In general, naphthalenes with triplet energies around 60 kcal/mol are almost ideally located to have triplet stability and yet to store a very considerable energy.

Two other questions can be expected to be important. The lifetime of the upper state responsible for the photocleavage will of course be a factor; unfortunately, we know little about this subject and any discussion would be mere speculation. A considerable amount is known about other types of chromophores (azulene, thiones)[25] and a similar degree of understanding would be desirable in the case of naphthalenes. The other aspect relates to the singlet state characteristics. Undoubtedly, excited singlets will be good candidates for two-photon one-laser reactions, and indeed there is some indication that in the case of benzil such processes play a role.[24] In the case of BNP (Table II) one-photon cleavage of the singlet is inefficient, reflecting the localization of the energy in the carbonyl chromophore. Two-photon processes may play a minor role in the one-laser (308 nm) cleavage of BNP.

Experiment Section

Materials and General Techniques. The synthesis of 1,3-bis(1-naphthyl)-2-propanone has been reported in an earlier publication.[3] Dibenzyl ketone and benzophenone were recrystallized before use. 1,3-Cyclohexadiene was vacuum distilled. Other reagents and solvents (Aldrich Gold Label) were used as received. Aberchrome-540 was purchased from Aberchromics Ltd. (Cardiff).

Fluorescence and phosphorescence spectra were recorded on a Perkin-Elmer LS-5 fluorescence spectrometer. Fluorescence lifetimes were measured on a PRA instrument. GC analyses were done on a Perkin-Elmer 8320 gas chromatograph with a 12-m BPI on vitreous silica capillary column. GC/MS spectra were recorded on a Hewlett Packard 5995 instrument equipped with a 10-m Ultra I (OV-101) capillary column. HPLC analyses were done on a Varian instrument equipped with a reverse-phase column and with methanol/water mixtures as eluent. Preparative separations were done on a Perkin-Elmer 10 liquid chromatograph with a Lobar Silica Gel 60 prepacked column.

Laser Photolysis. The laser photolysis facility and recent modifications required for two-laser experiments have been described in earlier publications.[26,27] All two-laser experiments reported herein used a Lumonics TE-860-2 excimer laser with a Xe-HCl gas mixture (308 nm, ~5-ns pulses, ≤80 mJ/pulse) as the synthesis laser for BNP triplets and a Candela flash pumped dye laser (Stilbene 420 dye in 50% aqueous methanol; 100-200 mJ/pulse; ~250 ns pulse width) for excitation of the triplet. The benzophenone sensitization experiments were carried out with use of a Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, ≤9mJ/pulse) for excitation.

Samples of BNP (0.2 mM in benzene) were contained in 7 × 7 mm^2 quartz cells and were degassed by nitrogen purging.

Lamp Irradiations. Samples of BNP in the appropriate solvent were degassed by nitrogen purging and irradiated with RPR 3000 lamps. Products were identified by comparison of GC, GC/MS, and HPLC traces to those of authentic samples. Quantitative product analysis was done by HPLC with 9-phenylanthracene as an internal standard (added after irradiation) and with a standard mixture of ketone plus products for calibration.

For quantum yield measurements, samples of BNP and valerophenone in benzene with matched optical densities at 313 nm were degassed by nitrogen purging and irradiated in a merry-go-round with a Hanovia 200 W mercury/xenon arc lamp and a potassium chromate filter to isolate the 313-nm line. Quantitative product analysis for BNP samples was done by HPLC, as above. The valerophenone actinometer samples were analyzed for acetophenone production ($\phi = 0.3$)[12] by GC with hexadecane as an internal standard.

Laser Product Studies. Samples of BNP in benzene (3 mL; 0.5 mM) were purged with nitrogen and irradiated with (i) 500-308-nm laser shots, (ii) 500 pairs of 308- and 430-nm pulses with a 500-ns delay between the two pulses, and (iii) 500 pairs of shots as in (ii) but with the laser sequence reversed. The samples were continuously purged with nitrogen during the laser irradiations to provide sample mixing. Continuous mixing is essential for the comparison of one-laser, two-laser, and reverse-sequence experiments to be valid. Quantitative analysis was done by HPLC.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance and to Professor H. G. Heller for the communication of unpublished results.

Registry No. 1,3-Bis(1-naphthyl)-2-propanone, 51042-38-7.

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(25) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings Publishing Co.: Menlo Park, CA, 1978.

(26) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(27) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

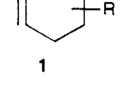
Biradical Reversion in the Intramolecular Photochemistry of Carbonyl-Substituted 1,5-Hexadienes

Clemens Schröder, Steven Wolff, and William C. Agosta*

Contribution from The Rockefeller University, New York, New York 10021-6399.
Received March 3, 1987

Abstract: We have studied the intramolecular photochemistry of dienones **10a,b–12a,b**. The initial rate of loss of alkene stereochemistry in recovered starting ketone provides a measure of the rate of reversion (k_r) of the biradical intermediate (Scheme I) relative to its conversion to products (k_p). Results are presented in Table I along with quantum yields for products (Φ_p) and for reversion (Φ_r) and the fraction of absorbed light not accounted for by these processes (Φ_{dif}). Both 1-acyl (**10a,b**) and 2-acyl (**11a,b**) hexadienes yield freely reverting biradicals. In these series both Φ_p and Φ_r increase on replacement of hydrogen by methyl at C(6), providing evidence for the postulated exciplex. The 3-keto hexadienes **12a,b** are quite different: (1) the biradical does not revert to starting ketone (<1%); (2) substitution of methyl for hydrogen at C(6) causes a decrease in Φ_p; and (3) initial bonding in the biradical is at C(β) of the enone. An explanation for the regiochemistry and relative Φ_p's of the three series is offered.

In previous studies we have investigated the role of structural features in control of the regiochemistry of intramolecular photochemical reactions of the carbonyl-substituted 1,5-hexadienes generalized as **1–3**.[1] These studies have led to rules predicting whether cyclization of the diene **4** leads to biradical **5** (crossed, 1,5 or 2,6 closure) or **6** (straight, 1,6 closure) or both. Collapse or disproportionation of these biradicals then leads to the observed



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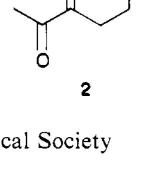

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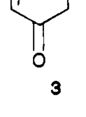

3

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(1) (a) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1291. (b) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1299. (c) Matlin, A. R.; Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1983**, *24*, 2961.

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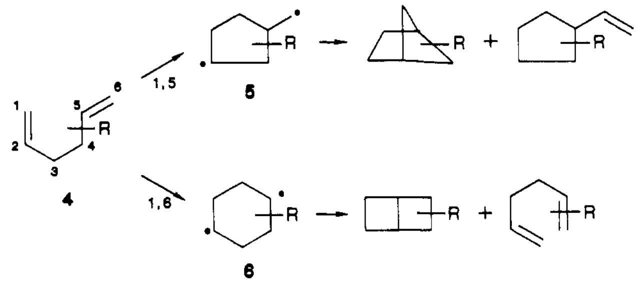
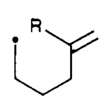
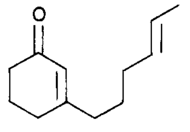
products. The mechanistic basis of these qualitatively useful predictive rules has not been clear, and one significant piece of mechanistic information lacking has been knowledge of whether the biradical undergoes reversion to starting dienone. For example, the cyclization of 5-hexenyl (**7**) and 5-alkyl-5-hexenyl (**8**) radicals, which is known to be irreversible and under kinetic control,[2] provides a good model for the regiochemical behavior of appropriately substituted 1-acyl-1,5-hexadienes (**1**) and 1,5-hexadien-3-ones (**3**).[1a] In both the radicals and the ketones C(5) substitution leads to increased C(6) closure, and for the ketones it is known that larger substituents at C(5) lead to more closure at C(6). In 2-acyl-1,5-hexadienes (**2**) this effect is absent, and these ketones undergo crossed closure regardless of the substitution at C(5).[1b] Similarly, there is good evidence that in crossed closure of **1** and **3** the initial bond formation is 1,5 rather than 2,6; in contrast, the failure of substitution at C(5) to influence regiochemistry in **2** suggests that initial closure in this case is 2,6.[1] Interpretation of these observations could be facilitated by knowledge of whether biradical formation is under kinetic or thermodynamic control in **1**–**3** and whether it differs among the three series; as we have pointed out, answering these questions is an obvious next step in resolving this problem.[3]





7: R = H
8: R = alkyl



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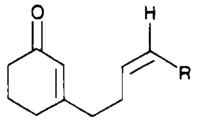

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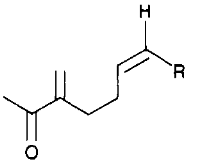

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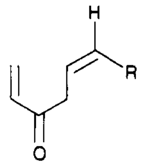
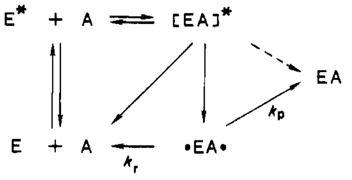


12

a, R = D; b, R = CH$_3$; c, R = H

Scheme I



This question of biradical reversion is an old one in the photochemical [2 + 2] cycloaddition. The mechanistic model generally assumed in discussion of the reaction is shown in Scheme I, where E, A, [EA], •EA•, and EA are enone, alkene, exciplex, biradical, and cycloaddition product, respectively; asterisked species are triplets; k_r and k_p are the rate of reversion of biradical to ground state species and of its conversion to products, respectively;[4-7] and the dashed arrow represents the alternative possibility that the exciplex collapse directly to products.[8,9] From analysis of kinetic data for the addition of cyclohexene to cyclopentenone and cyclohexenone, Loutfy and Mayo concluded that over half of the biradicals formed reverted to olefin and ground-state ketone ($k_r/k_p > 1$).[5] In fact it appears to be generally accepted that reversion of the biradical is a major source of inefficiency in the cycloaddition reaction,[6a] although the direct chemical evidence on this point suggests that this is not always the case. McCullough et al. reported in 1975 that in addition of (*Z*)-2-butene to 3-phenylcyclohexenone, recovered olefin contained $\sim$9% of its geometric isomer at $\sim$2% conversion, a finding in line with efficient reversion of the biradical after loss of stereochemistry.[10] In contrast, several years earlier Corey and his co-workers had noted that cycloaddition of either (*Z*)- or (*E*)-2-butene to cyclohexenone gave the same mixture of products and that there was no concomitant isomerization of (*Z*)-2-butene to its *E* isomer (<1%) during the reaction,[4a] results implying a biradical that does not revert but loses stereochemistry before closure to cyclobutane. Additional examples of each type of behavior in the intermolecular reaction are available.[6b] To our knowledge there is only a single report concerning reversion in an intramolecular [2 + 2] reaction. This is an investigation by Becker and his co-workers of the photochemistry of two 1-acyl-1,6-heptadienes, (*E*)-3-(4-hexenyl)cyclohexenone (**9**) and its *Z* isomer **9Z**, from which these investigators concluded that the two ketones give the same mixture of products and do not equilibrate during irradiation.[11] There is no obvious way to generalize this observation, however, particularly to hexadienes, which differ markedly in behavior from the heptadienes.[1,3,12]

We were interested then in investigating biradical reversion in representative members of the three classes of carbonyl-substituted hexadienes **1**–**3**, and we chose to examine the photochemistry of the six ketones **10a**,**b**–**12a**,**b**, where loss of stereochemistry of the deuterium or methyl group at C(6) in recovered starting ketone will signal reversion of the biradical intermediate. Ketones **11a**,**b** and **12a**,**b** are the simplest members of their series; use of the

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(2) (a) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974**, 2251. Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Chem. Commun.* **1974**, 472. Beckwith, A. L. J. *Colloq. Inst. C. N. R. S.* **1978**, *278*, 373. (b) For a more general review, see: Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Chapter 4.

(3) Matlin, A. R.; George, C. F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 3385. This paper contains related studies on carbonyl-substituted 1,6-heptadienes.

(4) (a) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570. (b) Wagner, P. J.; Bucheck, D. J. *Can. J. Chem.* **1969**, *47*, 713 and references cited therein.

(5) Loutfy, R. O.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559. References to earlier work by this group are given in this paper.

(6) (a) Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123. (b) Weedon, A. C. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1984; pp 61–143. (c) A general review of photochemical reactions involving biradical intermediates is available: Wagner, P. J. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, Chapter 20.

(7) Recently it has been suggested that in intermolecular photocycloaddition reactions of cyclohexenones the immediate precursor of biradical •EA• is a reactive ground-state species, possibly a ground-state *trans*-cyclohexenone, derived from triplet E*: Schuster, D. I.; Brown, P. B.; Capponi, L. J.; Rhodes, C. J.; Scaiano, J. C.; Tucker, P. C.; Weir, D. *J. Am. Chem. Soc.* **1987**, *109*, 2533. Application of this proposal to intramolecular cycloadditions of cyclohexenones such as **10a**,**b** remains to be explored; it appears not to be relevant to open-chain systems such as **11a**,**b** and **12a**,**b**.

(8) Shaik, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 3184 and references cited therein. The body of evidence cited above (ref 4–7 and references therein) supports the generally accepted idea that biradicals are intermediates in cycloadditions of the sort under discussion here. In the present work, loss of stereochemistry at C(6) in products at low conversion (see below) reinforces this conclusion.

(9) The mechanism in Scheme II usually also contain steps for formation of excimer and dimer. These steps are omitted here, since competing formation of dimer is absent in all the intramolecular cycloadditions under discussion.

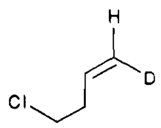
(10) McCullough, J. J.; Ramachandran, B. R.; Snyder, F. F.; Taylor, G. N. *J. Am. Chem. Soc.* **1975**, *97*, 6767.

(11) Becker, D.; Nagler, M.; Hirsh, S.; Ramun, J. *J. Chem. Soc., Chem. Commun.* **1983**, 371. From the data published it appears, however, that there is slow isomerization of the side-chain double bond; after 26 h about 15% alkenylcyclohexenone remains, and this is a 1:1 mixture of the *Z* and *E* isomers.

(12) (a) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932. (b) Liu, R. S. H.; Hammond, G. S. *Ibid.* **1967**, *89*, 4936.

corresponding open chain alkadienones as representatives of series **1** was precluded by the failure of 3,7-octadien-2-one to undergo [2 + 2] cycloaddition.[13] Preparation of ketones **10a,b–12a,b** and the mechanistic implications of their photochemical behavior are discussed below.

Preparation of 10a,b–12a,b. Both **10a** and **11a** were available from (*Z*)-4-chloro-1-butene-*1*-d_1 (**13**), which was prepared following a published procedure.[14,15] Reaction[1a] of the Grignard reagent from **13** with 3-ethoxycyclohexenone and subsequent acid hydrolysis gave **10a**. Alkylation of acetoacetic ester with the iodide derived from **13** yielded **15**;[16] this was then converted to **11a**, generally following an earlier route for similar α-methylene ketones.[17] Thus, keto ester **15** was ketalized, the ester group was reduced with hydride, and the product **16** was deketalized and dehydrated to furnish **11a**. It was also useful to have on hand **17**, the geometric isomer of **11a**, as a standard for nuclear magnetic resonance (NMR) measurements. This was prepared from keto ester **18**, available through alkylation of acetoacetic ester with 4-bromo-1-butyne.[17a] Steps as just described for preparation of **11a** then gave **19**, which on hydroboration and treatment with acetic acid-*O*-*d*,[14] followed by deketalization, furnished dienone **17**.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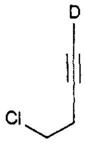
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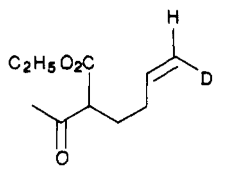
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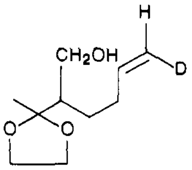
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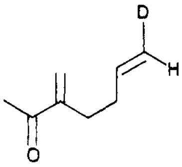
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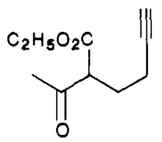
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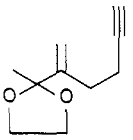
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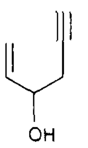
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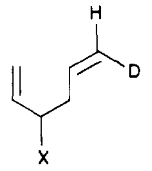

21: X = OSiC(CH$_3$)$_3$Ph$_2$
22: X = OH

Substrate **12a** was available in several steps from 1-hexen-5-yn-3-ol (**20**). We prepared **20** through addition of propargylmagnesium bromide to acrolein, as previously described.[18,19] Alcohol **20** was then converted to its *tert*-butyldiphenylsilyl ether,[20] the acetylenic protium was exchanged for deuterium, and the triple bond was reduced stereoselectively by hydroboration–protonolysis[14] to furnish **21**. Treatment of **21** with 40% aqueous hydrofluoric acid in tetrahydrofuran[21] provided satisfactory cleavage of the silyl ether, and direct oxidation of alcohol **22** with Jones's reagent[22] gave **12a**.

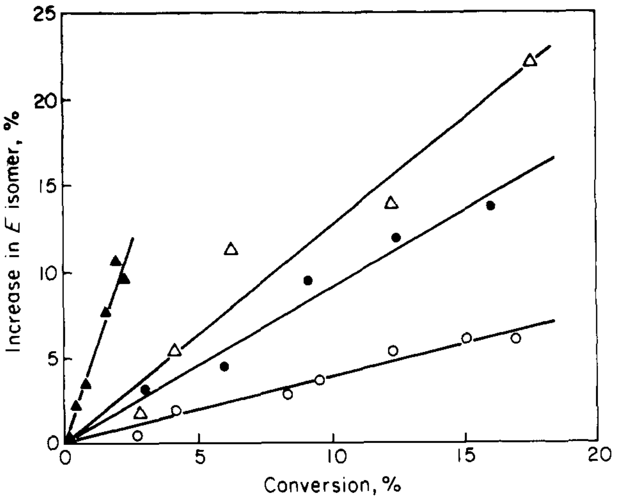
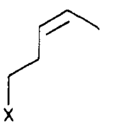
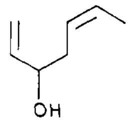


Figure 1. Increase in *E* isomer in recovered dienone as a function of conversion of dienone to photoproducts for **10a** (○), **10b** (●), **11a** (△), and **11b** (▲). For **12a,b** no scrambling of label in recovered dienone was observed.

Synthesis of the methyl-substituted substrates **10b–12b** began with (*Z*)-3-penten-1-ol (**23**) or the derived bromide **24**.[23,24] By way of the Grignard reagent from **24**, ketone **10b** was available by using the method for **10a**. Preparation of **11b** closely followed the route for **11a** and **17**, employing **24** in this case for alkylation of acetoacetic ester. For **12b** alcohol **23** was treated with pyridinium chlorochromate,[25] and the resulting aldehyde was allowed to react directly with vinylmagnesium bromide to form dienol **25**.[26] Oxidation then yielded **12b**, which had properties comparable with those reported for a sample prepared by another route.[27]


23 X = OH
24 X = Br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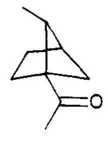
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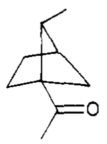
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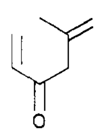
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After purification proton NMR measurements on these six ketones indicated that the stereochemical purity of each was 92–96% and that **10a–12a** contained less than ~2% of the corresponding undeuteriated species **10c–12c**, respectively.

Results. Ketones **10a,b** and **12a,b** were irradiated (wavelength > 340 nm) in benzene solution (~0.01 M). Conversion to photoproducts was followed by gas chromatography, and loss of stereochemical integrity both in products and in recovered dienone was followed by proton NMR measurements at 500 MHz. Similar

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[13] Irradiation of 3,7-octadien-2-one produces 4,7-octadien-2-one: Wolff, S., unpublished observations in these laboratories.

[14] Crawford, R. J.; Lutener, S. B.; Cockcroft, R. D. *Can. J. Chem.* **1976**, *54*, 3364.

[15] We were able to improve this materially in the final step (hydroboration–protonolysis of **14**) through substitution of pentane for ether as solvent in the workup.

[16] House, H. O.; Lee, L. F. *J. Org. Chem.* **1976**, *41*, 863.

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

[18] Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1971; p 168.

[19] Mercuric chloride is used in this procedure, and we improved the yield of **20** from 73 to 95% by removal of mercury salts in the workup by filtration through sand under pressure using flash chromatographic equipment (Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923).

[20] Hanessian, S.; Lavallee, P. *Can. J. Chem.* **1975**, *53*, 2975.

[21] Similar cleavage in acetonitrile as solvent has been described recently: Mascareñas, J. L.; Mouriño, A.; Castedo, L. *J. Org. Chem.* **1986**, *51*, 1269.

[22] Bowers, A.; Halsall, T. G.; Jones, E. R. H. *J. Chem. Soc.* **1953**, 2548. Djerassi, C.; Engle, R. R.; Bowers, A. *J. Org. Chem.* **1956**, *21*, 1547.

[23] Coxon, J. M.; Hartshorn, M. P.; Swallow, W. H. *J. Org. Chem.* **1974**, *39*, 1142 and references therein.

[24] Salomon, R. G.; Coughlin, D. J.; Ghosh, S.; Zagorski, M. G. *J. Am. Chem. Soc.* **1982**, *104*, 998.

[25] Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

[26] An independent preparation of **25** is on record: Boaretto, A.; Marton, D.; Tagliavini, G.; Gambaro, A. *Inorg. Chim. Acta* **1983**, *77*, L196. The infrared spectrum of our sample compares well with bands reported in this earlier work.

[27] Gibson, T. W.; Erman, W. F. *J. Org. Chem.* **1972**, *37*, 1148.

Table I. Ratio of Rate of Reversion Process (k_r) to Rate of Photoconversion (k_p), Quantum Yields (Φ_p and Φ_r), and Remaining Absorbed Light (Φ_{dif}) for **10a,b–12a,b**

ketone	k_r/k_p	Φ_p[a]	Φ_r[b]	Φ_{dif}[c] $[1 - (\Phi_p + \Phi_r)]$
10a	0.75	0.26	0.20	0.54
10b	1.81	0.32	0.58	0.10
11a	2.53	0.0048	0.012	0.98
11b	9.30	0.0059	0.055	0.94
12a	0.00	0.16	0.00	0.84
12b	0.00	0.13	0.00	0.87

[a] Quantum yield for products. [b] Quantum yield for reversion. [c] Remaining absorbed light.

experiments with **11a,b** (0.005 M) were performed in the presence of 0.1 M *m*-methoxyacetophenone or propiophenone as triplet sensitizer, since direct irradiation of **11c** leads to hydrogen abstraction occurring from a singlet state rather than to photocycloaddition.[1b,17] In some cases the reactions could be followed by NMR directly; in others removal and separation of aliquots by gas chromatography (GC) were necessary in order to obtain the required data; details and data are reported in the Experimental Section. Results for **10a,b** and **11a,b** are given in Figure 1, where the increase in *E* isomer in recovered dienone is plotted against conversion for the early portion of the reaction, before scrambling of stereochemistry in the substrate is extensive. It is assumed in all cases that the GC detector response factors are identical for *Z* and *E* isomers of the starting material and for the isomeric photoproducts formed. Previous experience[1,3] with similar reactions suggests that this introduces an error no greater than 5%. It is also assumed that the only products formed are the volatile isomers seen by GC, and experience suggests that here the error is also small. The linear least-squares plot is shown for each ketone; the fit is good, suggesting that the assumptions noted are generally acceptable.[28] There was no scrambling (<1%) in recovered **12a** or **12b** throughout their irradiation to high conversion. From these results one can estimate the ratios k_r/k_p, since, on the supposition that biradical reversion is equally likely to yield the *Z* or *E* isomer of the substrate, k_r/k_p in each case is equal to twice the slope given in Figure 1; these ratios are recorded in Table I. The label is scrambled in the products from all six substrates; for the products obtained at low conversion from **10a–12a**, NMR spectra indicate that there is essentially complete loss of stereochemistry at the deuteriated carbon atom.

Products from **10c**,[1a] **11c**,[17] and **12c**,[1a,27,29] which are the unlabeled versions of the three deuteriated ketones, have already been characterized, as have the major products from **12b**.[27,30] Since **10c** yields four isomeric products,[1a] a complex mixture from irradiation of **10b** was anticipated. These products are all isomeric with **10b** and proved to be difficultly separable; we have characterized them only sufficiently to be certain that the cycloaddition is well behaved. Irradiation of **11b** furnished a mixture of **26** and **27** (85:15 by NMR) that was obtained analytically pure but could not be separated under any conditions tried. All these substrates furnish volatile photoproducts in 80–95% yield.

In view of the unique behavior of **12a,b**, where the biradical does not revert to starting ketone, and also recalling our earlier observation that in the related 5-methyl-1,5-hexadien-3-one (**28**) photocycloaddition could be neither sensitized nor quenched,[1c] we carried out sensitization and quenching studies on **12c**. Here the reaction is efficiently sensitized at >340 nm by propiophenone and at 313 nm by acetone. Although reaction of **12c** is unaffected by piperylene, it is ~25% quenched by neat 2,3-dimethyl-1,4-butadiene and follows Stern–Volmer kinetics[31] over the investigated range of 1.73–8.84 M (neat) quencher with $k_q\tau \sim 0.034$ M^{-1}. We conclude that cyclization of **12c** occurs from a quenchable triplet, just as is well established for other [2 + 2] photocycloadditions.[6,32]

We have also determined quantum yields (±~8%) for products (Φ_p) from these ketones. The results are included in Table I and were obtained for benzene solutions irradiated in a merry-go-round apparatus at ~313 nm (potassium chromate filter) with concurrent formation of acetophenone from valerophenone serving as a chemical actinometer.[33] For **11a,b** the reactions were sensitized by propiophenone, and concentrations of sensitizer and ketone was adjusted so that sensitizer singlets were not quenched, but all sensitizer triplets were quenched.[34] If these conditions are met, the quantum yields measured should be independent of ketone concentration; this was true over the fourfold range of concentration examined in each case. From Φ_p and k_r/k_p we calculate quantum yields for reversion (Φ_r), which are also shown. The remaining fraction of absorbed light not accounted for by product formation and biradical reversion $[1 - (\Phi_p + \Phi_r)]$ is recorded as Φ_{dif}.

Discussion. As is shown in Table I, Φ_p and Φ_r vary widely with structure in these ketones. For **11a,b** and **12a,b** other processes account for most of the light absorbed. This is not unexpected, and Scheme II shows two pathways that must be considered in this regard. The first is unimolecular decay of the triplet to ground-state ketone, which occurs through twisting about the conjugated double bond.[35,36] Irradiation of open chain dienones, including 1-acyl,[37] 2-acyl,[38] and 3-keto[27,39] hexadienes, frequently leads to cis–trans equilibration at the conjugated double bond faster than intramolecular cycloaddition. Double bond isomerization is an important path for dissipation of energy in these ketones, and this must account for much, if not all, of Φ_{dif} for **11a,b** and **12a,b**. Open-chain α,β-unsaturated carbonyl compounds typically fail to react intermolecularly with alkenes,[6] but acyclic substrates of all three types **1–3** undergo intramolecular photocycloaddition without difficulty.[40] Steric constraints on double bond isomerization are relatively unimportant here; twisting is rapid, and this leads to short-lived triplets that can be captured by olefins in cycloaddition only when the reaction is intramolecular. Unimolecular decay must also be an important pathway for disposing of the remaining light in cyclohexenones **10a,b** as there is good evidence for transient, photochemically formed, ground-state *trans*-cyclohexenes and related excited-state species.[7,41,42] Since triplet lifetimes of cyclohexenones are longer than those of open-chain alkenones,[42a] it is not surprising that intramolecular capture of the triplet is more efficient in **10a,b** than in the other two series.

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(28) The plots shown in Figure 1 were calculated with the origin fixed and all points weighted equally. The resulting slopes and their errors are **10a** (0.38 ± 0.01), **10b** (0.90 ± 0.04), **11a** (1.26 ± 0.08), and **11b** (4.65 ± 0.36).

(29) Bond, F. T.; Jones, H. L.; Scerbo, L. *Tetrahedron Lett.* 4685 (1965); *Org. Photochem. Synth.* **1971**, *1*, 33.

(30) In addition to the previously noted [2 + 2] products from **12b**, we found a small amount of the disproportionation product, 3-vinylcyclopentanone, which was identified from its published spectroscopic properties: Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *J. Org. Chem.* **1984**, *49*, 3938.

(31) Wagner, P. J. In *Creation and Detection of the Excited State*; Marcel Dekker: New York, 1971; Vol. 1, Part A, p 173.

(32) We also reinvestigated and confirmed our earlier report (ref 1c) concerning the absence of triplet quenching and sensitization in photocycloaddition of **28**.

(33) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.

(34) Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 906. Zimmerman, H. E.; Schissel, D. N. *J. Org. Chem.* **1986**, *51*, 196.

(35) Wagner, P. J.; Buchek, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 5090 and references cited therein.

(36) It is possible that direct double bond isomerization of the singlet in competition with intersystem crossing also plays a role here: Morrison, H.; Rodriquez, O. *J. Photochem.* **1974**, *3*, 471.

(37) Wolff, S.; Barany, F.; Agosta, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2378. See also ref 1a.

(38) Wolff, S., unpublished results in these laboratories.

(39) Wilson, P.; Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1985**, *26*, 5883.

(40) Numerous examples are given in ref 1 and references cited therein.

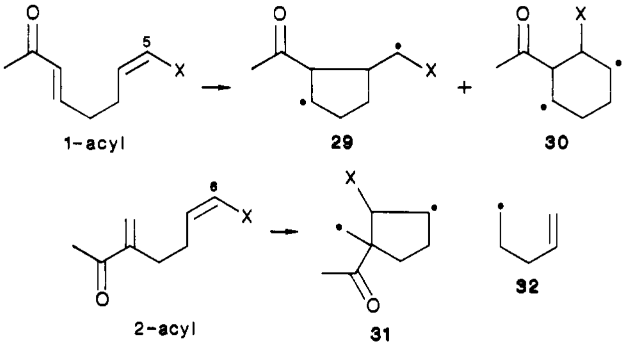
(41) Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 4329. Dauben, W. G.; van Riel, H. C. H. A.; Hauw, C.; Leroy, F.; Joussot-Dubien, J.; Bonneau, R. *Ibid.* **1979**, *101*, 1901. Dauben, W. G.; van Riel, H. C. H. A.; Robbins, J. D.; Wagner, G. J. *Ibid.* **1979**, *101*, 6383. Goodman, J. L.; Peters, K. S.; Misawa, H.; Caldwell, R. A. *Ibid.* **1986**, *108*, 6803. Bonneau, R. *J. Photochem.* **1987**, *36*, 311.

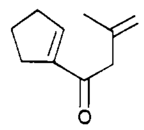
(42) (a) Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816. (b) Goldfarb, T. D. *J. Photochem.* **1978**, *8*, 29. Bonneau, R.; Fornier de Violet, P. *C. R. Acad. Sci.* **1977**, *284C*, 631.

Less is known about the second dissipative process given in Scheme II, which is decay of the exciplex formed between triplet enone and olefin to ground-state species. In their kinetic study of intermolecular cycloadditions Loutfy and Mayo specifically assumed without direct evidence that such decay was slow relative to conversion of the exciplex to biradical.[5] The role of exciplex decay in the photochemistry of **11** is mentioned below.

In discussing the remaining results we consider first **10a,b** and **11a,b**, deferring **12a,b** until later. In **10** and **11** the sum (Φ_p + Φ_r) increases by a factor of 2–3 on changing the C(6) substituent from hydrogen to methyl. For consistency with Scheme II, this implies one or both of two effects: methyl substitution leads to increased conversion of triplet enone (E*) to exciplex ([EA]*) and/or to decreased decay of exciplex to ground-state substrate (E+A). In the case of the well-documented exciplexes between alkenes and triplet carbonyl groups that lead to oxetanes, it is known that the rate of exciplex formation increases with decreasing ionization potential of the olefin.[43] Replacement of hydrogen by methyl in a terminal olefin lowers the ionization potential of the double bond ~0.5 eV,[44] and in the reaction of triplet butyrophenone with appropriate alkenes this change leads to an increase in the rate constant for quenching by a factor of 2–6.[43a] It is reasonable to assume a similar relationship in formation of the complexes postulated for **10** and **11**, so that the simplest interpretation of the noted increase in (Φ_p + Φ_r) is that it results from an increased rate of exciplex formation. This provides independent evidence for the intermediacy of an exciplex in these reactions of **10a,b** and **11a,b**.

We turn now to the biradical reversion itself and its implications. As noted in the introduction, there is good evidence that 1-acyl hexadienes undergo initial 1,6 and 1,5 (as opposed to 2,6) closure, 2-acyl hexadienes do not close 1,6, and there is suggestive evidence that 2-acyl hexadienes undergo initial 2,6 (as opposed to 1,5) closure.[1,45] The present work shows that the regiochemical differences between these two series are not attributable to some qualitative difference in behavior of the two types of biradical. If we accept the site of initial bonding in biradical formation just described as established, a simple explanation is available for the regiochemical behavior and relative quantum yields of the 1- and 2-acyl systems. In both systems initial bonding is preferentially to C(α) of the enone. In 1-acyl systems 1,5 bonding leads to **29**. If there is a substituent at C(5), the steric factors important in cyclization of 5-alkyl-5-hexenyl radicals (**8**)[2] will favor 1,6 closure to **30** as well. Since reversion occurs readily, C(5) substitution should also enhance 1,6 closure through stabilization of the resulting radical center at C(5). In contrast, for the 2-acyl system initial bonding at C(α) implies only 2,6 closure to **31**, since the alternative 2,5 bonding would lead to a cyclobutane. Another specific characteristic of the 2-acyl series is that Φ_p is relatively low.[1b] The data in Table I show that this is not merely because k_r/k_p is large; also, there is no reason to suppose that unusually short triplet lifetimes are responsible, since the lifetimes of triplet **11a,b** probably are not much different from those of **12a,b**.[42a] Furthermore, we have previously reported Φ_p for ketones **33**–**35**, which differ only in the placement of the carbonyl group and also show this effect: **33** (0.59), **34** (0.34), and **35** (0.055).[1a,b] It is instructive to compare these characteristics of the 2-acyl system with the thermal behavior of 4-pentenyl radical (**32**). Cyclization of **32** to cyclobutylmethyl is endothermic and not observed; closure of **32** to cyclopentyl is kinetically disfavored on stereoelectronic grounds and also fails to occur.[2b] These properties of **32** provide an attractive explanation for the low Φ_p's of 2-acyl hexadienes, since the steric and stereoelectronic factors disfavoring cyclization of **32** could also disfavor collapse of the exciplex to a biradical. This implies that some alternative reaction pathway for this exciplex must be available. In terms of Scheme I, this requires exciplex decay (or exciplex reversal, which is generally thought not to occur[5]) at a rate competitive with the disfavored collapse to biradical.[46] In the 2-acyl series Φ_p's are sufficiently low that exciplex decay can be significant here but still relatively unimportant, as has been presumed in the past,[5] in systems with Φ_p's of a few tenths.[47] These conclusions suggest that heptadienes can differ from hexadienes in the site of initial bonding as well as other aspects of their photochemistry, since Becker has concluded[11] that the 1-acyl heptadienes **9** and **9Z** close initially at C(β). There is also evidence, however, that some other 1-acyl heptadienes first close at C(α).[3]

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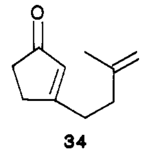
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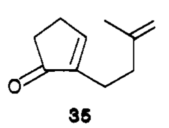
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We consider briefly possible mechanisms of scrambling of stereochemistry of the label in **10** and **11**. Biradical **29** permits scrambling of the label (X = D or CH_3) in substrate and products through inversion and rotation at the radical center prior to biradical reversion or collapse. The situation is somewhat more complicated with **30** and **31**. Here scrambling of the label on reversion results from conformational mobility of the ring. There are two conformations in which orbital overlap of the radical centers and the cleaving C(2)–C(6) bond are favorable, each leading to a different geometry about the C(5)–C(6) double bond in returned substrate. This is illustrated for **36**, which is one of the diastereomers of **31** (X = D). The two relevant half-chair conformations of **36** are **37** and **38**, which should cleave selectively to *E* (**17**) and *Z* (**11a**) dienones, respectively. Scrambling in products, however, results from formation of the two diastereomers

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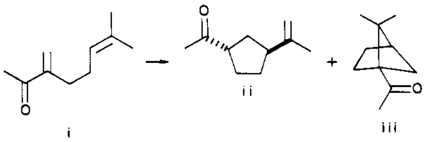
(43) (a) Kochevar, I.; Wagner, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 5742; **1972**, *94*, 3859. (b) Caldwell, R. A.; Sovocool, G. W.; Gajewski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549.

(44) Demeo, D. A.; El-Sayed, M. A. *J. Chem. Phys.* **1970**, *52*, 2622.

(45) The present results add to the evidence favoring 2,6 closure, for the alternative now is that both 1-acyl and 2-acyl systems close 1,5 with reversion, but only the 1-acyl series responds to the steric effect of alkyl substitution at C(5).

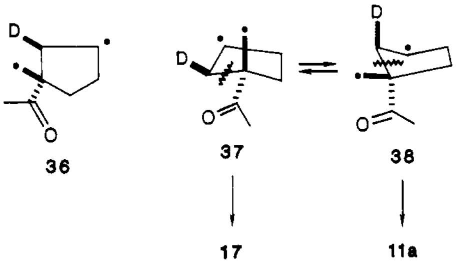
(46) The alternative explanation that formation of the exciplex rather than its conversion to biradical is retarded by the factors preventing cyclization of **32** would require that formation of the new covalent bond present in the biradical be well advanced in the exciplex.

(47) Exceptions to this proposed general rule of closure on the α carbon atom will be favored by appropriate structural features. Minor disproportionation products (≤5%) resulting from initial 2,6 bonding in 1-acylhexadienes have been noted previously (ref 1a), and the conversion of i to ii (~15%) and iii (~5%) provides an example of preferential 1,5 bonding in a 2-acyl hexadiene. Apparently, the *gem*-dimethyl substitution retards 2,6 closure and stabilizes the radical center at C(6) resulting from 1,5 closure sufficiently to favor the latter mode of cyclization. It is noteworthy that the yield of volatile products from i is abnormally low and that the reaction gives mostly polymer (unpublished work in these laboratories).



(48) It may well be significant that the trienes corresponding to **12b**, (*Z*)- and (*E*)-2-methylene-1,5-heptadiene, show this same behavior on sensitized photocyclization to *endo*- and *exo*-5-methyl-2-methylenebicyclo[2.1.1]hexane (ref 12b).

(49) Wolff, S.; Huecas, M. E.; Agosta, W. C. *J. Org. Chem.* **1982**, *47*, 4358.



of **30** and **31**, with X either cis or trans to the acyl group, in initial C(1)–C(6) or C(2)–C(6) bonding, respectively. Collapse of each of these then furnishes a different diastereomeric product, as, for example, **26** and **27** from **11b**.

The qualitative problem now remaining concerns the third class of ketones. The 3-keto dienes are set apart from the two systems just considered by three notable differences. First, there is no measurable scrambling of label in recovered starting **12a,b** even at high photochemical conversion, although the stereochemical integrity of the label is lost in products. This is consistent with formation of a biradical that does not revert but whose lifetime permits inversion and rotation at the radical center (as for **29**) before collapse.[48] Second, since 3-keto systems also close 1,6 and 1,5 (as opposed to 2,6), initial cyclization occurs specifically at C(β) of the enone.[1a] Third, on methyl substitution at C(6), Φ_p decreases rather than increases, contrary to expectation if an exciplex is involved. At present no explanation for these observations is available, but the results at hand for the 3-keto hexadienes do not fit well with the steps of Scheme II. We note that, unlike the other two classes, the structural relationship between enone and isolated olefin here has no counterpart in typical intermolecular [2 + 2] cycloadditions, since the carbonyl group is located between the two reacting double bonds. Just how this influences the photochemical reaction remains to be understood. Besides the reduced entropy of cyclization due to an additional sp^2 center in the chain, one possible consequence is that this location permits participation of the carbonyl group π electrons in the interaction of the two carbon–carbon double bonds.

Conclusion. It appears that the photochemistry of 1-acyl (**1**) and 2-acyl (**2**) hexadienes is quite similar up to formation of the biradical intermediate. There is evidence that each follows the mechanism outlined in Scheme II, with initial bonding at C(α) of the enone, and in our interpretation the significant effect of the acyl group is to determine whether C(α) is C(1) or C(2). This bonding requirement appears to control subsequent events and to lead to the observed differences between the two series, including the role of substituents on the C(5)–C(6) double bond, the regiochemistry of the reaction, and quantum yields for products. The 3-keto hexadienes (**3**), on the other hand, seem to follow a different pathway. This involves initial bonding at C(β), which is C(1). Subsequent events are again determined by this bonding requirement, with the result that substituent effects, regiochemistry, and quantum yields for 3-keto hexadienes resemble those of the 1-acyl series, which also closes on C(1).

Experimental Section

General Procedures. For preparative reactions procedures were as previously described.[3] Preparative GC employed the following 0.25-in. columns, all of which were prepared with Chromosorb W 45/60: (A) 0.6 m, 25% QF-1, (B) 2 m, 25% QF-1, (C) 3 m, 25% Carbowax 20 M, (D) 1.2 m, 25% Carbowax 20 M.

(*Z*)-4-Chloro-1-butene-*1*-d_1 (13). Hydroboration of chlorobutyne **14** was carried out as previously reported[14] on a 18.3-g scale. Workup was performed with solutions cooled to 0 °C and pentane as solvent. When pentane recovered from a previous run was used as solvent the yield of **13** was 11.0 g (60%), bp 74–76 °C.

(*Z*)-3-(3-Butenyl-*4*-d_1)cyclohex-2-en-1-one (10a). Magnesium (500 mg) was covered with 3 mL of THF, 100 μL of 1,2-dibromoethane was added, and the flask was immersed in an oil bath (60 °C). After the ethylene evolution had stopped, a solution of 905 mg (10 mmol) of chlorobutene **13** and 300 μL of 1,2-dibromoethane in 5 mL of THF was added dropwise, and the mixture was stirred 45 min at 60 °C. Then 1.4 g (10 mmol) 3-ethoxy-2-cyclohexenone in 7 mL of THF was added, and the resulting solution was heated at reflux for 30 min. After cooling at room temperature the mixture was quenched with ice–aqueous NH_4Cl and worked up with ether. The crude product was dissolved in 14 mL of methanol, and 1.4 mL of saturated oxalic acid solution was added. After 1.5 h at room temperature $NaHCO_3$ and 40 mL of H_2O were added, and the mixture was extracted three times with pentane; the organic extracts were washed with $NaHCO_3$ and brine and dried over $MgSO_4$, and the solvent was evaporated.

Distillation (0.2 Torr) afforded 904.3 mg of **10a** (60%), bp 95–97 °C. For **10a**: NMR (300 MHz, $CDCl_3$) δ 5.89 (s, 1 H, CO—CH=), 5.77 (m, 1 H, C*H*=CHD), 4.98 (d, J = 10.5 Hz, =C*H*D), 2.5–2.2 (m, 8 H, C*H*$_2$), 2.0 (m, 2 H, C*H*$_2$-CH$_2$-CO); NMR (500 MHz, C_6D_6) δ 5.88 (s, 1 H, CO—CH=) 5.53 (m, 1 H, C*H*=CHD), 4.89 (d, J = 10.1 Hz, 1 H, =C*H*D), 2.10 (t, J = 7.1 Hz, 2 H, C*H*$_2$-CO), 1.84 (m, 2 H, C*H*$_2$—CH=CHD), 1.75 (m, 2 H, C*H*$_2$—CH$_2$—CH=CHD) 1.55 (m, 2 H, C*H*$_2$—CH= ring), 1.41 (m, 2 H, C*H*$_2$—CH$_2$—CH= ring). These data are compatible with those for **10c**[1a] and indicate that labeling of **10a** is ~96% stereospecific and ~98% complete.

(*Z*)-3-(3-Pentenyl)cyclohex-2-en-1-one (10b). To a solution of the Grignard reagent, prepared from Mg (1.30 g, 53.4 mg-atom) and (*Z*)-1-bromo-3-pentene (6.37 g, 42.8 mmol) in ether (35 mL), was added 3-ethoxycyclohex-2-en-1-one (5.61 g, 40 mmol) following the method described previously.[1a] The crude alcohol (7.165 g) was treated with saturated oxalic acid (5 mL) in MeOH (50 mL) for 2 h. Standard workup gave a residue which was distilled to give **10b** (4.335 g, 66%), bp 86–89 °C (1 Torr). Further purification was achieved by GC (column D, 190 °C): IR 3070 (m), 2950 (s), 1675 (s), 1627 (m), 1250 (m), 1190 (m), 885 (m) cm^{-1}; NMR (300 MHz) δ 5.88 (s, 1 H), 5.55–5.32 (m, 2 H), 2.38–2.26 (m, 7 H), 2.03–1.97 (m, 2 H), 1.61 (dd, J = 1.5, 6.7 Hz, 3 H), 1.367 (m, 1 H). Anal. ($C_{11}H_{16}O$) C, H.

Ethyl 2-(3-Butenyl-*4*-d_1)acetoacetate (15). A mixture of **13** (11.0 g), NaI (19.8 g), and acetone (145 mL) was heated at reflux overnight. After filtration of NaCl and removal of acetone the residue was distilled to yield 13.0 g (59%) of the corresponding iodide, bp 95–98 °C (240 Torr). This (12.8 g) was used directly to prepared **15** according to the known procedure for the unlabeled ester;[16] yield 7.35 g (58%). IR and NMR spectra were as published,[16] except for the expected differences due to deuteriation.

(*Z*)-3-Methylene-6-hepten-2-one-*7*-d_1 (11a). According to the published procedure[1b] the above 7.35 g (40 mmol) of **15** was converted to the ethylene ketal, reduced with lithium aluminum hydride, and deketalized with ether and 5% aqueous H_2SO_4. The crude ketol **16** was formed in essentially quantitative yield. It was converted to the corresponding tosylate (95%) with tosyl chloride in pyridine,[1b] and this was directly eliminated with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in ether at −8 °C as described for closely related cases[49] to yield **11a** in 62% yield. This was purified by flash chromatography[50] at 0 °C. A sample of **11c** prepared by this route had the same properties as previously reported.[17] For **11a**: NMR (300 MHz) δ 6.02 (s, 1 H), 5.81–5.74 (m) with s at 5.77 (2 H), 4.95 (d, J = 10.2 Hz, 1 H), 2.36 (m, 2 H), 2.33 (s, 3 H), 2.18 (m, 2 H). The data are compatible with those of **11c** and indicate that labeling of **11a** is ~96% stereospecific and ~98% complete.

(*Z*)-3-Methylene-6-octen-2-one (11b). By way of published procedures,[17] ethyl acetoacetate (3.824 g, 29.4 mmol) was treated with (*Z*)-1-bromo-3-pentene (4.92 g, 33 mmol) to give the alkylated ester (2.378 g, 41%), bp 67–70 °C (1 mmHg): IR 3050 (m), 2995 (s), 2950 (s), 1750 (s), 1727 (s), 1455 (m), 1365 (m), 1245 (s), 1155 (s) cm^{-1}; NMR (60 MHz) δ 5.73–5.07 (m, 2 H), 4.16 (q, J = 7 Hz, 2 H), 3.27 (t, J = 7 Hz, 1 H), 2.15 (s, 3 H), 1.97 (m, 4 H), 1.58 (br d, J = 6 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H); MS, m/z 198.1301 (M$^+$, calcd for $C_{11}H_{18}O_3$, 198.1255). The keto ester (2.38 g) was ketalized with ethylene glycol, reduced with $LiAlH_4$, and deketalized with 5% H_2SO_4 to give the ketol (1.78 g, 99%): IR 3475 (br s), 3035 (m), 2950 (s), 1700 (s), 1350 (m), 1160 (m), 1040 (s) cm^{-1}; NMR (60 MHz) 5.58–5.05 (m, 2 H), 3.62 (br d, J = 6.5 Hz, 2 H), 3.33 (br, 1 H), 2.67 (br t, J = 6.5 Hz, 1 H), 2.18 (s, 3 H), 2.00–1.1 (m, with br d at 1.59, J = 5 Hz, 7 H). Treatment of the ketol with *p*-toluenesulfonyl chloride in pyridine, overnight at 0 °C, then for 3 h at 100 °C, gave, after bulb-to-bulb distillation (115–130 °C, 10 Torr), **11b** (1.114 g, 71%): IR 3120 (w), 3035 (m), 2940 (s), 1677 (s), 1625 (w), 1430 (m), 1355 (s), 827 (s) cm^{-1}; NMR (300 MHz) δ 5.93 (s, 1 H), 5.70 (s, 1 H), 5.44–5.24 (m, 2 H), 2.31–2.08 (m, with s at 2.27, 7 H), 1.57 (d, J = 5.8 Hz, 3 H). Anal. ($C_9H_{14}O$) C, H.

(*E*)-3-Methylene-6-hepten-2-one-*7*-d_1 (17). Following the procedure noted above for preparation of **11a**, keto ester **18** (6.54 g, 36.7 mmol)[17a] was ketalized and reduced with lithium aluminum hydride (overall 93%). The crude hydroxy ketal was converted to the tosylate[1b] and treated with DBN as noted above to furnish **19** (75%). For **19**: NMR (60 MHz) δ 5.3 (s, 1 H), 4.9 (s, 1 H), 3.8 (m, 4 H), 2.3 (br, 4 H), 1.8 (m, 1 H), 1.4 (s, 3 H). On a 0.94-mmol scale this was subjected directly to hydroboration and treatment with acetic acid-*O*-*d* as previously described.[14] Deketalization as above with ether–sulfuric acid then yielded **17** (29%

Table II. Photochemical Conversion and Stereochemical Scrambling in **10a,b–11a,b**

ketone	time, min	conversion, %	increase in *E* isomer, %
10a	4.0	2.7	0.4
	8.0	4.2	1.8
	12.0	8.3	2.8
	16.0	9.5	3.5
	20.0	12.3	5.3
	25.0	15.1	5.9
	30.0	16.9	5.9
10b	2.0	3.0	3.1
	4.0	6.0	4.4
	6.0	9.1	9.4
	8.0	12.4	11.8
	10.0	16.0	13.6
11a	90.0	2.8	1.7
	120.0	4.1	5.2
	180.0	6.2	11.2
	240.0	12.2	13.8
	360.0	17.4	22.2
11b	0.0	0.0	0.0[a]
	22.0	0.0	0.0[a]
	30.0	0.4	2.1
	40.0	0.9	3.4
	50.0	1.5	7.6
	60.0	1.8	10.4
	70.0	2.4	9.5

[a] Reaction of **11b** reproducibly showed an induction period of approximately this length.

from **19**). For **17**: NMR (300 MHz) δ 6.02 (s, 1 H), 5.83–5.72 (m, with t, J = 1.0 Hz, at 5.77, 2 H), 4.99 (dt, J = 17.3, 3.2 Hz, 1 H), 2.37 (m, 3 H), 2.34 (s, 3 H), 2.18 (m, 2 H).

1-Hexen-5-yn-3-ol (20). This was prepared following Brandsma's procedure[18] on a 300-mmol scale. After hydrolysis of the reaction mixture with aqueous NH_4Cl, the two-phase system was filtered through 5 cm of sand with use of flash chromatographic equipment.[19] The column was washed with methanol and the filtrate transferred to a separatory funnel. The phases were separated, and the aqueous phase was extracted six times with ether. The organic phases were combined and dried over $MgSO_4$, and ether was removed through a Vigreux column. The residue was distilled to yield 27.5 g (95%) of **20**, bp 76 °C (40 Torr).

(*Z*)-1,5-Hexadien-3-one-*6-d*$_1$ (12a). By a published procedure[20] **20** (5.02 g, 52.2 mmol) was converted to the *tert*-butyldiphenylsilyl ether on treatment with the silyl chloride in DMF (30 mL) containing imidazole (2.81 g), yield ~100%. A solution of ethylmagnesium bromide, prepared from Mg (3.7 g, 0.15 g-atom) and ethyl bromide (8.25 g, 75.7 mmol) in THF (35 mL), was added dropwise to a solution of this crude silyl ether (17.0 g, 50.5 mmol) in THF (30 mL). The resulting mixture was heated at reflux for 5 h, D_2O (4 mL) was then added, the mixture was stirred 5 min and then worked up with aqueous NH_4Cl and ether. This yielded 16.71 g (98%) of deuteriated silyl ether, whose NMR spectrum had lost the absorption at δ 1.9 (t, J = 2 Hz, 1 H) present in the starting material.

This material was subjected to hydroboration–protonolysis[14] to furnish **21** (yield 15 g, 89%). The silyl ether (3.36 g) was dissolved in THF (100 mL) and treated with 40% aqueous HF (70 mL); the mixture was stirred at room temperature overnight, cooled to −30 °C, and treated dropwise with KOH (112 g) in water (150 mL). The slightly basic mixture was extracted with ether (6×), the extracts were dried ($MgSO_4$), and part of the solvent was removed through a Vigreux column (bath temperature <70 °C). The remaining solution (~100 mL) was diluted with pentane (30 mL) and then treated with Jones's reagent[22] (5 mL). Over 45 min the mixture was allowed to warm to 5 °C with stirring. It was worked up in the usual way after destruction of excess oxidant at −10 °C with 2-propanol. Ether was removed through a Vigreux column as above and **12a** was separated from THF and purified by GC on column A at 55 °C, yield 630 mg. For **12a**: NMR (500 MHz, C_6D_6) δ 6.01 (dd, J = 17.6, 10.6 Hz, 1 H), 5.87 (m, 1 H), 5.79 (dd, J = 17.6, 1.2 Hz, 1 H), 5.15 (dd, J = 10.6, 1.2 Hz, 1 H), 4.97 (dt, J = 10.2, 1.3 Hz, 1 H), 2.8 (br, 2 H). These values agree well with those of **12c** prepared either by this route or by the previously published method[29] and indicated that deuteriation was ~96% stereospecific and ~98% complete.

(*Z*)-1,5-Heptadien-3-one (12b). A solution of (*Z*)-3-penten-1-ol (2.584 g, 30 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of pyridinium chlorochromate (75 mmol) in CH_2Cl_2 (70 mL) according to the method of Corey and Suggs.[25] After being stirred for 2.5 h, the reaction mixture was diluted with pentane (300 mL), centrifuged, and filtered through a small column of Florisil. The filtrate was added directly to an excess of vinylmagnesium bromide in THF (40 mL of a 1.0 M solution), and the mixture was diluted with ether (100 mL). Standard workup yielded an oil which was purified by flash chromatography[50] to yield **25** (0.53 g, 16%): IR 3615 (m), 3400 (br), 3070 (w), 3020 (s), 1212 (s), 1017 (m), 982 (s), 920 (s) cm^{-1}; NMR (300 MHz) δ 5.81 (ddd, J = 5.9, 10.7, 16.9 Hz, 1 H), 5.52 (m, 1 H), 5.35 (m, 1 H), 5.15 (m, 1 H), 5.03 (d, J = 10.4 Hz, 1 H), 4.03 (m, 1 H), 2.38 (s, 1 H), 2.23 (br, 2 H), 1.62 (d, J = 6.7 Hz, 3 H). A solution of **25** (0.50 g) in pentane (12 mL) and acetone (12 mL) was cooled to −10 °C and treated with Jones's reagent[22] (2 mL). The mixture was stirred for 10 min at −10 °C and for 20 min at 0 °C before excess oxidant was destroyed by the addition of 2-propanol. Standard extraction workup yielded a residue which was purified by GC on column B (85 °C) to give **12b**, whose spectral properties were comparable to those reported.[27]

Procedures for Photolyses. Ketones **10a,b** and **12a,b**, 0.01–0.08 M in degassed benzene (or C_6D_6) solution, were irradiated in a Rayonet apparatus with 350-nm lamps and water cooling or alternatively with a 450-W medium-pressure mercury-arc lamp through uranium glass (wavelength >340 nm). Ketones **11a,b**, 0.005 M in benzene containing 0.1 M propiophenone (for **11a**) or *m*-methoxyacetophenone (for **11b**), were irradiated in the Rayonet apparatus. For **10a,b** and **11a,b** conversion to products was followed, and separation of samples of recovered starting material was carried out, by GC on column B (**10a**, **11a,b**) or C (**10b**). The degree of scrambling in recovered starting material was then measured by NMR integration of the appropriate C(6) hydrogen (**10a** and **11a**) or methyl (**11b**) signals. For **10b** the degree of scrambling was determined directly by GC, since **10b** and its *E* isomer separate under the conditions used. For **12a,b** both conversion and stereochemistry of starting ketone were monitored by NMR measurements directly on the reaction mixture in C_6D_6. Integration of the appropriate C(6) signals in unreacted **12a,b** indicated no measurable loss of stereochemistry, even at >50% conversion; an estimated ~1% of the *E* isomer would have been detected. Results from the NMR and GC measurements for **10a,b** and **11a,b** are given in Table II and Figure 1. Examination of NMR spectra of products at low conversion (≤10%) indicated that the C(6) label was scrambled in all cases; for **10a–12a** the extent of scrambling was ~50%.

Acknowledgment. We thank the National Science Foundation for support of this research, the Deutscher Akademischer Austauschdienst for a postdoctoral NATO Science Fellowship to C.S., Laura Mieszerski for technical assistance, and Francis Picart, Susan Meyer, and Julie Wu for 500-MHz NMR spectra, which were determined on a spectrometer purchased with funds from the National Science Foundation, the National Institutes of Health, and the Keck Foundation.

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(50) Reference in footnote 19.