Table II. In Vitro Antitumor Assay of Alkylidene Cyclopentenediones **7** and **8** Compared with Cisplatin and Mitomycin C (IC_{50}, μg/mL)

cell line	cisplatin	mitomycin C	7	8
murine melanoma	7.7	2.5	15.1	11.1
human colon (HCT-116)	4.5	0.50	15.2	15.0
human nasopharyngyl	2.6	0.69	18.6	6.4
human colon (Moser)	6.3	2.2	15.2	17.4
murine lung	7.0	0.75	14.4	17.0
human colon (RCA)			12.5	13.2

lower yields attributed to the sensitivity of the very reactive alkylidene cyclopentenedione core. In some cases small amounts of the corresponding benzoquinone were also isolated. One trend was noted from the data in Table I—alkynes with electron-withdrawing groups attached gave poorer yields of alkylidene cyclopentenediones compared to the other alkynes.

A brief survey was made of the stereoselectivity of the reaction with respect to the geometry of the alkylidene double bond substituents and the substituents on the cyclopentenedione ring. Cationic maleoylcobalt complex **5b**, prepared analogously to **5a** (eq 3 and 4), was treated with 1-hexyne and cyclohexylacetylene to provide the cyclopentenediones shown in Table I, entries 9 and 10. In every case the reaction product proved to be a 1:1 mixture of double bond stereoisomers.

Alkylidene cyclopentenediones have been prepared previously by aldol dehydration and related sequences applied to cyclopentenediones[6] and by rearrangement of alkylidene furanones,[7] and an interesting zwitterionic route from an unsaturated ketene was recently disclosed.[8] The present method is rationalized by coordination of the alkyne to the cationic cobalt of complex **5** in place of the readily lost MeCN ligand. For reasons poorly understood at present, reaction of the alkyne-coordinated complex to give quinone must be slowed significantly for the PPh_3-ligated series **4** relative to the pyridine-ligated complexes **3**. Retardation of the quinone formation allows the slower terminal alkyne to vinylidene tautomerization to proceed, leading to the observed alkylidene cyclopentenedione products.

There has been some interest in the biological properties of alkylidene and arylidene cyclopentenediones with examples of antitumor[9] and anticoagulant[10] properties noted for the latter and fungicidal and bactericidal[11] properties noted for the former. Since the 5-alkylidene-cyclopent-2-ene-1,4-dione ring is very similar to the 5-alkylidene-4-hydroxycyclopent-2-enone core found in a number of very potent antitumor antibiotics of current interest (clavulones (claviridenones),[12] chlorovulones,[13] punaglandins[14]), two of the alkylidene cyclopentenediones of Table I were submitted for in vitro assay of cytotoxicity against six tumor cell lines.[15] The IC_{50} data for 5-pentylidene-2,3-dimethylcyclopent-2-ene-1,4-dione (**7**) and 5-(4-chlorobutylidene)-2,3-dimethylcyclopent-2-ene-1,4-dione (**8**) are shown in Table II with results for the clinically useful anticancer drugs cisplatin and mitomycin C given for comparison. Although subsequent in vivo testing of the two alkylidene cyclopentenediones showed no activity, the cytotoxicity results suggest that further assay of simple structures related to alkylidene cyclopentenediones could provide interesting biological leads.

Acknowledgment. This investigation was supported by PHS Grant No. CA-40157 awarded by the National Cancer Institute, DHHS. The effort of Dr. Suresh Iyer on some aspects of this project is gratefully acknowledged.

Supplementary Material Available: Experimental procedures consisting of the preparation of the cobalt complexes and reactions of the maleoylcobalt complexes **5a** and **5b** with terminal alkynes (13 pages). Ordering information is given on any current masthead page.

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Remarkable Enantioselective 1,4-Addition Reactions of Chiral Allylphosphonyl Anions (Ambident Nucleophiles) with Cyclic Enones (Ambident Electrophiles)

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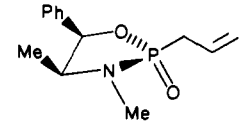
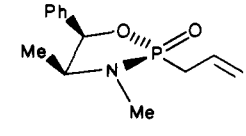
Despite the enormous amount of work on organophosphorus compounds,[1] relatively few studies have concerned asymmetric induction reactions involving chiral substrates of the phosphine oxide type.[2] In the course of our studies on asymmetric induction reactions involving allylic anions with enones,[3] we found that chiral allylphosphonyl anions of **1** and **2** undergo good enantioselective



1



2

(1) (a) *Methoden der Organischen Chemie. Organische Phosphorverbindungen II*; Regitz, M., Ed.; Stuttgart: New York, 1982. (b) Quin, L. D. *The Heterocyclic Chemistry of Phosphorus*; John Wiley & Sons: New York, 1981. (c) Trippette, S., Ed.; *Organophosphorus Chemistry*; The Chemical Society: Burlington House, London, Vol. 1-14.

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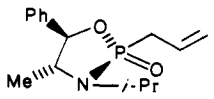
1,4-addition with cyclic enones of varying size;[4] however, replacing the methyl group at nitrogen of **1** with isopropyl group, i.e., anion of **3**, provides remarkable enantioselectivity in these reactions.



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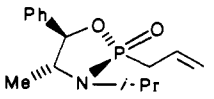
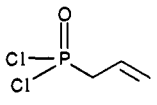


4

Chiral allyl sulfoxides undergo racemization at the sulfur atom via a reversible [2,3]-sigmatropic process;[5] hence, chiral allyl phosphine oxides were investigated. For the sake of simplicity and because of its ability to complex with the lithium counterion we chose allylphospholidines **1** and **2** as our initial substrates.

Treatment of allylphosphonyl dichloride (**5**)[6] with 1 equiv of (−)-ephedrine (**6**) and 2 equiv of Et_3N in toluene (g/8 mL) at −40 °C for 1 h and 25 °C for 12 h gave 90% yield of (2*S*,4*S*,5*R*)-2-allyl-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine 2-oxide (**1**)[7] (solid; mp 64–65 °C) and diastereomeric (2*R*)-**2** (oil) in a ratio of 1:1. Phospholidines **1** and **2** were separated



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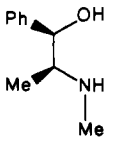
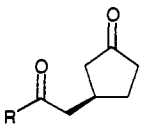
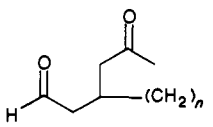


6

by column chromatography (ΔR_f 0.15; ethyl acetate). The configurations at phosphorus were assigned from the chemical shifts of the H-4 and H-5 signals in the ^1H NMR spectra.[8] The H-4 and H-5 resonate at lower field in **1** than in **2**; thus, the P=O group must be cis to H-4 and H-5 in **1**. Reaction of the phosphonylallyl anion of **1** (**1** and 1 equiv of *n*-BuLi in THF at −78 °C) and 2-cyclopentenone in THF at −78 °C for 30 min provided 80% yield of 1,4-γ-adduct **10** (entry 1, Table I). The absolute configuration at the newly formed stereogenic center of adduct **10** was determined by converting **10** to the known acid, (+)-(*R*)-3-oxocyclopentylacetic acid (**21*R***).[3,9] Ozonolysis of **10** in

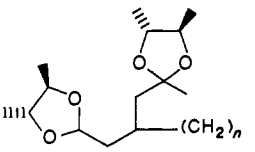


20*S*, R = H
21*R*, R = OH



22, *n* = 3
23, *n* = 4

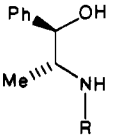
CH_2Cl_2 at −78 °C (80% yield) followed by oxidation of the resulting aldehyde **20*S*** with $AgNO_3$–KOH–H_2O–EtOH at 25 °C provided (+)-**21*R*** (90% yield). Treatment of aldehyde **20** with 3 equiv of (−)-(2*R*,3*R*)-2,3-butanediol and 0.05 equiv of *p*-toluenesulfonic acid in benzene under reflux produced bisdioxolane **24**. The optical purity (% ee) of **20** was measured from the ^{13}C NMR spectrum of **24**, the chemical shifts of the two diastereomers



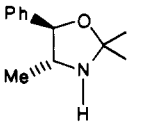
24, *n* = 2
25, *n* = 3
26, *n* = 4

being different. Table I summarizes the reactions of various cyclic enones with the anions derived from allylphospholidines. The optical yields of the products from the reactions of **1** and **2** are good (70–74% ee) but could be improved remarkably when phospholidine **3** was used.

In the transition state of these 1,4-addition reactions of lithiated phosphonylallyl anions with enones, chelation of the lithium ion with the O=P—N side can be avoided if the nitrogen of **1** possesses a bulky alkyl group. Hence, the better working model (1*R*,2*R*)-(−)-α-(1-isopropylaminoethyl)benzyl alcohol (**27**), $[\alpha]_D^{22°}$



27, R = *i*-Pr
28, R = H



29

= −129° (*c* 1.0; CH_2Cl_2), was investigated. The C-4 methyl group of **3** is anti to the C-5 phenyl and N-3 isopropyl groups. This structure provides the most stable oxazaphospholidine ring. Amine (−)-**27** was prepared by treating (1*R*,2*R*)-(−)-norpseudoephedrine hydrochloride (**28**)[10] with acetone–NaOAc–HOAc–H_2O–$NaBH_4$ at 0 °C[11] to provide oxazolidine **29** and amine **27** in a ratio of 9:1 (92% yield). Reduction of this crude mixture with $LiAlH_4$ in ether at 25 °C for 30 min gave 85% overall yield of pure (−)-**27**.[12] By the same procedure used for the preparation of **1** and **2**, phospholidinones **3** (solid; mp 55–57 °C, 45% yield) and **4** (oil, 45% yield) were synthesized and separated. Table I summarizes the respective reactions of the anions of **3** and **4** with 2-cyclopentenone, 2-cyclohexenone, and 2-cycloheptenone. Phospholidine **4** afforded poor diastereofacial selection; 1,4-γ-adducts (**15** and **16**) and 1,2-α-adducts (minor products) were formed in the reactions with 2-cyclohexenone and with 2-cycloheptenone (entries 6 and 7). However, **3**, the diastereomer of **4**, provided excellent optically pure 1,4-γ-adducts (88–98% ee; entries 8–10). It should be noted that the sulfinylallyl anion derived from (*R*)-*p*-tolyl allyl sulfoxide[3a] reacted with 2-cycloheptenone, to produce 1,2-γ-adduct as the major product. Only the 1,4-γ-adducts were obtained in reactions of **3** and cyclic enones.

The optical purities of all 1,4-γ-adducts (Table I) were determined from ^{13}C NMR spectra of the bisdioxolane derivatives of the corresponding δ-keto aldehydes as mentioned above. Similar to the sulfinylallyl anions the trans-W configuration (O=P—C—C—C) of the anion from **3** approaches enones from the si face.[3,4c] The 1,2-α-adducts formed, only in the reactions of **4** (entries 6 and 7), as minor products. The absolute configuration and optical purity of these adducts were not determined. However, ^{13}C NMR spectra of these adducts indicate two diastereomers.

This remarkable regio- and enantioselective (88–98% ee) 1,4-addition reactions of allyl phospholidine **3** with cyclic enones of

(4) The reactions of the carbanions of the allyldiphenylphosphine oxides with cyclopentenone have been reported. (a) Haynes, R. K.; Vonwiller, S. C. *J. Chem. Soc., Chem. Commun.* **1987**, 92. (b) Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *Tetrahedron Lett.* **1985**, *26*, 1565. (c) Binns, M. R.; Chai, O. L.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *Ibid.* **1985**, *26*, 1569. Reactions of phosphonylallyl anions with aldehydes and ketones: (d) Corey, E. J.; Cane, D. E. *J. Org. Chem.* **1969**, *34*, 3053.

(5) (a) Bickart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869. (b) Hoffmann, R. W. *Organic Sulfur Chemistry*; Freidlina, R. K., Skorova, A. E., Eds.; Pergamon Press: New York, 1981; p 69. (c) Evans, D. A.; Andrews, G. A. *Acc. Chem. Res.* **1974**, 147.

(6) Kinnear, A. M.; Perren, E. A. *J. Chem. Soc.* **1952**, 3437.

(7) All enantiomers are depicted with the absolute stereochemistry indicated. All new compounds displayed satisfactory ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{31}P NMR (160 MHz), UV, IR, and low-resolution mass spectra and satisfactory elemental analysis.

(8) (a) Cooper, D. B.; Hall, C. R.; Harrison, J. M.; Inch, T. D. *J. Chem. Soc., Perkin Trans.* **1977**, *1*, 1969. (b) Hall, C. R.; Inch, T. D.; Williams, N. E. *J. Chem. Soc., Perkin Trans.* **1982**, 639.

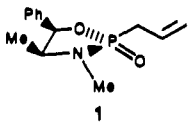
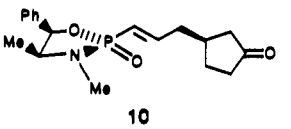
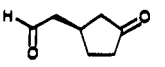
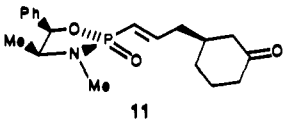
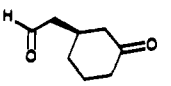
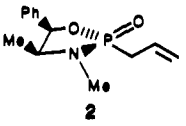
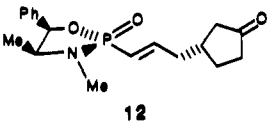
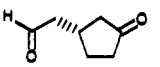
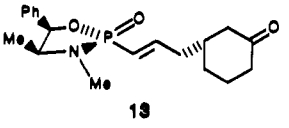
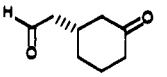
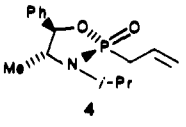
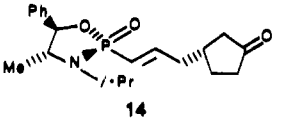
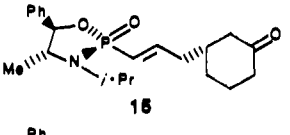
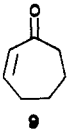
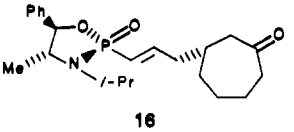
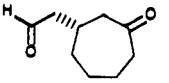
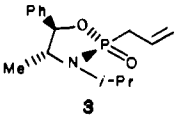
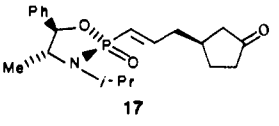
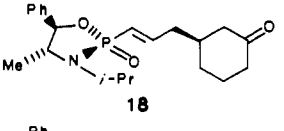
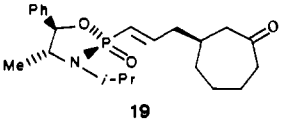
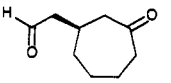
(9) Kuritani, H.; Takaoka, Y.; Shingu, K. *J. Org. Chem.* **1979**, *44*, 452.

(10) (−)-Ephedrine (**6**) and (−)-norpseudoephedrine hydrochloride (**28**) were purchased from Aldrich Chemical Company, Milwaukee, WI.

(11) Schellenberg, K. A. *J. Org. Chem.* **1963**, *28*, 3259. The reported method was modified to provide optimal yield; the procedure will be published in a full paper.

(12) Racemic **27** has been prepared by hydride reduction of the corresponding α-amino ketone: Baudet, M.; Gelbcke, M. *Anal. Lett.* **1979**, *12(B4)*, 325 and references cited therein. The optically active form has not been reported.

Table I. Asymmetric Additions of Allylphosphonyl Anions to α,β-Unsaturated Cyclic Enones

entry	phospholidine	enone	1,4-γ-adduct	% yield	aldehyde	% yield	$[\alpha]_D^{22}$, deg[a]	opt yield[b] % ee
1	 1	 7	 10	80	 20S	81	+105	70
2	1	 8	 11	82	 22S	82	+12	74
3	 2	7	 12	82	 20R	80	−111	74
4	2	8	 13	83	 22R	82	−11.7	73
5	 4	7	 14	75	20R	86	−42	28
6	4	8	 15	62[c]	22R	78	−4.6	28
7	4	 9	 16	45[c]	 23R	75	−43.6	64
8	 3	7	 17	79	20S	80	+148	98
9	3	8	 18	70	22S	82	+14.3	88
10	3	9	 19	71	 23S	81	+56	95

[a] c 1.0, CH_2Cl_2. [b] Optical yields were determined from ^{13}C NMR spectra of the corresponding bisdioxolane derivatives **24**, **25**, and **26** of the aldehydes **20**, **22**, and **23**. [c] The 1,2-α-adducts were also isolated (15% in entry 6 and 5% in entry 7), and the absolute configuration and optical purity were not determined. ^{13}C NMR spectra of these 1,2-α-adducts indicate two diastereomers.

various ring sizes complement and advance the related chemistry explored with sulfinylallyl anions.[3] Utilization of these reactions in natural product synthesis is apparent, since the resulting α,β-unsaturated phosphonates can be manipulated via the conjugate addition with organometallic reagents[13] followed by the Wittig reaction of the resulting phosphorus-stabilized carbanions.[14] The chiral β-hydroxyamine **27** may find application in as chiral ligands for asymmetric catalysis,[15] asymmetric olefination and alkylation,[2b] and as chiral reducing agents.[16]

Acknowledgment. We gratefully acknowledge the financial support from the National Science Foundation (CHE-8419265) and the National Institute of General Medical Sciences (GM36336). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support. We also thank the NSF for a grant for the purchase of the Perkin-Elmer 241 polarimeter.

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Supplementary Material Available: ^1H and ^{13}C NMR data for compounds **1–4**, **10–27**, and **29**, and experimental procedures of the reaction of **3** and **7** and ozonolysis of the 1,4-γ-adduct **17** (11 pages). Ordering information is given on any current masthead page.

Direct Observation of Photochemical Cleavage of a Cyclopropylalkoxycarbene to an Alkyne

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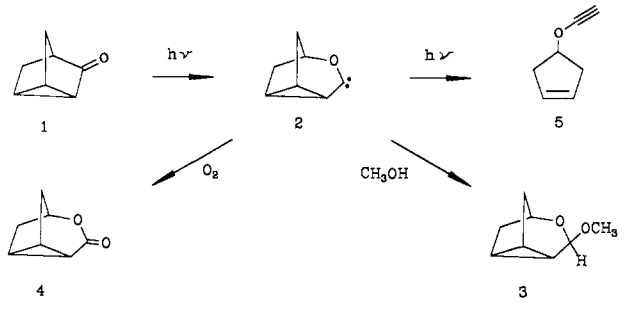
Alkoxycarbenes have drawn considerable interest in their relation to carbonyl photochemistry.[2] For example, the parent, hydroxymethylene, has been the subject of numerous theoretical studies vis-a-vis formaldehyde photochemistry.[3] Moreover, synthetic applications of photochemical carbonyl ring expansions to alkoxycarbenes have begun to appear.[4] We have recently published low-temperature spectroscopic investigations of methoxychlorocarbene[5] and phenoxychlorocarbene.[6] In these cases, however, the influence of the halogen on the spectroscopic and photochemical properties of the carbenes could not be easily separated from the oxygen perturbation of primary interest. We now wish to report the spectroscopic characterization of a nonhalogenated alkoxycarbene and its novel photochemistry.

Yates[2,7] has shown that irradiation of nortricyclanone (**1**) in solution gives products attributable to carbene **2**. For example, irradiation of **1** in MeOH solution gives acetal **3** and in the



1 2 5 4 3

presence of O_2 gives lactone **4**. We have now found that irradiation (285 nm) of tricyclic ketone **1**, in an N_2 matrix at 20 K, leads to slow disappearance of the starting IR absorptions and the growth of new bands (Figure 1).[8] Subsequent broad-band irradiation (>270 nm) destroys a number of the new bands (labeled C), with concomitant growth in others (labeled A). Starting

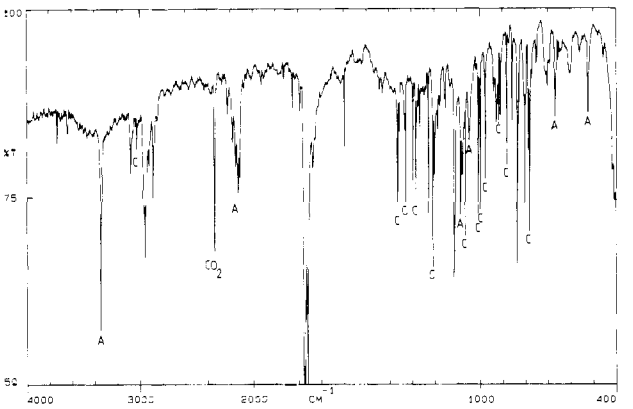
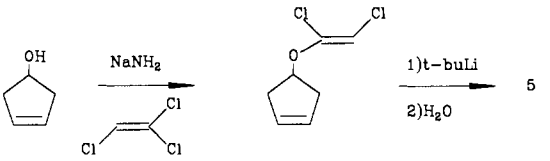


Figure 1. IR spectrum obtained on irradiation of N_2 matrix isolated **1** (1:800, 20 K) for 45 h at 285 ± 18 nm. Bands labeled C are assigned to carbene **2**, and those labeled A are assigned to acetylene **5**. Unlabeled bands are due to residual **1**.

material is also observed to grow on broad-band photolysis. Unfortunately, the combination of the slow photolysis of **1** and the photolability of the initial photoproduct limits the obtainable intensity of the intermediate. A UV spectrum obtained on the same matrix indicates a broad band, with λ_{max} at 396 nm, growing and disappearing with the initial photoproduct IR bands.

The observed photochemistry and the IR and UV spectra suggest that the initially formed intermediate C in the matrix photolysis of **1** is alkoxycarbene **2**. Trapping experiments confirm this. Irradiation (285 nm) of a 50-K 3-methylpentane matrix containing **1** and MeOH (3-mp:MeOH:**1** = 20:5:1) generated the same products as in the N_2 experiments above, along with new IR bands identical with those of independently prepared acetal **3**. Warming the matrix to 90 K caused the disappearance of the bands due to **2** and the growth of the bands of **3**.

The strong IR band at 3350 cm^{-1} hints that the major photoproduct of carbene **2** contains a terminal acetylene (A in Figure 1). Absorptions at ca. 2200 and 670 cm^{-1} support this assignment. Alkyne **5** was independently synthesized from cyclopent-1-en-3-ol as shown below, and was shown to be identical with the photoproduct.[9]



It is interesting to note the carbene IR absorptions in the region of 1300 cm^{-1} for **2**. We have previously found that oxymethylenes exhibit anomalously high-energy C–O stretches near these frequencies.[5,6] We have attributed the associated unusual force constants to partial C–O double-bond character as predicted theoretically.[5b] Methylene scissoring deformations can also come at these frequencies, however, and this region in the IR is fairly complicated. The IR spectrum of ^{18}O labeled **2**, generated from the corresponding ketone, indicates that the band at 1369 cm^{-1} is a predominantly C–O stretch with an isotopic shift of 17 cm^{-1}.[10] Quinkert[11] has suggested that transient absorptions observed at ca. 360 nm in the irradiations of cyclobutanones in low-temperature glasses were attributable to the corresponding cyclic oxacarbenes. Although the absorption maximum observed for **2** is at somewhat lower energy, the difference might arise from conjugation with the adjacent cyclopropane. It should be noted that in the case of Quinkert,[11] however, no additional evidence sup-

(1) Fellow of the Alfred P. Sloan Foundation, 1986–1988. Address correspondence to this author at the University of Nevada.

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(8) For general matrix isolation conditions and description of apparatus see ref 5b. Irradiations were performed with a Baush and Lomb monochromator or with appropriate cut-off filters. The IR spectra were obtained on a Beckman 4250 spectrometer interfaced with an IBM XT computer for data storage and manipulation.

(9) Compound **5**: ^1H NMR (200 MHz, $CDCl_3$) 5.7 (br s, 2 H), 4.85 (t of t, 1 H, J = 5.1, 3.3 Hz), 2.68 (br s, 4 H), 1.52 (s, 1 H) ppm; IR (Ar, 10 K) 3350, 2145, 2140, 1195, 1115, 925, 695, 670, 605, 525 cm^{-1}.

(10) Labeled **1** was produced by hydrolysis of the corresponding ethylene glycol ketal with $H_2O(^{18}O)$.

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