Photolysis of 21. Irradiation of **21** (180 mg) in benzene (65 mL) in the usual fashion was complete in 15 h. Preparative VPC (column J, 160 °C) afforded two products. **21a** (11%): IR 2970 (s), 2885 (s), 2860 (w), 1712 (s), 1375 (m), 1340 (m), 1310 (m), 1182 (m), 1152 (m), 1090 (m), 1048 (m) cm^{-1}; NMR^{44} (220 MHz) δ 2.25–1.46 (m, 12 H), 1.33 (s, 3 H), 0.88 (dd, H_A, J_{AB} = 7.0, $J_{AA'}$ = 8.2 Hz); mass spectrum, *m/z* 164.1192 (M^+, calcd for $C_{11}H_{16}O$, 164.1201). **21b** (76%): IR 2955 (s), 1707 (s), 1366 (w), 1312 (w), 1285 (w), 880 (w) cm^{-1}; NMR (220 MHz) δ 2.73 (dd, *J* = 6.1, 9.1 Hz, 1 H), 2.43 (dd, *J* = 9.2, 12.4 Hz, 1 H), 2.33 (dddd, *J* = 1.6, 3.6, 3.6, 15.2 Hz, 1 H), 2.15–1.62 (m, 9 H), 1.42–1.28 (m, 1 H); mass spectrum, *m/z* 164.1197 (M^+, calcd for $C_{11}H_{16}O$, 164.1201).

Pyrolysis of 21b. Pyrolysis of 50 mg in C_6H_6 (4 mL) in a sealed, evacuated tube at 175 °C for 3 h yielded (VPC analysis) only **21** and ~20% unreacted **21b**.

Quantum Yield Measurements. Solutions of the dienones were prepared in benzene–CH_3OH (95:5), and 3.0 mL of each solution was placed in a separate 13 × 100 mm Pyrex test tube fitted with a constricted neck. Each sample was degassed by purging with N_2 for 10 min before sealing. These samples were irradiated on a merry-go-round apparatus simultaneously with 0.1 M solutions (3.0 mL) of valerophenone in CH_3CH_2OH or C_6H_6 using the output of a 450-W Hanovia medium-pressure mercury lamp filtered through a 1-cm path of 0.002 M K_2CrO_4 in 1% aqueous K_2CO_3. Yields of the dienone products and acetophenone were determined by calibrated VPC on column K. Total conversion was kept below 10%.

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 Eric Orava for technical assistance, Bodil Braren and Francis Picart for 300-MHz spectra, and to S. T. Bella for microanalyses. The 300-MHz NMR spectrometer was purchased with assistance from the National Science Foundation and from the Camille and Henry Dreyfus Foundation.

Intramolecular Photochemical Reactions of 2-Acyl-1,5-hexadienes

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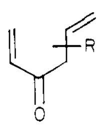
Received July 21, 1982

Abstract: Photolysis of the 2-acyl-1,5-hexadienes **6–11** (Table I) leads to regiospecific crossed cyclization, yielding derivatives of bicyclo[2.1.1]hexane. Unlike dienones of the related classes **1** and **2**, neither substitution at C(5) nor the presence of a ring influences the regiochemistry. Quantum yields for **9** and **10** also show an insensitivity to C(5) substitution and are six- to tenfold lower than for comparable dienones **1** and **2**. It is suggested that initial cyclization in these systems occurs from C(2) to C(6), rather than C(1) to C(5) as is preferred in **1** and **2**.

In the preceding paper[1] we reported on control of the regiochemistry of photochemical cyclization of 1,5-hexadien-3-ones (**1**) and 1-acyl-1,5-hexadienes (**2**) both through alkyl substitution at C(5) and also by incorporation of the conjugated double bond into a five- or six-membered ring. The "rule of five"[2] operates in the absence of these structural features, but with either of them present both modes of closure occur. The effects are roughly additive, and incorporation of both a C(5)-methyl group and a five-membered ring in either **1** or **2** leads to regiospecific 1,6 cyclization. Upon completing these studies with **1** and **2** we wished to extend our effort to a third type of hexadiene, 2-acyl-1,5-hexadienes (**3**), particularly because rather less was known about the photochemistry of these compounds. We were aware of only three relevant examples, **4**,[3] **5**,[4] and **6**,[5,6] all of which undergo only crossed closure from the triplet state. Of these, **4** and **5** appear to depart from the rules operating in ketones of types **1** and **2**, since **4** has a substituent at C(5) and **5** has its conjugated double bond in a cyclopentene ring. Unfortunately, however, these two compounds have features that render interpretation of this regiochemical behavior problematic. Diester **4** has two conjugated double bonds rather than one enone and one simple alkene, and the particular location of the cyclopentene ring in **5** may well introduce steric constraints absent in other substrates. We have now investigated several dienones of type **3** to test the operation of the substitution and ring effects discovered in **1** and **2**.[1] Our findings are reported below.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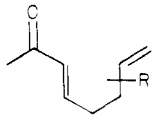

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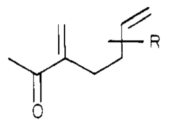

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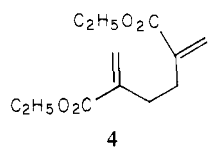

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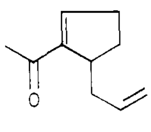

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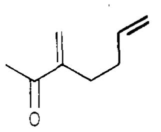

6

Results

We have prepared and photolyzed dienones **7–11** listed in Table I along with earlier results with **6**[5] for comparison. Unless otherwise noted below, conditions and methods used were those described in detail in the preceding paper.[1] Ketone **7** was reactive only at elevated temperature. Triplet sensitization for **6** and **7** is necessary to avoid singlet reactions,[6] and irradiation of sensitizer acetophenone and **7** at 80 °C leads to extensive hydrogen ab-

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[1] Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983** (preceding paper in this issue).

[2] Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932. Liu, R. S. H.; Hammond, G. S. *Ibid.* **1967**, *89*, 4936.

[3] Bloomfield, J. J.; Owsley, D. C. *Tetrahedron Lett.* **1973**, 1795. Reaction of **4** was triplet sensitized through irradiation in acetonitrile containing benzophenone.

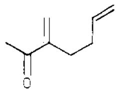
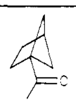
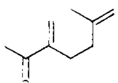
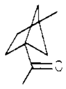
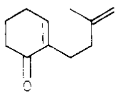
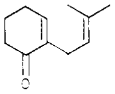
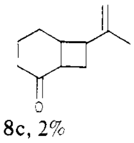
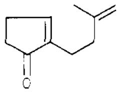
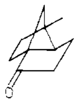
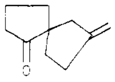
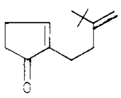
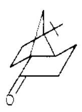
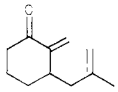
[4] Cormier, R. A.; Agosta, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 1867.

[5] Cormier, R. A.; Schreiber, W. L.; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 4873. Cormier, R. A.; Agosta, W. C. *Ibid.* **1974**, *96*, 618.

[6] Open-chain α-methylene ketones undergo intramolecular hydrogen abstraction from the singlet state, but their triplet [2 + 2] photocycloaddition reactions may be efficiently sensitized.[5]

0002-7863/83/1505-1299$01.50/0

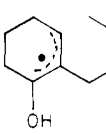
Table I. Products of Photolysis of 2-Acyl-1,5-hexadienes

dienone	quantum yield for major product	product, yield	
 6[a,b]		 6a, ~80%	
 7[b]		 7a, 12%[c]	
 8		 8a, 71%	 8b, 5%
		 8c, 2%	
 9	0.055	 9a, 50%	 9b, 6%
 10	0.075	 10a, 37%	
 11		 11a	

[a] From ref 5. [b] Triplet sensitized; see ref 6. [c] See text.

straction by acetophenone accounting for the low yield of **7a**. The results from **8–11** are for direct irradiation. Photolysis of **11** is quite slow, and thermal Cope rearrangement occurs particularly readily.[7] For these reasons this ketone was irradiated through Pyrex (λ >280 nm) at −20 °C in pentane solution, conditions under which the thermal rearrangement is effectively suppressed. Singlet reactivity is not a problem with **9** and **10**, but **8b,c** are believed to result from singlet γ-hydrogen abstraction to give **12**, followed by disproportionation or closure.[5] The reactions of **9** are efficiently sensitized by α-tetralone and quenched by 2,3-dimethyl-1,3-butadiene; the origin and significance of **9b** are discussed later. We have also determined representative quantum yields as before,[1] and these are included in Table I.

Preparative Experiments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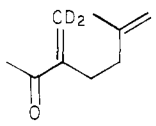
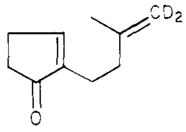
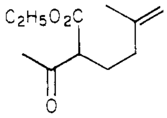

7D


9D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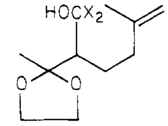
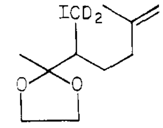
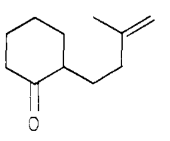

14, X = H
14D, X = D


15

Several methods were employed for synthesis of **7–11** and the two deuterated substrates **7D** and **9D**. The simple dienone **7** was prepared from alkylated acetoacetic ester **13**. This was ketalized and reduced with lithium aluminum hydride to yield **14**. Deketalization, tosylation, and exposure to hot pyridine then gave **7**.[8] For **7D** ketal **14D** was prepared by using lithium aluminum deuteride. Different conditions had to be developed for the elimination reaction in the deuterated series, since the label in **7D** is very easily scrambled through Cope rearrangement.[7] A satisfactory procedure was to convert **14D** to the corresponding iodide **15** by way of the ketal tosylate and then to employ 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)[9] for elimination of hydrogen iodide.[10] Use of aqueous oxalic acid at 0 °C permitted hydrolysis of the final ketal to **7D** without concomitant Cope rearrangement.

For **8** the corresponding cyclohexanone **16**, prepared throuugh alkylation of cyclohexanone *N,N*-dimethylhydrazone,[11] was converted to its silyl enol ether[12,13] and dehydrogenated.[13,14] This method failed for **9** and **10** because of difficulties in hydrolysis of the alkylated cyclopentanone dimethylhydrazones, but the desired cyclopentenones were available by way of bromo ketal **17**.[15] Lithium–halogen exchange using *tert*-butyllithium followed by alkylation with the appropriate alkenyl halide, **18** and **19** respectively, gave, after hydrolysis, **9** and **10** in poor yield. Iodide **19** was prepared from the tosylate of the corresponding alcohol **20**.[1] The deuterated iodide **21**[16] was substituted for **18** in preparation of **9D**.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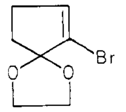
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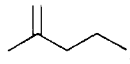
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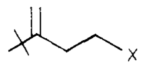
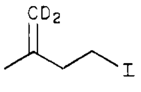

19, X = I
20, X = OH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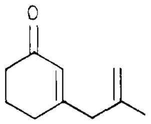
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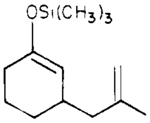
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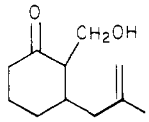
24

Preparation of the α-methylenecyclohexanone **11** began with addition of methallylmagnesium chloride to 3-ethoxycyclohexenone to furnish **22**.[17] Reduction of **22** with lithium in liquid ammonia and capture[18] of the regiospecifically formed enolate by chlorotrimethylsilane gave **23**, which yielded **24** upon reaction with methyllithium followed by formaldehyde.[19] Attempts to dehydrate **24** to **11** by way of the tosylate under the originally recommended conditions[20] at room temperature gave only the Cope rear-

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(7) Ketone **11** undergoes observable Cope rearrangement at room temperature, and we have observed that **7D** rearranges readily at 80–100 °C. For independent study of this process in ketones closely related to **11** and also of its catalysis by acid see: Dauben, W. G.; Chollet, A. *Tetrahedron Lett.* **1981**, *22*, 1583. For a review of the Cope rearrangement see: Rhoads, S. J.; Raulins, N. R. *Org. Reactions (N.Y.)* **1975**, *22*, 1.

(8) For discussion of this procedure see ref 5 and Spencer et al. (Spencer, T. A.; Watt, D. S.; Friary, R. J. *J. Org. Chem.* **1967**, *32*, 1234).

(9) Oediger, H.; Möller, F.; Eiter, K. *Synthesis* **1972**, 591.

(10) For other examples and discussion of this procedure see: Wolff, S.; Huecas, M. E.; Agosta, W. C. *J. Org. Chem.* **1982**, *47*, 4358.

(11) Corey, E. J.; Enders, D. *Tetrahedron Lett.* **1976**, 3.

(12) Miller, R. D.; McKean, D. R. *Synthesis* **1979**, 730.

(13) Fleming, I.; Paterson, I. *Synthesis* **1979**, 736.

(14) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.

(15) 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.

(16) Wolff, S.; Agosta, W. C. *J. Labeled Compd. Radiopharm.* **1982**, *19*, 959.

(17) Cantrell, T. S.; Haller, W. S.; Williams, J. C. *J. Org. Chem.* **1969**, *34*, 509.

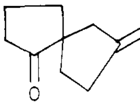
(18) Stork, G.; Singh, J. *J. Am. Chem. Soc.* **1974**, *96*, 6181.

(19) Stork, G.; d'Angelo, J. *J. Am. Chem. Soc.* **1974**, *96*, 7114.

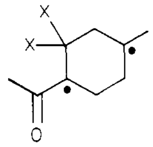
rangement[7] product **8** in a very slow reaction. However, we found that the desired elimination to **11** proceeds in essentially quantitative yield without rearrangement on treatment of the tosylate of **24** with DBN[9,10] at 0 °C.

Structures of Products

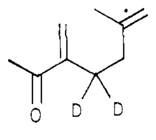
All new compounds reported in Table I have been fully characterized and show spectroscopic properties compatible with their assigned structures. For the major products **7a–11a** assignments are based on the same kinds of arguments presented in the preceding paper;[1] details are given in the Experimental Section. The structure of **8b** was deduced spectroscopically and then verified through comparison of its spectra with those already published[21] for this substance. The assignment for **8c** is based solely on spectra; it must be regarded as tentative, although quite credible in view of earlier observations,[5,22] along with the concomitant isomerization of **8** to **8b**. The structure of **9b** rests on spectra and oxidation by ruthenium tetraoxide[23] to spiro[4.4]nonane-1,7-dione (**25**), which was characterized by infrared and mass spectra.



25



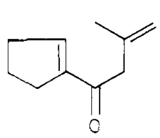
26, X = H
27, X = D



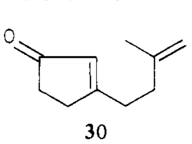
28

Discussion

From Table I it is obvious that **6–11** all cyclize with complete regiospecificity in the crossed fashion, quite independent of C(5) substitution or the presence of a ring. Apart from the earlier work with **6**, our first observation here was the isomerization of **7**, and we speculated that perhaps the failure to observe any 1,6 closure products resulted from an inability of the initial 1,6 cyclization intermediate, hindered bis tertiary biradical **26**, to collapse to a bicyclo[2.2.0]hexane. On fragmentation in either sense **26** only regenerates **7**, and thus 1,6 closure could possibly occur but go undetected through examination of the photolysis products. We tested this idea through irradiation of **7D**. Here 1,6 closure would yield **27**, and fragmentation would scramble the label with formation of both **7D** and **28**. In the event, however, photolysis of **7D** to partial conversion and recovery of unreacted starting ketone gave **7D** with the deuterium label intact; clearly no reversible 1,6 closure had occurred. Subsequent exploration of the chemistry of **8–10** confirmed that these 2-acyl-1,5-hexadienes (**3**) invariably followed the "rule of five". Furthermore, the reactions of this class are generally slower and have lower quantum yields for the products. Particularly interesting in this regard is a comparison of **9** with **29** and **30**, two ketones from our earlier study that represent series **1** and **2**. These three dienones share the same carbon skeleton and differ only in the location of the carbonyl group. Ketones **29** and **30** close regiospecifically 1,6 in quantum yields of 0.59 and 0.34, respectively.[1] In contrast, **9** yields no 1,6 closure products and is isomerized largely to **9a** in a quantum yield of 0.055. It is also noteworthy that not only does substitution at C(5) have no effect on the regiochemistry, but indeed replacement of C(5) methyl by *tert*-butyl (see **10**) results in a slight *increase* in quantum yield for the same type of product. This behavior differs from that of **31–33**, where the shift from hydrogen to methyl to *tert*-butyl at C(5) causes a progressive shift from 1,5 to 1,6 closure.[1] Taken together these observations point to some mechanistic difference in series **3** and suggest that in these dienones the initial bonding occurs from C(2) to C(6), rather than C(1) to C(5) as appears to be preferred for **1** and **2**.[1] If the first bond in photocyclization of **6** is C(2)–C(6) (see **34**), then no change in regiochemistry is expected on passing to **7** (see **35**).



29



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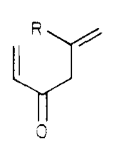
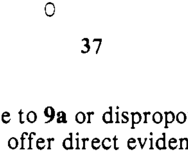
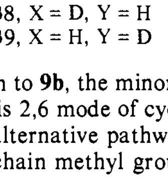


31, R = H
32, R = CH_3
33, R = $C(CH_3)_3$

Formation of side product **9b** from **9** appeared to provide independent support for the postulate of initial 2,6 closure. Since a plausible course of reaction for **9** is 2,6 closure to **36** followed by collapse to **9a** or disproportionation to **9b**, the minor product seemed to offer direct evidence for this 2,6 mode of cyclization. We were cognizant, however, of an alternative pathway to **9b**. Transfer of hydrogen from the side-chain methyl group to the β-carbon atom of cyclopentenone **9** would give biradical **37**, and this could collapse directly to **9b**. Such intramolecular abstractions in cyclopentenones are well documented.[24] It is true that they are disfavored when a seven-membered cyclic transition state is required,[25] as would be the case here, but indeed **9b** was found in only low yield. If this latter mechanism is operative, then formation of **9b** is of course irrelevant to the problem at hand. For this reason we investigated the origin of **9b** with some care. Photolysis of **9D** allows the desired discrimination, since 2,6 closure (see **36**) and disproportionation would lead only to **38**, while the hydrogen abstraction route (see **37**) would permit scrambling of the label and formation of both **38** and **39**. Upon irradiation **9D** was isomerized to an approximately 2:3 mixture of **38** and **39**. Both deuterated **9a** and recovered **9D** were cleanly labeled, indicating that scrambling of deuterium took place specifically in formation of **38** and **39** and implicating **37** as an intermediate. Thus, contrary to appearances, **9b** provides no useful information concerning the mechanism of closure to **9a**.



34, R = H
35, R = CH_3



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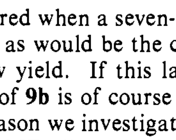
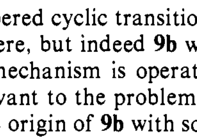
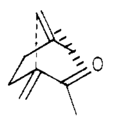


37



38, X = D, Y = H
39, X = H, Y = D

Seeking an explanation for preferential 2,6 closure of these 2-acyl dienes, we noted in examining molecular models that in the geometry required for initial 2,6 cyclization of **6–10** the carbonyl group can interact with the isolated double bond, as shown in **40**. Such interaction appears sterically and geometrically unfavorable for 1,5 and 1,6 closure of **6–10**, as well as for any mode of closure of the series **1** and **2** dienones. Secondary orbital overlap is considered an important influence on the course of



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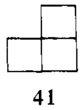

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various thermal transformations,[26] and we conjectured that perhaps carbonyl–olefin interaction occurs in **6–10**, overrides other considerations, and is responsible for 2,6 cyclization. If this were correct, a 2-acyl diene **3** in which such interaction was impossible might show the regiochemical behavior of series **1** and **2**. To explore this possibility we prepared the α-methylenecyclohexanone **11**, a 2-acylhexadiene with a constrained s-cis geometry of the enone that precludes this carbonyl–olefin interaction. If this then caused **11** to behave like series **1** or **2**, its 5-methyl substituent should favor some 1,6 closure. In the event, however, photocyclization of **11** led only to the crossed product **11a**, effectively disposing of the idea of regiochemical control through specific involvement of the carbonyl double bond. The result is nonetheless interesting because it reinforces the suggestion of initial 2,6, rather than 1,5, closure for 2-acyl dienes. As mentioned above,[7] thermal Cope rearrangement of **11** occurs at room temperature. This requires 1,6 closure that presumably is similar to the 1,6 closure so completely avoided on photolysis of **11**. Our observations with ketones **1** and **2** made it clear that partitioning between 1,5 and 1,6 closure of these substrates was controlled by steric effects and possibly radical stability. If these same factors operated for ketones **3**, it would be paradoxical to conclude that, even though **11** closes 1,6 extraordinarily readily in a thermal reaction, it cyclizes regiospecifically 1,5 on photolysis. We must conclude either (1) that 1,5 closure occurs in **11**, but for unexplained reasons it is totally unresponsive to steric hindrance and considerations of radical stability, or alternatively (2) that the initial bond forms from C(2) to C(6). We prefer the latter conclusion.

In closing we draw attention to two points. These photochemical studies with ketones of series **1–3** have permitted simple preparation of several novel tricyclic ring systems. We have employed one of these to provide easy access to tricyclo$[4.2.0.0^{1,4}]$ octane (**41**) and some of its derivatives,[27] and doubtless various additional studies of these new systems will also be fruitful. Finally, it is striking that the "rule of five" applies most reliably to these 2-acyl dienes, a class of hexadienes that played little part in derivation or earlier support for the rule.

Experimental Section

Materials and Equipment. General procedures have been previously described.[1] All VPC was carried out by using a Varian Aerograph Model 920 gas chromatograph with one of the following columns: (A) 25% QF-1, 10 ft; (B) 25% QF-1, 25 ft; (C) 25% QF-1, 2 ft; (D) 25% XF-1150, 6 ft; (E) 25% Carbowax 20 M, 5 ft; (F) 25% XF-1150, 3 ft; (G) 25% QF-1, 3 ft; (H) 25% Carbowax 20 M, 4 ft. All columns were packed in 0.25-in. aluminum tubing using 45/60 Chromosorb W, except columns E and H which employed 40/80 Chromosorb P.

6-Methyl-3-methylene-6-hepten-2-one (7). To a solution of sodium ethoxide prepared from sodium (1.98 g, 0.086 mol) in ethanol (80 mL) was first added ethyl acetoacetate (11.00 g, 84.6 mmol) at 0 °C and then 4-bromo-2-methyl-1-butene (13.15 g, 88.2 mmol) at 25 °C. The reaction mixture was heated at reflux overnight. After cooling and dilution with H_2O, it was extracted with ether (3×). The combined extracts were washed with H_2O and brine and were dried. Distillation afforded **13** (8.56 g, 51%); bp 72–77 °C (2 mm); IR 3075 (w), 2980 (m), 2935 (m), 1742 (s), 1717 (s), 1648 (m), 1441 (m), 1233 (s), 1142 (s), 884 (m) cm^{-1}; NMR (60 MHz) δ 4.67 (br s, 2 H), 4.14 (q, $J = 7$ Hz, 2 H), 3.23 (m, 1 H), 2.15 (s, 3 H), 1.93 (m, 4 H), 1.7 (m, 3 H), 1.27 (t, $J = 7$ Hz, 3 H). Anal. ($C_{11}H_{18}O_3$) C, H.

A mixture of **13** (7.05 g, 35.6 mmol), ethylene glycol (2.98 ml, 53.5 mmol), *p*-TsOH (17.8 mg), and benzene (80 mL) was heated to reflux overnight with removal of H_2O with a Dean–Stark trap. The reaction mixture was cooled, washed with aqueous $NaHCO_3$, and dried. The solvent was removed in vacuo to afford the ketal ester (8.74 g): IR 3070 (w), 2980 (s), 1737 (s), 1645 (w), 1205 (s), 1035 (s), 940 (w), 885 (m) cm^{-1}; NMR (60 MHz) δ 4.6 (br s, 2 H), 4.04 (q, $J = 7$ Hz, 2 H), 3.83 (m, 4 H), 2.63–1.48 (m, 8 H), 1.32 (s, 3 H), 1.23 (t, $J = 7$ Hz, 3 H). The crude ketal ester (8.74 g, 36.1 mmol) was dissolved in Et_2O (25 mL) and was added to $LiAlH_4$ (1.00 g) in Et_2O (100 mL) at a rate that caused gentle refluxing. Excess hydride was destroyed with saturated Na_2SO_4 solution and the reaction mixture was filtered and dried. Removal of solvent afforded **14** (6.20 g): IR 3540 (br), 3075 (w), 2970 (s), 2940 (s), 2885 (s), 1645 (w), 1032 (s), 937 (w), 882 (m) cm^{-1}; NMR (60 MHz) δ 4.65 (br s, 2 H), 3.92 (s, 4 H), 3.49 (m, 2 H), 2.67 (m, 1 H), 2.25–1.15 (m, with br s at 1.7 and s at 1.25, 11 H).

A mixture of crude **14** (7.87 g) in Et_2O (150 mL) and 5% H_2SO_4 (30 mL) was stirred vigorously at 25 °C overnight. The organic phase was separated, and the aqueous phase was saturated with salt and extracted with Et_2O. The combined organic phases were washed with $NaHCO_3$ and brine and were dried. Removal of solvent gave the ketol (4.18 g), which was dissolved in pyridine (50 mL) and treated with *p*-TsCl (5.61 g) for 1 h at 0 °C, 0.5 h at 25 °C, and 3.5 h at 100 °C. The reaction mixture was diluted with H_2O and extracted with pentane (3×). The pentane extracts were washed with dilute HCl, H_2O, $NaHCO_3$, and brine and were dried. The pentane was removed by distillation through a Vigreux column and the residue was bulb-to-bulb distilled to give the dienone. Preparative VPC (column A, 140 °C) afforded pure **7**: IR 3100 (w), 3000 (m), 2950 (m), 1681 (s), 1646 (w), 1625 (w), 1360 (m), 1115 (m), 925 (m), 882 (m) cm^{-1}; NMR (60 MHz) δ 5.87 (s, 1 H), 5.65 (br s, 1 H), 4.62 (br s, 2 H), 2.53–1.83 (m with s at 2.26, 7 H), 1.71 (br s, 3 H); mass spectrum, *m/z* 138.1047 (M^+, calcd for $C_9H_{14}O$, 138.1044).

Photolysis of 7. A solution of **7** (246 mg) in benzene (160 mL) containing acetophenone was heated to reflux and irradiated in the usual fashion for 14.5 h. VPC analysis (column B, 178 °C) indicated no remaining **7** and the formation of one product that was collected and identified as **7a**: IR 2950 (s), 2855 (s), 1705 (s), 1375 (m), 1355 (m), 1205 (w) cm^{-1}; NMR (220 MHz) δ 2.02 (s, 3 H), 1.88–1.82 (m, 2 H), 1.61–1.55 (m, 2 H), 1.50 (m, 2 H), 1.35 (m, 2 H), 1.21 (s, 3 H); mass spectrum, *m/z* 138.1044 (M^+, calcd. for $C_9H_{14}O$, 138.1044). No **7a** was formed when **7** and acetophenone were irradiated at room temperature.

Preparation of 7D. Reduction of the ketal ester described above with $LiAlD_4$ afforded **14D**. Without further purification, **14D** (6.20 g, 30.7 mmol) was dissolved in pyridine (80 mL) and treated with *p*-TsCl (7.30 g, 38.31 mmol) at 0 °C overnight. Standard workup afforded the tosylate (10.43 g, 95%). A mixture of the crude tosylate (7.60 g, 21.3 mmol) and NaI (25.6 g, 171 mmol) in hexamethylphosphoramide (120 mL) was heated at 50 °C for 22.5 h. After cooling, the reaction mixture was diluted with H_2O (900 mL) and brine (100 mL) and extracted with pentane (4×). The organic extracts were combined, washed with dilute $Na_2S_2O_3$ solution, H_2O, and brine, and dried. The solvent was removed by rotary evaporation to give **15** (6.11 g, 92%): NMR (60 MHz) δ 4.67 (br s, 2 H), 3.88 (s, 4 H), 2.28–1.08 (m with br s at 1.73 and s at 1.25, 11 H).

The dehydrohalogenation of **15** has been described.[10] A mixture of the diene ketal (223 mg) in CH_3OH (2 mL) and H_2O (0.2 mL) was treated with 1 N oxalic acid (0.2 mL) for 23 h at 4 °C. The reaction mixture was neutralized with $NaHCO_3$, diluted with brine, and extracted with pentane. The combined extracts were washed with H_2O and brine and dried. The solvent was removed in vacuo to give **7D** (169 mg). The dienone was further purified by preparative VPC using on-column injections (detector temperature 38 °C; oven temperature 55 °C; injector port heater off; He flow 120 mL/min). The NMR spectrum indicated >98% deuterium labeling and no Cope rearrangement: NMR (60 MHz) δ 4.62 (br s, 2 H), 2.52–1.87 (m with s at 2.27, 7 H), 1.72 (br s, 3 H).

Photolysis of 7D. Two NMR sample tubes containing **7D** (30–34 mg) and acetophenone (200 μL in C_6D_6, 450 μL) were degassed and sealed, and one was wrapped with opaque black tape. Both were heated in a water bath at 55 °C and irradiated for 5.5 h. NMR spectra indicated that they had equal amounts of **28** (<5%), resulting from thermal Cope rearrangement. The same experiment carried out at 15 °C for 22 h (λ >340 nm) and for 33.5 h (λ >280 nm) gave no **28**. Direct irradiation of **7D** in C_6D_6 for 22 h (λ >340 nm) and for 17.5 h (λ >280 nm) gave no **28**.

2-(3-Methyl-3-butenyl)cyclohexanone (16). The anion of cyclohexanone dimethylhydrazone (9.82 g, 70 mmol) was treated with 4-bromo-2-methyl-1-butene (13.3 g, 89.2 mmol) according to the procedure of Corey and Enders,[11] yielding the dimethylhydrazone of **16** (11.05 g, 76%): IR 3100 (w), 2955 (s), 2880 (s), 1648 (m), 1630 (m), 1442 (s), 1020 (m), 965 (m), 882 (s) cm^{-1}; NMR (60 MHz) δ 4.60 (br s, 2 H), 2.80–1.13 (m with s at 2.33 and br s at 1.7, 22 H). The hydrazone (10.4 g, 50 mmol) was oxidatively hydrolyzed in THF (500 mL) containing 1.0 N pH 7 phosphate buffer (150 mL) with three portions of $NaIO_4$ (23.5 g) in H_2O (150 mL) at 25 °C overnight. Distillation afforded **16** (6.89 g, 83%), bp 60–68° (0.5 mm); IR 3100 (w), 2960 (s), 2880 (s), 1715 (s), 1648 (w), 1445 (s), 1122 (m), 882 (s) cm^{-1}; NMR (60 MHz) δ 4.63 (br s, 2 H), 2.5–0.87 (m with br s at 1.72, 18 H); mass spectrum, *m/z* 166.1352 (M^+, calcd for $C_{11}H_{18}O$, 166.1358).

2-(3-Methyl-3-butenyl)cyclohex-2-enone (8). According to the published procedure,[12] **16** (499 mg, 3 mmol) was treated with hexamethyl-

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[26] For an example involving regiochemistry, see: Cohen, T.; Ruffner, R. J.; Shull, D. W.; Daniewski, W. M.; Ottenbrite, R. M.; Alston, P. V. *J. Org. Chem.* **1978**, *43*, 4052.

[27] Wolff, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1981**, 118; *J. Org. Chem.* **1981**, *46*, 4821.

disilazane (581 mg, 3.6 mmol) and iodotrimethylsilane (660 mg, 3.3 mmol) to afford the silyl enol ether (648 mg, 90%), bp 75–85 °C (0.5 mm). Without further purification the crude silyl enol ether (964 mg, 4 mmol) in CH_3CN (2 mL) was added to palladium acetate (712 mg, 3.17 mmol) and *p*-benzoquinone (122 mg, 1.13 mmol) in CH_3CN (14 mL) following the literature method.[14] The mixture was stirred at 25 °C overnight. The reaction mixture was diluted with pentane, filtered through Celite, washed with 5% aqueous NaOH, and dried. Bulb-to-bulb distillation (60–80 °C (0.05 mm)) afforded an oil (414 mg) that was shown to be a mixture of **8** and **16** by VPC (column D, 155 °C). Preparative VPC gave pure **8**: IR 3100 (w), 2950 (s), 1675 (s), 1640 (w), 1365 (m), 1248 (w), 1165 (m), 1095 (m), 882 (s) cm^{-1}; mass spectrum, *m/z* 164.1206 (M^+, calcd for $C_{11}H_{16}O$, 166.1201). Mixtures of **8** and **16** were also obtained upon treatment of the silyl enol ether with DDQ in the presence of 2,6-lutidine.[13]

Photolysis of 8. A solution of **8** (63 mg) in C_6H_6 (50 mL) was irradiated in the usual fashion for 11.5 h at which time VPC analysis (column E, 150 °C) indicated virtually no remaining **8** and the formation of two new components. The first was identified as **8a** (71%): IR 2960 (s), 2885 (s), 1770 (s), 1448 (m), 1375 (m), 1345 (m), 1240 (m), 980 (w) cm^{-1}; NMR[28] (220 MHz) δ 2.26–2.19 (m, 3 H), 2.11–1.45 (m, 9 H), 1.31 (dd, H_A, $J_{AB} = J_{AA'} = 6.6$ Hz); mass spectrum, *m/z* 164.1205 (M^+, calcd for $C_{11}H_{16}O$, 164.1201). The second component was a mixture of **8b** (5%) and **8c** (2%); these were separated on column F (150 °C). The NMR and IR spectra of **8b** were identical with those reported.[21] Data for **8c**: IR 3100 (w), 2955 (s), 1712 (s), 1645 (w), 1435 (m), 1330 (m), 1130 (m), 880 (m) cm^{-1}; NMR (220 MHz) δ 4.65 (m, 1 H), 4.60 (br s, 1 H), 2.87 (m, 1 H), 2.58 (m, 2 H), 2.34 (m, 2 H), 2.21–1.61 (m, with s at 1.65, 9 H); mass spectrum, *m/z* 164.1195 (M^+, calcd for $C_{11}H_{16}O$, 164.1201).

Attempted Pyrolysis of 8a at 190 °C. A solution of **8a** (~10 mg) in C_6H_6 (0.5 mL) was heated at 190 °C for 3 h in a sealed tube. VPC analysis indicated neither destruction of **8a** nor formation of any new product.

2-(3-Methyl-3-butenyl)cyclopent-2-enone (9). A solution of **17** (2.08 g, 10 mmol) and *tert*-butyllithium (5.95 mL of a 2.1 M solution, 12.5 mmol) was stirred at −78 °C for 1–5 h following the procedure of Smith et al.[15] The iodide **18** (4.90 g, 25 mmol) was added and the mixture was allowed to warm slowly to 25 °C overnight. Standard workup of the reaction mixture gave an oil (3.077 g), which VPC analysis (column C, 100 °C) indicated to be a mixture of unreacted **17**, **9**, and its ketal. The crude product was dissolved in CH_3OH (20 mL) and H_2O (2 mL) and was treated with 1 N oxalic acid (2 mL) overnight at 4 °C. The mixture was made basic with K_2CO_3, diluted with H_2O, and extracted with pentane. The pentane extracts yielded 2.00 g of an oil that was chromatographed on 90 g of neutral alumina (activity II–III). The dienone was eluted with 9:1 pentane:Et_2O. The fractions were combined and bulb-to-bulb distilled to afford pure **9** (124 mg, 8%): IR 3100 (w), 2945 (m), 1710 (s), 1648 (w), 1628 (w), 1441 (m), 881 (m) cm^{-1}; NMR δ 7.1 (m, 1 H), 4.63 (br s, 2 H), 2.65–1.9 (m, 8 H), 1.73 (s, 3 H); mass spectrum, *m/z* 150.1053 (M^+, calcd for $C_{10}H_{14}O$, 150.1044).

Photolysis of 9. Standard irradiation of a solution of **9** (124 mg) in C_6H_6 (65 mL) was followed by VPC analysis (column E, 160 °C), which indicated little starting material and the formation of one product peak after 14 days. This product was a mixture of **9a,b**; these were separated on column A (140 °C). Data for **9a** (50%): IR 2980 (s), 2935 (m), 2880 (m), 1730 (s), 1463 (m), 1448 (m), 1403 (w), 1375 (m), 1298 (m), 1159 (m), 1024 (m) cm^{-1}; NMR[28,29] (220 MHz) δ 2.64–2.47 (m, 1 H), 2.40 (dd, J = 9.0, 18.8 Hz, 1 H), 2.23 (ddd, H_B, J = 2.6, 2.6, 7.5 Hz), 2.5–1.57 (m, 7 H), 1.41 (dd, H_A, $J_{AB} = J_{AA'} = 7.1$ Hz), 1.15 (s, 3 H); mass spectrum, *m/z* 150.1042 (M^+, calcd for $C_{10}H_{14}O$, 150.1044). Data for **9b** (6%): IR 3095 (w), 2870 (s), 1735 (s), 1655 (w), 1405 (w), 872 (m) cm^{-1}; NMR (220 MHz) δ 4.80 (br s, 2 H), 2.52–1.77 (m, 11 H), 1.51 (m, 1 H); mass spectrum, *m/z* 150.1047 (M^+, calcd for $C_{10}H_{14}O$, 150.1044).

Efficient triplet sensitization of this photolysis was demonstrated. Irradiation through Pyrex for 1 h using a merry-go-round apparatus of a 0.014 M solution of **9** in benzene containing 9 mol equiv of α-tetralone gave 86% conversion to **9a,b**. The simultaneously irradiated control lacking sensitizer gave only 18% conversion with the same relative distribution of products.

The reaction was quenched with 2,3-dimethyl-1,3-butadiene. Irradiation of 0.014 M solution of **9** containing 0.056 M quencher as above led to 7% conversion to **9a,b**.

Oxidation of 9b. To a solution of RuO_4 in CCl_4 [prepared by shaking RuO_2 (50 mg) in a separatory funnel with 0.25 M $NaIO_4$ (10 mL), separation of the phases, and drying over Na_2SO_4] was added **9b** (~5 mg). After 0.5 h, excess oxidant was destroyed by the addition of 2-propanol and the reaction mixture was filtered through Celite. Solvent was removed by distillation and the residue was purified by preparative VPC (column C, 160 °C) to afford **25**: IR 2980 (s), 1750 (s), 1448 (w), 1405 (m), 1127 (m) cm^{-1}; mass spectrum, *m/z* 152.0859 (M^+, calcd for $C_9H_{12}O_2$, 152.0838).

Preparation of 9D. Following the procedure described above for **9**, ketal **17** (5.04 g, 24.6 mmol) in two batches was alkylated with **21**[16] (4.89 g, 24.7 mmol) to afford, after hydrolysis and column chromatography, **9D** (238 mg, 6%): NMR (60 MHz) δ 7.1 (br s, 1 H), 2.67–2.07 (m, 8 H), 1.7 (s, 3 H).

Photolysis of 9D. A solution of **9D** (143 mg) in C_6H_6 (90 mL) was irradiated for 10 days. Separation of the products and unreacted **9D** was accomplished as described above. The NMR spectrum of recovered **9D** indicated neither loss nor scrambling of the label. The NMR spectrum of the spiro ketone indicated a mixture consisting of ~40% **38** and ~60% **39**.

5-Iodo-2,2-dimethyl-3-methylenepentane (19). 4,4-Dimethyl-3-methylene-1-pentanol[1] (5.75 g, 44.8 mmol) was converted to the tosylate (11.46 g, 91%) by reaction in the usual fashion with *p*-TsCl (10.7 g, 56.0 mmol) in pyridine (75 mL) at 0 °C overnight. The crude tosylate was combined with NaI (12 g) in dimethylformamide (80 mL) and stirred at 53 °C for 4 h. The reaction mixture was cooled, diluted with H_2O, and extracted with pentane. The combined pentane extracts were washed with H_2O, dilute $Na_2S_2O_3$ solution, and brine and were dried. Pentane was removed by distillation through a Vigreux column and the residue was chromatographed on neutral alumina (80 g, activity I). The iodide was eluted in the first four 75-mL fractions. After concentration, the residue was distilled to afford pure **19** (7.83 g, 73%): bp 78–80 °C (8 mm); IR 3125 (w), 2995 (s), 2900 (m), 1628 (m), 1360 (m), 1160 (m), 890 (m) cm^{-1}; NMR (60 MHz) δ 4.92 (s, 1 H), 4.68 (br s, 1 H), 3.32–2.37 (m, 4 H), 1.07 (s, 9 H); mass spectrum, *m/z* 238.0224 (M^+, calcd for $C_8H_{15}I$, 238.0218).

2-(4,4-Dimethyl-3-methylenepentyl)cyclopent-2-enone (10). Following the procedure described above for the synthesis of **9** and **9D**, bromo ketal **17** (3.885 g, 19.0 mmol) was alkylated with **19** (7.83 g, 32.9 mmol) to yield 5.95 g of an oil composed of unreacted **17** and the ketal of **10**. After oxalic acid hydrolysis and chromatography on neutral alumina (150 g, activity II–III), bulb-to-bulb distillation afforded pure **10** (504 mg, 14%): bp ~100 °C (0.5 mm); IR 3120 (w), 3070 (w), 2990 (s), 2890 (m), 1705 (s), 1634 (m), 1444 (m), 1358 (m), 1194 (m), 884 (m) cm^{-1}; NMR (220 MHz) δ 7.17 (m, 1 H), 4.85 (s, 1 H), 4.67 (br s, 1 H) 2.53–2.50 (m, 2 H), 2.31–2.12 (m, 6 H), 1.06 (s, 9 H); mass spectrum, *m/z* 192.1529 (M^+, calcd for $C_{13}H_{20}O$, 192.1514).

Photolysis of 10. VPC analysis (column G, 150 °C) of the irradiation of **10** (65.5 mg) in C_6H_6 (70 mL) in the usual manner indicated little starting material after 9 days and the formation of one product. This was collected and identified as **10a** (37%): mp 54.5–55 °C; IR 2980 (s), 2900 (m), 1733 (s), 1478 (m), 1402 (w), 1358 (m), 1243 (m), 1011 (w) cm^{-1}; NMR[28] (220 MHz) δ 2.56–1.56 (m, 10 H), 1.40 (dd, H_A, $J_{AB} = J_{AA'} = 7.1$ Hz), 0.92 (s, 9 H); mass spectrum, *m/z*, 192.1510 (M^+, calcd for $C_{13}H_{20}O$, 192.1514).

An evacuated, sealed tube containing **10a** (~10 mg) in C_6H_6 (1 mL) was heated for 3 h at 175 °C. VPC analysis indicated no destruction of **10a**.

3-(2-Methyl-2-propenyl)cyclohex-2-enone (22). Addition of 3-ethoxycyclohex-2-enone (10.0 g, 71.3 mmol) to a solution of methallylmagnesium chloride [prepared from Mg (6.10 g) and metallyl chloride (18.1 g) in Et_2O (150 mL) at 0 °C] followed by treatment of the alcohol with 1 M oxalic acid as described for related systems[1] gave **22**[17] (9.744 g, 91%): bp 58–60 °C (0.1 mm); IR 3095 (w), 2965 (m), 1675 (s), 1625 (w), 1448 (w), 1425 (w), 888 (m) cm^{-1}; NMR (60 MHz) δ 5.73 (br s, 1 H), 4.88–4.65 (m, 2 H), 2.68 (s, 2 H), 2.48–1.55 (m with br s at 1.72, 9 H); mass spectrum, *m/z* 150.1033 (M^+, calcd for $C_{10}H_{14}O$, 150.1045).

3-(2-Methyl-2-propenyl)-1-(trimethylsiloxy)-1-cyclohexene (23). To Li (0.625 g, 0.09 mol) in liquid NH_3 at −78 °C was added a solution of **22** (4.50 g, 30 mmol) and *tert*-butyl alcohol (1.78 g, 24 mmol) in THF (150 mL).[18] Excess Li was destroyed by the addition of 2,3-dimethyl-1,3-butadiene; the solvents were removed, and the residue, redissolved in THF, was treated with chlorotrimethylsilane (9.78 g, 90 mmol)–triethylamine (9.11 g, 90 mmol) at −10 °C. Distillation yielded the silyl enol ether (5.29 g, 79%): bp 54–57 °C (0.5 mm); IR 3085 (w), 2950 (s), 1660 (m), 1362 (w), 1245 (s), 1184 (s), 834 (s) cm^{-1}; NMR (60 MHz) δ 4.65 (m, 3 H), 2.47–1.30 (m with br s at 1.72, 12 H), 0.1 (s, 9 H); mass spectrum, *m/z* 224.1616 (M^+, calcd for $C_{13}H_{24}OSi$, 224.1597).

3-(2-Methyl-2-propenyl)-2-methylenecyclohexanone (11). Following the published procedure,[19] the silyl enol ether (3.39 g, 15.1 mmol) in THF was treated successively with methyllithium (1.1 equiv) for 1 h at 0 °C and then gaseous formaldehyde (2–3 g) at −78 °C. Standard workup

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(28) See structure **28** in ref 1 for identification of protons H_A, H_B, etc.

(29) Identification of H_A and H_B was possible because these signals are absent in the spectrum of **9a** obtained from **9D**.

afforded an oil (2.96 g), which was chromatographed on silica gel (110 g, activity II–III). Elution with 95:5 CH_2Cl_2:Et_2O (fractions 11–28) gave **24** (1.35 g, 49%): IR 3610 (m), 3100 (w), 2950 (s), 1700 (s), 1650 (w), 1070 (w), 1050 (w), 882 (m) cm^{-1}; NMR (60 MHz) δ 4.67 (br s, 2 H), 4.00–3.37 (m, 2 H), 2.83–1.00 (m with br s at 1.7, 14 H). Treatment of the ketol (368.4 mg, 2.02 mmol) with *p*-TsCl (564 mg, 2.96 mmol) in pyridine (5 mL) in the usual way afforded the tosylate (643 mg, 95%). Without further purification, a solution of the tosylate in Et_2O (15 mL) was cooled to 0 °C and treated with 1,5-diazabicyclo[4.3.0]non-5-ene (475 μL) for 0.75 h. The mixture was diluted with pentane, washed with H_2O, dilute aqueous acetic acid, H_2O, and $NaHCO_3$, and dried. All operations were carried out with precooled reagents in a cold room. Removal of solvent in vacuo at 0 °C afforded **11** (317 mg, 100%): IR 3095 (m), 2955 (s), 1695 (s), 1647 (m), 1615 (m), 1445 (m), 930 (m), 885 (s) cm^{-1}; NMR (60 MHz) δ 5.67 (dd, $J_1 = J_2 = 1.5$ Hz, 1 H), 5.00 (dd, $J_1 = J_2 = 1.5$ Hz, 1 H), 4.73 (br s, 1 H), 4.65 (br s, 1 H), 3.00–1.33 (m with br s at 1.73, 12 H).

Photolysis of 11. A solution of **11** (317 mg) in pentane (150 mL) containing a small amount of $NaHCO_3$ was irradiated at −20 °C through Pyrex glass. The disappearance of **11** and formation of one product were detected by VPC analysis (column A, 145 °C). After 34.5 h, product destruction was noted, and the photolysis was ended. Preparative VPC (column H, 150 °C) gave three components. The first was identified as **11a** (40% based on unrecovered **11**): IR 2960 (s), 2880 (s), 1705 (s), 1450 (m), 1378 (m), 1345 (m), 1176 (w), 1133 (w) cm^{-1}; NMR[28] (300 MHz) δ 2.35–2.20 (m, 4 H), 2.10–1.99 (m, 1 H), 1.97–1.63 (m with dd at 1.83, H_A, $J_{AB} = 6.2$, $J_{AA'} = 9.5$ Hz and dd at 1.65, $H_{B'}$, $J_{A'B'} = 6.8$, $J_{B'D} = 2.5$ Hz, 4 H), 1.53 (dddd, $J = 3.4, 12.6, 12.6, 12.8$ Hz, 1 H), 1.39 (ddd, H_B, $J_{AB} = 6.2$, $J_{BE} = 2.3$, $J_{BE'} = 1.4$ Hz), 1.30 (ddd, H_E, $J_{DE} = 10.8$, $J_{EE'} = 3.7$, $J_{BE} = 2.8$ Hz), 1.18 (s, 3 H), 1.17 (dd, $H_{A'}$, $J_{A'B'} = 6.7$, $J_{AA'} = 9.5$ Hz). Anal. ($C_{11}H_{16}O$) C, H. The second component was **8a** (1%) and the third **8** (36%) arising from thermal Cope rearrangement on gas chromatography of unreacted **11**.

A sealed, evacuated tube containing **11a** (~10 mg) in C_6H_6 (1 mL) was heated at 190 °C for 3 h. VPC analysis indicated neither destruction of **11a** nor formation of other products.

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Activation of Carbon Dioxide with Aluminum Porphyrin and Reaction with Epoxide. Studies on (Tetraphenylporphinato)aluminum Alkoxide Having a Long Oxyalkylene Chain as the Alkoxide Group

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Abstract: (Tetraphenylporphinato)aluminum alkoxide ((TPP)AlOR) having a long oxyalkylene chain as the alkoxide group was prepared by the polymerization of epoxide with (tetraphenylporphinato)aluminum chloride as catalyst. The reactivity of this aluminum alkoxide toward carbon dioxide was markedly enhanced in the presence of 1-methylimidazole. Carbon dioxide thus trapped with the (porphinato)aluminum alkoxide was found to be activated enough to react with epoxide to afford cyclic carbonate. The spectroscopic investigation of the reaction system, favored by the enhanced solubility of the metalloporphyrin due to the long oxyalkylene chain, indicated that cyclic carbonate was formed by the insertion of carbon dioxide followed by that of epoxide into the aluminum–oxygen bond of (TPP)AlOR to give the aluminum alkoxide (TPP)Al–O–CHR–CH_2–O–CO–OR and subsequent intramolecular attack of this aluminum alkoxide toward the adjacent linear carbonate linkage, regenerating the starting alkoxide, (TPP)AlOR.

Chemical fixation of carbon dioxide is of great interest in connection with resource utilization and in relation to biochemical photosynthesis. Fundamental studies on the reactions of carbon dioxide have made much progress in recent years,[1] but the examples of catalytic reactions have been rather limited. An interesting reaction with potential utility is the reaction of carbon dioxide and epoxide using organometallic catalyst systems to give alternating copolymer, an aliphatic polycarbonate, from these monomers.[2,3] In the series of our studies on this and the related reactions of carbon dioxide, we found a remarkable effect of visible light on the reaction of (tetraphenylporphinato)aluminum ethyl (**1a**) with carbon dioxide.[4] Such an effect is considered to be related to electron transfer in the initial stage of photosynthesis.

Another interesting finding we made is on the reactivity of (tetraphenylporphinato)aluminum methoxide ((TPP)AlOMe, **1b**) with carbon dioxide.[5] (TPP)AlOMe traps carbon dioxide readily and reversibly at room temperature in the presence of 1-methylimidazole. The trapped carbon dioxide is activated enough to react with epoxide at room temperature to afford the corre-

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