experiments were carried out at the Center for Fast Kinetics Research, The University of Texas, Austin, 78712. The Center is supported jointly by the Biotechnology Branch of the Division of Research Resources of NIH (RR 00886) and by the University of Texas, Austin.

Supplementary Material Available: Kinetic data for reactions of bis(viologens) and spectral equilibria data for disproportionation of $PTQ^{3+}\cdot$ and $BTQ^{3+}\cdot$ and reactions of ETQ^{4+} with $DQ^{+}\cdot$, BTQ^{4+} with $DQ^{+}\cdot$, and PTQ^{4+} with $ETQ^{2+}\cdot\cdot$ (8 pages). Ordering information is given on any current masthead page.

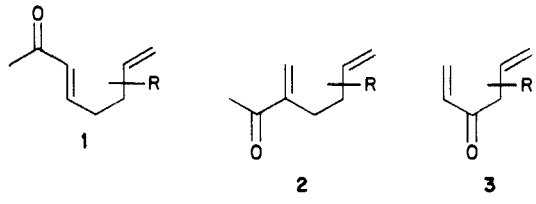
Regiochemical Control in Intramolecular Photochemical Reactions of 1,6-Heptadienes: Carbonyl-Substituted 1-(4-Alkenyl)-1-cyclopentenes

Albert R. Matlin,[†] Clifford F. George,[‡] Steven Wolff,*[†] and William C. Agosta*[†]

Contribution from the Laboratories of The Rockefeller University, New York, New York 10021-6399, and Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375-5000. *Received September 23, 1985*

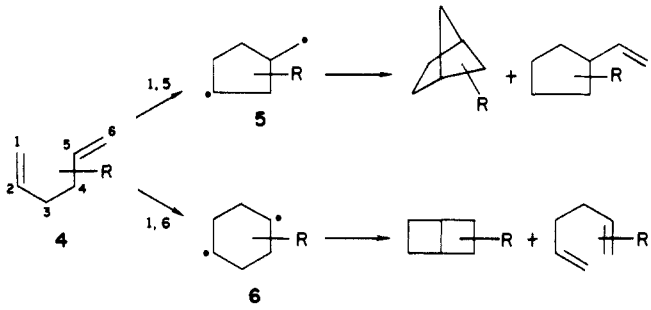
Abstract: The regiochemistry of intramolecular photochemical reaction has been studied in three series of ketones of types **10–12**, with particular attention to the effect of alkyl substitution on the side-chain double bond [C(6) and C(7)]. Results for 13 ketones are summarized in Tables I–III and permit these generalizations: (1) ketones **10** follow the "rule of five" and always give straight closure, (2) ketones **11** respond to substitution at C(6) with crossed closure, and (3) ketones **12** respond to substituion at C(6) with reduced crossed closure. Several anomalies would be clarified if initial 1,7 bonding can occur, and this possibility is discussed.

In previous studies we have investigated the role of structural features in control of the regiochemistry of the intramolecular photochemical reactions of carbonyl-substituted 1,5-hexadienes of the general structures **1–3**.[1-4] There is a well-known gener-



1 **2** **3**

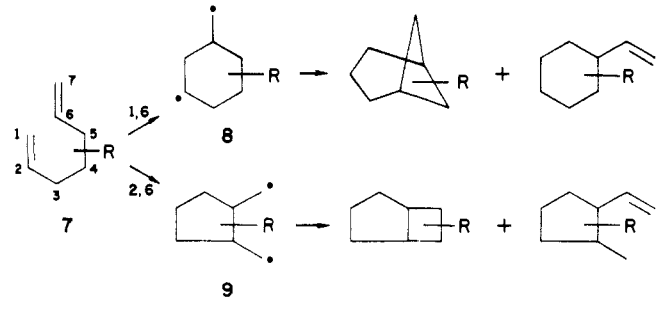
alization,[5] the "rule of five", that irradiation of hexadienes (**4**) leads preferentially to 1,5 (crossed) closure, with intermediate formation of biradical **5** that then leads to products through collapse or disproportionation. All indication of the alternative



4 **5** **6**

1,6 (straight) closure to **6** is frequently completely absent. We found, however, that in 1-acyl-1,5-hexadienes (**1**) and 1,5-hexadien-3-ones (**3**) incorporation of the conjugated double bond into a five- or six-membered ring or substitution of the diene with an alkyl group at C(5) causes 1,6 closure to become competitive.[1,3] These effects are additive, and in molecules containing both features highly regioselective 1,6 closure can occur. Interestingly, neither effect influences the regiochemistry of the third class of hexadienes, 2-acyl-1,5-hexadienes (**2**), and all representatives of this group that were studied close in the crossed fashion.[2] More recently we have found that substitution of a trimethylsilyl, but not a *tert*-butyl, group at C(1) in series **3** also favors 1,6 closure.[4]

We wished to pursue a similar investigation of regiochemical effects in 1,6-heptadienes (**7**), particularly since these compounds have seen much more use as intermediates in the synthesis of natural products than have their lower homologues.[6] In **7** the



7 **8** **9**

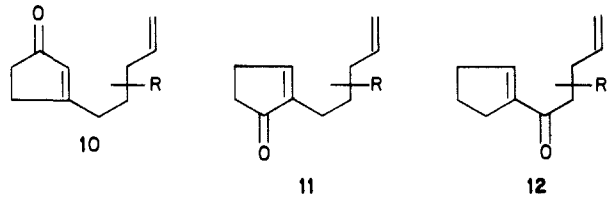
rule of five predicts straight closure by way of **9** to be favored over crossed closure to **8**.[5] It was attractive to examine the three types of carbonyl-substituted heptadienes homologous to **1–3**, but for these new studies we chose to focus our effort specifically on compounds in which the conjugated double bond was incorporated

[†] The Rockefeller University.
[‡] Naval Research Laboratory.

(1) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1292. This paper contains references to reviews and discussions pertinent to the general topics of the present report.
(2) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1299.
(3) Matlin, A. R.; Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1983**, *24*, 2961.
(4) Wilson, P.; Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1985**, *26*, 5883.
(5) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932. Liu, R. S. H.; Hammond, G. S. *Ibid.* **1967**, *89*, 4936. A theoretical treatment has recently appeared: Gleiter, R.; Sander, W. *Angew. Chem.* **1985**, *97*, 575; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 566.
(6) See for example: Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135.

0002-7863/86/1508-3385$01.50/0

in a five-membered ring. The three classes then become **10–12**.



There were good reasons for restricting substrates in this fashion; from our earlier work with hexadienes it was clear that the single most effective influence on regiochemistry came from incorporation of the conjugated double bond in a cyclopentene ring,[1] and it seemed reasonable that a similar situation might obtain with heptadienes. Furthermore, there was already ample evidence in the work of others that placement of the enone double bond in a six-membered ring or simple substitution at C(6) or both did not alter the regiochemistry of cyclization for either 1-acyl-[7,8] or 2-acyl-1,6-heptadienes.[9,10] For the 3-keto series no such information was available, but it had been reported that on irradiation at $\lambda \geq 280$ nm simple acyclic 1,6-heptadien-3-ones polymerize rather than undergo any intramolecular photocyclization.[11,12] In the paragraphs below we describe the preparation and photochemistry of 13 dienones of series **10–12**. To some extent, the behavior of these systems is reminiscent of that of the hexadienes, but the consequences of structural change prove to be rather more complicated with these higher homologues. As before, the results permit useful generalizations about the influence of structure on regiochemistry, are pertinent to the detailed mechanisms of these photochemical processes, and raise several questions for future study.

Results

In Tables I–III are gathered data on the 13 dienones of the general structures **10**, **11**, and **12**, respectively, that were prepared and irradiated in this study. Typically, dilute solutions (~0.01 M) of these compounds in purified hexanes were illuminated through a uranium glass filter ($\lambda > 340$ nm) at ~25 °C. As noted before,[1] irradiation at higher temperature had little effect on the product distributions or yields; reaction was appreciably faster, however, at the higher temperature, and occasionally this was preparatively convenient. Products and unreacted starting ketones were isolated by preparative vapor-phase chromatography (VPC) or flash chromatography.[13] Structures of these products and preparation of the starting ketones are discussed below. In Tables II and III products are segregated according to the regiochemistry of closure; the 1-acyl series **10** (Table I) yielded only products of straight closure. Dienones **23** and **25** underwent some intramolecular hydrogen abstraction to form **23c** and **25c**, and these extraneous minor products are also included in Table III. Dienone **19** gave ~3% of a characterized but unidentified third isomeric product, **19c**. Yields given are based on isolated material in most cases, and ratios of straight and crossed closure calculated from these yields are listed for convenience. We also determined approximate quantum yields for the reactions of ketones **14**, **18**, and **22**. These three substrates share the same carbon skeleton and differ only in the location of the carbonyl group. The results, which are included in Tables I–III, were obtained for benzene solutions irradiated in a merry-go-round apparatus at ~313 nm (potassium chromate filter[14]) with the concurrent formation of acetophenone

Table I. Products of Photolysis of 3-(4-Alkenyl)-2-cyclopenten-1-ones (**10**)

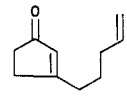
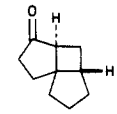
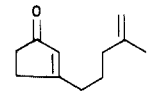
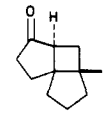
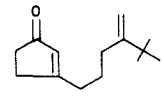
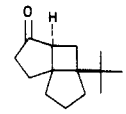
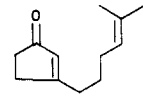
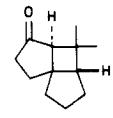
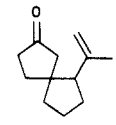
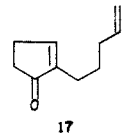
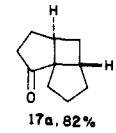
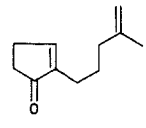
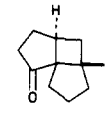
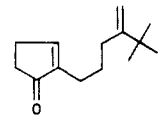
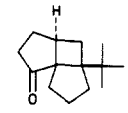
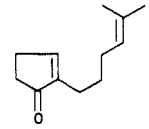
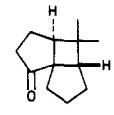
dienone	product, yield (quantum yield)
 13	 13a, 92%
 14	 14a, 93% (0.60)
 15	 15a, 92%
 16	 16a, 50%  16b, 40% (mixture of diastereomers)

Table II. Products of Photolysis of 2-(4-Alkenyl)-2-cyclopenten-1-ones (**11**)

dienone	ratio of straight/crossed closure	product, yield (quantum yield)	
		straight closure	crossed closure
 17	only straight	 17a, 82%	
 18	73/27	 18a, 46% (0.21)	 18b, 17% (0.08)
 19	80/20	 19a, 73%	 19b, 18%
 20	only straight	 20a, 88%	

(7) (a) Cargill, R. L.; Dalton, J. R.; O'Connor, S.; Michels, D. G. *Tetrahedron Lett.* **1978**, 4465. Fetizon, M.; Lazare, S.; Pascard, C.; Prange, T. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1407. Yoshioka, M.; Ishii, K.; Wolf, H. R. *Helv. Chim. Acta* **1980**, *63*, 571. Oppolzer, W.; Zutterman, F.; Bättig, K. *Ibid.* **1983**, *66*, 522. Hoye, T. R.; Martin, S. J.; Peck, D. R. *J. Org. Chem.* **1982**, *47*, 331. (b) Becker, D.; Nagler, M.; Hirsh, S.; Ramun, J. *J. Chem. Soc., Chem. Commun.* **1983**, 371.

(8) Pirrung, M. *J. Am. Chem. Soc.* **1981**, *103*, 82.

(9) Oppolzer, W.; Bird, T. G. C. *Helv. Chim. Acta* **1979**, *62*, 1199. Birch, A. M.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1980**, 1195. Bloomfield, J. J.; Owsley, D. C. *Tetrahedron Lett.* **1973**, 1795.

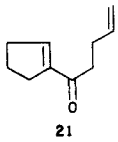
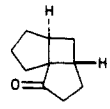
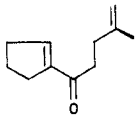
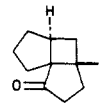
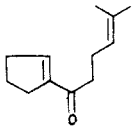
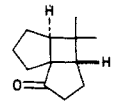
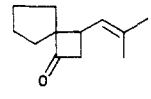
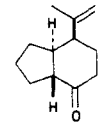
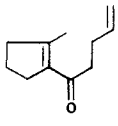
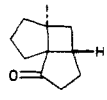
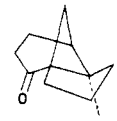
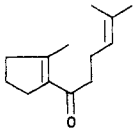
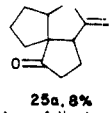
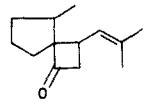
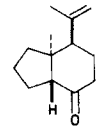
(10) For a structurally constrained 2-acyl system that yields both straight and crossed products, see ref 6.

(11) Gibson, T. W.; Erman, W. F. *J. Org. Chem.* **1972**, *37*, 1148.

(12) In this brief summary we have omitted from consideration a number of substrates related to 5-allyl-2-cyclopentenone that are constrained structurally and that in many cases can be considered either 3-keto- or 1-acylheptadienes; regiochemical behavior of these systems has proved complicated: Frõstl, W.; Margaretha, P. *Helv. Chim. Acta* **1976**, *59*, 2244. Oppolzer, W.; Burford, S. C. *Ibid.* **1980**, *63*, 788. McMurry, T. B. H.; Gowda, G. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1516. Barker, A. J.; Pattenden, G. *Tetrahedron Lett.* **1980**, *21*, 3513. Also excluded are heteroatom-substituted systems in which regiochemical behavior seems to be influenced by the heteroatom: Ikeda, M.; Takahashi, M.; Uchino, T.; Ohno, K.; Tamura, Y. *J. Org. Chem.* **1983**, *48*, 4246.

(13) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

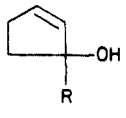
Table III. Products of Photolysis of 1-(1-Cyclopenten-1-yl)-4-alken-1-ones and 1-(2-Methyl-1-cyclopenten-1-yl)-4-alken-1-ones (**12**)

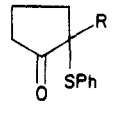
dienone	ratio of straight/crossed closure	product, yield (quantum yield) straight closure		crossed closure
 **21**	60/40	 **21a**, 57%		 **21b**, 38%
 **22**	90/10	 **22a**, 84% (0.37)		 **22b**, 9% (0.04)
 **23**	39/61	 **23a**, 33%	 **23c**, 5% (H abstraction)	 **23b**, 52%
 **24**	65/35	 **24a**, 46%		 **24b**, 25%
 **25**	16/84	 **25a**, 8% (mixture of diastereomers)	 **25c**, 18% (mixture of diastereomers) (H abstraction)	 **25b**, 42%

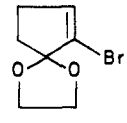
from valerophenone[14] serving as a chemical actinometer.

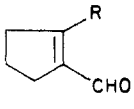
Preparative Experiments

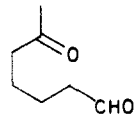
Series **10** dienones **13–16** were available through addition of the appropriate alkenyl Grignard reagent (RMgBr) to cyclopentenone followed by oxidative rearrangement of the intermediate allylic alcohol **26** with chromium trioxide in aqueous sulfuric acid.[15]

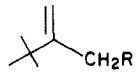

26


27, R = H
28, R = alkenyl


29


30, R = H
31, R = CH_3


32


33, R = CH_2CH_2Br
34, R = CH_2CH_2OH
35, R = H

Series **11** ketones **17**, **18**, and **20** were prepared from 2-(phenylthio)cyclopentanone (**27**).[16] Alkylation[17] of **27** using sodium hydride and the appropriate alkenyl bromide (RBr) furnished **28**, and this was converted to the desired substrate on oxidation with sodium periodate and subsequent elimination of the sulfoxide at 50 °C.[18] The related *tert*-butyl compound **19** was prepared by way of bromo ketal **29**.[19] Lithium–halogen exchange using *tert*-butyllithium followed by alkylation with the appropriate alkenyl halide gave, after hydrolysis, cyclopentenone **19**. Series **12** ketones **21–23** were available through additions of the appropriate Grignard reagent to 1-cyclopentenecarboxaldehyde (**30**) and subsequent oxidation using pyridinium chlorochromate,[20] all following an established procedure.[3,21] For the methylated homologues **24** and **25**, substituted aldehyde **31**[22] was employed, and the final oxidation was performed using oxalyl chloride and dimethyl sulfoxide in methylene chloride.[23] Aldehyde **31** was prepared through cyclization[24] of 6-oxoheptanal (**32**).[22]

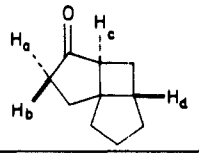
The only previously unreported halide required in these syntheses was **33**; this was prepared from **34** by way of the tosylate. Alcohol **34** was conveniently available on reaction of ethylene oxide with the anion formed on treatment[25] of 2-*tert*-butylpropene (**35**) with potassium *tert*-butoxide and butyllithium.

Structure of Products

With the exception of **13a**,[26] all the photoproducts reported in Tables I–III are new compounds; they have been fully characterized and show spectroscopic properties compatible with their assigned structures. Additional evidence for these assignments

(14) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.
(15) Büchi, G.; Egger, B. *J. Org. Chem.* **1971**, *36*, 2021. McCurry, P. M., Jr.; Singh, R. K. *Ibid.* **1974**, *39*, 2317.
(16) Seebach, D.; Teschner, M. *Chem. Ber.* **1976**, *109*, 1601.
(17) Coates, R. M.; Pigott, H. D.; Ollinger, J. *Tetrahedron Lett.* **1974**, 3955.
(18) Trost, B. M.; Salzmann, T. N. *J. Am. Chem. Soc.* **1973**, *95*, 6840.
(19) Guaciaro, M. A.; Wovkulich, P. M.; Smith, A. B., III, *Tetrahedron Lett.* **1978**, 4661. Smith, A. B., III; Branca, S. J.; Pilla, N. N.; Guaciaro, M. A. *J. Org. Chem.* **1982**, *47*, 1855.
(20) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.
(21) Smith, A. B., III; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 1961.
(22) Inouye, Y.; Inomata, S.; Ishihara, Y.; Kakisawa, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 208.
(23) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.
(24) White, J. D.; Ruppert, J. F.; Avery, M. A.; Torii, S.; Nokami, J. *J. Am. Chem. Soc.* **1981**, *103*, 1813.
(25) Schlosser, M.; Hartmann, J.; David, V. *Helv. Chim. Acta* **1974**, *57*, 1567.
(26) Cargill, R. L.; Sears, A. B. *Tetrahedron Lett.* **1972**, 3555.

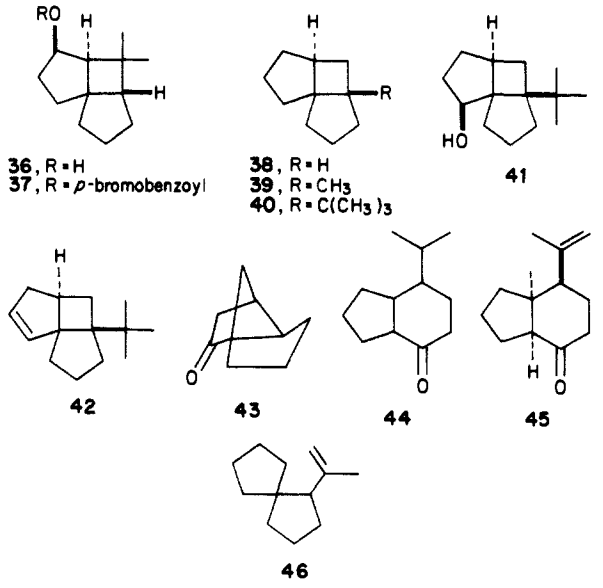
Table IV. Comparison of Selected Proton NMR Signals of Adducts **13a–16a**

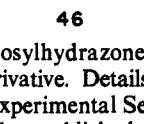


dienone	chemical shift, ppm multiplicity coupling constants			
	H_a	H_b	H_c	H_d
13a	2.36 dddd J = 2.2, 2.4, 7.2, 17.8 Hz	2.79 ddd J = 9.8, 12.3, 17.8 Hz	2.23 ddd J = 0.75, 4.2, 10.5 Hz	2.54 dd J = 6.6, 14.3 Hz
14a	2.36 dddd J = 2.0, 2.0, 9.7, 18.7 Hz	2.69 ddd J = 9.8, 11.9, 18.7 Hz	2.22 ddd J = 1.8, 4.4, 10.8 Hz	$H_d = CH_3$
15a	2.68–2.38 irresolvable 3 H, m	2.68–2.38 irresolvable 3 H, m	2.20 ddd J = 0.5, 5.0, 10.3 Hz	$H_d = C(CH_3)_3$
16a	2.39 dddd J = 1.7, 5.0, 10.3, 19.0 Hz	2.54 ddd J = 9.5, 9.5, 19.0 Hz	2.01 br s	2.11 d J = 8.7 Hz

comes from two X-ray structure determinations, a variety of chemical transformations, and three instances of identical products arising from two different substrates.

X-ray studies established the structures of **16a** and **19b**. Ketone **16a** was reduced stereospecifically to **36** by lithium triethylborohydride at −78 °C, and the alcohol was converted to the *p*-bromobenzoate **37**, which provided crystals suitable for X-ray





analysis. For **19b** the tosylhydrazone (**19bT**) proved to be a satisfactory crystalline derivative. Details of these crystallographic studies are given in the Experimental Section and supplementary material. With **16a** firmly established, proton nuclear magnetic resonance (NMR) comparisons at 300 MHz strongly supported the assignments for the related ketones **13a** and **14a**. NMR comparisons were also useful within the isomeric series of **17a** and its derivatives **18a**, **20a**, and **22a**, all of which gave similar spectra. These spectra are gathered in Tables IV and V, where the noted similarities are apparent; it is also clear that the spectra of the two *tert*-butyl-substituted ketones **15a** and **19a** provided little useful information. In addition, the close relation between crossed product **21b** and its methyl homologues **22b** and **24b** was evident from their NMR spectra (see Experimental Section). The two series of ketones in Tables IV and V were then correlated through conversion of ketones in each series to the corresponding hydrocarbons, tricyclo[5.3.0.0^{1,5}]decane[27] (**38**) and its alkylated derivatives **39** and **40**. Wolff–Kishner reduction[28] of **13a** and **21a** yielded **38**, and similar treatment of **14a** and **22a** gave **39**. Ketone **15a** was likewise reduced to **40**, but in **19a** the nearby *tert*-butyl group rendered the carbonyl inert to Wolff–Kishner conditions. Instead, **19a** was reduced with lithium aluminum hydride to **41**, which was dehydrated in hot hexamethylphosphoramide[29] to furnish **42**. Hydrogenation of this olefin then completed the second route to **40**. The three identities, **17a** ≡ **21a**, **18a** ≡ **24a**, and **20a** ≡ **23a**, are good evidence for these three structures, since in each case the alternative crossed cycloaddition products from these pairs of substrates would not be identical, and it is not obvious what unforeseen rearrangement would lead to a pair of identical products in any of the three cases.

Confirmation of the structure of **21b** came through independent synthesis. Ring expansion of **43**[1] with diazomethane in methanol containing lithium chloride furnished an authentic sample of **21b**.[30] The structure and stereochemistry of **23b** rest on reduction of the side-chain double bond and correlation of the resulting isopropyl ketone with synthetic material. This work, which is described elsewhere,[31] led eventually to assignments for all four 7-isopropyl-4-hydrindanones (**44**) and estimates of the free energy difference for each of the two pairs of diastereomers subject to equilibration. The assignment for **25b**, the methyl homologue of **23b**, follows from analogy, comparison of spectra of the two hydrindanones, and the observation that **25b** is very readily epimerized to its more stable isomer **45**. This epimerization is expected, since it permits the axial isopropenyl group of **25b** to adopt an equatorial conformation. A similar situation was encountered with **23b**.[31] Spiro ketone **16b** was isolated as a ~1:1 mixture of diastereomers; in keeping with expectation, Wolff–Kishner reduction of this mixture yielded a single hydrocarbon, **46**.

(27) We refer to the straight and crossed tricyclic photoproducts in Tables I–III as derivatives of tricyclo[5.3.0.0^{1,5}]decane (**38**) and tricyclo[4.3.1.0^{2,6}]-decane, respectively. The current Chemical Abstracts names for the two parent hydrocarbons are octahydro-1*H*-cyclobuta[1,2:1,4]dicyclopentene (**38**) and hexahydro-3a,7-methano-3a*H*-indene.

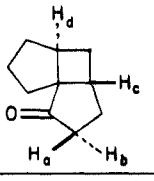
(28) Murray, R. K., Jr.; Babiak, K. A. *J. Org. Chem.* **1973**, *38*, 2556.

(29) Monson, R. S. *Tetrahedron Lett.* **1971**, 567. Monson, R. S.; Priest, D. N. *J. Org. Chem.* **1971**, *36*, 3826.

(30) Similar ring expansion of bicyclo[2.1.1]hexan-2-one and its 1-methyl derivative has been carried out: Gibson, T. *J. Org. Chem.* **1972**, *37*, 700.

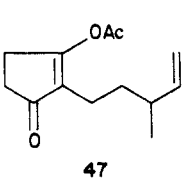
(31) Matlin, A. R.; Agosta, W. C., submitted for publication.

Table V. Comparison of Selected Proton NMR Signals of Adducts **18a–22a**

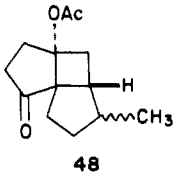


dienone	chemical shift, ppm multiplicity coupling constants			
	H_a	H_b	H_c	H_d
18a (24a)	2.39 ddd J = 4.0, 9.6, 18.6 Hz	2.60 ddd J = 9.6, 9.6, 18.8 Hz	2.36 m	$H_d = CH_3$
19a		2.64 m		$H_d = C(CH_3)_3$
20a (23a)	2.38 ddd J = 2.4, 10.2, 19.3 Hz	2.68 ddd J = 10.1, 11.2, 19.3 Hz	$H_c = CH_3$	2.22 d J = 8.75 Hz
21a (17a)	2.37 ddd J = 3.0, 9.1 17.8 Hz	2.81 ddd J = 9.4, 11.3, 17.8 Hz	2.43 dd J = 8.3, 13.5 Hz	2.60 dd J = 7.6, 14.0 Hz
22a	2.31 ddd J = 5.3, 9.6, 17.7 Hz	2.72 ddd J = 9.1, 9.3, 17.7 Hz	2.09 dd J = 8.9, 12.4 Hz	2.58 ddd J = 1.9, 6.6, 15.1 Hz

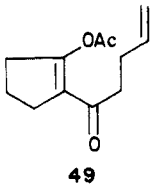
Finally, with the exception of the minor products **19c**, **23c**, and **25c**, all these compounds are [2 + 2] photocycloaddition or disproportionation products expected from biradicals **8** and **9**. The structures are also compatible with the two directly relevant previous observations known to us. The structure of **17a** is in accord with the behavior reported for **47**, which on irradiation



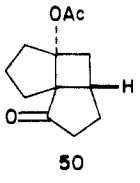
47



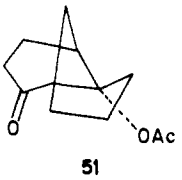
48



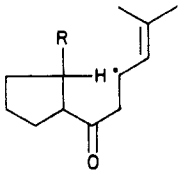
49



50



51



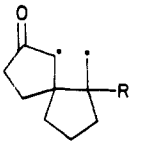
52

isomerizes to a diastereomeric mixture of straight closure products **48**.[32] Similarly, the formation of **21a,b** has precedent in the analogous isomerization of **49** to **50** and **51**,[33,34] the structures of which were established by X-ray crystallography.[33] Spiro ketones **23c** and **25c** can be accounted for by competitive abstraction of allylic hydrogen by the β-carbon atom of the enone system to yield biradical **52** which then collapses. Such hydrogen abstraction products appear in series **12** only from dienones **23** and **25** presumably because interaction of the two double bonds is sterically retarded in these two cases by the terminal methyl substituents. Intramolecular abstraction reactions of this sort in acylcyclopentenes have numerous precedents.[21,35]

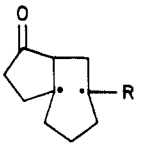
(32) Oppolzer, W.; Wylie, R. D. *Helv. Chim. Acta* **1980**, *63*, 1198.
(33) Begley, M. J.; Mellor, M.; Pattenden, G. *J. Chem. Soc., Chem. Commun.* **1979**, 235; *J. Chem. Soc., Perkin Trans. 1* **1983**, 1905.
(34) Seto, H.; Hirokawa, S.; Fujimoto, Y.; Tatsuno, T. *Chem. Lett.* **1983**, 989. More recently related studies have appeared: Seto, H.; Fujimoto, Y.; Yoshioka, H.; Tatsuno, T *Chem. Pharm. Bull.* **1984**, *32*, 3751.
(35) Smith, A. B., III; Foster, A. M.; Agosta, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 5100.

Discussion

Several features of the results in the tables are noteworthy, particularly in comparison with our earlier studies of hexadienes.[1,2] As before, in two of the series the regiochemistry of closure is sensitive to structure, while the third group follows the rule of five without fail. Earlier this third group was the 2-acylhexadienes (**2**). Now, however, it is the 1-acylheptadienes (**10**) (Table I) that are unique. The lack of regiochemical effect in the series **13–15**, as hydrogen is replaced by methyl and then *tert*-butyl, suggests that the initial cyclization here may not be 2,6 (see **9** and **53**) but rather 1,7 (see **54**). Closure of a seven-membered ring is, of

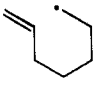


53

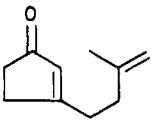


54

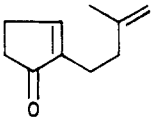
55



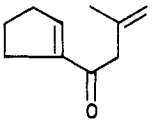
56



57



58



59

course, typically disfavored,[36] but in the absence of structural information about the intramolecular exciplex that precedes bond formation in these photochemical processes, it is not obvious that 1,7 cyclization must be avoided here. We return to this matter below.

Turning to Tables II and III, we note that both straight and crossed closure occur. From comparison of **17** with **18** and **21** with **22**, it is apparent that an alkyl group at C(6) plays a significant role in determining this regiochemistry. In the 2-acyl series (Table II) the effect is to increase crossed closure (**18** vs. **17**). Unlike hexadienes **1** and **3**, however, the effect does not increase with the size of the substituent (**19** vs. **18**). In Table III, C(6) substitution actually works in the opposite sense and *sup-*

(36) A theoretical treatment is available: DeTar, D. F.; Luthra, N. P. *J. Am. Chem. Soc.* **1980**, *102*, 4505.

presses crossed closure (**22** vs. **21**). These observations signal additional complexities in the heptadienes relative to hexadienes that remain to be elucidated, but a simple possible explanation is again that initial 1,7 bonding can be a significant process in these isomerization. Comparison of **21** with **24** and **23** with **25** confirms that substitution at C(1) has rather little regiochemical influence. Not surprisingly, geminal dimethyl groups at C(7) (**20**, **23**, **25**) seem to favor closure at C(6) from both C(1) and C(2). This may be simply a steric effect; the possibility remains open, however, that stabilization of a radical center at C(7) plays a role, since, as with the hexadienes, it is not yet clear whether formation of the first bond is reversible in these intramolecular cyclizations.[37] This present uncertainty should be kept in mind in assessing all these results.

In interpreting the photochemistry of hexadienes,[1] we found a useful model in the cyclization of 5-hexenyl (**55**) and in the regiochemical effects of alkyl substitution at C(5) and C(6) in this radical.[38] Unfortunately, much less information is available concerning 6-heptenyl (**56**), and the effect of alkyl substitution at C(6) or C(7) in this species is unknown. One pertinent comparison between **55** and **56** can be made, however. The relative rates of 1,5 and 1,6 closure in 5-hexenyl (**55**) are 50:1, but for 6-heptenyl (**56**) the ratio of 1,6 to 1,7 closure is only 10:1.[38] Since it is well established that appropriate structural features can induce regiospecific 1,6 closure in hexadienes,[1] this reduced rate ratio for **56** implies that structural features could favor 1,7 cyclization in heptadienes even more readily. This line of thought lends welcome support to the suggestions made above that initial 1,7 closure may occur in certain cases.

The quantum yields for **14** (0.60), **18** (0.29), and **22** (0.41) may be compared with the values previously determined for the corresponding hexadienes **57** (0.36), **58** (0.06), and **59** (0.59). It is noteworthy that in the heptadienes there is no unusually low quantum yield and that the series that fails to respond to change in substituents at the isolated double bond has the highest quantum yield in the heptadienes (**14**) but the lowest in the hexadienes (**58**).

In summary, these findings, together with previous work, permit several generalizations. Ketones **10** (1-acyl series) follow the rule of five and yield straight closure products regardless of substitution at C(6). The five-membered ring in the present examples had no effect. Ketones **11** (2-acyl series) respond to C(6) substitution with crossed closure, qualitatively similar to behavior previously observed in 1-acyl- and 3-ketohexadienes.[1,2] Ketones **12** (3-keto series) are also sensitive to C(6) substitution but respond in the fashion opposite to that of ketones **11**. The five-membered ring appears necessary for these substituent effects to operate in both **11** and **12**. Several anomalies in these reactions would be clarified if initial 1,7 bonding can occur. Initial bonding in the three other senses appears to occur; there is direct evidence from disproportionation products for instances of initial 2,6 (**16b**, **25a**) and 1,6 (**23b**, **25b**) bonding, and initial 2,7 bonding provides the simplest rationalization for crossed products **18b** and **19b**.

It is clear at this point that control of regiochemistry in cyclization of the heptadienes is more complex than in the hexadienes. An obvious next step is determination of whether cyclization is under kinetic or thermodynamic control and whether this control varies with structure. We are currently studying systems that should answer these questions both for hexadienes and for heptadienes.

Experimental Section

General Procedures. ^{1}H NMR spectra were recorded at 300 MHz in $CDCl_3$, and IR spectra were taken in CCl_4 except where noted. Analytical VPC was carried out on a Varian Aerograph 1400 employing a 5 ft × 0.125 in. 1.5% OV-101 on 100/120 Chrom G-HP and a Hewlett-Packard integrating recorder Model 3390A. Preparative GC was carried out on a Varian Aerograph 920 with one of the following columns: (A) 10% OV-101, (B) 10% Carbowax 20 M, and (C) 25% QF-1. Columns were packed in 0.25 in. × 5 ft aluminum tubing with 80/100 Chrom W-HP. Compounds were also purified by flash chromatography[13] (FC) on silica gel (230–400 mesh) using a mixture of hexanes and ether as indicated (hexanes:ether). All preparative irradiations were carried out with a Hanovia 450-W medium-pressure Hg lamp using either toroidal vessels or test tubes to contain solutions of the dienones. The substrates were dissolved in nitrogen-purged hexanes (1–2 mg/mL) and were irradiated through a uranium glass filter until conversion was complete. In many cases, the reaction of the final 5–10% of substrate required 1–2 days. The reactions were monitored by analytical VPC. After photolysis the solvent was removed by distillation, and the residue was taken up in ether and passed through a short column of Florisil to remove any polymeric material. Analytically pure samples were isolated by either VPC or FC. Unless otherwise indicated, products were obtained as colorless oils.

General Synthesis of Dienones 10. The Grignard of the appropriate alkenyl bromide (~30 mmol) was formed in ether (25 mL) and then cooled to 0 °C. Cyclopentenone (27 mmol) was dissolved in ether (20 mL) and added dropwise. The reaction mixture was allowed to warm to room temperature and was then stirred for 1.5 h. The reaction was quenched by pouring the mixture onto an ice/NH_4Cl mixture. The solution was extracted 3 times with ether, and the ether layer was washed with $NaHCO_3$ (aqueous) and brine. Drying over $MgSO_4$ and concentration gave an alcohol which was immediately carried on without purification or characterization. The alcohol was dissolved in ether (70 mL) and cooled to 0 °C. Chromium trioxide (3.5 g) was dissolved in 35 mL of 5% H_2SO_4 and then added dropwise to the ether solution with rapid stirring. After 1 h the reaction mixture was extracted 3 times with pentane, and the organic layer was washed with $NaHCO_3$ (aqueous) and brine. The pentane solution was dried over $MgSO_4$ and concentrated to a light-yellow oil. The desired dienone **10** was then purified by FC.

Synthesis of 13. Cyclopentenone (2.2 g, 27 mmol) was reacted with the Grignard derived from 5-bromo-1-pentene (4 g, 27 mmol) by following the general procedure. The crude alcohol was then oxidized to give after FC (1:1) 500 mg (12% overall) of **13**: ^{1}H NMR δ 5.96 (1 H, q, J = 1.4 Hz), 5.80 (1 H, ddt, J = 17.0, 10.3, 6.7 Hz), 5.06 (2 H, m), 2.58 (2 H, m), 2.42 (4 H, m), 2.12 (2 H, m), 1.70 (2 H, quintet, J = 7.5 Hz); IR 3095 (m), 2950 (s), 2870 (m), 1705 (s), 1620 (s), 1430 (m), 1180 (m), 910 (m) cm^{-1}; MS, m/z 150.1044 (M^+ calcd. for $C_{10}H_{14}O$, 150.1045).

Irradiation of 13. Dienone **13** (250 mg) was illuminated for 80 h to give 230 mg (92%) of **13a**. An analytical sample was isolated by GC (A, 130 °C, 10 min): ^{1}H NMR δ 2.79 (1 H, ddd, J = 9.8, 12.3, 17.8 Hz), 2.54 (1 H, dd, J = 6.6, 14.3 Hz), 2.36 (1 H, dddd, J = 2.2, 2.4, 7.2, 17.8 Hz), 2.23 (1 H, ddd, J = 0.75, 4.2, 10.5 Hz), 2.0–1.4 (10 H, m); IR 2975 (s), 2950 (s), 2870 (m), 1735 (s), 865 (m) cm^{-1}. Anal. ($C_{10}H_{14}O$) C, H.

Wolff–Kishner Reduction of 13a and 21a. Ketone **13a** (230 mg, 1.5 mmol), hydrazine (750 μL), KOH (1 g), and ethylene glycol (3 mL) were heated to 100 °C for 1 h and then at 195 °C for 4 h. The reaction mixture was then cooled to room temperature, diluted with H_2O, and extracted 3 times with pentane. The pentane extracts were washed with H_2O and brine and dried over $MgSO_4$. The solvent was removed by distillation to give 96 mg (47%) of **38**. An analytical sample was prepared by GC (A, 90 °C, 9 min): ^{1}H NMR δ 2.02 (2 H, q, J = 7.0 Hz), 1.8 (4 H, m), 1.60–1.31 (10 H, m); ^{13}C NMR (75 MHz) δ 56.17, 39.56, 36.47, 33.38, 29.07, 26.06; IR ($CDCl_3$) 2950 (s), 2880 (m), 2860 (m) cm^{-1}. Anal. ($C_{10}H_{16}$) C, H. Similar reduction of 190 mg of **21a** yielded 99 mg (52%) of **38**.

Synthesis of 14. Cyclopentenone (2.3 g, 28 mmol) was reacted with the Grignard derived from 5-bromo-2-methyl-1-pentene[8] (5 g, 30.6 mmol) by following the general procedure. The crude alchol was then oxidized as described above to give after FC (1:1) 430 mg (9.5% overall). An analytical sample was provided by GC (A, 160 °C, 8 min): ^{1}H NMR δ 5.97 (1 H, m), 4.76 (1 H, s), 4.70 (1 H, s), 2.6 (2 H, m), 2.43 (4 H, m), 2.08 (2 H, t, J = 7.3 Hz), 1.73 (3 H, s); IR 3100 (w), 2950 (s), 1710 (s), 1435 (m), 1175 (m), 985 (m) cm^{-1}. Anal. ($C_{11}H_{16}O$) C, H.

Irradiation of 14. Dienone **14** (210 mg) was irradiated for 67 h to give 195 mg (93%) of **14a**: ^{1}H NMR δ 2.69 (1 H, ddd, J = 9.8, 11.9, 18.7 Hz), 2.36 (1 H, dddd, J = 2.0, 2.0, 9.7, 18.7 Hz), 2.22 (1 H, ddd, J = 1.8, 4.4, 10.8 Hz), 2.07 (1 H, dd, J = 11.7, 11.7 Hz), 2.06 (1 H, ddd, J = 2.0, 9.7, 13.9 Hz), 1.9–1.6 (6 H, m), 1.5 (1 H, m), 1.36 (1 H, m), 1.15 (3 H, s); IR 2985 (s), 2890 (m), 2860 (m), 1735 (s), 860 (w) cm^{-1}. Anal. ($C_{11}H_{16}O$) C, H.

Synthesis of 15. Cyclopentenone (1.1 g, 13.5 mmol) was treated with the Grignard derived from **33** (3.5 g, 17.0 mmol). The crude alcohol was

(37) For bimolecular [2 + 2] photocycloaddition, reversion is a major source of inefficiency: Loutfy, R. O.; De Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559. Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123. In at least one case, however, the first step in intramolecular [2 + 2] cycloaddition of a 1-acyl-substituted heptadiene has proved to be irreversible.[7b]

(38) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Chem. Commun.* **1974**, 472. Beckwith, A. L. J. *Colloq. Int. C. N. R. S.* **1978**, *278*, 373; *Radicaux Libres Org., Colloq., 1977*. Related theoretical studies are available: Bischof, P. *Helv. Chim. Acta* **1980**, *63*, 1434.

rearranged and oxidized by following the general procedure to give after FC (2:1) 432 mg (16% overall) of **15**: ^{1}H NMR δ 5.91 (1 H, s), 4.84 (1 H, s), 4.63 (1 H, s), 2.53 (2 H, m), 2.35 (4 H, m), 2.02 (2 H, t, J = 7.8 Hz), 1.70 (2 H, quintet, J = 7.7 Hz), 0.99 (9 H, s); IR 2960 (s), 2860 (m), 1710 (s), 1180 (w), 890 (m), 860 (m) cm^{-1}; MS, m/z 206.1696 (M$^+$ calcd for $C_{14}H_{22}O$, 206.1671).

Irradiation of 15. Dienone **15** (50 mg) was dissolved in 75 mL of hexanes and irradiated for 62 h. The solution was then filtered through Celite and concentrated to give 46 mg (92%) of **15a**. An analytical sample was obtained by preparative GC (A, 140 °C, 14 min): ^{1}H NMR δ 2.68–2.37 (3 H, m), 2.20 (1 H, ddd, J = 0.5, 5.0, 10.3 Hz), 2.10 (1 H, ddd, J = 1.7, 5.2, 12.9), 1.98–1.84 (2 H, m), 1.82–1.56 (5 H, m), 1.46 (1 H, m), 0.92 (9 H, s); IR 2940 (s), 2855 (m), 1725 (s) cm^{-1}; MS, m/z 206.1659 (M$^+$, calcd for $C_{14}H_{22}O$, 206.1671).

Wolff–Kishner Reduction of 15a. Ketone **15a** (8.2 mg) was reduced as described above for **13a** to furnish **40**, purified by GC (C, 105 °C): IR 2960 (s), 1475 (m), 1385 (m), 1358 (m), 1210 (s), 658 (w) cm^{-1}; NMR δ 2.14 (1 H, ddd, J = 2.76, 6.78, 13.5 Hz), 2.07–1.89 (3 H, m), 1.80–1.37 (11 H, m), 0.89 (9 H, s); MS (CI), m/z 191.1775 [(M − H)$^+$, calcd for $C_{14}H_{23}$, 191.1800].

Synthesis of 16. Cyclopentenone (1.64 g, 20 mmol) was reacted with the Grignard derived from 6-bromo-2-methyl-2-hexene[39] (4 g, 22.6 mmol), and the resultant alcohol was oxidized by following the general procedure. Purification by FC (1:1) gave 760 mg (21%) of dienone **16**. An analytically pure sample was prepared by GC (A, 155 °C, 12 min): ^{1}H NMR (benzene-d_6) δ 5.82 (1 H, s) 5.05 (1 H, t, J = 6.7 Hz), 2.02 (2 H, m), 1.84 (6 H, m), 1.65 (3 H, s), 1.49 (3 H, s), 1.26 (2 H, quintet, J = 7.5 Hz); IR 2990 (m), 2950 (s), 2880 (m), 1710 (s), 1615 (s), 1430 (m), 1175 (m) cm^{-1}; MS, m/z 178.1398 (M$^+$, calcd for $C_{12}H_{18}O$, 178.1358).

Irradiation of 16. Dienone **16** (743 mg) was irradiated for 108 h to give 596 mg (90% yield at 89% conversion) of two photoproducts. Analytically pure samples were isolated by GC (B, 160 °C, 8 and 12 min). First eluted was **16a** (55%): ^{1}H NMR δ 2.54 (1 H, ddd, J = 9.5, 9.5, 19.0 Hz), 2.39 (1 H, dddd, J = 1.7, 5.0, 10.3, 19.0 Hz), 2.14 (1 H, m), 2.11 (1 H, d, J = 8.7 Hz), 2.01 (1 H, br s), 1.99 (1 H, m), 1.70–1.55 (5 H, m), 1.45 (1 H, m), 1.04 (3 H, s), 1.03 (3 H, s); IR ($CDCl_3$) 2950 (s), 2860 (m), 1715 (s) cm^{-1}. Anal. ($C_{12}H_{18}O$) C, H. The second component (45%) was isolated as a mixture (~1:1) of diastereomers **16b**: ^{1}H NMR δ 4.89 (1 H, s), 4.73 (1 H, s), 2.42 (1 H, J = 8.3 Hz), 2.25 (2 H, m), 2.2–1.55 (10 H, m), 1.76 and 1.71 (3 H, s); IR ($CDCl_3$) 2970 (s), 2875 (m), 1730 (s) cm^{-1}. Anal. ($C_{12}H_{18}O$) C, H.

Preparation of 37. Ketone **16a** (40 mg, 0.2 mmol) was dissolved in 1 mL of THF and cooled to −78 °C. Lithium triethylborohydride (1 M) (1 mL) was slowly added, and the mixture was stirred at −78 °C for 1 h. The solution was allowed to warm to room temperature, and then 3 N NaOH (5 mL) and 30% H_2O_2 (5 mL) were added. The reaction mixture was stirred vigorously for 20 min. Dilution with water and extraction with ether gave, after drying over $MgSO_4$ and concentration, 38 mg (95%) of the desired alcohol **36**: ^{1}H NMR (benzene-d_6) δ 4.02 (1 H, ddd, J = 7.4, 7.4, 11.2 Hz), 2.06 (1 H, dddd, J = 7.7, 12.1, 12.1, 12.1 Hz), 1.87 (1 H, m), 1.67 (5 H, m), 1.45 (4 H, m), 1.32 (3 H, s), 1.2 (1 H, m), 0.96 (3 H, s), 0.85 (1 H, s); IR 3630 (m), 3450 (br), 2940 (s), 2850 (m), 1090 (m) cm^{-1}. Alcohol **36** (10 mg, 0.06 mmol) was dissolved in 1 mL of pyridine along with *p*-bromobenzoyl chloride (39 mg, 0.18 mmol), and the solution was stirred overnight at room temperature. The reaction mixture was diluted with water and extracted 3 times with ether. The combined extracts were washed with 3 N HCl, $NaHCO_3$, and brine. The solution was dried over $MgSO_4$ and concentrated. The desired ester was purified by FC (10:1) and crystallized at low temperature from hexanes: mp 78–80 °C; ^{1}H NMR (60 MHz, CCl_4) δ 7.6 (4 H, dd, J = 9, 21 Hz), 5.13 (1 H, q, J = 8 Hz), 2.37–0.63 (12 H, m), 1.2 (3 H, s), 0.9 (3 H, s). This material was used for X-ray structural studies.

Wolff–Kishner Reduction of 16b. The ~1:1 mixture of **16b** (100 mg) was dissolved in degassed ethylene glycol along with KOH and anhydrous hydrazine. The mixture was heated to 100 °C for 1 h and then 180 °C for 3 h. The reaction mixture was cooled to room temperature, diluted with water, and extracted with pentane. The pentane extracts were washed with H_2O and brine. The solution was dried over $MgSO_4$, and the solvent was distilled off. The residue was purified by GC (A, 110 °C, 8 min) to give 60 mg (65%) of **46**: ^{1}H NMR δ 4.79 (1 H, m), 4.66 (1 H, m), 2.35 (1 H, t, J = 7.5 Hz), 1.9–1.2 (14 H, m), 1.73 (3 H, s); ^{13}C NMR (75 MHz) δ 147.6, 111.5, 54.8, 53.6, 39.8, 39.6, 33.6, 30.3, 24.4, 23.7, 22.9, 22.7; IR 3050 (w), 2950 (s), 2860 (m), 1630 (w), 1445 (w), 1365 (w), 885 (m) cm^{-1}. Anal. ($C_{12}H_{20}$) C, H.

General Procedure for the Synthesis of Dienones 11. NaH (1.1 equiv) was placed in a dry round-bottom flask and washed 3 times with pentane. After most of the pentane was removed, freshly distilled THF was added. α-(Phenylthio)cyclopentanone (1 equiv) dissolved in THF was slowly added to the NaH suspension.[17] After hydrogen evolution ceased, HMPA (5 equiv) was added. The appropriate alkenyl bromide (2–3 equiv) was dissolved in THF and added to the reaction mixture. The solution was stirred at room temperature for 3 h and then heated at 50 °C for 3 days. The reaction mixture was then cooled to room temperature and quenched with NH_4Cl. Water was added, and the mixture was extracted with ether. The organic phase was washed with water and brine and dried over $MgSO_4$, and the solvent was removed in vacuo. The crude **28** was purified by FC. $NaIO_4$ (2–4 equiv) was dissolved in a minimum amount of water and added to a solution of **28** in methanol.[18] The reaction mixture was stirred for 3 days at room temperature. The white solid precipitate was filtered, and the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and heated to 50 °C for 3 h, and then the solvent was removed. The oily residue was taken up in ether and washed with water and brine, dried over $MgSO_4$, and concentrated. The crude material was then subjected to FC and then preparative GC to give the desired dienones **11**.

Synthesis of 17. α-(Phenylthio)cyclopentanone (2 g, 10.4 mmol) was treated with NaH (12 mmol) and 5-bromo-1-pentene (2.47 g, 16.6 mmol) by following the general procedure to give after FC (6:1) 316 mg (11%) of **28**: ^{1}H NMR δ (60 MHz, CCl_4) 7.3 (5 H, s), 5.67 (1 H, m), 5.0 (1 H, m), 4.73 (1 H, m), 2.73–1.0 (12 H, m); IR 3075 (m), 2955 (s), 2860 (m), 1730 (s), 1640 (w), 1435 (m), 1155 (m), 910 (m), 860 (m) cm^{-1}. The α-(phenylthio) ketone (306 mg, 1.2 mmol) was treated with $NaIO_4$ (390 mg, 1.8 mmol) by following the general procedure to give after purification (FC, 4:1; GC, B, 150 °C, 12 min) 50 mg (20%) of the desired dienone **17**: ^{1}H NMR δ 7.32 (1 H, septet, J = 1.3 Hz), 5.82 (1 H, dd t, J = 17.0, 10.2, 6.7 Hz), 5.0 (2 H, m), 2.57 (2 H, m) 2.40 (2 H, m), 2.19 (2 H, m), 2.08 (2 H, m); IR 3070 (w), 2930 (s), 2860 (m), 1705 (s), 1635 (m), 1440 (m), 990 (m), 910 (s), 865 (m) cm^{-1}; MS, m/z 150.1045 (M$^+$, calcd for $C_{10}H_{14}O$, 150.1045).

Irradiation of 17. Dienone **17** (50 mg) was irradiated for 18 h to give 41 mg (82%) of the tricyclic ketone **17a**, which was identical with **21a** described below.

Synthesis of 18. α-(Phenylthio)cyclopentanone (1.7 g, 8.85 mmol) was reacted with 5-bromo-2-methyl-1-pentene (2.77 g, 17 mmol) by following the general procedure to give 1.4 g (58%) of **28** after FC (4:1): ^{1}H NMR (60 MHz, CCl_4) δ 7.3 (5 H, s), 4.62 (2 H, s), 2.77–1.07 (12 H, m), 1.67 (3 H, s); IR 3070 (m), 2960 (s), 2940 (s), 1730 (s), 1155 (m), 880 (s), 680 (m) cm^{-1}. The alkylated ketone (1.74 g, 6.4 mmol) was treated with $NaIO_4$ (5 g, 23 mmol) by following the general procedure to give after purification (FC, 4:1; GC, A, 130 °C, 10 min) 330 mg (28%) of dienone **18**: ^{1}H NMR δ 7.32 (1 H, m), 4.72 (1 H, s), 4.68 (1 H, s), 2.57 (2 H, m), 2.40 (2 H, m), 2.18 (2 H, t, J = 7.0 Hz), 2.04 (2 H, t, J = 7.6 Hz), 1.72 (3 H, s), 1.63 (2 H, m); IR 3060 (w), 2930 (s), 2850 (m), 1710 (s), 885 (m), 860 (m) cm^{-1}; MS, m/z 164.1202 (M$^+$, calcd for $C_{11}H_{16}O$, 164.1201).

Irradiation of 18. Dienone **18** (34 mg) was dissolved in 50 mL of dry benzene and illuminated for 6 days to give two products (21.4 mg, 63%). The products were isolated by GC (B, 140 °C). First eluted (8 min) was **18a** (75%): ^{1}H NMR δ 2.6 (1 H, ddd, J = 9.6, 9.6, 18.8 Hz), 2.39 (1 H, ddd, J = 4.0, 9.6, 18.6 Hz), 2.36 (1 H, m), 2.15 (2 H, m), 1.87 (5 H, m), 1.65 (1 H, d, J = 4.9 Hz), 1.61 (1 H, d, J = 5.0 Hz), 1.38 (1 H, m),1.05 (3 H, s); IR ($CDCl_3$) 2950 (s), 1710 (s) cm^{-1}; MS, m/z 164.1202 (M$^+$, calcd for $C_{11}H_{16}O$, 164.1201).

Second eluted (13 min) was **18b** (25%): ^{1}H NMR δ 2.54 (1 H, ddd, J = 2.5, 8.8, 18.9 Hz), 2.31 (1 H, dd, J = 10.0, 18.8 Hz), 2.2–1.9 (6 H, m), 1.8 (3 H, m), 1.75–1.55 (4 H, m), 1.0 (3 H, s); IR ($CDCl_3$) 2950 (s), 2920 (s), 2860 (m), 1720 (s) cm^{-1}; MS, m/z 164.1201 (M$^+$, calcd for $C_{11}H_{16}O$, 164.1201).

Synthesis of 19. To a solution of *t*-BuLi (49.4 mL of a 1.7 M solution in pentane, 84 mmol) in THF (250 mL), cooled to −78 °C under a N_2 atmosphere, was added bromo ketal **29** (8.20 g, 40 mmol).[19] The mixture was stirred for 4 h at this temperature; alkenyl bromide **33** (12.65 g, 61.7 mmol) and HMPA (50 mL) were added, and the reaction mixture was allowed to warm to 25 °C overnight. Standard workup yielded 15.7 g of crude alkylated ketal. This was taken up in MeOH (120 mL) and H_2O (10 mL) and treated with saturated oxalic acid solution (5 mL) at 4 °C overnight. Most of the MeOH was removed in vacuo, and H_2O was added before extraction with pentane. The combined extracts were washed with $NaHCO_3$ and brine and were dried. Distillation yielded 5.813 g (70%): bp 93–97 °C (0.5 mm); IR 3100 (w), 2970 (s), 2875 (m), 1707 (s), 1630 (m), 1356 (m), 992 (w), 887 (m) cm^{-1}; NMR δ 7.33 (m, 1 H), 4.87 (s, 1 H), 4.69 (d, J = 1.1 Hz, 1 H), 2.59–2.56 (m, 2 H), 2.42–2.39 (m, 2 H), 2.24–2.19 (m, 2 H), 2.09–2.03 (m, 2 H), 1.71–1.58 (m, 2 H), 1.05 (s, 9 H); MS, m/z 206.1647 (M$^+$, calcd for $C_{14}H_{22}O$, 206.1671).

Irradiation of 19. A solution of **19** (897 mg) in C_6H_6 (200 mL) was irradiated until GC analysis (column C, 170 °C) indicated no remaining starting material (1 week) and the formation of three products. The

benzene was removed by distillation, and the residue was bulb-to-bulb distilled to give 847 mg (94%) of a mixture of photoproducts. These were separated by preparative GC to give the following. **19a** (78%): IR 2960 (s), 2875 (m), 1720 (s), 1362 (w), 1150 (w) cm^{-1}; NMR (300 MHz) δ 2.69–2.59 (1 H, m), 2.38–2.15 (3 H, m), 2.03–1.73 (7 H, m), 1.54–1.40 (2 H, m), 0.88 (9 H, s); MS, m/z 206.1672 (M^+, calcd for $C_{14}H_{22}O$, 206.1671). **19b** (19%): IR 2960 (s), 2880 (m), 1728 (s), 1363 (m), 1188 (m), 908 (m) cm^{-1}; NMR (300 MHz) δ 2.46–2.32 (3 H, m), 2.22–1.54 (10 H, m), 0.90 (9 H, s); MS, m/z 206.1646 (M^+, calcd for $C_{14}H_{22}O$, 206.1671). **19c** (3%): IR 2940 (s), 2835 (m), 1720 (s), 1645 (m), 1360 (m), 900 (w) cm^{-1}; NMR (300 MHz) δ 6.67 (1 H, ddd, J = 3.17, 3.17, 6.22 Hz), 3.06–2.94 (m, 1 H), 2.56 (1 H, dddd, J = 2.98, 6.13, 9.12, 19.21 Hz), 2.36–2.06 (4 H, m), 1.92 (1 H, ddd, J = 3.96, 3.96, 14.36 Hz), 1.78–1.58 (3 H, m), 1.51–1.31 (2 H, m), 0.90 (9 H, s); MS (CI), m/z 207.1721 [$(M + H)^+$, calcd for $C_{14}H_{23}O$, 207.1749]. No structure was assigned to **19c**.

Reduction of 19a. A solution of the ketone (278 mg) in Et_2O (6 mL) was added to a suspension of $LiAlH_4$ (~200 mg) in Et_2O (15 mL) at −78 °C under a N_2 atmosphere. After completion of the addition, the reaction was allowed to warm to 25 °C and was worked up in the usual way to afford a quantitative yield of **41**. Further purification was accomplished by preparative GC (C, 165 °C): IR 3630 (m), 2960 (s), 1455 (w), 1380 (w), 1355 (m), 895 (w) cm^{-1}; NMR (300 MHz) δ 4.15 (1 H, dd, J = 6.7, 11.7 Hz), 2.47–2.33 (1 H, m), 2.17–2.05 (2 H, m), 1.91–1.71 (5 H, m), 1.62–1.35 (6 H, m), 1.01 (9 H, s); MS (CI), m/z 207.1757 [$(M - H)^+$, calcd for $C_{14}H_{23}O$, 207.1749].

Dehydration of 41. The alcohol (280 mg) was dehydrated in hot HMPA (5 mL) according to a published procedure.[29] GC analysis (C, 105 °C) of the residue remaining after removal of pentane indicated two peaks (~1:1), which were collected by preparative VPC. The first eluted component was identified as **42**: IR 3040 (w), 2955 (s), 2870 (m), 2840 (m), 1475 (m), 1385 (m), 1361 (m), 1213 (s) cm^{-1}; NMR (300 MHz) δ 5.70–5.63 (2 H, m), 2.72–2.63 (2 H, m), 2.16–2.04 (2 H, m), 1.90–1.33 (7 H, m), 0.85 (9 H, s); MS (CI), m/z 191.1779 [$(M + H)^+$, calcd for $C_{14}H_{23}$, 191.1800]. The NMR spectrum of the second component indicated the presence of two *tert*-butyl groups. This material was not investigated further.

Hydrogenation of 42. A solution of the olefin (15 μL) in MeOH (2 mL) was hydrogenated for 1.5 h at 1 atm by using 5% Pd/C (17 mg) as catalyst. The product was isolated by dilution with H_2O and extraction with pentane. This material was spectroscopically identical with **40** described above.

Synthesis of 20. α-(Phenylthio)cyclopentanone (1.3 g, 6.7 mmol) was treated with 6-bromo-2-methyl-2-hexene[39] (2.6 g, 14.6 mmol) by following the general procedure to give after FC (6:1) 1.14 g (60%) of **28**: ^1H NMR (60 MHz, CCl_4) δ 7.25 (5 H, s), 4.98 (1 H, m), 2.4–1.0 (12 H, m), 1.65 (3 H, s), 1.55 (3 H, s); IR 3055 (w), 2970 (s), 2855 (m), 1730 (s), 860 (m), 785 (m) cm^{-1}. The alkylated α-(phenylthio)cyclopentanone (425 mg, 1.5 mmol) was oxidized with $NaIO_4$ (642 mg, 3.0 mmol) and eliminated by following the general procedure to give after purification (FC, 4:1; GC, A, 140 °C, 13.5 min) 55 mg (21%) of **20**: ^1H NMR δ 7.3 (1 H, s), 5.11 (1 H, t, J = 7.1 Hz) 2.57 (2 H, m), 2.4 (2 H, m), 2.18 (2 H, m), 2.01 (2 H, q, J = 7.3 Hz), 1.69 (3 H, s), 1.60 (3 H, s), 1.52 (2 H, quintet, J = 7.7 Hz); IR ($CDCl_3$) 2950 (m), 2910 (s), 2835 (m), 1690 (s), 1625 (w), 1435 (m) cm^{-1}. Anal. ($C_{12}H_{18}O$) C, H.

Irradiation of 20. Dienone **20** (47.5 mg) was irradiated for 46 h to give 41.8 mg (88%) of ketone **20a**, the properties of which were the same as those given below for **23a**.

General Procedure for Synthesis of Dienones 12. The Grignard reagent was formed from the appropriate alkenyl bromide (25 mmol) in 25 mL of ether. The solution was then cooled to 0 °C, and aldehyde **30** or **31**[22] (21 mmol) in 25 mL of ether was added dropwise. The solution was stirred for an additional 0.5 h and then quenched by pouring it into an ice–H_2O mixture. The solution was neutralized with 5% HCl and washed successively with H_2O, $NaHCO_3$, and brine. Drying over $MgSO_4$ followed by solvent removal gave the requisite alcohols. These were not purified but were oxidized directly by using either pyridinium chlorochromate[20] or Swern oxidation.[23] Product ketones were purified by FC.

Synthesis of 21. 1-Cyclopentenecarboxaldehyde (**30**) (1.9 g, 21 mmol) was reacted with the Grignard derived from 4-bromo-1-butene (3.4 g, 25 mmol) by following the general procedure to give 3.08 g (95%) of the alcohol: NMR (60 MHz) δ 6.3–5.5 (4 H, m), 5.3–4.9 (4 H, m), 4.3 (1 H, t, J = 6.5 Hz), 2.6–1.5 (10 H, m); IR ($CDCl_3$) 3635 (m), 3455 (br), 3090 (w), 2940 (s), 2860 (s), 1635 (m) cm^{-1}. This alcohol (1 g, 6.6 mmol) was oxidized (PCC) to give after FC (4:1) 320 mg (32%) of dienone **21**: ^1H NMR δ 6.74 (1 H, s), 5.85 (1 H, m), 5.0 (2 H, m), 2.76 (2 H, t, J = 7.2 Hz), 2.55 (4 H, m), 2.38 (2 H, m), 1.92 (2 H, quintet, J = 7.6 Hz); ^{13}C NMR (75 MHz) δ 198.19, 145.61, 143.23, 137.51, 114.97, 38.10, 33.89, 30.62, 28.43, 22.75; IR ($CDCl_3$) 3090 (w), 2980 (s), 2850 (m), 1655 (s), 1610 (m) cm^{-1}; MS, m/z 150.1038 (M^+, calcd for $C_{10}H_{14}O$, 150.1045).

Irradiation of 21. Dienone **21** (120 mg) was irradiated for 9 h, giving 114 mg (95%) of a mixture of two photoproducts. The products were isolated by preparative GC (B, 130 °C). First eluted (11 min) was **21a** (60%): ^1H NMR δ 2.81 (1 H, ddd, J = 9.4, 11.3, 17.8 Hz), 2.60 (1 H, dd, J = 7.6, 14.0 Hz), 2.43 (1 H, dd, J = 8.3, 13.5 Hz), 2.37 (1 H, ddd, J = 3.0, 9.1, 17.8 Hz), 1.9–1.75 (6 H, m), 1.7–1.45 (4 H, m); ^{13}C NMR 221.57 (s), 59.16 (s), 42.36 (d), 37.64 (t), 36.57 (d), 32.97 (t), 31.14 (t), 29.79 (t), 27.44 (t), 26.62 (t); IR ($CDCl_3$) 2970 (s), 2880 (m), 1715 (s) cm^{-1}; MS, m/z 150.1037 (M^+, calcd for $C_{10}H_{14}O$, 150.1045). Second eluted (17 min) was **21b** (40%): ^1H NMR δ 2.64 (1 H, dddd, J = 6.0, 10.3, 18.7, 0.5 Hz), 2.51 (1 H, ddd, J = 3.7, 9.41, 18.8 Hz), 2.41 (1 H, m), 2.29 (1 H, m), 2.2–1.88 (7 H, m), 1.75 (2 H, q, J = 5.6 Hz), 1.44 (1 H, m); ^{13}C NMR (75 MHz) 213.5 (s), 64.96 (s), 50.0 (d), 33.68 (d), 33.04 (t), 31.73 (t), 29.41 (t), 28.19 (t), 27.69 (t), 27.17 (t); IR ($CDCl_3$) 2955 (s), 2880 (m), 1695 (s) cm^{-1}; MS, m/z 150.1046 (M^+, calcd for $C_{10}H_{14}O$, 150.1045).

Independent Synthesis of 21b. Ketone **39**[1] (70 mg, 0.5 mmol) was dissolved in 50 mL of methanol containing LiCl (2 g). Diazomethane (~2.5 mmol) in ether was added, and the reaction was left standing overnight. The solution was acidified with 3% HCl and taken up in ether. The ethereal solution was washed with H_2O, $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and the solvent removed. Analysis by GC showed that two products were formed in very low yield. The entire sequence was repeated 5 times, and the major product was isolated by GC. This material proved to be identical by ^1H NMR and IR spectroscopies by GC retention time with **21b**.

Synthesis of 22. The Grignard derived from 4-bromo-2-methyl-1-butene (1.8 g, 12 mmol) was reacted with 1-cyclopentenecarboxaldehyde (**30**) (1 g, 10.4 mmol) by following the general procedure to give 1.6 g (94%) of the alcohol: ^1H NMR δ 5.58 (1 H, s), 4.69 (2 H, s), 4.23 (1 H, t, J = 6.4 Hz), 2.3 (4 H, m), 2.1–1.5 (6 H, m), 1.73 (3 H, s); IR 3650 (w), 3420 (br), 3090 (w), 2960 (s), 2860 (s), 1680 (m), 1640 (m), 1440 (m), 1365 (m), 875 (s) cm^{-1}. This alcohol (800 mg, 4.8 mmol) was oxidized with PCC. Purification by FC (4:1) gave 200 mg (25%) of the desired dienone **22**: ^1H NMR δ 6.75 (1 H, s), 4.73 (1 H, s), 4.68 (1 H, s), 2.80, (2 H, t, J = 7.7 Hz), 2.56 (4 H, t, J = 7.8 Hz), 2.32 (2 H, t, J = 7.8 Hz), 1.9 (2 H, quintet, J = 7.6 Hz), 1.75 (3 H, s); IR 3100 (w), 2975 (s), 2860 (m), 1670 (s), 1615 (m), 1440 (m), 1370 (m), 889 (m) cm^{-1}. Anal. ($C_{11}H_{16}O$) C, H.

Irradiation of 22. Ketone **22** (184 mg) was illuminated for 16 h to give 84% of **22a** and 9% of **22b**. **22a**: ^1H NMR δ 2.72 (1 H, ddd, J = 9.3, 9.1, 17.7 Hz), 2.58 (1 H, ddd, J = 1.9, 6.6, 15.1 Hz), 2.31 (1 H, ddd, J = 5.3, 9.6, 17.7 Hz), 2.09 (1 H, dd, J = 8.9, 12.4 Hz), 2.05–1.7 (5 H, m), 1.55 (4 H, m), 1.03 (3 H, s); ^{13}C NMR (75 MHz) δ 220.98, 62.25, 41.18, 39.66, 37.74, 37.57, 36.13, 32.22, 27.04, 26.54, 22.75; IR ($CDCl_3$) 2960 (s), 2875 (m), 1715 (s) cm^{-1}. Anal. ($C_{11}H_{16}O$) C, H. **22b**: IR 2960 (s), 2865 (m), 1710 (s), 1450 (w), 1370 (w), 1208 (w), 1065 (w), 1005 (w), 900 (w) cm^{-1}; NMR (300 MHz) δ 2.61 (ddd, J = 6.0, 9.8, 18.5 Hz, 1 H), 2.55 (m, 1 H), 2.50 (ddd, J = 3.9, 9.3, 18.9 Hz, 1 H), 2.14–1.75 (m, 9 H), 1.38 (m, 1 H), 1.06 (s, 3 H); MS, m/z 164.1137 (M^+, calcd for $C_{11}H_{16}O$, 164.1201).

Wolff–Kishner Reduction of 22a and 14a. Ketone **22a** (207 mg, 1.3 mmol), anhydrous hydrazine (~750 mL), KOH (1 g), and ethylene glycol (3 mL) were heated together for 1 h at 100 °C and then for 3.5 h at 175 °C. The mixture was cooled to room temperature, diluted with water, and extracted 3 times with pentane. The combined pentane extracts were washed with NH_4Cl, $NaHCO_3$, and brine solutions. Drying over $MgSO_4$ and removal of the solvent by distillation gave 75 mg (40%) of the hydrocarbon **39**. An analytical sample was obtained by preparative GC (A, 110 °C, 10 min): ^1H NMR δ 2.13 (1 H, dd, J = 6.6, 15.7 Hz), 1.9–1.7 (5 H, m), 1.7–1.5 (4 H, m), 1.44 (2 H, m), 1.35–1.15 (3 H, m), 0.97 (3 H, s); IR 2955 (s), 2930 (s), 2860 (s), 2845 (s), 1460 (m), 1440 (m), 1370 (w) cm^{-1}. Anal. ($C_{11}H_{18}$) C, H. Similar reduction of **14a** also yielded **38b**.

Synthesis of 23. The Grignard derived from 5-bromo-2-methyl-2-pentene (1.9 g, 12 mmol) was reacted with 1-cyclopentenecarboxaldehyde (**30**) (1 g, 10.4 mmol) by following the general procedure to give 1.8 g (96%) of the alcohol: ^1H NMR (60 MHz, CCl_4) δ 5.53 (1 H, s), 5.1 (1 H, t, J = 8 Hz), 4.13 (1 H, t, J = 6 Hz), 2.6–1.2 (10 H, m), 1.70 (3 H, s), 1.6 (3 H, s); IR 3640 (m) 3400 (br), 2940 (s), 2855 (s), 1440 (m), 1375 (m) cm^{-1}. This alcohol (1 g, 5.6 mmol) was oxidized (PCC) to give after FC (6:1) 750 mg (41%) of dienone **23**: ^1H NMR δ 6.72 (1 H, s), 5.11 (1 H, m), 2.67 (2 H, t, J = 7.5 Hz), 2.55 (4 H, m), 2.30 (2 H, m), 1.92 (2 H, quintet, J = 7.6 Hz), 1.68 (3 H, s), 1.62 (3 H, s); IR 2960 (s), 2840 (s), 1665 (s), 1240 (m), 860 (s) cm^{-1}; MS, m/z 178.1349 (M^+, calcd for $C_{12}H_{18}O$, 178.1358).

(39) Le Bel, N. A.; Banucci, E. G. *J. Org. Chem.* **1971**, *36*, 2440.

Irradiation of 23. Dienone **23** (800 mg) was irradiated for 8 h, producing three products (712 mg, 89%). Two of the products were isolated by preparative GC (B, 160 °C). First eluted (12 min) was **23c** (6%): ^{1}H NMR δ 5.14 (1 H, m), 3.20 (1 H, dd, J = 9.1, 17.1 Hz), 3.05 (1 H, ddd, J = 6.7, 9.2, 9.2 Hz), 2.71 (1 H, dd, J = 6.65, 17.06 Hz), 1.76 (3 H, d, J = 1.0 Hz), 1.66 (3 H, d, J = 1.1 Hz), 1.8–1.5 (8 H, m); IR 2980 (s), 1780 (s), 1230 (s), 860 (s) cm^{-1}; MS, m/z 178.1339 (M$^+$, calcd for $C_{12}H_{18}O$, 178.1358). Second eluted (15.5 min) was **23a** (37%): ^{1}H NMR 2.68 (1 H, ddd, J = 10.1, 11.2, 19.3 Hz), 2.38 (1 H, ddd, J = 2.4, 10.2, 19.3 Hz), 2.22 (1 H, d, J = 8.6 Hz), 2.12 (1 H, d, J = 8.75 Hz), 2.05–1.45 (8 H, m); ^{13}C NMR (75 MHz) δ 224.43, 55.80, 54.51, 48.07, 39.07, 33.83, 32.24, 28.65, 27.86, 26.10, 24.51, 20.48; IR ($CDCl_3$) 2970 (s), 2880 (m), 1712 (s) cm^{-1}. Anal. ($C_{12}H_{18}O$) C, H. The third product **23b** (57%) was isolated by FC (6:1): ^{1}H NMR δ 5.00 (1 H, t, J = 1.4 Hz), 4.94 (1 H, s), 2.67 (2 H, m), 2.52 (1 H, ddd, J = 6.3, 11.5, 15.5 Hz), 2.33 (1 H, ddd, J = 5.5, 4.5, 15.4 Hz), 2.18 (1 H, m), 2.1–1.4 (8 H, m), 1.86 (3 H, s); IR 3090 (w), 2960 (s), 2870 (m), 1715 (s), 910 (m), 880 (7); MS, m/z 178.1361 (M$^+$, calcd for $C_{12}H_{18}O$, 178.1358).

Synthesis of 24. 2-Methylcyclopent-1-enecarboxaldehyde (**31**) (1 g, 9 mmol) was treated with the Grignard reagent derived from 4-bromo-1-butene (1.5 g, 11 mmol) and then oxidized (Swern). The crude material was purified by FC (6:1) to give 530 mg (35% overall) of **24**: ^{1}H NMR δ 5.87 (1 H, dd t, J = 6.5, 10.3, 17.1 Hz), 5.01 (2 H, m), 2.68 (2 H, m), 2.61 (2 H, t, J = 7.4 Hz), 2.49 (2 H, m), 2.38 (2 H, m), 2.09 (3 H, s), 1.84 (2 H, quintet, J = 7.6 Hz); IR 3070 (w), 2950 (s), 2845 (m), 1675 (s), 1615 (m), 915 (m), 860 (m) cm^{-1}; MS, m/z 164.1205 (M$^+$, calcd for $C_{11}H_{16}O$, 164.1201).

Irradiation of 24. Dienone **24** (89 mg) was irradiated for 35 h to give two products (63 mg, 71%). The products were isolated by preparative GC (B, 140 °C). First eluted (9 min) was **24a** (65%), which is identical with **18a** described above. Second eluted (17 min) was **24b** (35%): ^{1}H NMR δ 2.58 (1 H, dddd, J = 0.6, 6.7, 11.3, 18.4 Hz), 2.45 (1 H, m), 2.38–1.85 (m, 8 H), 1.71 (1 H, d, J = 10.5 Hz), 1.51–1.41 (1 H, m), 0.82 (3 H, s); ^{13}C NMR δ 213.54, 67.60, 52.48, 36.73, 37.18, 33.11, 30.39, 26.86, 25.63, 23.63, 19.50; IR ($CDCl_3$) 3050 (m), 2950 s), 2860 (m), 1690 (s) cm^{-1}; MS, m/z 164.1226 (M$^+$, calcd for $C_{11}H_{16}O$, 164.1201).

Synthesis of 25. 2-Methylcyclopent-1-enecarboxaldehyde (**31**) (1.0 g, 9.0 mmol) was treated with the Grignard derived from 5-bromo-2-methyl-2-pentene (1.6 g, 9.8 mmol), and the resulting alcohol was directly oxidized (Swern). The crude product was purified by FC (10:1) to give 340 mg (20% overall) of the desired dienone **25**: ^{1}H NMR δ 5.12 (1 H, t, J = 1.3, 7.1 Hz), 2.66 (2 H, m), 2.5 (4 H, m), 2.28 (2 H, q, J = 7.3 Hz), 2.09 (3 H, s), 1.83 (2 H, quintet, J = 7.6 Hz), 1.69 (3 H, s), 1.68 (3 H, s); IR 2955 (s), 2920 (s), 2850 (m), 1675 (s), 1620 (m), 1375 (m), 860 (m) cm^{-1}; MS, m/z 192.1500 (M$^+$, calcd for $C_{13}H_{20}O$, 192.1514).

Irradiation of 25. Dienone **25** (175 mg) was dissolved in 200 mL of benzene and irradiated for 30 h to give 120 mg (69%) of a mixture of three photoproducts. The products were isolated by FC (20:1). First eluted was **25c** (26%) as a mixture of diastereomers from which one isomer could be separated: ^{1}H NMR δ 5.13 (1 H, d t, J = 1.3, 9.1 Hz), 3.08 (2 H, m), 2.61 (1 H, m), 2.08–1.5 (7 H, m), 1.76 (3 H, d, J = 1.0 Hz), 1.67 (3 H, d, J = 1.2 Hz), 1.06 (3 H, d, J = 6.9 Hz); IR ($CDCl_3$) 2960 (s), 2930 (m), 2865 (m), 1765 (s) cm^{-1}; MS, m/z 192.1514 (M$^+$, calcd for $C_{13}H_{20}O$, 192.1514). Second eluted was **25a** (12%) as a mixture of diastereomers from which one isomer could be separated: ^{1}H NMR δ 5.02 (1 H, s), 4.89 (1 H, s), 2.65 (1 H, dd, J = 7.1, 11.5 Hz), 2.2–1.4 (11 H, m), 1.86 (3 H, s), 0.89 (3 H, d, J = 7.0 Hz); IR 2955 (s), 1730 (m), 1245 (s), 860 (s) cm^{-1}; MS, m/z 192.1512 (M$^+$, calcd for $C_{13}H_{20}O$, 192.1514). Third eluted was **25b** (62%): ^{1}H NMR δ 4.98 (1 H, t, J = 1.2 Hz), 4.94 (1 H, s), 2.82 (1 H, m), 2.49 (1 H, ddd, J = 7.8, 6.3, 16.4 Hz), 2.34 (2 H, J = 5.1 Hz), 2.3–2.06 (2 H, m), 1.86 (3 H, s), 1.63 (5 H, m), 1.43 (1 H, m), 0.84 (3 H, s); IR 3070 (w), 2955 (s), 2875 (m), 1715 (s), 1245 (m), 890 (m), 860 (s) cm^{-1}; MS, m/z 192.1518 (M$^+$, calcd for $C_{13}H_{20}O$, 192.1514). Attempts to purify **25b** by preparative GC (B, 150 °C, 24 min) led to epimerization, giving the cis-fused hydrindanone **41**: ^{1}H NMR δ 4.56 (1 H, t, J = 1.6 Hz), 4.77 (1 H, d, J = 1.8 Hz), 2.76 (1 H, dd, J = 3.8, 12.5 Hz), 2.52–2.22 (5 H, m), 2.25–1.78 (3 H, m), 1.72 (3 H, q, J = 0.7 Hz), 1.66 (2 H, m), 1.5 (1 H, m), 1.07 (3 H, s); IR ($CDCl_3$) 3075 (w), 2965 (s), 2945 (s), 2880 (m), 1700 (s), 1635 (w), 1435 (m), 1370 (m), 1115 (w) cm^{-1}; MS, m/z 192.1528 (M$^+$, calcd for $C_{13}H_{20}O$, 192.1514).

Synthesis of Alcohol 34. According to the procedure of Schlosser,[25] 2-*tert*-butylpropylene (6.5 g, 66 mmol), potassium *tert*-butoxide (7.4 g, 66 mmol), and 10 mL of hexanes were placed in a flask, and butyllithium (2.5 M, 26.4 mL, 66 mmol) was slowly added to the well-stirred mixture. The exothermic reaction was accompanied by the appearance of a yellow color. The solution was stirred for 48 h at room temperature. The reaction mixture was cooled to 0 °C, and ethylene oxide (4.0 mL, 80 mmol) dissolved in 40 mL of THF was slowly added. After all the ethylene oxide was added the reaction mixture was stirred for an additional 2 h. The mixture was then poured into a well-stirred solution of NH_4Cl in ice water. The mixture was extracted twice with ether, washed with sodium bicarbonate and brine solution, and dried over $MgSO_4$ and the solvent removed in vacuo. Distillation (100–110 °C, 20 torr) gave 6.18 g (67%) of the desired alcohol **34**: ^{1}H NMR (60 MHz, CCl_4) δ 4.83 (1 H, s), 4.66 (1 H, d), 3.59 (2 H, t, J = 6 Hz), 2.23–1.23 (4 H, m), 1.12 (9 H, s); IR 3620 (w), 3400 (br), 2965 (s), 2865 (s), 780 (s) cm^{-1}. This was used directly in the following step.

Synthesis of Bromide 33. *p*-Toluenesulfonyl chloride (14.3 g, 75 mmol) was dissolved in 50 mL of pyridine and cooled to 0 °C. Alcohol **34** (9.7 g, 68 mmol) was dissolved in 25 mL of pyridine and added to the reaction mixture. The solution was stirred for 16 h at 4 °C. The reaction mixture was diluted with H_2O and taken up in ether. The solution was washed 3 times with 5% HCl, water, and brine solution. The ethereal solution was dried over $MgSO_4$ and the solvent removed in vacuo. The crude tosylate was used immediately in the next step without characterization. Lithium bromide (13 g, 150 mmol) was dissolved in 100 mL of dry acetone. The tosylate was dissolved in 50 mL of acetone and added to the reaction flask, and the mixture was heated at reflux for 3 h. The reaction mixture was cooled to room temperature, diluted with water, and then extracted 3 times with pentane. The pentane extracts were washed with brine and dried over $MgSO_4$, and the solvent was removed by distillation. Distillation of the residue at reduced pressure gave 9 g (65% overall) of the desired bromide **33** (85–89 °C, 19 torr): ^{1}H NMR (60 MHz, CCl_4) δ 4.88 (1 H, s), 4.63 (1 H, 3), 3.37 (2 H, t, J = 6.5 Hz), 2.15 (4 H, m), 1.08 (9 H, s); IR 3085 (w), 2965 (s), 2870 (m), 1630 (m), 800 (s), 755 (s) cm^{-1}. Anal. ($C_7H_{13}Br$) C, H.

Quantum Yields. These were carried out on benzene solutions of dienones **14**, **18**, and **22** by following the procedure previously reported.[1]

Crystal Data and Data Collection. $C_{19}H_{23}O_2Br$ (**37**), M_r = 363.30, triclinic $P\bar{1}$, $F(000)$ = 376, a = 7.741 (1) Å, b = 9.135 (1) Å, c = 12.879 (2) Å, α = 84.69 (1)°, β = 85.75 (1)°, γ = 71.36 (1)°, cell volume = 858.2 (2) Å^3, Z = 2, calculated density = 1.406 mg/mm^3, and crystal dimensions = 0.35 × 0.20 × 0.10 mm.

$C_{21}H_{30}N_2O_2S$ (**19bT**, the tosylhydrazone of **19b**), M_r = 374.54, triclinic $P\bar{1}$, $F(000)$ = 404, a = 7.513 (1) Å, b = 10.422 (2) Å, c = 14.846 (3) Å, α = 70.08 (1)°, β = 84.86 (2)°, γ = 73.73 (2)°, cell volume = 1049.2 (3) Å^3, Z = 2, calculated density = 1.185 mg/mm^3, and crystal dimensions = 0.30 × 0.10 × 0.08 mm.

Data for **37** and **19bT** were collected on a Nicolet R3m diffractometer at T = 295 K, λ = 0.710 69 Å (Mo Kα) (**37**), and λ = 1.541 78 Å (Cu Kα) (**19bT**). Lattice parameters were determined from 24 centered reflections with 20° ≤ 2θ ≤ 25° (**37**) and 30° ≤ 2θ ≤ 70° (**19bT**). The data collection ranges were $-8 \le h \le 3$, $-9 \le k \le 9$, and $-13 \le l \le 13$ (**37**) and $0 \le h \le 8$, $-10 \le k \le 10$, and $-16 \le l \le 16$ (**19bT**). sin (θ)/λ_{max} = 0.54 Å^{-1} (**37**) and 0.56 Å^{-1} (**19bT**). Three standards monitored every 60 reflections varied 1.6% (**37**) and 3.6% (**19bT**) over data collection. Data were collected in the $\theta/2\theta$ mode with a scan width at 2°; the scan rate was a function of the count rate (4°/min minimum, 30°/min maximum). For **37**, 3433 reflections were measured, 2239 unique (R_{int} = 0.008) and 1583 observed with $F_o > 3\sigma(F_o)$; for **19bT**, 3342 reflections were measured, 3085 unique (R_{int} = 0.023) and 2807 observed with $F_o > 3\sigma(F_o)$. An additional 80 reflections were rejected due to peak overlap from crystal defects (**19bT**). Lorentz and polarization corrections were applied, μ = 2.73 mm^{-1} (**37**) and μ = 1.45 mm^{-1} (**19bT**). An empirical absorption correction was made to **37**.

The structures were solved by direct methods. The least-squares refinement program used program SHELXTL.[40] The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(|F_o| + g(F_o)^2)$ is included to account for random instrumental error (g is estimated to be 0.0002). There were 241 parameters refined for **37** and 250 for **19bT**, including atomic coordinates and anisotropic temperature factors for all non-H atoms. Hydrogens were fixed at ideal positions except for the amine hydrogen in **19bT**. The hydrogen isotropic temperature factors were fixed at 1.1 times the equivalent isotropic temperature factor of the atom to which they are bonded in **37** and 1.2 times that in **19bT**. The final residuals for **37** were R = 0.057 and R_w = 0.040, with an error in an observation of unit weight of 1.39. The respective parameters for **19bT** are R = 0.089, R_w = 0.130, and S = 5.29. The final Fourier excursions were 0.50 and −0.38 e Å^{-3} (**37**) and 0.48 and −0.50 e Å^{-3} (**19bT**). The largest shifts to error parameter in the final cycle were 0.15 (**37**) and −0.28 (**19bT**). Atomic scattering factors are from the International Tables for Crystallography.[41] The final values for the atomic positional and thermal parameters are available as supplementary material. In Figures 1 and

(40) Sheldrick, G. M. SHELXTL 1980, minicomputer programs for structure determination, University of Göttingen, Federal Republic of Germany.

(41) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975, Vol. IV.

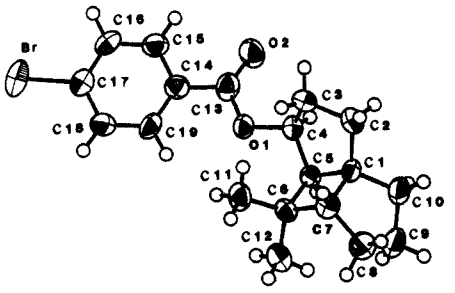


Figure 1. ORTEP drawing of 37 showing 50% probability ellipsoids.

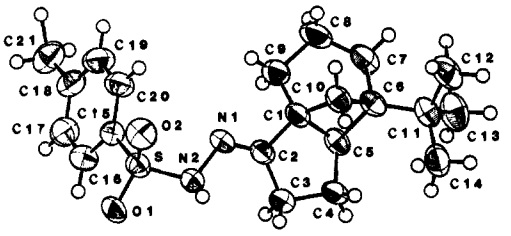


Figure 2. ORTEP drawing of **19bT** showing 50% probability ellipsoids.

2 are shown ORTEP drawings for **37** and **19bT**, respectively.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to Phyllis Wilson for technical assistance and to Francis Picart for 300-MHz NMR spectra. The 300-MHz spectrometer was purchased with assistance from the National Science Foundation and the Camille and Henry Dreyfus Foundation.

Registry No. 13, 22627-71-0; **13a**, 39865-63-9; **14**, 101761-44-8; **14a**, 101761-45-9; **15**, 101761-46-0; **15a**, 101761-47-1; **16**, 101761-48-2; **16a**, 101761-49-3; **16b** (isomer 1), 101761-50-6; **16b** (isomer 2), 101761-51-7; **17**, 99261-30-0; **17a**, 101761-52-8; **18**, 101761-53-9; **18a**, 101761-54-0; **18b**, 101761-55-1; **19**, 101761-56-2; **19a**, 101761-57-3; **19b**, 101761-58-4; **19bT**, 101761-61-9; **20**, 101761-59-5; **20a**, 101761-60-8; **21**, 43011-53-6; **21b**, 101761-62-0; **22**, 101761-63-1; **22a**, 101761-64-2; **22b**, 101761-65-3; **23**, 101761-66-4; **23b**, 101761-67-5; **23c**, 101761-68-6; **24**, 43011-51-4; **24b**, 101761-69-7; **25**, 101761-70-0; **25a**, 101761-71-1; **25b**, 101761-72-2; **25c**, 101761-73-3; **27**, 52190-40-6; **28** (R = 1-penten-5-yl), 101761-74-4; **28** (R = 2-methyl-1-penten-5-yl), 101761-75-5; **28** (R = 2-methyl-2-hexen-6-yl), 101761-76-6; **29**, 68241-78-1; **30**, 6140-65-4; **31**, 81328-61-2; **33**, 101761-77-7; **34**, 101761-78-8; **34** tosylate, 101761-61-9; **35**, 594-56-9; **36**, 101761-81-3; **37**, 101761-80-2; **38**, 101761-79-9; **39**, 101761-83-5; **40**, 101761-84-6; **41**, 101761-82-4; **42**, 101761-85-7; **45**, 101761-86-8; **46**, 101761-87-9; cyclopentenone, 930-30-3; 5-bromo-1-pentene, 1119-51-3; 5-bromo-2-methyl-1-pentene, 41182-50-7; 6-bromo-2-methyl-2-hexene, 30316-02-0; *p*-bromobenzoyl chloride, 586-75-4; 6,7-dihydro-6-(5,5-dimethyl-4-methylenehexyl)-1,4-dioxaspiro[4.4]nonane, 101761-88-0; 4-bromo-1-butene, 5162-44-7; 2-(3-buten-1-yl)cyclopent-1-enemethanol, 101761-89-1; 4-bromo-2-methyl-1-butene, 20038-12-4; 2-(3-methyl-3-buten-1-yl)cyclopent-1-enemethanol, 101761-90-4; 5-bromo-2-methyl-2-pentene, 2270-59-9; 2-(4-methyl-3-penten-1-yl)cyclopent-1-enemethanol, 101761-91-5; ethylene oxide, 75-21-8.

Supplementary Material Available: Tables of atomic coordinates, bond angles, thermal parameters, and observed and calculated structure factors for **37** and **19bT** (35 pages). Ordering information is given on any current masthead page.

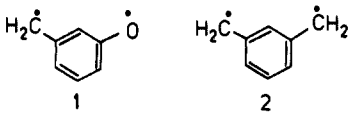
Stereochemistry of Additions of *m*-Quinomethane to Olefins and Acyclic Dienes

Thomas A. Inglin and Jerome A. Berson*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. *Received November 18, 1985*

Abstract: The *m*-quinomethane biradical has a triplet ground state, as judged by the temperature dependence of the intensity of its EPR signal. When generated by pyrolysis or photolysis of 6-methylenebicyclo[3.1.0]hex-3-en-2-one, it adds to olefinic trapping agents to give phenolic indans. Retention of configuration dominates by a factor of 13–17 with *cis*-1,2-dimethoxyethene and by a factor of >100 with *trans*-1,2-dimethoxyethene. With the 2,4-hexadienes, which undergo addition to give phenolic 1-propenylindans, retention again is the favored pathway, but the preference is lower (up to 6-fold). The propenyl stereochemistry in the product is completely retained. A comparison with known results of cycloadditions of trimethylenemethane (singlet) biradical and of *m*-quinodimethane shows that *m*-quinomethane additions are intermediate between the other two in cis stereospecificity. A mechanistic rationale for this ordering is discussed.

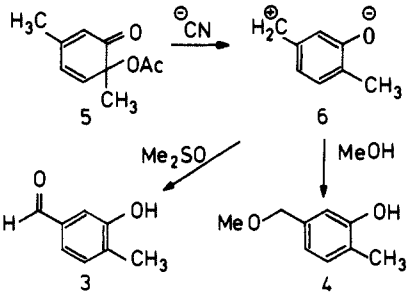
The moment is propitious for a comparison of the stereochemistry of the cycloadditions of the polar non-Kekulé molecule *m*-quinomethane **1**, MQM,[1,2] with that recently reported[3] for the



1 2

parent hydrocarbon *m*-quinodimethane **2**, MQDM. Understanding of the structure, spin state, and reaction mechanisms of non-Kekulé molecules could emerge from such studies, which form the subject matter of the present paper.

Scheme I



Substituted variants of **1** were invoked as reactive intermediates as long ago as 1964, when Leitich and Wessely[4] explained the

(1) Rule, M.; Matlin, A. R.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098.
(2) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787.
(3) (a) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 1867. (b) Goodman, J. L.; Berson, J. A. *Ibid.* **1985**, *107*, 5409. (c) Goodman, J. L.; Berson, J. A. *Ibid.* **1985**, *107*, 5424.

0002-7863/86/1508-3394$01.50/0