were isolated by flash chromatography (9:1, hexanes/diethyl ether) in a combined yield of 24%. Preparative GC (160 °C) gave analytical samples of **15** and **16**.

Bicyclic adduct *cis*-15: ^1H NMR 6.21 (dt *J* = 7.4, 14.0, 1H), 5.55 (d *J* = 14.0 Hz, 1H), 2.56 (m, 2H), 2.40 (m, 2H), 2.21 (m, 1H), 2.15–1.85 (m, 2H), 1.50–1.25 (m, 2H), 0.14 (s, 9H); ^{13}C NMR 221.2, 145.5, 130.9, 54.2, 45.5, 44.0, 33.8, 37.5, 33.5, 32.9, 25.5, 0.1; IR 1732, 1608; HRMS calcd for C₁₄H₂₄OSi (*M*⁺) 236.1596, obsd. 236.1595.

Bicyclic adduct *trans*-16: ^1H NMR 5.95 (dt *J* = 6.0, 18.4, 1H), 5.67 (dt *J* = 1.1, 18.4, 1H), 2.52 (m, 2H), 2.35 (m, 2H), 2.16 (m, 1H), 2.10–1.78 (m, 4H), 1.67 (m, 2H), 1.35 (m, 2H), 0.02 (s, 9H); ^{13}C NMR 221.5, 143.7, 132.6, 54.0, 45.6, 44.1, 37.7, 37.5, 33.6, 33.1, 25.6, –1.3; IR 1732, 1617; HRMS calcd for C₁₄H₂₄OSi (*M*⁺) 236.1596, obsd 236.1596.

Irradiation of Cyclooctadienone with 2,3,3-Trimethyl-1-butene. Cyclooctadienone (267 mg, 6.5 mmol) and 2,3,3-trimethyl-1-butene (5 g, 51 mmol) were dissolved in 130 mL of methylene chloride and irradiated for 11 h. Bicyclic adduct **14** was isolated by flash chromatography (18:1 hexanes, ethyl acetate) and an analytical sample was obtained by preparative GC (160 °C).

Bicyclic adduct 14: ^1H NMR 4.92 (brs, 1H), 4.65 (brs, 1H), 2.68–2.50 (m, 2H), 2.50–2.43 (m, 1H), 2.40–2.10 (m, 2H), 2.08–1.82 (m, 4H), 1.80–1.30 (m, 4H), 1.04 (s, 9H); ^{13}C NMR 222.1, 154.8, 107.3, 53.6, 46.6, 43.9, 37.3, 36.1, 33.6, 33.5, 32.8, 29.1, 25.6; IR 1730, 1637 cm^{-1} HRMS calcd for C₁₅H₂₄O (*M*⁺) 220.1827 obsd 220.1825.

Irradiation of Cyclooctadienone with Isoprene. Cyclooctadienone (736 mg, 6.0 mmol) and isoprene (12 mL, 141 mmol) were dissolved

in 120 mL of dichloromethane and irradiated for 2 h. The bridged keto alkene was isolated by flash chromatography (9:1 hexanes, diethyl ether) in 50% yield and an analytical sample was obtained by preparative GC (160 °C).

Adduct 17: ^1H NMR 5.45 (brs, 1H), 2.35–2.15 (m, 5H), 2.15–2.03 (m, 3H), 1.87 (m, 1H), 1.75 (s, 3H), 1.58–1.17 (m, 5H); ^{13}C NMR 224.7, 134.4, 121.5, 55.7, 54.8, 44.2, 44.1, 36.9, 35.4, 35.2, 33.1, 28.5, 25.9; IR 1732 (s), 1600 (w), 1457 (m) cm^{-1} ; HRMS calcd for C₁₃H₁₈O (*M*⁺) 190.1358, obsd 190.1358.

Irradiation of Cyclooctadienone with 2,3-Dimethyl-1,3-butadiene. Cyclooctadienone (267 mg, 2.2 mmol) and 2,3-dimethyl-1,3-butadiene (387 mg, 4.7 mmol) were dissolved in 70 mL of methylene chloride and irradiated for 8 h. Photoadduct **18** was isolated by flash chromatography (5:1 hexanes:ethyl acetate) in 55% yield and an analytical sample was obtained by preparative GC (160 °C).

Adduct 18: ^1H NMR 2.28–2.19 (m, 4H), 2.19–2.08 (m, 2H), 1.84 (m, 2H), 1.73 (s, 6H), 1.55–1.13 (m, 6H); ^{13}C NMR 225.1, 127.3, 55.0, 43.3, 39.6, 34.9, 26.0, 24.0; IR 1736 cm^{-1} ; HRMS calcd for C₁₄H₂₀O (*M*⁺) 204.1514, obsd 204.1511.

Irradiation of Cyclooctadienone with Methanol. Cyclooctadienone (500 mg, 4.1 mmol) was dissolved in 150 mL of methanol and irradiated for 4 h in the Rayonet. The photolysis mixture showed five products by GC–MS. The major product (288 mg) was isolated by flash chromatography (3:1 hexanes/diethyl ether) and identified as the methoxyketone **7**.^{17b} Irradiation of an analytical sample of 0.01M methanol solution of cyclooctadienone for 5 min at room temperature produced two products, **7** and **28** in a 1.3:1 ratio.

Keto ether 7: ^1H NMR 3.43 (s, 3H), 3.37 (dd *J* = 1.6, 6.5, 1H), 2.60 (m, 1H), 2.45 (m, 2H), 2.10–1.78 (m, 3H), 1.78–1.46 (m, 3H), 1.33 (m, 1H); ^{13}C NMR 216.2, 87.2, 57.9, 44.9, 41.0, 35.6, 33.9, 31.2, 25.4; IR 1745; MS *m/e* 154 (10, *M*⁺).

Photolysis of 2-methoxybicyclo[3.3.0]octan-3-one 7. Following the procedure described by Haseltine,^{17b} ketone **7** (160 mg) was dissolved in 20 mL of hexanes and photolyzed for 8.5 h in the Rayonet using the 300-nm lamps. Flash chromatography (4:1, hexanes/diethyl ether) provided bicyclic[3.3.0]octan-3-one. ^1H NMR 2.65 (m, 2H), 2.53–2.32 (m, 2H), 2.04–1.79–1.45 (m, 4H), 1.43–1.27 (m, 2H); ^{13}C NMR 221.1, 44.6, 39.5, 33.3, 25.4; IR 1732.

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Supporting Information Available: 200 MHz ^1H NMR spectra of compounds **11a**, **11b**, **11d**, **11e**, **12a**, **12b**, **12c**, **12d**, **13**, **14**, **15**, **16**, **17**, **18**, **19a**, **19b**, **19c**, **19d**, and **20b**; 50 MHz ^{13}C NMR spectra of compounds **12a**, **12b**, **12c**, **20a**; full sets of Cartesian coordinates, dipole moments and energies as calculated using Gaussian94 at the 6-31G*/B3LYP level for **6**, **24**, **25** singlet and **25** triplet (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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