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Base-Catalyzed Endo-Mode Cyclization of Allenes: Easy Preparation of Five- to Nine-Membered Oxacycles

Chisato Mukai,* Masaru Ohta, Haruhisa Yamashita, and Shinji Kitagaki

Division of Pharmaceutical Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

cmukai@kenroku.kanazawa-u.ac.jp

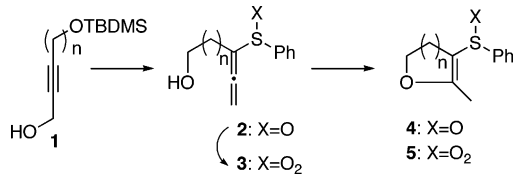
Received July 6, 2004

A reliable and efficient procedure for constructing five- to eight-membered oxacycles has been developed. Allenes with both a phosphoryl group and a suitable δ-hydroxyalkyl side chain at the C_1-position underwent an endo mode ring-closing reaction to give five- to seven-membered oxacycles. Changing the phosphoryl group to a phosphono functionality facilitated the preparation of eight-membered congeners. Introduction of a *cis* double bond to the alkyl side chain of the starting allenes made possible the easy formation of medium-sized oxacycles, such as the dihydrooxocin and tetrahydrooxonin frameworks, regardless of the electron-withdrawing group ($POPh_2$, $PO(OEt)_2$, SOPh, and SO_2Ph) at the C_1-position.

Introduction

Various kinds of oxacycles have been shown to be the major component of many biologically important natural products.[1] In a previous paper,[2] we reported a novel and efficient method for the preparation of five- to seven-membered oxacycles **4** ($n = 1-3$) from propargyl alcohol derivatives **1** ($n = 1-3$) (Scheme 1). This procedure involves the known [2,3]-sigmatropic rearrangement of the propargyl alcohol with benzenesulfenyl chloride (PhSCl),[3] followed by the novel base-catalyzed endo-mode ring closure of the resulting allenyl sulfoxides **2** ($n = 1-3$).[4] However, the ring-closing reaction of **2** ($n = 4$) under the standard basic conditions, leading to the construction of eight-membered oxacycles **4** ($n = 4$), was unsuccessful. To overcome this drawback, the sulfonyl functionality, which was anticipated to increase the reactivity of the allenyl moiety as a formal Michael acceptor, was used as an electron-withdrawing group for this endo-mode ring-closing reaction. Thus, the allenyl sulfone derivatives **3** ($n = 1-4$), prepared by oxidation of the allenyl sulfoxides **2** ($n = 1-4$), were subjected to basic conditions resulting in the formation of the five- to eight-membered oxacycles **5** ($n = 1-4$) in high yields.[5]

SCHEME 1



A similar protocol using phosphorus reagents[6] instead of PhSCl would provide oxacycles with a phosphoryl or a phosphono functionality, which should be very useful for further manipulations if the endo-mode ring-closing reaction proceeded as anticipated.[7,8] In addition, several natural products possess a monocyclic eight- or nine-membered oxacycle as a core framework with an internal double bond.[1] Therefore, it would be interesting to investigate the synthesis of medium-sized oxacycles with an internal double bond by applying the newly developed endo-mode ring-closing reaction of allenes. Thus, our endeavors were directed toward (i) the examination of the ring-closing reaction of allenylphosphine oxides as well as allenylphosphonate derivatives and (ii) the preparation of eight- and nine-membered oxacycles with an internal double bond (dihydrooxocin and tetrahydrooxonin, respectively).

* To whom correspondence should be addressed. Tel: +81-76-234-4411. Fax: +81-76-234-4410.

(1) (a) Moore, R. E. In *Marine Natural Products: Chemical and Biological Perspectives*; Scheuer, P. J., Ed.; Academic Press: New York, 1978; Vol. 1, pp 43−124. (b) Faulkner, D. J. *Nat. Prod. Rep.* **1986**, *3*, 1−33. (c) Yasumoto, T.; Murata, M. *Chem. Rev.* **1993**, *93*, 1897−1909. (d) Faulkner, D. J. *Nat. Prod. Rep.* **1996**, *13*, 75−125.

(2) Mukai, C.; Yamashita, H.; Hanaoka, M. *Org. Lett.* **2001**, *3*, 3385−3387.

(3) Horner, L.; Binder, V. *Liebigs Ann. Chem.* **1972**, *757*, 33−68.

(4) Parsons reported an exo-mode ring-closing reaction of allenyl sulfoxide derivatives; see: (a) Pairaudeau, G.; Parsons, P. J.; Underwood, J. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1718−1720. (b) Gray, M.; Parsons, P. J.; Neary, A. P. *Synlett* **1992**, 597−598. (c) Gray, M.; Parsons, P. J.; Neary, A. P. *Synlett* **1993**, 281−282. (d) Parsons, P. J.; Stefinovic, M. *Synlett* **1993**, 931−932. (e) Edwards, N.; Macritchie, J. A.; Parsons, P. J.; Drew, M. G. B.; Jahans, A. W. *Tetrahedron* **1997**, *53*, 12651−12660.

(5) Dai described an exo-mode cyclization of the allenyl sulfone derivatives resulting in a formation of the five-membered oxacycles: Dai, W.-M.; Lee, M. Y. H. *Tetrahedron* **1998**, *54*, 12497−12512.

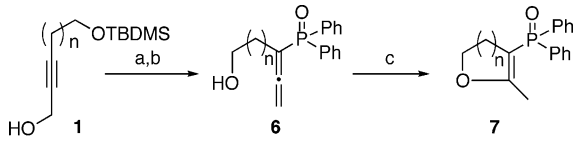
(6) (a) Nicolaou, K. C.; Maligres, P.; Shin, J.; de Leon, E.; Rideout, D. *J. Am. Chem. Soc.* **1990**, *112*, 7825−7826. (b) Curtin, M. L.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 5278−5287.

(7) A similar endo-mode ring-closing reaction of trisubstituted allenylphosphine oxides, leading to the dihydrofuran skeleton, has been reported: Pravia, K.; White, R.; Fodda, R.; Maynard, D. F. *J. Org. Chem.* **1996**, *61*, 6031−6032.

(8) Brel reported an exo-mode cyclization of the allenylphosphonate derivatives leading to a furan framework: Brel, V. K. *Synthesis* **2001**, 1539−1545.

10.1021/jo0488614 CCC: $27.50
Published on Web 09/04/2004

TABLE 1. Ring Closure of 6[a]

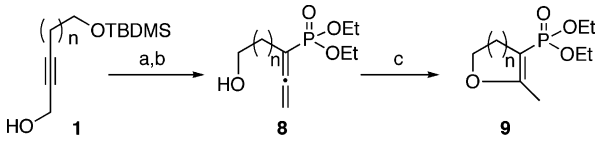


a: n=1, **b**: n=2, **c**: n=3, **d**: n=4

entry	*n*	product	yield (%)	product	yield (%)
1	1	**6a**	82	**7a**	81
2	2	**6b**	71	**7b**	89
3	3	**6c**	70	**7c**	78
4	4	**6d**	74	*b*	

[a] Reaction conditions: (a) Ph_2PCl, Et_3N, THF, −78 °C; (b) PPTS, MeOH, rt; (c) tBuOK, ^{t}BuOH, 30 °C. [b] The reaction mixture was heated at 60 °C, and 2-octyne-1,8-diol was obtained in 63% yield.

TABLE 2. Ring Closure of 8[a]



a: n=1, **b**: n=2, **c**: n=3, **d**: n=4

entry	*n*	product	yield (%)	product	yield (%)
1	1	**8a**	81	**9a**	98
2	2	**8b**	77	**9b**	71
3	3	**8c**	83	**9c**	94
4	4	**8d**	76	**9d**	81[d]

[a] Reaction conditions: (a) $(EtO)_2PCl$, Et_3N, $CHCl_3$, reflux; (b) PPTS, MeOH, rt; (c) ^{t}BuOK, ^{t}BuOH, 30 °C; (d) the reaction mixture was heated at 60 °C. When the reaction was carried out at rt, **9d** was obtained in 75% yield.

Results and Discussion

The known propargyl alcohol **1**[2] was treated with chlorodiphenylphosphine (Ph_2PCl) in THF at −78 °C in the presence of Et_3N to give the corresponding allenylphosphine oxides with a siloxy group, which were subsequently exposed to PPTS in MeOH at room temperature to give **6** (Table 1). Treatment of **6a** with ^{t}BuOK in ^{t}BuOH at 30 °C for 10 min (the previously optimized conditions for allenyl sulfoxides **2**[2]) effected endo-mode ring closure to produce the dihydrofuran derivative **7a** in 81% yield (entry 1). The dihydropyran and tetrahydrooxepin frameworks **7b** and **7c** were also constructed under similar conditions in acceptable yields (89% and 78%, respectively) (entries 2 and 3). However, exposure of **6d** ($n = 4$) to standard basic conditions led to complete recovery of the starting material. Heating the reaction mixture at 60 °C furnished 2-octyne-1,8-diol[2] in 63% yield, which was presumably formed through the retro [2,3]-sigmatropic rearrangement of **6d**, followed by hydrolysis.[9] Thus, the endo-mode ring-closing reaction of allenylphosphine oxides **6** could be used to prepare five- to seven-membered oxacycles, but not medium-sized oxacycles.

We next investigated the ring-closing reaction of phosphonate derivatives **8**. According to the procedure described for the conversion of **1** to **6**, propargyl alcohol **1a** was treated with chlorodiethoxyphosphine [$(EtO)_2PCl$] in THF at room temperature. However, no reaction took place and **1a** was completely recovered intact. After several reaction conditions were screened, $CHCl_3$ was found to be a suitable solvent for this transformation. Thus, a solution of **1a** and $(EtO)_2PCl$ in $CHCl_3$ was refluxed for 1 h to give, after desilylation, **8a** in 81% yield. Similarly, **8b**−**d** were prepared in acceptable yields (Table 2). Exposure of **8a** to ^{t}BuOK at 30 °C for 10 min produced the ring-closed product **9a** in 98% yield (entry 1). The six- and seven-membered oxacycles **9b** and **9c** were also formed through an endo-mode process from the corresponding allenylphosphonates **8b** and **8c** (entries 2 and 3). Furthermore, the endo-mode ring-closing reaction of **8d** proceeded at 30 °C for 6 h to give the eight-membered oxacycle **9d** in 75% yield. The reaction time (6 h) was significantly shortened with heating at 60 °C (20 min) to give **9d** in 81% yield (entry 4). Interestingly, consecutive retro-[2,3]-sigmatropic rearrangement and hydrolysis, which occurred with the allenylphosphine oxide **6d**, was not observed even at 60 °C. These results indicate that the endo-mode ring-closing reaction of the allenylphosphonates **8** could be used to prepare five- to eight-membered oxacycles.

To summarize the present and previous results,[2] the behavior of allenyl sulfoxides **2** under endo-mode ring-closing conditions is quite similar to that of allenylphosphine oxides **6**, resulting in the formation of five- to seven-membered oxacycles. These procedures were not suitable for the construction of medium-sized oxacycles. In contrast to these results, both the starting allenyl sulfone **3** and the allenylphosphonates **8** were easily transformed into five- to eight-membered oxacycles.

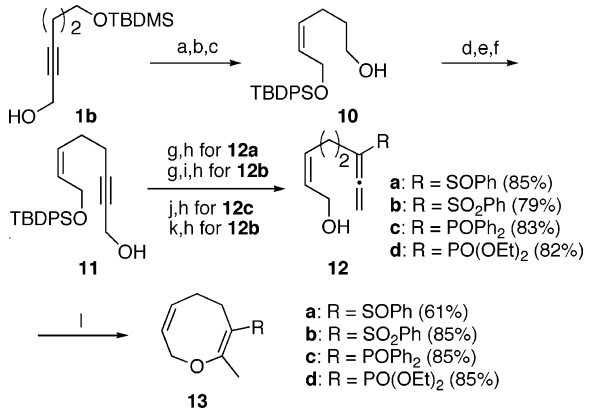
The next phase of this program involved the application of the endo-mode ring-closing reaction to the construction of medium-sized oxacycles with an additional double bond, such as the dihydrooxocin and tetrahydrooxonin frameworks. The starting allenes **12** were prepared as follows. Hydrogenation of compound **1b** with nickel boride (Ni_2B)[10] gave the allyl alcohol derivative which was subsequently treated with TBDPSCl and PPTS to afford **10**[11] in 81% overall yield. Oxidation of **10** was followed by dibromoolefination and treatment with base to leave the acetylide,[12] which was quenched by paraformaldehyde to furnish **11** in 73% yield. Upon exposure to PhSCl at −78 °C, **11** underwent the formation of sulfenic ester and [2,3]-sigmatropic rearrangement to give, after desilylation, **12a** in 85% yield. A similar protocol with Ph_2PCl and $(EtO)_2PCl$ instead of PhSCl provided **12c** (83%) and **12d** (82%), respectively. In the preparation of the sulfonyl derivative **12b**, the resulting sulfoxide, derived from the reaction of **11** with PhSCl, was oxidized with $(NH_4)_6Mo_7O_{24}/H_2O_2$[13] and then desilylated to give **12b** in 79% yield.

With the desired four allyl alcohol derivatives **12** in hand, the ring-closing reaction was then carried out. According to the standard basic conditions, **12a** was

(9) A similar result was observed when the corresponding allenyl sulfoxide **2** ($n = 4$) was exposed to ^{t}BuOK in ^{t}BuOH at 60 °C.

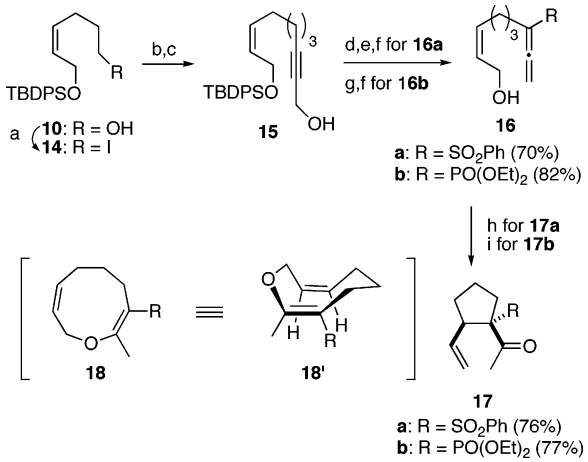
(10) Brown, C. A.; Ahuja, V. K. *J. Org. Chem.* **1973**, *38*, 2226−2230.
(11) Hayashi, N.; Noguchi, H.; Tsuboi, S. *Tetrahedron* **2000**, *56*, 7123−7137.
(12) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769−3772.
(13) Schultz, H. S.; Freyermuth, H. B.; Buc, S. R. *J. Org. Chem.* **1963**, *28*, 1140−1142.

SCHEME 2[a]



[a] Reaction conditions: (a) $Ni(OAc)_2$, H_2, $NaBH_4$, $H_2N(CH_2)_2NH_2$, NaOH, EtOH, rt; (b) TBDPSCl, imid, DMF, 0 °C to rt; (c) PPTS, MeOH−THF (1:1), rt, (81%); (d) SO_3·Py, DMSO, Et_3N, CH_2Cl_2, 0 °C to rt; (e) PPh_3, CBr_4, CH_2Cl_2, −20 °C; (f) ^{n}BuLi, $(HCHO)_n$, THF, −78 °C to rt, (73%); (g) PhSCl, Et_3N, THF, −78 °C; (h) 10% HCl, MeOH, rt; (i) H_2O_2, $(NH_4)_6Mo_7O_{24}$·$4H_2O$, EtOH, 0 °C; (j) Ph_2PCl, Et_3N, THF, −78 °C; (k) $(EtO)_2PCl$, Et_3N, $CHCl_3$, reflux; (l) ^{t}BuOK, ^{t}BuOH, 30 °C.

SCHEME 3[a]



[a] Reaction conditions: (a) PPh_3, I_2, imid, 0 °C to rt, (quant); (b) THF−DMPU, LiC≡$CCH_2OTBDMS$, −78 °C to rt; (c) PPTS, MeOH−THF (1:1), rt, (61%); (d) PhSCl, Et_3N, THF, −78 °C; (e) H_2O_2, $(NH_4)_6Mo_7O_{24}$·$4H_2O$, EtOH, 0 °C; (f) 10% HCl, MeOH, rt; (g) $(EtO)_2PCl$, Et_3N, $CHCl_3$, reflux; (h) ^{t}BuOK, ^{t}BuOH, 30 °C; (i) ^{t}BuOK, ^{t}BuOH, 60 °C.

treated with ^{t}BuOK in ^{t}BuOH at 30 °C to give the 5,6-dihydro-2*H*-oxocin **13a** in 61% yield. Similar treatment of **12c** produced **13c** in 85% yield. These results are in contrast to those observed in the ring-closing reaction of sulfoxides **2** and phosphine oxides **6**, in which the eight-membered products were not detected. The sulfonyl and phosphonate derivatives **12b** and **12d** provided the corresponding dihydrooxocin derivatives **13b** and **13d** in high yields, as expected. Thus, the introduction of a *cis* double bond to the starting allenes facilitated the formation of an eight-membered oxacyclic ring system via the endo-mode ring closure.

Based on the observations in Scheme 2, we expected that we could readily obtain the 4,5,6,9-tetrahydrooxonin skeleton (nine-membered oxacycle). Thus, the starting allenyl sulfone **16a** and allenylphosphonate **16b** with an allyl alcohol moiety were prepared by conventional means (Scheme 3). Treatment of **16b** with ^{t}BuOK in ^{t}BuOH at 30 °C gradually produced the new product,[14] but the reaction rate was too slow for the starting material to disappear completely. When the reaction mixture was heated at 60 °C, the starting material completely disappeared and the unexpected cyclopentane derivative **17b**[15] was obtained in 77% yield instead of the expected tetrahydrooxonin **18** (R = $PO(OEt)_2$). Molecular model considerations of compound **18** provided clues to better understand the production of the cyclopentane skeleton. The formation of **17b** from **16b** could be interpreted in terms of the initial formation of the 4,5,6,9-tetrahydrooxonin **18** (R = $PO(OEt)_2$) via the endo-mode ring-closing reaction, which would spontaneously undergo thermal [3,3]-sigmatropic rearrangement[16] (see conformer **18′**), resulting in the exclusive formation of the cyclopentane framework. Upon exposure to ^{t}BuOK in ^{t}BuOH at 30 °C, **16a** underwent a similar consecutive ring-closing reaction and the thermal [3,3]-sigmatropic rearrangement to give **17a**[15] in 76% yield.

To prevent an unfavorable [3,3]-sigmatropic rearrangement of the resulting 4,5,6,9-tetrahydrooxonin skeleton, we focused on preparing 2,3,6,7-tetratahydrooxonins. The Wittig reaction of the aldehyde **19**[17] with the alkylidenetriphenylphosphorane,[18] derived from **20**, was followed by desilylation to give **21** in 83% yield. Introduction of a hydroxymethyl group at the triple bond terminus was realized by exposure of **21** to ^{n}BuLi and paraformaldehyde to give **22** in 93% yield. According to the procedure described for the preparation of allenes **12** from **11** in Scheme 2, compound **22** was subjected to [2,3]-sigmatropic rearrangement with a proper reagent to produce, after deprotection, the corresponding allenes **23** in good yields. The standard basic conditions (^{t}BuOK in ^{t}BuOH at 30 °C) effected the rapid endo-mode ring closure of the sulfoxide derivative **23a** to furnish 2,3,6,7-tetrahydro-9-methyl-8-phenylsulfinyloxonin (**24a**) in 71% yield as a single isomer. Similarly, treatment of **23c** and **23d** with ^{t}BuOK produced the corresponding nine-membered oxacyclic frameworks **24c** and **24d**, respectively, in acceptable yields (Scheme 4). In the case of the sulfonyl derivative **24b**, the endo-mode ring-closing reaction proceeded as expected to furnish the ring-closed products in 66% yield as a mixture of **24b** and its isomer **24b′** with an *exo*-methylene moiety in a ratio of ca. 2:1.[19] This result was different from those observed in the ring-closing

(14) The newly formed product was identified as **17b**.

(15) The stereochemistry of compound **17** was undetermined. On the basis of molecular model considerations, we tentatively assumed that the relative stereochemistry between the acetyl and vinyl groups was cis.

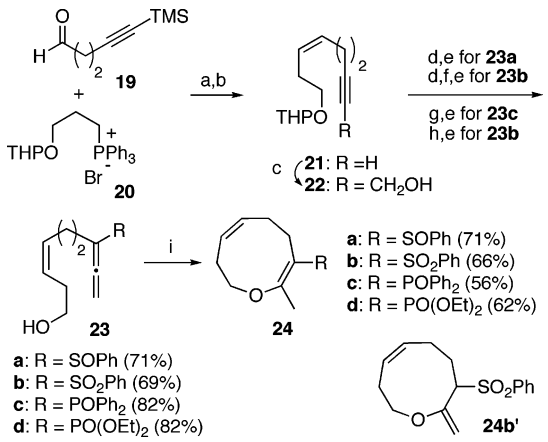
(16) For [3,3]-sigmatropic rearrangement of the acyclic vinyl ether derivatives, which have an allyl moiety with an electron-withdrawing group, see: (a) Cookson, R. C.; Gopalan, R. *J. Chem. Soc., Chem. Commun.* **1978**, 608. (b) Denmark, S. E.; Harmata, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 4972−4974. (c) Denmark, S. E.; Marlin, J. E. *J. Org. Chem.* **1991**, *56*, 1003−1013.

(17) Staab, H. A.; Meissner, U. E.; Weinacht, W.; Gensler, A. *Chem. Ber.* **1979**, *112*, 3895−3906.

(18) Schow, S. R.; McMorris, T. C. *J. Org. Chem.* **1979**, *44*, 3760−3765.

(19) Both isomers **24b** and **24b′** could be isolated by chromatography. Compounds **24b** and **24b′** were independently exposed to the ring-closing conditions to give a similar mixture of **24b** and **24b′** in a ratio of ca. 2:1.

SCHEME 4[a]



[a] Reaction conditions: (a) KHMDS, THF, −78 °C; (b) K_2CO_3, MeOH, rt, (83%); (c) ^{n}BuLi, $(HCHO)_n$, THF, −78 °C to rt, (93%); (d) PhSCl, Et_3N, THF, −78 °C; (e) *p*-TsOH, MeOH, rt; (f) H_2O_2, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, EtOH, 0 °C; (g) Ph_2PCl, Et_3N, THF, −78 °C; (h) $(EtO)_2PCl$, Et_3N, $CHCl_3$, reflux; (i) ^{t}BuOK, ^{t}BuOH, 30 or 60 °C.

reaction of **23a**,**c**,**d**, in which ring-closed products **24a**,**c**,**d** possessing an endo-olefin moiety were isolated as a sole isolable product. Thus, a new procedure for constructing the 2,3,6,7-tetrahydrooxonin skeleton was developed via the endo-mode ring-closing reaction of allenes.

In summary, we have developed a reliable and efficient procedure for constructing various types of oxacycles via an endo-mode ring-closing reaction. Allenyl sulfoxide and allenylphosphine oxide derivatives gave five- to seven-membered oxacycles. On the other hand, allenyl sulfone and allenylphosphonate congeners produced the corresponding five- to eight-membered oxacycles. In addition, the introduction of a *cis* double bond to the alkyl side chain of the starting allenes made possible the easy formation of medium-sized oxacycles with an additional double bond, such as the dihydrooxocin and tetrahydrooxonin frameworks, regardless of the electron-withdrawing group at the C_1-position of the starting allenes. The application of this simple and efficient method to the synthesis of bioactive compounds is now in progress.

Experimental Section

3-(Diphenylphosphinyl)-3,4-pentadien-1-ol (6a). To a solution of 5-(*tert*-butyldimethylsiloxy)-2-pentyn-1-ol (**1a**) (215 mg, 1.00 mmol) and Et_3N (0.42 mL, 3.1 mmol) in THF (10 mL) was gradually added a solution of chlorodiphenylphosphine (663 mg, 3.00 mmol) in THF (1.0 mL) at −78 °C. After being stirred for 30 min at the same temperature, the reaction was quenched by addition of water, and the resulting mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of the crude product in MeOH (10 mL) was added PPTS (25 mg, 0.10 mmol) at room temperature, and the mixture was stirred overnight. MeOH was evaporated off, and the residue was taken up in AcOEt, which was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with AcOEt gave **6a** (235 mg, 82%) as colorless needles: mp 107.5−108 °C (hexane−AcOEt); IR 3337, 1965, 1935 cm^{-1}; ^1H NMR δ 7.79−7.70 (4H, m), 7.58−7.42 (6H, m), 4.68 (2H, dt, J = 11.2, 2.3 Hz), 3.80 (2H, t, J = 5.3 Hz), 2.59−2.48 (2H, m); ^{13}C NMR (acetone-d_6) δ 211.6 (J_{C-P} = 7.3 Hz), 133.0 (J_{C-P} = 104.9 Hz), 132.7 (J_{C-P} = 2.4 Hz), 132.4 (J_{C-P} = 8.5 Hz), 129.2 (J_{C-P} = 12.2 Hz), 95.6 (J_{C-P} = 100.1 Hz), 77.1 (J_{C-P} = 13.4 Hz), 61.8 (J_{C-P} = 3.7 Hz), 32.9 (J_{C-P} = 4.9 Hz); MS *m*/*z* 284 (M^+, 33); HRMS calcd for $C_{17}H_{17}O_2P$ 284.0966, found 284.0957. Anal. Calcd for $C_{17}H_{17}O_2P$: C, 71.82; H, 6.03. Found: C, 71.52; H, 6.05.

General Procedure for Ring Closure of Allenylphosphine Oxides 6. To a solution of **6** (2.00×10^{-1} mmol) in ^{t}-BuOH (2.0 mL) was added ^{t}BuOK (3.00×10^{-1} mmol) at 30 °C. After being stirred for 10 min, the reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with AcOEt afforded the corresponding oxacycles **7**. Chemical yields are summarized in Table 1.

3-(Diphenylphosphinyl)-2-methyl-4,5-dihydrofuran (7a): colorless needles; mp 101−102 °C (Et_2O); IR 1628 cm^{-1}; ^1H NMR δ 7.74−7.40 (10H, m), 4.38 (2H, t, J = 9.6 Hz), 2.73−2.60 (2H, m), 1.97−1.92 (3H, m); ^{13}C NMR δ 168.6 (J_{C-P} = 19.5 Hz), 133.3 (J_{C-P} = 108.7 Hz), 131.5 (J_{C-P} = 2.5 Hz), 131.3 (J_{C-P} = 9.8 Hz), 128.4 (J_{C-P} = 12.2 Hz), 96.1 (J_{C-P} = 123.3 Hz), 69.8 (J_{C-P} = 11.0 Hz), 33.2 (J_{C-P} = 9.7 Hz), 13.8; MS *m*/*z* 284 (M^+, 100); HRMS calcd for $C_{17}H_{17}O_2P$ 284.0966, found 284.0961. Anal. Calcd for $C_{17}H_{17}O_2P$: C, 71.82; H, 6.03. Found: C, 71.50; H, 5.97.

5-(Diphenylphosphinyl)-6-methyl-3,4-dihydro-2*H*-pyran (7b): colorless oil; IR 1614 cm^{-1}; ^1H NMR δ 7.72−7.44 (10H, m), 4.08−4.05 (2H, m), 2.03 (3H, d, J = 1.3 Hz), 1.83−1.76 (4H, m); ^{13}C NMR δ 164.7 (J_{C-P} = 18.3 Hz), 133.8 (J_{C-P} = 105.0 Hz), 131.6 (J_{C-P} = 9.8 Hz), 131.4 (J_{C-P} = 2.4 Hz), 128.4 (J_{C-P} = 11.0 Hz), 96.7 (J_{C-P} = 112.3 Hz), 66.3, 24.3 (J_{C-P} = 9.7 Hz), 22.1 (J_{C-P} = 8.5 Hz), 20.6 (J_{C-P} = 3.7 Hz); MS *m*/*z* 298 (M^+, 92); HRMS calcd for $C_{18}H_{19}O_2P$ 298.1123, found 298.1123. Anal. Calcd for $C_{18}H_{19}O_2P\cdot{}^1/_2H_2O$: C, 70.35; H, 6.56. Found: C, 70.38; H, 6.73.

3-(Diphenylphosphinyl)-2-methyl-4,5,6,7-tetrahydrooxepin (7c): colorless needles; mp 101−102 °C (Et_2O); IR 1607 cm^{-1}; ^1H NMR δ 7.80−7.40 (10H, m), 4.15 (2H, t, J = 5.9 Hz), 2.14−2.00 (5H, m), 1.90−1.78 (2H, m), 1.64−1.50 (2H, m); ^{13}C NMR δ 171.8 (J_{C-P} = 19.6 Hz), 133.8 (J_{C-P} = 105.0 Hz), 131.6 (J_{C-P} = 9.8 Hz), 131.4, 128.5 (J_{C-P} = 12.2 Hz), 107.7 (J_{C-P} = 103.7 Hz), 71.5, 29.6, 29.3 (J_{C-P} = 9.8 Hz), 24.5 (J_{C-P} = 7.3 Hz), 21.8; MS *m*/*z* 312 (M^+, 83); HRMS calcd for $C_{19}H_{21}O_2P$ 312.1279, found 312.1271. Anal. Calcd for $C_{19}H_{21}O_2P$: C, 73.06; H, 6.78. Found: C, 73.12; H, 6.89.

3-(Diethoxyphosphinyl)-3,4-pentadien-1-ol (8a). To a solution of **1a** (49.8 mg, 2.32×10^{-1} mmol) and Et_3N (0.10 mL, 0.72 mmol) in $CHCl_3$ (2.0 mL) was gradually added a solution of diethyl chlorophosphite (90%, 121 mg, 0.70 mmol) in $CHCl_3$ (1.0 mL) at room temperature. The reaction mixture was refluxed for 1 h and then diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of the crude product in MeOH (2.0 mL) was added PPTS (5.8 mg, 2.3×10^{-2} mmol) at room temperature, and the mixture was stirred overnight. MeOH was evaporated off, and the residue was taken up in AcOEt, washed with brine, dried, and concentrated to dryness. Chromatography of the residue with AcOEt gave **8a** (41.2 mg, 81%) as a colorless oil: IR 3398, 1965, 1936 cm^{-1}; ^1H NMR (C_6D_6) δ 4.62 (2H, dt, J = 13.2, 2.6 Hz), 4.50 (1H, brs), 4.06−3.83 (6H, m), 2.66−2.47 (2H, m), 1.06 (6H, t, J = 6.9 Hz); ^{13}C NMR (C_6D_6) δ 212.2 (J_{C-P} = 6.1 Hz), 91.3 (J_{C-P} = 188.0 Hz), 76.1 (J_{C-P} = 15.9 Hz), 62.6 (J_{C-P} = 6.1 Hz), 61.3 (J_{C-P} = 6.1 Hz), 32.7 (J_{C-P} = 6.1 Hz), 16.3 (J_{C-P} = 6.1 Hz); MS *m*/*z* 220 (M^+, 3.2); HRMS calcd for $C_9H_{17}O_4P$ 220.0865, found 220.0857. Anal. Calcd for $C_9H_{17}O_4P\cdot{}^1/_2H_2O$: C, 47.16; H, 7.92. Found: C, 47.20; H, 7.98.

Ring Closure of Allenylphosphonates 8. According to the procedure described for ring closure of **6**, compounds **8** was exposed to the standard ring-closing conditions. Chemical yields of oxacycles **9** are summarized in Table 2.

7-(Diethoxyphosphinyl)-8-methyl-3,4,5,6-tetrahydro-2*H*-oxocin (9d): colorless oil; IR (neat) 1634 cm^{-1}; ^1H NMR

(C_6D_6) δ 4.06−3.82 (4H, m), 3.60 (2H, t, J = 5.3 Hz), 2.69−2.51 (2H, m), 2.34 (3H, d, J = 1.3 Hz), 1.69−1.56 (2H, m), 1.50−1.20 (4H, m), 1.07 (6H, t, J = 7.1 Hz); ^{13}C NMR (C_6D_6) δ 165.3 (J_{C-P} = 29.3 Hz), 115.8 (J_{C-P} = 181.9 Hz), 70.9 (J_{C-P} = 2.4 Hz), 60.9 (J_{C-P} = 4.9 Hz), 30.1, 28.6, 27.5, 26.4 (J_{C-P} = 7.4 Hz), 16.9, 16.4 (J_{C-P} = 6.1 Hz); MS m/z 262 (M^+, 32); HRMS calcd for $C_{12}H_{23}O_4P$ 262.1334, found 262.1340. Anal. Calcd for $C_{12}H_{23}O_4P$: C, 54.95; H, 8.84. Found: C, 54.82; H, 8.93.

(*Z*)-6-(*tert*-Butyldiphenylsiloxy)-4-penten-1-ol (10).[11] $NaBH_4$ (167 mg, 4.41 mmol) was added to a solution of EtOH (4.0 mL) containing 2 N aqueous NaOH (0.2 mL) at room temperature. After being stirred for 10 min, the mixture was filtered through a Celite pad. The filtrate (0.26 mL) was then added dropwise to a suspension of $Ni(OAc)_2 \cdot 4H_2O$ (55.6 mg, 2.23×10^{-1} mmol) in EtOH (5.0 mL) with vigorous stirring under a hydrogen atmosphere. A solution of ethylenediamine (0.04 mL) and **1b** (189 mg, 8.27×10^{-1} mmol) in EtOH (2.0 mL) was added to a solution of Ni_2B, thus formed, in EtOH. After being stirred for 1 h, the mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane−AcOEt (4:1) to afford the crude alkene (178 mg). To a solution of the crude alkene (165 mg) and imidazole (117 mg, 1.72 mmol) in DMF (1.0 mL) was added TBDPSCl (236 mg, 8.58×10^{-1} mmol) at 0 °C, and the mixture was warmed to room temperature. The mixture was stirred for 2 h at ambient temperature, diluted with water, and extracted with Et_2O. The extract was washed with water and brine, dried, and concentrated to dryness. To a solution of the crude product in MeOH−THF (1:1, 7.0 mL) was added PPTS (18 mg, 7.2×10^{-2} mmol) at room temperature, and the mixture was stirred overnight. The solvent was evaporated off, and the resulting residue was taken up in AcOEt, which was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (4:1) gave **10** (227 mg, 81%) as a colorless oil: ^{1}H NMR δ 7.74−7.65 (4H, m), 7.48−7.35 (6H, m), 5.64 (1H, dtt, J = 10.9, 6.3, 1.3 Hz), 5.51−5.38 (1H, m), 4.26 (2H, dd, J = 6.3, 0.7 Hz), 3.57 (2H, t, J = 6.3 Hz), 2.01 (2H, qd, J = 7.3, 1.3 Hz), 1.62−1.48 (3H, m), 1.05 (9H, s); ^{13}C NMR δ 135.6, 133.7, 130.7, 129.6 129.5, 127.6, 61.9, 60.0, 32.0, 26.8, 23.6, 19.1.

(*Z*)-8-(*tert*-Butyldiphenylsiloxy)-6-octen-2-yn-1-ol (11). To a solution of **10** (1.12 g, 3.16 mmol), DMSO (2.8 mL), and Et_3N (2.2 mL, 16 mmol) in CH_2Cl_2 (16 mL) was added $SO_3 \cdot$Py (2.25 g, 14.1 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. The reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to leave the crude aldehyde. To a solution of PPh_3 (3.30 g, 12.6 mmol) in CH_2Cl_2 (9.0 mL) was added CBr_4 (2.09 g, 6.30 mmol) at 0 °C, and the reaction mixture was stirred for 5 min. A solution of the crude aldehyde in CH_2Cl_2 (3.0 mL) was then added to a solution of the ylide at −20 °C. The mixture was stirred overnight, diluted saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane−AcOEt (20:1) to afford the crude dibromo derivative. To a solution of the dibromo derivative in THF (16 mL) was added ^{n}BuLi (1.39 M in hexane, 5.7 mL, 7.9 mmol) at −78 °C. The reaction mixture was stirred for 30 min, and paraformaldehyde (280 mg, 9.40 mmol) was added to the resulting solution of the acetylide. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched by addition of saturated aqueous NH_4Cl, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (6:1) gave **11** (869 mg, 73%) as a colorless oil: IR 3609 cm^{-1}; ^{1}H NMR δ 7.73−7.68 (4H, m), 7.48−7.36 (6H, m), 5.74−5.64 (1H, m), 5.51−5.41 (1H, m), 4.28 (2H, dd, J = 6.3, 1.0 Hz), 4.20−4.17 (2H, m), 2.22−2.05 (4H, m), 1.63 (1H, t, J = 6.3 Hz), 1.06 (9H, s); ^{13}C NMR δ 135.5, 133.7, 130.6, 129.6 128.6, 127.6, 85.6, 78.8, 60.3, 51.3, 26.8, 26.6, 19.1, 18.9; FABMS m/z 379 (M^+ + 1, 8.5). Anal. Calcd for $C_{24}H_{30}O_2Si$: C, 76.14; H, 7.99. Found: C, 75.98; H, 8.12.

(*Z*)-6-(Phenylsulfinyl)-2,6,7-octatrien-1-ol (12a). To a solution of **11** (105 mg, 2.77×10^{-1} mmol) and Et_3N (0.12 mL, 0.86 mmol) in THF (2.8 mL) was gradually added a solution of benzenesulfenyl chloride (60.7 mg, 4.19×10^{-1} mmol) in THF (1.0 mL) at −78 °C. After the mixture was stirred for 2 h, the reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residual oil was passed through a short pad of silica gel with CH_2Cl_2 to afford the crude sulfoxide. Aqueous HCl (10%, 1.0 mL) was added to a solution of the crude sulfoxide in MeOH (3.0 mL) at room temperature. After being stirred for 1 h, the reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (2:1) gave **12a** (58.8 mg, 85%) as a colorless oil: IR 3429, 1969, 1944 cm^{-1}; ^{1}H NMR δ 7.66−7.40 (5H, m), 5.64−5.49 (1H, m), 5.43−5.17 (3H, m), 4.14−3.97 (2H, m), 2.34−1.84 (4H, m); ^{13}C NMR δ 205.8, 143.3, 130.9, 130.6, 129.9, 129.1, 124.5, 112.2, 82.4, 58.3, 25.4, 23.0; MS m/z 248 (M^+, 3.6); HRMS calcd for $C_{14}H_{16}O_2S$ 248.0871, found 248.0872.

(*Z*)-6-(Phenylsulfonyl)-2,6,7-octatrien-1-ol (12b). According to the procedure for the preparation of **12a**, **11** (105 mg, 2.77×10^{-1} mmol) was converted the corresponding sulfoxide with a siloxy group. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (620 mg, 5.00×10^{-1} mmol) and 30% H_2O_2 (1.4 mL) were combined at 0 °C and stirred for 15 min. This newly adjusted bright yellow solution was added dropwise to a solution of the crude sulfoxide in EtOH (2.5 mL) at 0 °C. After being stirred for 2 h, the reaction mixture was diluted with water and extracted with Et_2O. The extract was washed with brine, dried, and concentrated to dryness. Aqueous HCl (10%, 1.0 mL) was added to a solution of the crude product in MeOH (2.0 mL) at room temperature. After being stirred for 2.5 h, the reaction mixture was diluted with water and extracted with AcOEt, which was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with CH_2Cl_2−AcOEt (8:1) gave **12b** (57.8 mg, 79%) as a colorless oil: IR 3611, 3533, 1969, 1940 cm^{-1}; ^{1}H NMR δ 7.93−7.78 (2H, m), 7.67−7.45 (3H, m), 5.69−5.25 (4H, m) 4.11 (2H, dd, J = 6.9, 0.7 Hz) 2.40−2.10 (4H, m); ^{13}C NMR δ 207.9, 139.9, 133.5, 130.2, 130.0, 129.1, 128.1, 112.4, 84.6, 58.3, 26.7, 25.4; MS m/z 264 (M^+, 1.0); HRMS calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0815.

Ring Closure of Allene Derivatives 12. According to the procedure described for ring closure of **6**, compounds **12** was exposed to the standard ring-closing conditions. Chemical yields of oxacycles **13** are summarized in Scheme 2.

8-Methyl-7-(phenylsulfinyl)-5,6-dihydro-2*H*-oxocin (13a): colorless oil; IR 1620 cm^{-1}; ^{1}H NMR δ 7.57−7.35 (5H, m), 5.78−5.50 (2H, m), 4.79 (1H, dd, J = 13.5, 7.6 Hz), 4.56 (1H, dd, J = 13.5, 6.9 Hz), 2.69−2.21 (6H, m), 1.83−1.57 (1H, m); ^{13}C NMR δ 158.8, 144.0, 136.9, 130.0, 128.7, 124.5, 122.6, 120.4, 65.3, 30.1, 20.6, 19.1; MS m/z 248 (M^+, 14); HRMS calcd for $C_{14}H_{16}O_2S$ 248.0871, found 248.0873.

8-Methyl-7-(phenylsulfonyl)-5,6-dihydro-2*H*-oxocin (13b): colorless oil; IR 1607 cm^{-1}; ^{1}H NMR δ 7.87−7.73 (2H, m), 7.61−7.42 (3H, m), 5.92 (1H, dt, J = 10.9, 5.6 Hz), 5.55 (1H, dtt, J = 10.9, 6.6, 1.3 Hz), 4.69 (2H, d, J = 6.6 Hz), 2.61−2.46 (2H, m), 2.77 (2H, t, J = 6.3 Hz), 2.20 (3H, s); ^{13}C NMR δ 163.8, 142.7, 136.1, 132.5, 128.9, 126.8, 122.6, 120.8, 67.4, 29.1, 26.9, 19.8; MS m/z 264 (M^+, 32); HRMS calcd for $C_{14}H_{16}O_3S$ 264.0820, found 264.0817. Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.34; H, 6.11.

(*Z*)-1-(*tert*-Butyldiphenylsiloxy)-6-iodo-2-hexene (14). To a solution of **10** (366 mg, 1.03 mmol) in CH_2Cl_2 (10 mL)

were added PPh_3 (325 mg, 1.24 mmol) and imidazole (84.3 mg, 1.24 mmol). I_2 (310 mg, 1.24 mmol) was then added to the reaction mixture at 0 °C, and the mixture was warmed to room temperature. After being stirred for 1 h, the reaction mixture was diluted with saturated aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (10:1) gave **14** (479 mg, quant) as a colorless oil: ^{1}H NMR δ 7.74−7.66 (4H, m), 7.48−7.34 (6H, m), 5.67 (1H, dtt, J = 11.2, 6.3, 1.7 Hz), 5.35 (1H, dtt, J = 11.2, 7.3, 1.3 Hz), 4.28 (2H, dd, J = 6.3, 1.3 Hz), 3.07 (2H, t, J = 6.9 Hz), 2.03−1.90 (2H, m), 1.85−1.71 (2H, m), 1.05 (9H, s); ^{13}C NMR δ 135.6, 133.7, 130.7, 129.6, 128.5, 127.6, 60.2, 33.2, 28.3, 26.8, 19.1, 6.1; FABMS m/z 464 (M^+, 1.1); HRMS calcd for $C_{22}H_{29}IOSi$ 464.1032, found 464.1039. Anal. Calcd for $C_{22}H_{29}IOSi$: C, 56.89; H, 6.29. Found: C, 56.51; H, 6.30.

(*Z*)-9-(*tert*-Butyldiphenylsiloxy)-7-nonen-2-yn-1-ol (15). ^{n}BuLi (1.39 M in hexane, 1.20 mL, 1.67 mmol) was added to a solution of 3-(*tert*-butyldimethylsiloxy)propyne (325 mg, 1.91 mmol) in THF−DMPU (6:1, 2.8 mL) at −78 °C, and the reaction mixture was stirred for 1 h. A solution of **14** (592 mg, 1.27 mmol) in THF−DMPU (1.0 mL) was then added to the solution of acetylide, and the mixture was warmed to room temperature. After being stirred overnight, the reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. PPTS (32 mg, 0.13 mmol) was added to a solution of the crude product in MeOH−THF (1:1, 13 mL) at room temperature, and the mixture was stirred overnight. MeOH−THF was evaporated off, and the residue was taken up in AcOEt, which was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (4:1) gave **15** (306 mg, 61%) as a colorless oil: IR 3609 cm^{-1}; ^{1}H NMR δ 7.73−7.64 (4H, m), 7.47−7.34 (6H, m), 5.64 (1H, dtt, J = 11.2, 6.3, 1.3 Hz), 5.37 (1H, dtt, J = 11.2, 7.3, 1.7 Hz), 4.30−4.22 (2H, m), 4.14 (2H, t, J = 2.0 Hz), 2.13 (2H, tt, J = 7.3, 2.0 Hz), 2.03−1.91 (2H, m), 1.48 (2H, quin, J = 7.3 Hz), 1.04 (9H, s); ^{13}C NMR δ 135.5, 133.8, 130.1, 129.7, 129.6, 127.6, 85.9, 78.6, 60.2, 51.2, 28.2, 26.8, 26.5, 19.1, 18.0; FABMS m/z 393 (M^+ + 1, 4.5); HRMS calcd for $C_{25}H_{32}O_2Si$ 392.2172, found 392.2143. Anal. Calcd for $C_{25}H_{32}O_2Si$: C, 76.48; H, 8.22. Found: C, 76.21; H, 8.53.

1-[(1*R,2*S**)-1-(Diethoxyphosphinyl)-2-ethenylcyclopentyl]ethan-1-one (17b).** To a solution of **16b** (29.9 mg, 1.09 × 10^{-1} mmol) in ^{t}BuOH (5.5 mL) was added ^{t}BuOK (18.3 mg, 1.63 × 10^{-1} mmol) at 30 °C. After being stirred for 20 min at 60 °C, the reaction mixture was cooled to room temperature, diluted with water, and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with AcOEt gave **17b** (22.9 mg, 77%) as a colorless oil: IR 1701 cm^{-1}; ^{1}H NMR δ 5.82−5.72 (1H, m), 5.13 (1H, dt, J = 17.1, 1.0 Hz), 5.03 (1H, dt, J = 10.3, 1.0 Hz), 4.19−4.11 (4H, m), 3.20−3.10 (1H, m), 2.52−2.39 (1H, m), 2.27 (3H, s), 2.15−2.02 (1H, m), 2.02−1.93 (1H, m), 1.83−1.69 (2H, m), 1.62−1.53 (1H, m), 1.32 (6H, q, J = 7.3 Hz); ^{13}C NMR δ 204.7 (J_{C-P} = 2.4 Hz), 137.7 (J_{C-P} = 2.4 Hz), 116.4, 64.8 (J_{C-P} = 136.7 Hz), 62.6 (J_{C-P} = 7.3 Hz), 62.5 (J_{C-P} = 8.5 Hz), 49.8 (J_{C-P} = 2.4 Hz), 32.1 (J_{C-P} = 7.3 Hz), 30.7, 30.0, 23.5 (J_{C-P} = 4.9 Hz), 16.4 (J_{C-P} = 6.1 Hz); MS m/z 274 (M^+, 1.7); HRMS calcd for $C_{13}H_{23}O_4P$ 274.1334, found 274.1333. Anal. Calcd for $C_{13}H_{23}O_4P\cdot{}^1/_2H_2O$: C, 55.11; H, 8.54. Found: C, 54.86; H, 8.26.

(*Z*)-8-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-5-octen-1-yne (21). To a solution of **20**[18] (3.64 g, 7.50 mmol) in THF (13 mL) was added KHMDS (0.75 M in toluene, 9.1 mL, 6.8 mmol) at −78 °C, and the reaction mixture was stirred for 20 min. Aldehyde **19**[17] (386 mg, 2.50 mmol) in THF (2.5 mL) was then added to a solution of the ylide, which was stirred for 15 min. The reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane−AcOEt (20:1) to give the crude enyne. K_2CO_3 (690 mg, 5.00 mmol) was added to a solution of the crude enyne in MeOH (13 mL) at room temperature. The mixture was stirred for 3 h, and K_2CO_3 was filtered off. The filtrate was diluted with saturated NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (20:1) gave **21** (434 mg, 83%) as a colorless oil: IR 3308 cm^{-1}; ^{1}H NMR δ 5.59−5.43 (2H, m), 4.62−4.56 (1H, m), 3.92−3.68 (2H, m), 3.55−3.35 (2H, m), 2.42−2.17 (6H, m), 1.95 (1H, t, J = 2.6 Hz), 1.90−1.43 (6H, m); ^{13}C NMR δ 129.3, 127.2, 98.5, 83.8, 68.3, 66.7, 62.0, 30.5, 27.9, 26.3, 25.3, 19.4, 18.6; FABMS m/z 208 (M^+, 1.5); HRMS calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1461. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.62; H, 9.75.

(*Z*)-9-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-6-octen-2-yn-1-ol (22). To a solution of **21** (434 mg, 2.08 mmol) in THF (10 mL) was added ^{n}BuLi (1.44 M in hexane, 1.70 mL, 2.45 mmol) at −78 °C. The reaction mixture was stirred for 2 h, and then paraformaldehyde (188 mg, 6.24 mmol) was added. The mixture was warmed to room temperature and stirred for 15 h. The reaction mixture was diluted with saturated aqueous NH_4Cl and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane−AcOEt (8:1) gave **22** (463 mg, 93%) as a colorless oil: IR 3609, 3422 cm^{-1}; ^{1}H NMR δ 5.57−5.42 (2H, m), 4.64−4.57 (1H, m), 4.22 (2H, s) 3.93−3.68 (2H, m), 3.56−3.38 (2H, m), 2.43−2.03 (7H, m), 1.90−1.42 (6H, m); ^{13}C NMR δ 129.5, 127.0, 98.5, 85.1, 78.8, 66.9, 62.0, 50.7, 30.4, 27.7, 26.3, 25.2, 19.2, 18.8; FABMS m/z 238 (M^+, 3.4); HRMS calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1566.

2-Methyl-3-(phenylsulfinyl)-4,5,8,9-tetrahydrooxonin (24a). According to the procedure described for ring closure of **16b**, the ring-closing reaction of **23a** was performed. The title compound was obtained in 71% yield as a colorless oil: IR 1638 cm^{-1}; ^{1}H NMR δ 7.53−7.36 (5H, m), 5.53 (1H, dt, J = 10.6, 8.3 Hz), 5.33−5.18 (1H, m), 3.99 (2H, dd, J = 5.9, 4.3 Hz), 2.39−1.92 (9H, m); ^{13}C NMR δ 159.0, 143.4, 133.8, 130.0, 128.8, 127.3, 125.5, 124.3, 68.2, 27.2, 25.9, 21.0, 15.7; MS m/z 262 (M^+, 2.0); HRMS calcd for $C_{15}H_{18}O_2S$ 262.1028, found 262.1032. Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92. Found: C, 68.30; H, 7.07.

2-Methyl-3-(phenylsulfonyl)-4,5,8,9-tetrahydrooxonin (24b) and 2-Methylene-3-(phenylsulfonyl)-2,3,4,5,8,9-hexahydrooxonin (24b′). According to the procedure described for ring closure of **16b**, the ring-closing reaction of **23b** was performed. Title compounds were obtained as a separable mixture. **24b** (44%): a colorless oil; IR 1624 cm^{-1}; ^{1}H NMR δ 7.89−7.76 (2H, m), 7.61−7.43 (3H, m), 5.59 (1H, dt, J = 10.6, 7.6 Hz), 5.46 (1H, dt, J = 10.6, 8.2 Hz), 4.02 (2H, t, J = 5.3 Hz), 2.46 (2H, t, J = 6.3 Hz), 2.40 (3H, s), 2.26 (2H, dt, J = 8.2, 6.3 Hz), 2.16 (2H, dt, J = 7.6, 5.3 Hz); ^{13}C NMR δ 163.4, 142.1, 133.4, 132.7, 128.9, 127.0, 126.2, 124.9, 68.6, 27.2 26.7, 26.2, 16.6; MS m/z 278 (M^+, 2.4); HRMS calcd for $C_{15}H_{18}O_3S$ 278.0977, found 278.0981. Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.50; H, 6.63. **24b′** (22%): colorless needles; mp 108−109 °C (hexane); IR 1641 cm^{-1}; ^{1}H NMR δ 7.94−7.78 (2H, m), 7.66−7.42 (3H, m), 5.68−5.36 (2H, m), 4.74 (1H, d, J = 2.3 Hz), 4.60 (1H, dd, J = 2.3, 1.3 Hz), 4.00−3.83 (2H, m), 3.67 (1H, ddd, J = 11.9, 5.9, 1.3 Hz), 2.54−1.90 (6H, m); ^{13}C NMR δ 152.1, 138.0, 133.5, 132.3, 129.2, 128.7, 126.6, 97.4, 70.2, 66.1, 25.7, 24.0, 22.2; MS m/z 278 (M^+, 9.6); HRMS calcd for $C_{15}H_{18}O_3S$ 278.0977, found 278.0966. Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.36; H, 6.56.

3-(Diphenylphosphinyl)-2-methyl-4,5,8,9-tetrahydrooxonin (24c). According to the procedure described for ring closure of **16b**, the ring-closing reaction of **23c** was performed. The title compound was obtained in 68% yield as colorless needles: mp 129−131 °C (Et_2O); IR 1614 cm^{-1}; ^{1}H NMR δ 7.73−7.37 (10H, m), 5.70−5.46 (2H, m), 4.01 (2H, t, J = 5.3

Hz), 2.29−2.04 (7H, m), 1.87−1.76 (2H, m).^{13}C NMR δ 165.1 (J_{C-P} = 19.6 Hz), 133.7 (J_{C-P} = 105.0 Hz), 133.3, 131.8 (J_{C-P} = 9.7 Hz), 131.4 (J_{C-P} = 2.5 Hz), 128.4 (J_{C-P} = 10.9 Hz), 126.5, 113.9 (J_{C-P} = 102.6 Hz), 67.7, 27.9 (J_{C-P} = 11.0 Hz), 27.4, 26.9 (J_{C-P} = 2.4 Hz), 17.2 (J_{C-P} = 2.5 Hz); MS *m*/*z* 338 (M^+, 45); HRMS calcd for $C_{21}H_{23}O_2P$ 338.1436, found 338.1433. Anal. Calcd for $C_{21}H_{23}O_2P$: C, 74.54; H, 6.85. Found: C, 74.38; H, 7.03.

3-(Diethoxyphosphinyl)-2-methyl-4,5,8,9-tetrahydrooxonin (24d). According to the procedure described for ring closure of **16b**, the ring-closing reaction of **23d** was performed. The title compound was obtained in 62% yield as a colorless oil: IR 1626 cm^{-1}; ^{1}H NMR δ 5.73−5.55 (2H, m), 4.13−3.91 (6H, m), 2.41−2.10 (9H, m), 1.30 (6H, t, J = 6.9 Hz); ^{13}C NMR δ 164.8 (J_{C-P} = 30.5 Hz), 133.8, 126.1, 110.8 (J_{C-P} = 184.3 Hz), 67.5, 61.0 (J_{C-P} = 4.9 Hz), 27.2, 26.9 (J_{C-P} = 3.6 Hz), 26.4 (J_{C-P} = 7.4 Hz), 16.5, 16.3 (J_{C-P} = 7.3 Hz); MS *m*/*z* 274 (M^+, 19); HRMS calcd for $C_{13}H_{23}O_4P$ 274.1334, found 274.1338.

Acknowledgment. This work was supported in part by a Grant-in Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, to which we are thankful.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **12a**,**b**,**d**, **13a**,**d**, **16a**,**b**, **22**, **23a**−**d**, and **24d** and characterization data for compounds **6b**−**d**, **8b**−**d**, **9a**−**c**, **12c**,**d**, **13c**,**d**, **16a**,**b**, **17a,** and **23a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0488614